High-Pressure Structural Studies of Strontium

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Declaration

This thesis has been composed by myself and it has not been submitted in any previous application for a degree. The work reported within was executed by me, unless otherwise stated.

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Abstract

The use of high pressure as a parameter for the investigation of solid state phenomena has become increasingly important throughout the various scientific disciplines. Among the materials that are of fundamental interest, but that are not yet fully understood, are the elemental metals, especially those alkali and alkaline earth metals. These metals exhibit a pressure induced $s \to d$ electron transfer, resulting in a rich variety of high-pressure crystalline phases. Despite the wide interest in these elements, the systematics of their high-pressure structural behaviour has been poorly understood until comparatively recently. Strontium is one of the alkaline earth elemental metals in which very few high pressure structural studies has been carried out, either experimentally or theoretically. Previous structural work has shown that strontium undergoes a sequence of phase transitions up to 46 GPa. The relatively complex structures of Sr-IV and Sr-V, stable above 35 GPa and 46 GPa respectively, could not be solved and doubts remained about the correct assignment of the Sr-III structure. It is only comparatively recently, however, that experimental techniques have been developed to allow the detailed structural characterisation of these phases.

To resolve these remaining uncertainties, the author has carried out a re-examination of the high-pressure structures and transitions in strontium using angle-dispersive powder-diffraction techniques with the image-plate area detector on station 9.1 at the SRS Daresbury Laboratory. The experimental set up has also been improved so that data of sufficient quality could be obtained to allow the structures of these high pressure phases to be both correctly identified and accurately refined. The previously reported structure of Sr-III was found to be wrongly identified as having an orthorhombic $Imma$ symmetry (with a structure similar to that of Si-III) and this has now been correctly identified as having the archetypal $\beta$-tin ($I4_1/amd$) structure. The higher pressure
phase of Sr, Sr-IV, has also been solved and the structure solution showed that it has a very complex monoclinic structure. This is the first time that this complex monoclinic structure has been reported in an element. Finally, the crystal structure of Sr-V has also been closely studied in comparison with the recently reported Ba-IV structure — based on the similarity of the diffraction patterns observed. The Sr-V structure is indeed found to be essentially the same as that of Ba-IV and it also has an intra-phase structural transition similar to those observed in Ba-IV.

Along with the experimental work, computational studies of condensed matter systems is also a very active area of research. These calculations can be used to investigate the behaviour of materials under extreme conditions and can probe physical phenomena that are not readily measured experimentally. However, calculations still rely heavily on accurate experimentally-determined structural information since they are, as yet, not capable of predicting crystal structures directly and require a starting model. Computational studies of the new high-pressure Sr structures have also been presented in this thesis and they show good agreement with experiment.
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Chapter 1

Introduction

1.1 High-Pressure Structural Studies

Pressure and temperature are the most important variables for understanding the physical and chemical properties of condensed matter. The importance of these thermodynamic variables as experimental parameters arises from the fact that distances between atoms or molecules in a material are strongly dependent on these parameters. While temperature more strongly effects atomic thermal motion and consequently has only an indirect effect on interatomic distances, pressure on the other hand, has a direct effect and is "clean" in the sense that it has only an indirect effect on the energy of the system. For example, at room temperature, one of the most intensively studied elements silicon (Si) can transform to six different phases over the pressure range up to 50 GPa. On the other hand, at ambient pressure, Si only exists in the Si-I diamond structure from essentially 0 K to its melting point at 1683 K. Pressure is, therefore, the more important experimental variable for governing interatomic distance. In a readily accessible pressure range, application of pressure on a number of solids has been shown to reduce the interatomic distances by as much as 10%-20%. For example, Cs can be compressed to 26% of its ambient pressure volume at 12 GPa [1, 2]. Consequently, pressure can cause dramatic changes in atomic electronic energy states and lead to an alteration of the physical and chemical properties of materials. With increasing pressure, band gaps are reduced and many insulators and semiconductors become metals. Most of the naturally occurring elements are metals at atmospheric pressure and many
of the remainder are themselves transformed to metals by the application of pressure. For example, Si transforms from an ambient-pressure semiconducting cubic structure to a metallic tetragonal \( \beta \)-tin structure at 12 GPa. Hydrogen is also believed to be metallic at very high pressures. This element is studied widely as it is the simplest and most abundant element and also because it is the prototypical system of the insulator-to-metal transition. On Earth, hydrogen is commonly found as a diatomic molecular gas but on Jupiter, where the interior pressure is millions of times greater than that at our planet's surface, hydrogen is believed to exist as a liquid metal. Hydrogen can be cooled to a liquid below 20 K and a solid below 14 K. In all these states, hydrogen is still an electrical insulator. Theoretically, metallic hydrogen can be achieved when high pressure reduces the energy gap between the filled valence-electron band and the unfilled conduction-electron band. These predictions have stimulated an extremely active, and hotly contested, area of high-pressure condensed matter physics. It is also interesting to note that many simple substances form a rich variety of high-pressure structures. Among them, water (H\(_2\)O) has been shown to manifest at least ten crystal structures under nonambient conditions. As well as studying the behaviour of existing substances at high pressure, many new novel materials can be synthesised under the extreme conditions of high-temperature and high-pressure. Subsequently, the study of high-pressure transformations and the stability of dense materials has been an active area of research for many decades.

The scope of high-pressure studies has grown continually with the development of new techniques for generating high pressures along with the growth in the range of measurements that can be performed under these conditions. Piston-cylinder and opposed-anvil devices were used by the Nobel laureate P.W. Bridgman in the first half of last century to measure the compressibility and electrical transport properties of materials to pressures up to 10 GPa [3, 4]. His research laid the foundations for a large proportion of present-day work in the field of high pressure. Following Bridgman, H.G. Drickamer and his co-workers extended high-pressure measurement up to 50 GPa with the development of supported-taper anvil devices. Multi-anvil devices were also developed in Japan by N. Kawai and S. Endo in 1970 [5] for high-pressure experiments and are still widely used for many high-pressure studies particularly those involving the synthesis of materials. However, these high pressure devices are relatively large and require a ded-
icated laboratory and substantial operating resources. The study of materials at high pressure was revolutionised by the advent of the diamond-anvil cell (DAC), introduced in 1959 by Weir et al [6], which not only increased the range of pressure attainable, but also allowed high-pressure studies to be undertaken in non-specialised laboratories. This development has made more precise physical measurements under high pressure possible with a much wider range of techniques (e.g. optical and x-ray spectroscopy, x-ray diffraction) than was possible with the earlier hydraulically-driven devices.

In high-pressure research, various means of measurement can be performed in order to study the high-pressure behaviour of materials. The basic effect of pressure is to reduce the volume of the sample and therefore increase overlap between adjacent electronic orbitals. This increased overlap leads to a number of consequences change in their structure and physical properties. Structural studies of materials under high pressure is one of the most fundamental studies and probably the most important step to understanding the behaviour and properties of materials under high pressure. The main objective for high-pressure structural studies is to take the sample up to the desired pressure and perform the measurement for a precise determination of high-pressure structure. The crystalline sample used in structural studies can be either a single crystal sample or a powder sample. Single-crystal techniques remain the ideal method for extremely accurate structural studies both at ambient and high pressure. However, in high-pressure work, single-crystal samples often pulverise after passing through a phase transition and they can often break up when the pressure is no longer ideally hydrostatic. Powder samples, on the other hand, can be taken to extremely high pressures and are naturally unaffected by phase transitions involving a large volume collapse. However, powder-diffraction data are one-dimensional in nature which makes structure solution far from routine and also less accurate than single-crystal methods. Neutron and x-ray diffraction with either powder or single-crystal samples are the most widely used experimental techniques for structural studies. The major difference between these two diffraction techniques is that x-rays are scattered by the electrons in the crystal but neutrons are scattered by the nuclei of the atoms. In neutral atoms, there are Z electrons outside the nucleus and Z protons in the nucleus. The unique properties of neutrons offers significant advantages in many important cases. However, since neutrons scatter from the nuclei in the atomic cores rather that via the electromagnetic
interaction with the atomic electrons, the neutron scattering factor, therefore, varies irregularly with atomic number whereas the x-ray scattering factor increases systematically in proportion to the atomic number (always coupling much more strongly to the heavy elements). Neighbouring atoms in the periodic table often have sufficient difference in their neutron scattering factors to aid the study of the degree of order in alloys, for example, but their x-ray atomic scattering factors are usually quite close to each other. In addition, it is possible to change atoms visibility to neutrons, without appreciably changing the bonding or chemistry of particular atom, by changing isotope. Thus, particular sites in materials can be labeled for investigation of their coordinates and motion. Neutrons are especially sensitive to the lightest and arguably most important element of all, hydrogen, (H), while hydrogen is virtually transparent to x-rays. Therefore, neutron diffraction is also a suitable method for gaining information about light atoms in the presence of heavy ones.

The fact that neutrons are uncharged means not only that they can penetrate deeply into the target but also that they come close to the nuclei — there is no Coulomb barrier to be overcome. Consequently, neutron techniques allow an accurate structure determination but with the low flux of neutron sources a large sample volume is required to produce resolvable diffracted intensities and consequently, for high pressure experiments, the maximum pressure that can be reached is much more limited in comparison to x-ray diffraction techniques. For x-ray diffraction, single-crystal techniques allow high-pressure studies to be conducted routinely with a sealed-tube source where entire sample is diffracting and sample volume is of the same order as that used for ambient-pressure studies. However, this is not the case for powder techniques where only a fraction of the small sample volume diffracts the x-ray beam. With such a small sample volume diffracting the x-ray beam, a higher flux of x-rays is needed in order to acquire a reasonably intense diffracted signal from a powder sample. These problems were overcome by the advent of synchrotron radiation. Synchrotron radiation not only provides a high x-ray flux but it also offers a wide range of radiation from hard x-ray wavelengths through to the infrared which offers several possible measurement techniques. It also provide a high beam energy (short wavelength), particularly beneficial for its high penetration power.

For high-pressure diffraction experiments, the major impact goes to the energy-dispersive
techniques (EDX), which exploit the full "white" beam of the synchrotron. This technique was widely used for high-pressure structural studies because of its advantage in pressure cell design for its anvil supported and hence highest pressure gained, this feature will be fully explained later in chapter 2. This method uses the wide range of x-ray radiation emitted from the storage ring to allow diffraction patterns to be collected as a function of x-ray energy at a fixed angle, $\theta$. However, patterns collected from this method are usually accompanied by a number of unavoidable limitations such as fluorescence peaks from the sample, electronic escape peaks from the detector itself and the energy resolution of the detector, which limits the resolution of the powder patterns. By collecting the data at a fixed angle, the diffracted x-ray beam collected is therefore diffracted from a very small volume in the sample which can cause poor powder averaging. This will also be described in chapter 2 in more detail. Therefore, it is not the ideal method for an accurate structural determination. This problem was overcome by the use of image-plate (IP) area detectors in high-pressure powder-diffraction. In this technique, the x-ray beam is monochromated to a suitable wavelength before it strikes the sample and the diffracted intensities are collected on the image plate as two dimensional Debye-Scherrer rings. This method is an angle-dispersive technique (ADX). As it is desirable to collect as much of the Debye-Scherrer rings as possible, the pressure cells used for this technique are required to have a wider exit compare to those used for EDX. This leads to relatively poor anvil support and therefore lower pressures are expected for pressure cells designed for ADX. The diffraction patterns collected by ADX methods give more reliable intensities compared to those obtained from EDX techniques. This is due to the fact that the intensities measured by ADX techniques are obtained by integrating around the Debye-Scherrer rings that are diffracted from a larger fraction of the sample and hence a better powder averaging can be obtained. Diffraction patterns collected from this technique also allow far higher resolution as the resolution is not limited by energy resolution of the detector but the pixel size itself. The ADX approach is therefore the most successful method for the determination of crystal structures and is widely used in ambient pressure studies. As the aim of this thesis is to understand the behaviour of Sr to relatively modest pressures and to determine the structures accurately, all the experimental work presented in this thesis was undertaken using high-pressure angle-dispersive x-ray powder diffraction techniques with synchrotron radiation.
Approximately three-quarters of the known elements in the periodic table are metals. In order to understand behaviour of materials under high pressure, the understanding of the behaviour of metals at ambient and high pressure is necessary, especially for those simplest metals located on the left hand side of the periodic table named as alkali and alkaline earth metals. It is sometime found that the outermost valence electrons in a solid can be treated as if they were essentially free electrons. This is particularly true in that class of materials known as metals, in which the outer most valence electrons are not involved in chemical bonding. The fact that the valence electrons in metals behave like free electrons accounts for many of the electrical, thermal and optical properties of metals. Consider solid metallic sodium (Na). Each atom contain 11s electrons, indicated as $1s^2\ 2s^2\ 2p^6\ 3s$. But 10 of these are in states which are tightly bound to the nucleus to form an ion of positive charge and the final outermost $3s$ electron can be considered to be essentially free to move around through out the solid. It is the same $3s$ electron that sodium gives up in chemical bonding to become a $\text{Na}^+$ ion. In fact, these valence electrons are not completely free since they still move in the presence of the positively charged ions that are located on the crystal lattice of the metal. Alkali and alkaline earth metals are thought to be the closest to ideal metals as they are nearly-free electron metals at ambient pressure. With increasing pressure, these metals undergo major changes in their electronic structure, becoming $d$-transition metals, and they lose their nearly-free electron character. Alkali and alkaline earth metals have, therefore, drawn considerable interest, both theoretically and experimentally, from scientists in a range of disciplines. P.W. Bridgman's early work on electrical resistance measurements suggested that, under pressure, the simple alkali metals might take on the characteristics of transition metals.

Compression of metals causes changes in electrical conductivity and bonding affinity accompanying the alterations in their electronic structures and in effect, these metals assume the properties of other elements. An excellent illustration of this behaviour is exhibited by caesium which undergoes a series of pressure-induced electronic transitions with increasing pressure [2, 7]. At ambient pressure caesium has the bcc structure. Under pressure it transforms to the fcc structure, which is a close-packed arrangement of the atoms. On further pressure increase it transforms to another fcc structure and then to a tetragonal structure. This tetragonal structure is not close-packed and therefore the
arrangement of the atoms in the structure becomes more open as the lattice contracts. This structural transition sequence is thought to be induced by a series of electronic transitions where electrons change between different electron shells with pressure. In Cs, the rapid decrease in lattice parameter during the transition to the fcc structure is caused by the 6s electrons being driven towards the nucleus and as a result the compressibility is very large. However after the transition to the tetragonal phase, all the electrons have moved into the 5d shell and compression of the structure becomes much more difficult as further pressure increase can not be accommodated by further electronic transitions.

Although, there is a long established interest in the high-pressure behaviour of these metals, the structures of most of the high-pressure phases have only been identified relatively recently.

Investigation of the high-pressure electrical transport properties of Sr was first car-
CHAPTER 1. INTRODUCTION

ried out by P.W. Bridgman in his piston-cylinder apparatus [8]. He observed a sharp maximum in the resistance of strontium at about 4 GPa which was later confirmed by Stager and Drickamer [9]. Bridgman also reports a volume anomaly near 6 GPa [10, 11] although this suggested phase transition was not confirmed by his own subsequent resistance measurements [12]. The structure of strontium at ambient pressure was first determined by Simon and Vohsen [13] who found that it has a cubic close packed (fcc) structure with $a = 6.04(5)$ Å and subsequent determinations of the lattice constant with higher precision were carried out by King giving $a = 6.075(4)$ Å [14]. The high pressure x-ray diffraction study of Sr by McWhan and Jayaraman shows a transition to the Sr-II phase at 4.2 GPa, in good agreement with the resistance measurements, which was later identified as having the body-centred cubic (bcc) structure [15]. Using high-pressure energy-dispersive x-ray powder-diffraction, Olijnyk and Holzapfel found that the Sr-II (bcc) phase transforms to a new structure close to 26 GPa at room temperature, Sr-III, which they expected to be an orthorhombic distortion of the simple cubic structure. However, the x-ray data were not good enough for a satisfactory indexing. A more recent study by Winzenick and Holzapfel at 31.3 GPa has identified Sr-III as having an orthorhombic structure with Imma symmetry [16], similar to that of the high-pressure phase of Si [17] and Ge [18]. This transition is probably also seen in resistance measurements by Dunn and Bundy with an opposed-anvil apparatus, where a kink was observed in the 35 GPa resistance isobar at about 200K [19]. Olijnyk and Holzapfel also observed that Sr adopts another unknown structure, Sr-IV, in the pressure range 35 to 46 GPa. They report that Sr finally transforms to Sr-V above 46 GPa, the highest pressure attained in their study [20]. They also suggest some similarity between the Sr-V and the Ba-IV powder patterns. Therefore, high-pressure x-ray diffraction studies aimed at resolving these unknown structures are urgently required to understand the high-pressure systematics of this important group of elements.

In this thesis, a high-pressure structural study of Sr has been performed and the high-pressure phases of Sr-III, Sr-IV and Sr-V have been identified. Sr-III has the tetragonal $\beta$-tin structure [21], and not an orthorhombic Imma structure as has been previously reported [16]. This is the first observation of the ideal $\beta$-tin structure in a non-group IV element. The structure solution of the Sr-IV phase is presented in this thesis. Sr-IV has a complex monoclinic superstructure of $\beta$-tin and has not been observed
previously in elemental metals [22]. The Sr-V phase exhibits the remarkable zeolite-like self-hosting structure first observed in Ba and Rb. In an attempt to gain a more detailed understanding of these transitions, pseudopotential calculations have also been performed.

1.2 Thesis Outline

Chapter 2: High-Pressure Powder-Diffraction Techniques A concise description of the background to high-pressure powder-diffraction techniques will be given along with a discussion of the techniques used for the experimental work. This will include details of the experimental set-up and the pressure cells used. Although the author was not involved in the development of these methods, it is necessary to describe the experimental procedures in detail as they are used to perform all the diffraction experiments presented in this thesis.

Chapter 3: Sr-III: The Tetragonal $\beta$-tin Structure A review of the work conducted on Sr will be presented in this chapter. It will concentrate on the high-pressure structural studies of Sr conducted by the author up to the Sr-III phase. A detailed account will be given on the structure solution of Sr-III. The importance of angle-dispersive x-ray diffraction techniques using the image-plate system as the key to structure solution will also be discussed.

Chapter 4: Sr-IV: The Complex Monoclinic Superstructure The structure solution of Sr-IV will be presented in this chapter along with the unexpectedly complex behaviour through the III/IV phase transition. This chapter will mainly give details on the powder diffraction work performed by the author on Sr-IV and the techniques introduced to obtain the high resolution data required to solve the complex and unusual behaviour of this high-pressure phase.

Chapter 5: Sr-V: The Remarkable Self-hosting Structure Firstly, the prototype Ba-IV structure is discussed in detail as it shares the principal structural features of the Sr-V phase. Based on the observed similarity between the Ba-IV and Sr-V powder-diffraction patterns, the Sr-V phase was found to have the archetypal Ba-IV self-hosting structure. Details on a transition in the guest structure of Sr-V will also be presented.
Chapter 6: Computational Work on the High-pressure Phases of Strontium
The principles of total-energy pseudopotential calculations will be briefly introduced and the results of such calculations on the high-pressure structures of Sr will be discussed.

Chapter 7: Conclusions A brief summary of the work and results presented in this thesis will be given along with a discussion on the possible future studies that can be made on the high-pressure phases of strontium.
Chapter 2

High-Pressure Powder Diffraction Techniques

2.1 Introduction

This chapter provides an introduction to the physics of powder diffraction and experimental techniques for high-pressure crystallography. Details of the high pressure cells and beamline equipment used for the high pressure experiments at the Synchrotron Radiation Source at Daresbury Laboratory are also given in this chapter. The experimental set-up has been implemented and developed by members of the high-pressure experimental group of the University of Edinburgh over the past decade. The author was not involved in the early development of the beamline equipment but has introduced new and a unique data collection techniques to improve the data quality. This was a key to the structure solution of Sr-IV (as will be discussed later in chapter 4). However, it is important to describe the details of the experimental set-up and the data processing procedures as these techniques are used for all the work described in this thesis.

2.2 Theory of Powder Diffraction

All techniques involving the diffraction of radiation by crystalline materials depend on Bragg’s law for describing the relationship between the angle of the incident beam to
Chapter 2. High-Pressure Powder Diffraction Techniques

Figure 2.1: The principles of Bragg's law.

The intensity of the diffracted beam depends on the arrangement of atoms within the
layers from which the incident beam is being diffracted. The details on atomic positions can be then extracted from the relative intensities of these diffracted beams which are related to $F^2$, where $F$ is the structure factor and is defined by

$$F = \sum_{n=1}^{N} f_n e^{2\pi i(hx_n + ky_n + lz_n)} \tag{2.2}$$

where $N$ is the number of atoms in the unit cell, $f_n$ is the scattering factor of the $n^{th}$ atom and $x_n, y_n, z_n$ are the fractional coordinates of the $n^{th}$ atom. By using Bragg’s law (equation 2.1) the size and shape, or lattice type, of the unit cell can be calculated. The atomic positions then can be derived from the measured intensities using the structure factor (equation 2.2). These principles, therefore, form the basis of crystal structure determination.

In powder diffraction, there are two distinct experimental techniques which arise from varying either $\lambda$ or $\theta_{hkl}$ in Bragg’s law. For energy-dispersive x-ray diffraction (EDX), where a polychromatic “white” beam is used, $\theta_{hkl}$ is held constant and the diffraction data are collected as a function of wavelength, $\lambda$, which is determined from the energy of the radiation ($E = hc/\lambda$). The discrimination between the reflections is performed using detectors with energy sensitivity (e.g. an intrinsic Ge detector) which disperses the diffracted photons in the energy spectrum. In angle-dispersive x-ray diffraction (ADX), the highly collimated monochromatic (fixed wavelength) beam impinges on the sample and the reflections produce powder diffraction rings with various 2$\theta$ angles about the incident beam. These rings are measured by moving the point detector through $\theta$ or by area detectors such as photographic film or image-plates (IP).

The ADX technique is widely used for almost all ambient condition powder diffraction and also for low-temperature and high-temperature studies. For high-pressure experiments, samples are usually contained in pressure generating equipment such as the diamond-anvil cell (DAC) which have very restricted incident and diffracted beam apertures. The crucial advantages of EDX, which utilise point detectors, over ADX techniques, with area detectors, are the minimal requirements for angular access to the sample. The small opening of the cell for x-ray access leaves maximum support to the anvils for reaching maximum pressures. Therefore, since the advent of synchrotron
radiation sources in the early 1980s, EDX techniques were the preferred option for high-pressure measurements made with DACs. However, structure refinement from EDX data usually suffers from the limitation of the detector which gives relatively poor resolution compared to conventional scanning point-detectors or area detectors used in ADX techniques. Additionally, the pattern collected from EDX is usually contaminated by fluorescence lines from the sample and escape peaks from the detector itself. In order to obtain good energy resolution, a very narrow range of the defined scattering angle is required. In such a case, the diffraction pattern is collected from only a few crystallites in the sample chamber and thus a poor powder averaging is expected. Also, energy dependent absorption in the DAC components leads to unreliable intensities. Therefore, this technique is not an ideal method for accurate structure determination.

On the other hand, the ADX approach is much more successful for accurate and detailed structural studies, and is the most widely used method for crystal structure determination at ambient conditions. The simplest method for collecting an ADX diffraction pattern is by using photographic film. The diffraction pattern from the powder sample is then recorded as a series of concentric rings. Two-dimensional data collection not only increases efficiency, but it also provides more reliable peak intensities when the intensities are integrated along each of the diffraction rings. This integration procedure reduces the effect of coarse crystallinity and preferred orientation (where crystallites are not randomly oriented but align along a particular axis). The preferred orientation effect can be easily observed as the variation in intensity around the Debye-Scherrer rings. Intensity information from ADX has been used extensively for high-pressure crystal structure determination. All the data collected for this thesis were using ADX techniques combined with an image-plate area detector which shares the same basic principles with photographic film and will be described in detail in section 2.5.3.

2.3 Criteria for Accurate Structure Determination

The most important step for experimental science is to establish the criteria needed for a successful experiment. The following factors are required for accurate structure determination using high-pressure powder-diffraction techniques.
CHAPTER 2. HIGH-PRESSURE POWDER DIFFRACTION TECHNIQUES

(a) As much of the full diffraction pattern should be collected to the highest possible resolution.

(b) The background should be low and smoothly varying so that the intensities from the diffraction peaks can be fitted using the Rietveld method, described in section 2.5.5.

(c) The pattern should be contamination free.

(d) The powder pattern should be corrected for the effects of absorption as well as other experimental conditions affecting the diffracted intensity (such as incident beam polarisation).

(e) The powder should comprise small randomly oriented crystallites to avoid preferred orientation effects or poor powder averaging.

The experimental techniques and beamline equipment that have been developed by members of the group to meet these requirements will be discussed at the end of this chapter.

2.4 Pressure Cells and High-Pressure Techniques

Research at high pressure is very much dependent upon experimental techniques. Every significant technique advancement has resulted in a substantial expansion of our knowledge concerning the behaviour of matter under high pressures. P.W. Bridgman of Harvard University pioneered the study of matter under high pressures for more than half a century until 1961 [23]. He implemented a piston-cylinder apparatus for high-pressure measurement. He also introduced a gasket system for confining a sample between two anvils made of tungsten carbide (an extremely hard material with high compressive strength) opposing each other along a single axis. He surrounded the sample with silver chloride, a soft, solid material that can transmit pressure to the sample in a relatively isotropic manner. A major disadvantage of his massive hydraulically-driven Bridgman anvil cell and earlier designed piston-cylinder devices is that they were too large and heavy to be practical for routine x-ray diffraction measurements. Nevertheless, this type of pressure generating equipment, and similar hydraulically-driven devices, dominated high-pressure science until the advent of diamond-anvil cell (DAC)
in 1959.

The DAC was first introduced for high-pressure studies by Weir et al. in 1959 [6] for infrared absorption measurements and independently by John C. Jamieson [24] for high-pressure x-ray powder-diffraction work. Since then, the DAC has been developed for many kinds of measurement, among them, powder diffraction by Piermarini and Weir [25], for example, and for single-crystal x-ray diffraction by Block and Weir [26, 27], for example. The use of a metal gasket for hydrostatic pressure generation by Van Valkenburg [28], pressure transmitting media by Piermarini et al. [29], and the ruby fluorescence technique for pressure calibration by Barnett et al. [30], initiated a new era in high pressure science where high pressures can be generated easily by applying a fairly modest load by means of bolts. High-pressure studies could then be routinely performed in non-specialised laboratories.

2.4.1 The Diamond-Anvil Cells

There are various designs and types of DAC but they all share the same basic principles. The sample is placed in a pressure chamber created by a hole drilled in a hardened metal gasket that is situated between two flat parallel diamond faces (or culets). Pressure is applied by forcing the diamonds together. A pressure calibrant is placed in the chamber beside the sample and the free volume in the chamber is filled with a pressure-transmitting medium, which is usually a fluid. Figure 2.2 shows the essential details of a gasketed diamond-anvil pressure cell (DAC). The main distinctions between the various types are the pressure generating mechanism and the means by which the diamonds are aligned and supported. Jayaraman has written a comprehensive review of the DAC and the work performed using these devices [31]. Three types of DAC have been used to carry out the experiments described in this thesis: Merrill-Bassett pressure cells [32], a cell designed by Mao and Bell (1980) [33], and the DXR series of pressure cells designed by Adams (1992) [34]. These types pressure cells have a full conical-aperture, where the diamond supports have a cone opening for the transmission of the diffracted x-rays over a wide angle. This type of DAC is optimised for high-pressure ADX powder diffraction where the full Debye-Scherrer rings can be observed. However, a slot-aperture gives better support to the diamonds and consequently can be used to extended the pressure
Figure 2.2: The main components of a Diamond-Anvil Cell, with a metal gasket for confinement of the sample and pressure medium.

range, although there is a greater restriction on the proportion of the Debye-Scherrer rings that can be recorded.

The Merrill-Bassett (M-B) cells were designed for single-crystal work: i.e. the cell was small enough, and light enough, to be mounted on four-circle goniometers or x-ray cameras. Figure 2.3 shows an exploded view of the M-B DAC. The diamond anvils are mounted on beryllium (Be) backing discs which are sufficiently strong and are transparent to x-rays. However, beryllium has disadvantages, most notably it is highly

Figure 2.3: Schematic diagram of a Merill-Bassett diamond-anvil pressure cell. (1) Stainless steel body (2) beryllium discs (3) gasket (4) diamond anvils (From Merrill and Bassett (1974)) [32]
toxic and can, therefore, only be machined in specialised and licensed workshops. The beryllium discs each have a 0.8 mm diameter hole drilled through them to provide optical access to the sample and to allow the use of the ruby fluorescence pressure measuring technique. The Be discs are held in a steel body. On one side, the beryllium disc is held in place by three grub screws for translational alignment. However, there is no means of aligning the culets so that they can be made parallel to one another. The two halves of the cell are kept in alignment by three guide pins and the pressure is applied by tightening the three Allen screws situated at the corners of the cell body. This type of cell has a 50° half-angle cone opening to allow a maximum 2θ of 50° for powder-diffraction or 100° for single-crystal diffraction. With 600 μm culet diamonds, the top pressure for the M-B DAC is in the region of ~15-18 GPa, and with smaller 400 μm culets a pressure of ~25 GPa can be readily achieved.

The cell designed by Mao and Bell (1980) has further modifications to the M-B cell. This enlarged version of the M-B cell was originally designed for low-temperature experiments. Figure 2.4 shows a schematic diagram of this type of pressure cell. Based
Figure 2.5: (a) A cross-section of the DXR4 pressure cell. (b) A cross-section of the DXR6 pressure cell (c) The DXR6 pressure cell. (From Adams (1992))
on the same principles of the M-B DAC, the Mao-Bell cell has two circular halves, each of which has a diamond culet mounted on a Be disc which is in turn supported by a conical-aperture. Both halves of the cell are drawn together using Allen screws. With four guide pins and two pairs of left- and right-handed Allen screws, the pressure is applied by consecutively tightening a pair of oppositely threaded screws. This helps to keep the diamond culets well aligned during the application of pressure, thereby increasing the pressure limit. However, there are no additional improvements for diamond alignment so parallel alignment of the diamond culets is not possible. The Mao-Bell cell has an opening angle of 40° and with 400 μm diamond culets, a pressure of ~35GPa can be reached routinely.

The DXR cells designed by Adams (1992), are based on the piston-cylinder arrangement. They provide facilities for both tilt and translational alignment of the diamonds. As these design features allow very high pressures to be achieved, it is the cell type used most often for the work presented in this thesis. Beryllium is used as the diamond support material, as in the M-B designs. One disc is fitted into a ball-and-socket mechanism in the piston and the other is held with four grub screws in the cell body. Each disc is dome shaped to provide angle-independent x-ray absorption. The piston has three screws for tilt adjustment and the four grub screws in the cell body provide translation alignment for the opposing anvil. Pressure is applied by two oppositely threaded screws which push a steel plate onto the piston and drive it down the cylinder-shaped body of the cell. The DXR cell has an opening angle of 40° and with the provision of a more accurate and stable alignment in comparison to both the M-B and Mao-Bell cells, smaller diamond culets can be fitted (300μm and 200μm culet diamonds are usually used in the DXR cells). A top pressure of ~50 GPa is expected for 300 μm diamonds culet and ~80 GPa for 200 μm diamonds cule. Figure 2.5 shows both of the DXR4 and DXR6 pressure cells.

2.4.2 Diamond Anvils

Diamond is the hardest known substance and has been chosen as an anvil material for this property. It is also relatively transparent to a wide range of electromagnetic radiation, from the infrared through to hard x-rays. Diamonds are classified into two
types (I and II) depending on the level and nature of their impurities [35]. Type I diamonds contain nitrogen (~0.1% or more), and type II diamonds are nitrogen free, although they do contain traces of a variety of impurities at the parts per million level. A further subdivision of type-I diamonds is based on the way in which the nitrogen atoms aggregate. If there is a high nitrogen concentration, and if the diamond has been at a high temperature for a geologically long period of time, the nitrogen atoms tend to cluster as groups, defining type Ia diamonds, and are the most common form recovered in mining. Type Ib diamonds usually contain less nitrogen, and the residual nitrogen atoms do not form clusters. Type I diamonds are relatively cheap and are usually sufficient for the DACs used for x-ray diffraction applications [36] as the nitrogen impurities are not important. In fact, it has been demonstrated that type Ia diamonds which contain a resonable concentration of evenly dispersed nitrogen-platelet impurity, are more resistant to plastic deformation and consequently make good anvils for the Mbar region [37]. Type II diamonds are considerably more expensive than type I diamonds but as they have low luminescence, they are usually used for light scattering studies and are essential for IR spectroscopy.

Early diamond anvil designs are based on the modified brilliant cut where the diamond tips are polished to provide anvil culets. This type of anvil is widely available on the gemstone market and is low in price but does not necessarily give optimum per-
formance for DAC applications. Anvils specially designed for DAC applications have an enlarged table diameter, compared to brilliant cut stones of the same weight, and have an increased anvil angle. This recent design, the so called Drukker-cut, is shown in figure 2.6(a). With this type of diamond anvil, higher pressures can be achieved using the same DAC and culet diameter before anvil failure. The anvil flat is usually set parallel to the (100) or the (110) plane of the diamond. For the highest possible pressures, the end-flat is often bevelled \((2^\circ \rightarrow 5^\circ)\) \([37, 39]\), as shown in figure 2.6(c), so that stress concentration at the edges are reduced and the gasket support to the culets is optimised \([40]\).

### 2.4.3 The Gasket

The introduction of the gasket into the diamond anvil apparatus is a very important development in the history of the DAC. The gasket serves many critical functions in the DAC. It encapsulates the sample in the pressure cell and builds a gradient from ambient to the peak pressure, and most importantly, it provides a support for the anvil tips. In diamond cells, the gasket outside the flat culet area forms a thick ring that supports the anvils like a belt apparatus. Without this support the anvils fracture at modest pressures. The gaskets are generally prepared from a metal sheet of approximately 250 \(\mu m\) thickness which is preindentated between the anvils to the required thickness, usually 40-50 \(\mu m\). A hole is then drilled with a diameter of 50-200 \(\mu m\), typically by spark erosion in the centre of the indent. The metal surrounding the hole is extruded as pressure is applied, and so the gasket forms a pressure chamber in the DAC. Among the many types of metal that can be used, Inconel, an alloy of Ni:Cr:Fe=72:16:8, is extremely popular \([41]\), as is hardened stainless-steel, tool-steel or alloys such as Cu-Be. Tungsten has been chosen as a gasket material in all the experimental studies presented in this thesis due to its hardness, which helps to contain samples at high pressure, and its high x-ray absorption which helps to shield the detector from a considerable fraction of the background scatter produced by the cell components. Once the gasket hole has been prepared and the gasket has been replaced on the diamond, the hole is filled with the powder sample and the pressure transmitting medium.
2.4.4 Hydrostatic Pressure Transmitting Media

The free volume in the pressure chamber is usually filled with a pressure transmitting medium. Fluid media transmit hydrostatic pressure to a sample: i.e. the stress is uniform in all directions. For accurate structure determination at high pressure, it is essential that the sample is contained within a hydrostatic environment. Therefore, it is important that the pressure transmitting medium should remain a fluid over the required pressure range. Several pressure transmitting media have been tested for their hydrostatic limits by Piermarini et al [29]. A mixture 4:1 of methanol:ethanol (one of the most commonly used media) was found to freeze at 10.4 GPa although it appeared to remain sufficiently soft to provide quasi-hydrostatic conditions up to \(~20\) GPa where it become steadily less hydrostatic. For the high pressure work presented in this thesis, dry white mineral oil was used as a pressure transmitting fluid to prevent sample oxidation.

2.4.5 Pressure Measurement

In early high-pressure work, the conventional method for pressure determination is that where a reference material with a known equation of state is used. For this reason, NaCl is one of the most commonly used materials for pressure calibration [42]. The reference material is mixed with the sample and from the shift of its diffraction peaks with pressure, the unit cell volume of the reference material can be calculated and the pressure subsequently determined using its equation of state. With this method, the powder pattern will contain contamination peaks from the reference material and the method is, therefore, not ideally suited for accurate structure determination (according to the criteria previously stated in section 2.3).

A more convenient method for pressure measurement in a DAC is the ruby fluorescence technique, first introduced by Forman in 1972 [43]. Using well-established freezing points of several liquids and a range of solid-solid transitions at well-known fixed points, he demonstrated that the \(R\) lines of ruby (\(Cr^{3+}\) doped \(Al_2O_3\)) shift linearly with hydrostatic pressure in the range of 0.1-2.2 GPa, and that the \(R\) lines broaden if the ruby experiences nonhydrostatic stresses. Further work by Barnett et al. has made the
ruby fluorescence technique a very rapid and convenient method for the measurement of pressure [30]. With this method, the pressure reference material makes virtually no contribution to the powder pattern as the ruby is a single-crystal, is a weak x-ray scatterer and has an extremely small volume relative to the sample (the ruby is $\sim 10 \mu m$ in diameter relative to a sample volume diameter of $\sim 100 \mu m$). When the light from a He-Cd laser is focused on the ruby chip the $R$ fluorescence lines are excited. These ruby lines, $R_1$ and $R_2$, have wavelengths of 692.7 nm and 694.2 nm respectively at ambient pressure. The lines shift linearly to longer wavelengths with pressure over the range 0.0-2.2 GPa [43]. More recently, Piermarini and Block [44] calibrated the shift of the ruby lines against the equation of state of NaCl and they found that the shift appears to be linear up to 29 GPa. This can not be extended beyond 29 GPa as NaCl undergoes a phase transformation to the CsCl structure. At very high pressures ($\sim 100$ GPa) Mao et al observed a slight non-linearity in the pressure dependence of the wavelength shift of the $R$ lines and that linear scale underestimates the pressure [45]. They have proposed:

$$P = 380.8 \left[ \left( \frac{\Delta \lambda}{694.2} + 1 \right)^5 - 1 \right]$$  \hspace{1cm} (2.3)

where $P$ is pressure in GPa and $\Delta \lambda$ is the shift in nanometers of the $R_2$ ruby line from its ambient pressure value at 694.2 nm. A plot of the ruby line shift, $\Delta \lambda$, is shown in figure 2.7, where the dotted line represents a linear extrapolation according to Piermarini et al. and the solid line is given by equation 2.3. The pressure measurement apparatus used at Daresbury, where most of the work for this thesis has been performed, is shown in figure 2.8.

The system, manufactured by Dilor, uses a He-Cd laser to excite the ruby fluorescence. The laser light travels through a fibre optic cable and is focused onto the ruby in the DAC. The fluorescent light from the ruby then travels back along the same path and is deflected by a beam-splitter into the spectrometer. The spectrum received by the fibre optic cable consists of several fluorescence lines of different wavelengths and a background signal. This fluorescence is then dispersed by a grating onto a photo-diode array and the collected spectrum is displayed and recorded on a personal computer. The pressure is then calculated from the shift of the $R_2$ line using equation 2.3.
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Figure 2.7: Ruby fluorescence line shifts with pressure, $\Delta \lambda$ (nm) vs pressure (GPa) (From Mao et al. 1978) [45].

Figure 2.8: Schematic diagram showing the ruby pressure measurement equipment at SRS Daresbury.
The main disadvantage of this method is that the pressure can not be measured at the same time as the diffraction pattern is recorded. This can cause errors in pressure determination due to pressure variations during exposure. However, this error can be easily minimised by measuring the pressure immediately before and after the diffraction pattern has been recorded.

2.5 Experimental Setup and Data Processing

2.5.1 Image-Plate Set-up on Station 9.1

The set-up for high-pressure powder diffraction developed by the Edinburgh group is designed for use on station 9.1 at SRS, and is based on the original image-plate techniques, first introduced by the group of Shimomura et al. [46]. The main improvement over the original Japanese techniques is that full-conical aperture DACs are used which allow complete Debye-Scherrer rings to be observed. Also software for two-dimensional data processing has been developed [47]. These developments will be described in section 2.5.2. The principal components of the beamline equipment for station 9.1 are shown in figure 2.9.

Station 9.1 is situated roughly 15 m from a 5 T superconducting "wiggler" magnet. A double-bounce channel cut Si(111) monochromator is used to select the required wavelength for ADX. There is, however, a significant amount of \( \lambda /3 \) diffraction from the Si monochromator. The x-ray beam then passes through tungsten carbide slits which reduce the beam dimensions to 0.5 mm x 0.5 mm. Lead shielding encloses the beam emerging from the monochromator housing to reduce the background caused by air-scatter, until it is finally collimated to a circular beam of 50-100 \( \mu \text{m} \) diameter by a platinum pinhole. Platinum is selected for the pinhole material as it provides enhanced attenuation of the \( \lambda /3 \) harmonic in the incident beam. The platinum K absorption edge strongly attenuates wavelengths shorter than 0.1582 Å (i.e. \( \lambda /3 \) when \( \lambda =0.4745 \) Å). Typically, the experiments presented in this thesis are conducted with a wavelength of 0.4654 Å (the Cd edge). With a longer wavelength, the \( \lambda /3 \) component would pass through the platinum and the pattern would be contaminated with the low-angle \( \lambda /3 \) diffraction pattern from the gasket material.
2.5.2 Sample Alignment

Based on similar techniques employed by Shimomura et al. at the Photon Factory [46], an optical method is used to align the sample accurately on the x-ray beam. These techniques have been extensively developed by members of the Edinburgh group in the past decade to meet the requirement for the highly accurate high-pressure structure determinations.

To align the sample to the x-ray beam, the pressure cell is mounted on the sample stage. The telescope is focused on the sample through the diamond. The cell is removed from the sample stage and replaced by a piece of x-ray sensitive paper which is mounted on its own holder. This holder allows the position of the paper to be adjusted so the paper can be focused when viewed through the telescope without altering the telescope setting. After a 90 second exposure to the x-ray beam, a small black mark, indicating the position of the beam, can be seen through the telescope. The telescope is then moved vertically and horizontally perpendicular to the beam direction until the crosshair is aligned with the centre of the mark. The pressure cell is then replaced, and the sample stage is adjusted vertically and horizontally until the centre of the sample coincides with the telescope crosshairs. The sample is now aligned with the x-ray beam and ready for exposure. The telescope is removed during the exposure. However, with this procedure, significant contamination scatter from the gasket is still possible as a tilt of either the telescope optic axis or the normal to the diamond table face can shift the image of the sample (i.e. its apparent position) away from its true position. The
Edinburgh group has developed techniques to overcome this significant problem. The key to this new technique is the provision of an alignment laser. To align the laser to the x-ray beam, two pieces of x-ray sensitive paper are used. One piece is held in place over the end of the tube on the lead shielding, and the other is placed close to the laser at the far end of the optical bench. When exposed, both pieces of paper indicate the path of the x-ray beam. A hole is the carefully pierced through the mark on the paper closest to the laser and the laser is adjusted so that its beam passes through this hole and illuminates the mark on the other paper held on the shielding tube. The laser beam is then coincident with the x-ray beam. The beamline equipment is then aligned to the laser.

The pressure cell alignment procedure relies heavily on the accuracy of the telescope. It has been shown [48] that the principal sources of error in such a procedure are related to the high refractive index of the diamond anvils. If the telescope axis is not exactly parallel to the x-ray beam and the diamond face closest to the telescope is not exactly perpendicular to the beam, then the image seen through the telescope is significantly shifted. The alignment of the telescope is therefore a necessary step at the start of the experiment. To align the telescope's optic axis to the laser beam (and hence the x-ray beam), the objective lens is replaced by a mirror and the eyepiece is removed so that the laser beam can pass through the telescope tube. The tube is then adjusted so that the laser is reflected back to the source. The same technique is also applied to the pressure cell where the laser is reflected from the back of the diamond. To ensure that all the different types of pressure cell are always placed at the same position on the sample stage, each cell has its own holder. It is the holder that is shimmed at the start of the experiment to ensure that the diamond through which the sample is viewed is aligned accurately with the beam. The whole pressure cell alignment procedure takes approximately 10 minutes and the accuracy is sufficiently good to allow a beam of 75 μm diameter to pass cleanly through a 100 μm diameter gasket.

2.5.3 Image-Plate Area Detector

Before the advent of the image-plate detector (IP), high-pressure x-ray powder diffraction studies have seldom been used to obtain accurate structural information due to
the poor quality of the measured intensity data. As a detector, X-ray film has been used to record x-ray diffraction patterns from the earliest days of structural crystallography. Photographic materials consist of a light-sensitive emulsion coated on a glass or plastic film. The emulsion contains light sensitive crystals of silver halide suspended in gelatin. On exposure, the silver halide crystals that receive radiation form a latent image. Subsequent chemical treatment converts the exposed silver halide crystals into a black deposit of silver. After development, devices known as a microdensitometers are used to obtain the optical density (or transmission) data required for quantitative analysis of the images on the photographic film. These devices vary somewhat in their design, but they are all based on a simple optical system that projects a visible light beam through a small region of the film. As the film is moved in front of the light beam or the beam is moved across the film, a photodetector measures the relative intensity of the light transmitted through the film. The results are plotted or printed directly, or digitised for further processing by a computer. The IP, originally developed for medical imaging, shares essentially the same principles as photographic film as they are both two-dimensional detectors. The IP has played an important role in high-pressure angle-dispersive powder diffraction over the last decade due to its superior performance for diamond-anvil cell work. The main features are its high sensitivity to the short wavelengths needed to penetrate pressure cells (<0.7 Å). At this wavelength, the IP can detect intensity levels as low as 10 photons per pixel (≈ 0.1 × 0.1 mm²) while the minimum number of photons detectable by x-ray film is said to be of the order of thousands. The IP also has a large dynamic range on the order of ~10⁵, about three orders of magnitude greater than film, and low intrinsic noise (about 300 times less than photographic film). The IP data are also naturally digitised. These properties make the IP an ideal detector for high pressure ADX experiments and for accurate structure determination.

The IP consists of phosphor materials BaFBr:Eu²⁺ bonded onto a flat aluminium backing plate and covered with a layer of transparent plastic to protect the active part of the IP. The IPs used for the experiments detailed in this thesis have dimensions of 20 cm × 25 cm (approximately A4 size). The x-ray photons incident on the phosphor screen create excited electron states, which emit visible light when stimulated by a He-Ne laser. This phenomenon is called photostimulated luminescence. The electronic transition
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generates the luminescence with an intensity proportional to that of the original x-ray. For station 9.1 at SRS, Daresbury, the IP is kept in a light-tight cassette during exposure. This cassette is situated about 300 mm from the sample stage. At this distance, it allows the IP to collect diffraction patterns up to 30° in 2θ. A piece of thin lead is placed on the cassette at the beam position to absorb the intense λ component of the incident beam. However, the beam stop is partially transparent to the λ/3 component which leaves a mark on the IP indicating the incident beam position. This mark is useful for data integration as detailed in section 2.5.4. After exposure, the IP is removed from the cassette and inserted into the IP reader (a Molecular Dynamics 400A Phosphor Imager is used in all the studies at SRS). A He-Ne laser is used to stimulate the phosphor during reading, the emitted light being collected by a fibre-optic bundle and detected by a photomultiplier tube, where the intensity is converted into a voltage and subsequently a digital signal. The amplified and digitally processed signal is stored on a microcomputer which controls the IP scanning process. It takes approximately 10 minutes for a standard A4 size IP to be read. An 11 Mbyte data file consisting of 2816 × 2052 pixels is created. (the pixel dimensions are approximately 88 μm × 87 μm.) The plate can be used repeatedly, since exposure to visible radiation restores it to its initial condition.

During the scanning process, spatial and intensity distortions are introduced into the data by the scanning mechanism. Therefore, these distortions need to be calibrated before any subsequent data analysis. With a Molecular Dynamics reader, the IP is read by mechanically tracking the plate over a laser, which raster scans perpendicular to the mechanical motion. The spatial distortion in the direction perpendicular to the raster direction arises from the uneven step of the wire pulley mechanism that draws the IP over the laser. The other source of spatial distortion is related to the laser. The fixed laser is rastered across the plate by a motorised mirror mechanism that reflects the laser beam onto the IP. This causes a variation in the distance that the laser beam has to travel from the mirror to the IP when the laser is rastered across the plate and so causes the laser spot size to change as the beam sweeps across the plate. Also, the constant angular velocity of the mirror maps to a variable linear velocity of the beam across the plate. This affects the real size and separation of the pixels across the plate. The distortion in the laser raster is, however, largely reproducible.
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The spatial calibration for both distortions is generally performed by placing a metal foil, usually nickel foil, with a grid of holes with a known spacing and size (2 mm apart with 200 μm holes) onto the IP. A parallel beam of x-rays with an area greater than that of the IP is then allowed to expose the plate through the foil [49]. Provided that the energy of the incident beam is not too high, the x-ray beam will be absorbed by the nickel and pass through the holes leaving an image of uniformly spaced spots on the IP. The IP is then scanned in the normal manner and the location in, pixels, of the spots is determined, usually by fitting a function to each spot location. Since the exact pixel position of each spot can be calculated, it is possible to calculate the spatial distortion at the position of each spot. The spatial distortion at pixel positions between the spots can then be determined by interpolation.

The intensity distortions come from non-uniform sensitivity of the reader optics along the laser raster direction and the non-linear intensity response of the reader. To calibrate the non-uniform sensitivity of the reader optics, a strip of IP is exposed to a uniform incident intensity and then read in the normal manner. The data are integrated along the exposed strip in the direction perpendicular to the laser scan direction to produce an intensity variation graph across the strip in the laser raster direction. This graph is then used to normalise the IP data subsequently scanned by the reader. These distortions are periodically calibrated by Molecular Dynamics engineers.

2.5.4 Data Processing

This section describes the operation of the image-plate data analysis software, called EDIPUS [50], which has recently been developed by Dr. S. A. Belmonte from the previous version called PLATYPUS [47], originally written by Dr. R. O. Piltz (which has been used by the Edinburgh High Pressure Group for the past decade). The program runs on the "X Windows System" with a graphical-user-interface (GUI), which allows the user to view easily and integrate the raw IP data. The main feature of this program is that it produces a 1-d powder pattern from a 2-d image after applying corrections for spatial distortion, IP tilt and incident beam polarization.

In practice, the IP is not perfectly perpendicular to the incident beam. This results in the circular Debye-Scherrer rings being recorded as ellipses on the IP. The diffraction
peaks in the integrated pattern will be broad or even split if this is not corrected for. To calculate the tilt of the IP, the image is sectored into 60 azimuthal sectors about the centre of the pattern. The centre of the pattern is usually obtained by fitting the incident beam spot as described in the previous section. However, if there is no beam spot on the pattern, the program allows the user to refine the centre of the pattern along with the plate tilt. Provided that the IP is tilted with respect to the incident beam, the peaks in these 60 sectors will not all line-up. A routine called “sharpen” is then applied to adjust the tilt parameters, which change the effective radial position of the data points in each sector, until all the peaks in every sector line-up.

The next step is to “rebin” the data into the final 1-d pattern. In this process, an effective radius from the centre of the pattern is calculated for every pixel in the image. The calculation is performed to take into account the plate tilts and spatial distortion, and the intensity of the pixel is added to the appropriate bin. Generally, the pixel will overlap two bins so the intensity (I) is partitioned and added to the appropriate bin. For a pixel at radius $r$, where $r_1 < r < r_2$, the intensity is partitioned so that the intensity $(r-r_1) \times I$ is added to $r_1$ and $(1-(r-r_1)) \times I$ is added to $r_2$. In the rebinning process, to increase the speed of image processing, full calculation of pixel radius and intensity correction are carried out on every 16th pixel and the radius and intensity correction of the intervening pixels are calculated by quadratic interpolation. The integrated profile is then obtained in the form of a 1-d pattern.

However, this profile is still in the form of intensity vs. radius in pixels. Before carrying out any further data analysis, the data needed to be converted into intensity against scattering angle ($2\theta$), which requires that the distance between the sample and image-plate be known accurately. For each pressure cell, the sample to plate distance is obtained by collecting a diffraction pattern from a sample with known lattice parameters. From the lattice parameters of the calibrant and the known wavelength, the $2\theta$ values of the observed diffraction peaks can be calculated. A polynomial function is then fitted to the measured pixels positions of the observed reflections and this function is used to convert the pixels to $2\theta$.

However, converting from pixels to $2\theta$ using a polynomial function produces unequal $2\theta$ steps. This makes the converted data unsuitable for most available Rietveld refinement
packages, which require equal 2θ spacing. A program has been written by Dr. S. A. Belmonte [50] to overcome this problem. The program includes all the required data conversions and applies the interpolation into equally spaced 2θ steps.

2.5.5 Crystal Structure Determination and Refinement

The first step towards solving an unknown crystal structure from its powder pattern is the determination of the lattice type and lattice parameters. This is usually performed by extracting the 2θ positions of the diffraction peaks from the data using a peak fitting program such as XFIT [51]. Indexing programs are then used to find possible unit cells and indexing by a trial-and-error method. The indexing programs DICVOL [52, 53] and CRYSFIRE [54] were used by the author for the structure solutions presented in this thesis. Such programs require a list of very accurately measured 2θ values otherwise the programs will fail to find the correct solution. However, this step can sometimes be achieved by picking a unit cell that is, in some way, related to the unit cell of a known adjacent (i.e. lower or higher pressure) phase. After a unit cell has been determined, investigation of the indexing and systematic absences are carried out to pin down the possible space groups. The next step is to find approximate atomic coordinates. This is achieved by trial-and-error and can, sometimes, be inferred from correlations in the relative intensities of groups of principal reflections. Structure refinement of the initial, crude, model can then be performed in order to obtain the final, accurate, structure. H.M. Rietveld introduced a least-squares method for whole-pattern fitting to refine accurate crystal structures from powder data in 1969. This method was originally used for neutron powder diffraction studies [55] and then extended to x-ray powder diffraction [56]. In Rietveld refinement, the powder pattern is calculated from starting values of the lattice parameters and atomic coordinates along with other experimental parameters such as peak width variation, preferred orientation of the sample etc. The parameters of the profiles are varied until the match between the observed and calculated profiles is optimised simultaneously over the whole pattern using the least-squares method. The quantity minimised in the least-squares refinement is the residual, $\chi^2$, in:
where \( w_i \) is statistical weight at point \( i \), often set to \( 1/y_i \) based on counting statistics, \( y_{oi} \) is the observed intensity at point \( i \) and \( y_{ci} \) is the calculated intensity.

A powder diffraction pattern of a crystalline material may be viewed as a collection of individual reflection profiles, each of which has a peak height, a peak position, and an integrated area which is proportional to the Bragg intensity, \( I_K \), where \( K \) represents the Miller indices, \( h, k, l \) for a Bragg reflection. \( I_K \) is proportional to the square of the absolute value of the structure factor, \( |F|^2 \), previously mentioned in section 2.2. It is a crucial feature of the Rietveld method that no effort is made in advance to allocate observed intensity to any particular Bragg reflections nor to resolve overlapped reflections. Therefore, the principal disadvantage of the Rietveld method is that the starting structural parameters must be reasonably close to the correct values for the least-squares algorithm to function properly.

There are a number of methods used to assess the quality of the fit from \( \chi^2 \), two of which are given below:

\[
R_{wp} = \sqrt{\frac{\chi^2}{\sum_i w_i y_{oi}^2}} \quad (2.5)
\]

\[
S = \sqrt{\frac{\chi^2}{N - P}} \quad (2.6)
\]

where \( R_{wp} \) is the weighted residual and is independent of the scaling of the input data. \( S \) is the goodness-of-fit which takes into account the number of data points \( N \) and the number of the refined parameters \( P \). The ideal value of \( S \) is 1. If \( S \gg 1 \) then the model is not a good description of the data and if \( S < 1 \) then there are more parameters being refined than are justified by the data. The value of \( S \) then gives an idea of how well the model describes the data and whether the number of parameters refined is justified by the input data.

It is important to realise that in Rietveld refinement, the best solution is found by the
iteration where a trial set of parameters is tested at each iteration to try to minimise \( \chi^2 \). Thus, it is possible to find a set of parameters where \( \chi^2 \) is minimised locally but it is not at its true global minimum. And it is impossible to tell whether \( \chi^2 \) is at a local minimum or not. The local minimum is the lowest point in some limited region of the domain surface and the global minimum is the lowest point anywhere on the whole domain surface. It is also important to note that this method is a structure refinement method. It is not a structure solution method. All the refinements presented in this thesis are performed by the Rietveld refinement package GSAS [57].

2.6 Concluding Remarks

This chapter has provided the basis of the high-pressure powder diffraction techniques developed by members of the High Pressure Group of the University of Edinburgh and used by author to carry out the experiments compiled in this thesis. However, minor, but crucial, data sets were collected on station ID-9 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, which were performed on a slightly different set-up but were still based on essentially the same ADX and image-plate techniques.
Chapter 3

Sr-III: The Tetragonal $\beta$-tin Structure

3.1 Introduction

This chapter begins with a brief chronological review of the high-pressure structural systematics of Sr which have drawn considerable interest from researchers of various disciplines for a substantial period of time. Earlier work on high-pressure structural studies of Sr by Holzapfel et al. were all based on EDX techniques which usually suffered from the limitations of the detectors, leading to unreliable data, unsuitable for structural refinement. In contrast, with the previous high-pressure structural studies of Sr, the structural pressure dependence of strontium has been studied by the author using angle-dispersive powder diffraction techniques with the image-plate area detector system. The two-dimensional diffraction data has allowed the clear identification of an accompanying minor phase in the Sr-III phase stability range which has enabled the structure of Sr-III to be assigned correctly. Although the work on the structure solution of Sr-III was not solely performed by the author, nevertheless, the author was closely involved in the experimental work and carried out further studies to both understand the detailed nature of the Sr-III structure and its relationship with essentially identical structures in other materials and to provide an initial identification of the accompanying phase. This accompanying phase persists up to the Sr-V phase where it undergoes a further phase transition.
3.2 High-Pressure Structural Studies of Sr

The alkaline-earth metals Ca, Sr and Ba are well known for having pressure-induced $s \rightarrow d$ electron transfer and they have a rich variety of high-pressure crystal structures. The study of this phenomenon and the high-pressure structures of these divalent metals has been a challenge in condensed matter physics for both experimental and theoretical methods for some time. In the early high-pressure work on Sr, P.W. Bridgman used electrical resistance measurements to pinpoint a transition at 4 GPa in 1938 [8].

A higher pressure range investigation using piston-cylinder apparatus with resistance measurement has been performed by Stager and Drickamer up to 50 GPa [9] to confirm this transition. This high pressure structure, Sr-II, was subsequently identified as having a body-centred cubic structure by McWhan and Jayaraman using x-ray powder-diffraction experiment at 4.2 GPa using piston-cylinder apparatus [15]. However, it was not until 1984 that systematic high-pressure structural investigations of Sr were carried out by Olijnyk and Holzapfel in their original high-pressure energy dispersive powder diffraction studies [20]. The following sequence was reported: the transition from the ambient pressure Sr-I (fcc) structure to the Sr-II (bcc) structure was observed at 3.5 GPa; and the phase was found to transform to a relatively simple, but unsolved Sr-III phase at 26 GPa; Sr-III was found to transform to a more complex Sr-IV phase at 35 GPa. At 46 GPa the highest pressure reached, they reported another phase transformation, to Sr-V, that appears to have a very similar diffraction pattern to that of Ba-IV.

A more recent study by Winzenick and Holzapfel [16] has identified Sr-III as having an orthorhombic structure with Imma symmetry at 31.3 GPa, similar to that of the high-pressure phase of Si [17] and Ge [18].

These previous studies on the high-pressure phases of Sr were conducted with energy-dispersive x-ray powder diffraction techniques [20]. The accompanying limitations of these techniques such as low resolution, contamination of the powder pattern from fluorescence and escape peaks and the lack of texture information leads to severe difficulties in correctly identifying the high-pressure phases. In view of these experimental problems, a full re-examination of the high-pressure structures and transitions in strontium has been carried out using angle-dispersive powder-diffraction techniques with the image-plate detector on station 9.1 at the SRS Daresbury Laboratory.
3.3 Experimental Details

The samples, of 99.96+ % purity, were obtained from either Johnson Matthey or Aldrich Chemicals in the form of vacuum distilled large granules stored in sealed glass ampoules under argon. The granules were removed from the ampoules prior to use and subsequently stored in white mineral oil which was initially dried and stored under vacuum. Suitably sized samples for loading into the diamond-anvil cells were cut from the granules under dried white mineral oil so that any residual surface oxide was carefully removed. Diamond-anvil cells of the Diacell DXR-5 and DXR-6 designs and of the Mao-Bell design were used. The Druker cut diamond anvils had either 400 μm or 300 μm culets and the preindented tungsten gaskets had spark-eroded holes of 100 μm diameter. Samples were loaded with dried white mineral oil as a pressure-transmitting medium to prevent oxidation, and the pressure was measured to ± 0.1 GPa using the ruby-fluorescence techniques. Diffraction data were collected at the Synchrotron Radiation Source, Daresbury, with a wavelength of 0.4654 Å. The incident beam was collimated by a platinum pinhole to a diameter of 75 μm. The two dimensional powder patterns collected on the image plates were read on a Molecular Dynamics 400A PhosphorImager and then integrated to give conventional one-dimensional diffraction profiles. Details of the experimental setup and pattern integration software have been described previously in chapter 2.

3.4 The Behaviour of Sr at Relatively Low Pressure

The purpose of collecting and refining data in a relatively low pressure range was to determine the sample quality and to calculate the relative volume for comparison with higher-pressure studies. In order to understand the behaviour of Sr at high pressure, it is also important to have a full understanding at lower pressures. At ambient pressure, the Sr diffraction data show clean Sr-I (fcc) patterns indicating that the samples were suitable for the high-pressure experiments. Rietveld refinements were also performed in this phase for its full pressure range up to 3.5 GPa where it transforms to the Sr-II (bcc) phase. Figure 3.1 shows a Rietveld refinement of the Sr-I (fcc) structure at 1.4 GPa with a lattice parameter \( a = 5.87109(10) \) Å and \( R_{wp} = 0.0246 \).
Figure 3.1: Rietveld refinement of the Sr-I (fcc) structure at 1.4 GPa. The red dotted line shows the observed profile and the green solid line shows the calculated profile. The tick marks below the profiles show the peak positions and the difference between the observed and calculated profiles is indicated under the tick marks. The inset shows a face centred cubic close pack structure.

Figure 3.2: Rietveld refinement of the Sr-II (bcc) structure at 12 GPa. The red dotted line shows the observed profile and the green solid line shows the calculated profile. The tick marks below the profiles show the peak positions and the difference between the observed and calculated profiles is indicated under the tick marks. The inset shows a body centred cubic structure.
On compression, the Sr-II (bcc) phase was first observed in a mixed-phase sample with Sr-I (fcc) at 3.5 GPa, in excellent agreement with the transition pressure of 3.5 GPa observed by Olijnyk and Holzapfel [20]. Rietveld refinements were also performed in this phase for the full range up to the transition to the Sr-III phase. Figure 3.2 shows the Rietveld refinement of Sr-II at 12 GPa with a lattice parameter $a = 4.08384(4) \, \text{Å}$ and $R_{wp} = 0.0257$. The result of Rietveld refinement for Sr-I and Sr-II are presented in figure 3.3. In this pressure range, Sr transforms from the Sr-I metallic phase at ambient pressure to semi-metallic under pressure, and remains in that state up to about 3.5 GPa when it transforms to Sr-II where it becomes metallic again [9]. This transition, therefore, strongly suggests that there might be an accompanying electronic transition which can also be seen from its high compressibility in the lower pressure range before it becomes less compressible at higher pressure. Figure 3.3 reveals a very compressible Sr at lower pressure range. At 23 GPa, the relative volume of Sr is reduced to only 47% of its original volume.

The transformation from Sr-II to Sr-III initially appeared at approximately 24.4 GPa and manifested itself by the formation of bright spots on the two-dimensional diffraction patterns. On subsequent pressure increase a larger number of spots appeared as more Sr-II transformed to Sr-III with an accompanying decrease in the intensity of the Sr-II contribution to the diffraction pattern. Recrystallisation of Sr-II to Sr-III was complete.
CHAPTER 3. SR-III: THE TETRAGONAL $\beta$-TIN STRUCTURE

Figure 3.4: The integrated profile of the powder diffraction pattern taken at 34.8 GPa. The principal smooth lines are indicated by arrows. The inset shows a close up of the first three main peaks revealing the difference in texture. The strongest of the smooth lines from the additional phase is indicated by the white arrow in the inset.

at 26.8 GPa, which is in good agreement with the pressure of 26 GPa determined by Olijnyk and Holzapfel [20]. However, the two dimensional images obtained from the IP revealed two different types of Debye-Scherrer rings — smooth rings and spotty rings. It is important to note that this texture information, which was obtained from the IP data, can not be detected by EDX techniques and hence would not have been observed previously. The integrated profile and the two-dimensional image are shown in figure 3.4. This two-dimensional image clearly distinguishes the majority phase spotty lines from the formation of an additional smooth phase accompanying the Sr-II to Sr-III transition.

In order to re-examine the $Imma$ structure as the solution for Sr-III, the first attempts were made to fit the whole Sr-III pattern using the $Imma$ structure proposed by Winzenick and Holzapfel [16]. Figure 3.5 shows a comparison of the calculated pattern with the observed pattern, using the cell of Winzenick and Holzapfel, collected from the same sample at 34.8 GPa. Clear discrepancies between the observed and calculated splittings of the peaks corresponding to the 031 and 301 reflections can be seen. Moreover, the 200 reflection of the orthorhombic $Imma$ cell does not correspond with the spotty lines of the recrystallised phase but most closely coincides with the
strongest smooth line from the accompanying phase. This indicates that the Imma structure proposed by Winzenick and Holzapfel is based on a mixed phase of smooth and spotty pattern which is also suggested by a number of un-indexed peaks in their original powder patterns that can be identified with the accompanying smooth phase. Figure 3.6 shows a Imma structure proposed by Winzenick and Holzapfel.

In table 3.1, subsequent unit cell indexing of only the spotty lines determined that they could be indexed on a body-centred tetragonal cell, where all the reflections with \( h + k + l = \) even are present, with cell dimensions \( a = 5.5010(8) \) Å, \( c = 2.9571(8) \) Å at 34.8 GPa. The systematic absences were consistent with the \( I4_1/amd \) spacegroup of the \( \beta \)-tin structure \( (0, \frac{1}{2}, \Delta = \frac{1}{4}) \) and so a Rietveld refinement of the pattern was then undertaken for the full pressure range, assuming this structural model, and a correction for preferred orientation. The Imma structure can also be viewed as an orthorhombic distortion of the \( \beta \)-tin structure. (i.e. when \( a = b \) and \( \Delta = 0.25 \) the Imma structure becomes \( I4_1/amd \)) The result from Rietveld refinement is shown in figure 3.7 and it is apparent that, apart from the extra peaks from the additional "smooth" phase, the \( \beta \)-tin structure gives an excellent fit to the data. Any shift away from the ideal \( \beta \)-tin coordinates so that \( \Delta \) is increased from its ideal value of 0.25 [17, 18], places
### Table 3.1: The indexing of only spotty lines at 34.8 GPa given a tetragonal structure with lattice parameters $a = 5.5010(8) \text{ Å}$ and $c = 2.9571(8) \text{ Å}$.

<table>
<thead>
<tr>
<th>$h \ k \ l$</th>
<th>Observed $2\theta$</th>
<th>Calculated $2\theta$</th>
<th>Difference $2\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 0 0</td>
<td>9.710</td>
<td>9.706</td>
<td>0.003</td>
</tr>
<tr>
<td>1 0 1</td>
<td>10.252</td>
<td>10.251</td>
<td>0.001</td>
</tr>
<tr>
<td>2 2 0</td>
<td>13.740</td>
<td>13.743</td>
<td>-0.004</td>
</tr>
<tr>
<td>2 1 1</td>
<td>14.130</td>
<td>14.135</td>
<td>-0.005</td>
</tr>
<tr>
<td>3 0 1</td>
<td>17.169</td>
<td>17.175</td>
<td>-0.006</td>
</tr>
<tr>
<td>1 1 2</td>
<td>19.391</td>
<td>19.386</td>
<td>0.005</td>
</tr>
<tr>
<td>4 0 0</td>
<td>19.496</td>
<td>19.483</td>
<td>0.013</td>
</tr>
<tr>
<td>3 2 1</td>
<td>19.754</td>
<td>19.764</td>
<td>-0.010</td>
</tr>
<tr>
<td>4 2 0</td>
<td>21.811</td>
<td>21.809</td>
<td>0.001</td>
</tr>
<tr>
<td>4 1 1</td>
<td>22.062</td>
<td>22.062</td>
<td>0.001</td>
</tr>
<tr>
<td>3 1 2</td>
<td>23.842</td>
<td>23.841</td>
<td>0.001</td>
</tr>
<tr>
<td>4 3 1</td>
<td>26.081</td>
<td>26.085</td>
<td>-0.004</td>
</tr>
</tbody>
</table>
Figure 3.6: The *Imma* structure with atoms in the 4(e) positions at \((0, \frac{1}{2}, \Delta)\) relative to the origin chosen here. The origin has been moved from its standard position to facilitate comparison with the \(\beta\)-tin structure. The solid lines indicate nearest neighbours.

Intensity into systematically absent reflections. This may also explain why the *Imma* structure of Winzenick and Holzapfel has \(\Delta\) equal to the ideal \(\beta\)-tin value as otherwise intensities would have been predicted for reflections at positions where no diffraction peaks were observed in their data. Figure 3.7 shows the Rietveld refinement of Sr-III with the \(\beta\)-tin structure at 30.2 GPa with lattice parameters \(a = 5.59607(18)\), \(c = 3.01349(17)\) and \(R_{wp} = 0.0420\). Therefore, Sr-III is now identified as having a tetragonal \(\beta\)-tin structure and not orthorhombic *Imma* as previously reported. The orthorhombic structure previously proposed is shown to be a wrong identification based on a mixed phase. Additional support for this conclusion comes from the observation that the proportion of the smooth component varies considerably from sample to sample, and is sometimes almost absent giving an excellent fit to the \(\beta\)-tin structure as shown in figure 3.8.

The \(c/a\) ratio for the \(\beta\)-tin Sr cell is 0.5378 at 34.8 GPa which is similar to those observed in Sn (\(c/a = 0.5455\) at ambient pressure) [58], Si (\(c/a = 0.5498\) at 11.7 GPa) [17] and Ge (\(c/a = 0.5575\) at 12.6 GPa) [18]. The only other known high-pressure structure with the "\(\beta\)-tin" spacegroup and coordinates outside the group-IV elements
Figure 3.7: Rietveld refinement of Sr-III at 30.2 GPa with the \(\beta\)-tin structure. The principal smooth lines have been indicated by arrows.

Figure 3.8: Rietveld refinement of the Sr-III \(\beta\)-tin structure at 32.7 GPa with almost no smooth phase present.
Table 3.2: The results from Rietveld refinement of the \( \beta \)-tin structure over the whole pressure range of Sr-III. The \( c/a \) ratio is of a comparable value to those of group-IV elements.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>( a )</th>
<th>( c )</th>
<th>( c/a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.9</td>
<td>5.6863(5)</td>
<td>3.0615(3)</td>
<td>0.538</td>
</tr>
<tr>
<td>28.4</td>
<td>5.65132(14)</td>
<td>3.04417(12)</td>
<td>0.5386</td>
</tr>
<tr>
<td>30.2</td>
<td>5.59607(18)</td>
<td>3.01349(17)</td>
<td>0.5385</td>
</tr>
<tr>
<td>31.2</td>
<td>5.56294(19)</td>
<td>2.99116(11)</td>
<td>0.5376</td>
</tr>
<tr>
<td>32.7</td>
<td>5.53877(13)</td>
<td>2.97941(11)</td>
<td>0.5379</td>
</tr>
<tr>
<td>35.0</td>
<td>5.53002(2)</td>
<td>2.96748(14)</td>
<td>0.5366</td>
</tr>
<tr>
<td>36.3</td>
<td>5.46133(3)</td>
<td>2.90878(14)</td>
<td>0.5326</td>
</tr>
</tbody>
</table>

is that of Cs-IV, which has an elongated unit cell with lattice parameters \( a = 3.349(6) \) Å and \( c = 12.487(3) \) Å at 8.0 GPa [1]. The axial ratio, \( c/a \), of the tetragonal Cs-IV structure therefore has the value of 3.728 at 8.0 GPa, significantly different from the "ideal" \( \beta \)-tin structure. Rietveld refinements were also performed over the full pressure range of Sr-III to ensure that this proposed structure gives an acceptable fit over the pressure region where the Sr-III phase is stable. The results show an evidence of Sr-III structure being "ideal" \( \beta \)-tin structure and is shown in table 3.2. The \( c/a \) ratio is found to be constant and comparable to those of group-IV elements throughout this pressure range. The marked discrepancy in the \( c/a \) ratio for Cs is also reflected in the structural conformation, as shown in figure 3.9, where each atom has 8-fold-coordination rather than having the 6-fold-coordination of Sn, Si, Ge and Sr. Therefore, Sr is the first non-group-IV element to be shown to have the "ideal" \( \beta \)-tin structure. The variation of relative volume, \( V/V_0 \), with pressure, calculated from the lattice parameters, is shown in figure 3.10. The decreasing compressibility in Sr-III phase can be readily seen from the plot. This occurrence was also observed in Cs-IV phase and can be explained as a reduction in electronic transition accompanying the structural phase transition.

The sequence of phase transitions with increasing pressure, fcc \( \rightarrow \) bcc \( \rightarrow \) \( \beta \)-tin, reduces the coordination number from 12(fcc) to 8(bcc) to 6(\( \beta \)-tin). This decrease in the number
Figure 3.9: (a) The "ideal" $\beta$-tin structure of Sr-III and (b) the "non-ideal" $\beta$-tin structure of Cs-IV. The nearest neighbour coordinations, 6 for Sr-III and 8 for Cs-IV, are indicated by the solid lines.

Figure 3.10: Variation of relative volume of Sr as a function of pressure up to 36 GPa.
of neighbours is a well known behaviour in the group I and II metals and is attributed to \( s \to d \) transfer. At still higher pressures the overlap between the core electrons will dominate, and a close packed structure is then expected.

Work is continuing to identify the smooth accompanying phase and its possible relationship with the \( \beta \)-tin phase. The smooth phase first manifests itself close to the bcc \( \to \beta \)-tin transition from a contaminant free “clean” bcc pattern. As the pressure is increased the “low-pressure smooth phase” appears to have a similar compressibility to Sr-III as shown in figure 3.10 and it persists up to and through the Sr-III \( \to \) Sr-IV \( \to \) Sr-V transitions. This “low-pressure smooth phase” stays stable up to 57 GPa where it starts to transform to a “high-pressure smooth phase”. This high pressure smooth phase persists up to 75 GPa, the highest pressure reached in these Sr studies. The “high-pressure smooth phase” reveals only three detectable reflections, as will be clearly shown in chapter 5, and therefore it is impossible to index. On pressure decrease the diffraction pattern from the low-pressure smooth form progressively weakens until, at about 10 GPa, only a clean bcc pattern remains. Every sample run in the fcc phase prior to the higher pressure experiments revealed no detectable level of contamination (i.e. SrO which has a NaCl structure at ambient pressure and transforms to a CsCl-type structure at 36 GPa [59]). This behaviour strongly suggests that the smooth phase is another structural form of Sr, rather than simply a contaminant.

Initial attempts to solve the structure of the accompanying smooth phase have been carried out. Using a pattern collected at 35.2 GPa reveals seven low pressure smooth phase peaks. Indexing of only these smooth lines showed that this phase has a primitive orthorhombic unit cell with lattice parameters \( a = 6.692(3) \) Å, \( b = 5.9138(13) \) Å and \( c = 4.8322(11) \) Å at 35.2 GPa. Assuming the same density with previous phase, this structure should contain 8 atoms in the unit cell. The result from the indexing program DICVOL [52, 53] reveals a very tentative indexing and is shown in table 3.3. However, the intensities of the accompanying phase are very weak as is apparent in figures 3.4 and 3.11 and the phase fraction varies from sample to sample—although it is always by far the minority phase. Therefore, at least with the available data, a full structure solution for this phase is not possible. Figure 3.12 shows the compressibility of this proposed orthorhombic structure in comparison with the tetragonal \( \beta \)-tin structure.
Figure 3.11: The attempt to index low-pressure accompanying phase. The indexing suggests a primitive cell and the yellow arrow indicates the strongest peak (120).

Figure 3.12: Relative volume as a function of pressure.
### Table 3.3: The indexing of only smooth lines at 35.2 GPa given primitive orthorhombic structure with lattice parameters $a = 6.692(3)$ Å, $b = 5.9138(13)$ Å, $c = 4.8322(11)$ Å.

<table>
<thead>
<tr>
<th>h k l</th>
<th>observed $2\theta$</th>
<th>calculated $2\theta$</th>
<th>difference $2\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2 0</td>
<td>9.569</td>
<td>9.568</td>
<td>0.001</td>
</tr>
<tr>
<td>2 1 1</td>
<td>10.375</td>
<td>10.377</td>
<td>-0.002</td>
</tr>
<tr>
<td>0 0 2</td>
<td>10.711</td>
<td>10.714</td>
<td>-0.003</td>
</tr>
<tr>
<td>1 1 2</td>
<td>12.212</td>
<td>12.208</td>
<td>0.004</td>
</tr>
<tr>
<td>2 2 1</td>
<td>12.863</td>
<td>12.861</td>
<td>0.002</td>
</tr>
<tr>
<td>0 3 1</td>
<td>14.197</td>
<td>14.198</td>
<td>-0.002</td>
</tr>
<tr>
<td>2 1 3</td>
<td>18.422</td>
<td>18.418</td>
<td>0.004</td>
</tr>
</tbody>
</table>

### 3.5 Concluding Remarks

Finally, it is important to note the key role of the two-dimensional image-plate data in distinguishing the smooth diffraction pattern of the accompanying phase from the spotty pattern of Sr-III. This additional information proved crucial in determining conclusively that Sr-III has the "ideal" $\beta$-tin structure and not the orthorhombic Imma structure as previously suggested. The Sr-III structure is stable up to about 37 GPa where it transforms to a complex structure, recently solved by the author. This will be fully described in the next chapter. The behaviour of the accompanying smooth phase strongly suggests that it is a minority phase of Sr itself and not a contaminant. Apparently it was also observed by Winzenick and Holzapfel in their EDX experiment and led to the wrong identification of the Sr-III phase.
Chapter 4

Sr-IV: The Complex Monoclinic Superstructure

4.1 Introduction

In this chapter, further investigation of the high-pressure crystal structures of strontium have been carried out using angle-dispersive x-ray powder diffraction techniques combined with the image-plate area detector system. Phase IV of Sr has only been previously observed once by Olijynk and Holzapfel [20] and the structure solution is still unknown. The powder pattern is clearly very complex. A modification of the existing image-plate set-up was introduced and it was made so that the higher resolution data required for solving the complex Sr-IV structure could be collected. This is described later in this chapter. Three different models are proposed to explain the structural behaviour of Sr-IV. These models have been tested in detail against high-pressure powder diffraction data collected at the SRS and ESRF Synchrotron radiation facilities [60].

Among the recently determined high-pressure structures of elemental metals, there are a number of rather complex superstructures of much simpler underlying phases. For example, Cs is reported to have an orthorhombic superstructure of fcc[61]. The Sr-IV phase also exhibits this behaviour as the proposed Sr-IV structure can also be viewed as a superstructure of the Sr-III tetragonal $\beta$-tin structure.
4.2 Experiment and Technique Developments

Previous studies on the high-pressure phases of Sr-IV, by Olijnyk and Holzapfel [20], have used energy-dispersive x-ray powder diffraction techniques with their accompanying limitations (e.g. the resolution is limited by the energy discrimination of the detector; and contamination of the powder pattern from fluorescence peaks and escape peaks from the detector itself). Another disadvantage of the EDX technique is that the powder patterns obtained lack texture information which has led to severe difficulties in identifying the high pressure phases. In the previous chapter, this was shown to be crucial, as the high pressure phase of Sr-III was found to be misinterpreted in the work of Olijnyk and Holzapfel [16]. The lack of texture information did not allow the mixed-phase pattern to be correctly identified. To correctly identify the structure of Sr-IV we have undertaken angle-dispersive powder-diffraction studies with the image-plate detector on station 9.1 at the SRS Daresbury Laboratory. The sample preparation and cell loading techniques have been performed in the same manner as has been previously described. Diacell DXR5 or DXR6 diamond-anvil cells were used with either 200 μm or 300 μm diamond culets and the preindented gaskets had spark-eroded holes of 100 μm diameter. The diffraction data were collected at a wavelength of 0.4654 Å. The resulting two dimensional images were integrated using the program EDIPUS to produce conventional one dimensional powder patterns [47].

On pressure increase, the Sr-III (β-tin) phase starts to transform to a more complex structure at 36.7(4) GPa when a peak starts to grow on the low-angle side of the first β-tin peak, the (200)β-tin, and then moves to a lower Bragg angle with increasing pressure. The growth of this peak is complete at 37.7(2) GPa where it splits into two weak peaks. The Sr-IV patterns show a smoother texture than those of the β-tin phase. However, the 2d images still show intensity variation around the Debye-Scherer rings. The accompanying smooth phase still remains smooth and unchanged throughout the Sr-III to Sr-IV phase transition.

The exposures have been taken at a sample to image plate distance of about 300 mm, which is used for most of the experiments performed at SRS, Daresbury. The integrated profiles obtain from this sample to plate distance are usually sufficient for indexing. However, the integrated profiles for Sr-IV exhibit a very complex powder pattern and
Figure 4.1: The integrated profile of Sr-IV taken at 39.3 GPa. The star indicates the strongest peak from the accompanying smooth phase which is stable through the Sr-IV pressure range. The inset shows a two-dimensional image of the pattern which reveals clusters of un-resolved peaks.

the smooth accompanying phase still persists throughout the transition. With the existing experimental setup at SRS Daresbury Laboratory, the complex structure of Sr-IV can not be identified. An integrated pattern with the standard sample to plate distance is shown in figure 4.1 and the inset shows the two-dimensional image of the pattern. Close ups of regions of the same pattern reveal clusters of un-resolved peaks, as illustrated in figure 4.2.

Figure 4.2 shows two expanded regions from figure 4.1 (the pattern taken at 39.3 GPa). In figure 4.2(a), the first peak on the lower angle side has an asymmetry which suggests that there may be further overlapping peaks. Additionally, the second peak on the higher angle side also has a long tail which suggests that there could be weak peaks in that region as well. In figure 4.2(b), the peak on the higher angle side clearly shows that at least two strong peaks are situated too close together to be resolved and consequently only one broad peak is revealed. The trial and error software package, DICVOL [52, 53, 54], was used attempt the indexing of the Sr-IV pattern. However, the program failed to give a satisfactory indexing for the available data.

In angle-dispersive powder-diffraction techniques, as previously stated, it is necessary
Figure 4.2: Close ups of regions of the integrated profile of Sr-IV taken at 39.3 GPa, shown in figure 4.1.

Figure 4.3: A schematic diagram of the diffraction geometry. The second IP holder has been introduced by the author in order to acquire a higher resolution diffraction pattern.

to obtain accurate peak positions for indexing. The complex powder pattern of Sr-IV clearly shows that the data collected so far using the current experimental setup suffers from peak overlap and insufficient resolution. Therefore, these data can not be used for indexing and hence some technique development is required in order to improve the resolution of the recorded powder patterns. The full schematic diagram of the experimental setup can be seen in figure 2.9. The diffraction geometry of the ADX techniques developed by the author is shown in figures 4.3 where the powder patterns are collected as a series of concentric rings about the incident beam on the IP.

In figure 4.3, $2\theta$ is related to $\lambda$ by Bragg’s law, previously shown in equation 2.1.
Figure 4.4: Two-dimensional image plate data collected from station 9.1 SRS, Daresbury (a) with the primary IP holder and a sample to plate distance of 300 mm (the standard distance) and (b) with the secondary IP holder and a sample to plate distance of 600 mm.

Therefore, in order to record a diffraction pattern to the highest Bragg angle possible, x-rays of a relatively short wavelength are required, i.e. the shorter the wavelength, $\lambda$, the smaller Bragg angle $\theta$. As previously mentioned, all the measurements performed at SRS, Daresbury use an x-ray wavelength of 0.4654 Å with a sample to IP distance of about 300 mm. This allows ADX powder patterns to be collected up to 30° with reasonably sharp and well-resolved peaks, usually sufficient for structure determination. However, it has been shown that this is not the case for the very complex patterns of Sr-IV. Figure 4.3 illustrates that, for a fixed wavelength, by increasing the sample to IP distance, a higher resolution image can be recorded. With the limitation of the current experimental setup and space available in station 9.1, the maximum possible sample to IP distance is roughly 600 mm which allows about a quarter of the Debye-Scherrer rings to be recorded up to about 22° using an A4 size IP. Two-dimensional powder patterns collected from the same sample at the same pressure using the regular primary IP holder and the secondary holder are shown in Figure 4.4.

Figure 4.4(a) reveals the almost full Debye-Scherrer rings usually collected with the
Figure 4.5: Integrated profile of Sr-IV pattern collected with primary IP holder. Insets show close ups of regions which are crucial for indexing.

primary holder and figure 4.4(b) shows data collected from the secondary IP holder. With the well-resolved patterns collected by this new setup, peak positions can be measured precisely. The integrated profiles from both IP holders are shown in figures 4.5 and 4.6.

In the integrated powder pattern for the primary IP holder, figure 4.5, the insets clearly shows signs of un-resolved peaks throughout the pattern, while in the integrated powder pattern from the secondary IP holder shows well-resolved peaks. The resolution of the Debye-Scherrer rings is limited by the resolution of IP itself which has a pixel size of $\sim 0.08 \times 0.08 \text{ mm}^2$. By increasing sample to IP distance, the IP area used to collect the same fraction of the Debye-Scherrer ring is also increased, as previously shown in figure 4.4. This means that the number of pixels used to collect the same fraction of the pattern is increased. Therefore, higher resolution data can be recorded. This also can be clearly seen from the study of full width at half maximum (FWHM) from patterns collected at different sample to IP distance. FWHM is the width of the peak measured at the half of maximum intensity for a particular peak. In order to determine the resolution acquired from the different sample to IP distance, the first strongest peak
Figure 4.6: Integrated profile of Sr-TV pattern collected with newly introduced IP holder. Insets show the same close up regions as figure 4.5 for comparison.

has been chosen for comparison. At a sample to IP distance of 300 mm, FWHM of the strongest peak is 0.0845° while the FWHM of the same peak, collected at 600 mm, is 0.0561°. This demonstrates that by increasing the sample to IP distance from 300 mm to 600 mm with the current experimental set up at SRS, Daresbury, FWHM can be expected to reduced by ~30%, resulting in a higher resolution and a more resolved pattern. In the next section, this high resolution data is shown to be crucial for solving the complex high pressure structure. However, this setup required a longer exposure (i.e. less photons are detected by the same pixel) and was therefore not used for most of the experiment.

4.3 Results and Discussion

4.3.1 Indexing the Complex Monoclinic Structure

Powder patterns of Sr-IV have been re-collected using the new IP holder. The powder patterns were integrated and one-dimensional profiles were obtained using the techniques already outlined [47]. The peak profile fitting program, XFIT [51], was used to
measure peak positions and then the indexing program, DICVOL [52, 53], was used to search for a possible indexing. As the transition is apparently second-order in character, the relationship between Sr-III and Sr-IV needed to be understood before the structure of the Sr-IV phase could be solved. By monitoring the pressure dependence of the observed peaks in the powder patterns collected through the Sr-III to Sr-IV transition one might be able to find some plausible geometrical relationship between the unit cells of both phases given by these reflections. The $(200)_{\beta-tin}$ reflection, the first strong peak in the pattern, remains intense and sharp up to the Sr-V transition and the $(220)_{\beta-tin}$ reflection, the second strong peak, becomes split. This suggests that the distortion of the underlying $\beta$-tin structure to form that of the Sr-IV phase must somehow allow the d-spacing of the former $\beta$-tin reflections $(200)_{\beta-tin}$ and $(020)_{\beta-tin}$ to remain equal up to the Sr-V phase. Therefore, the plane defined by $(200)_{\beta-tin}$ and $(020)_{\beta-tin}$ in the Sr-IV structure must remain rectangular: i.e. $[200]_{\beta-tin}$ and $[020]_{\beta-tin}$ define diagonal directions of a rectangular plane in Sr-IV. With the knowledge that the Sr-IV structure must preserve the same d-spacing for the $(200)_{\beta-tin}$ and $(020)_{\beta-tin}$ reflections, false solutions from the indexing programme could be eliminated. A very persuasive unit cell given by the indexing program which fits the integrated Sr-IV pattern at 46.4 GPa (figure 4.6) is a monoclinic cell with lattice parameters $a = 5.655(2)$, $b = 7.776(3)$, $c = 5.346(3)$ and $\beta = 97.11(6)$ (see table 4.1).

To establish the relationship between the monoclinic cell and the previous $\beta$-tin phase, the proposed structure has been re-calculated for the pattern collected at 35.6 GPa, where the transformation initially develops with lattice parameters $a_{Mono} = 5.91436$, $b_{Mono} = 7.81940$, $c_{Mono} = 5.91386$ and $\beta = 97.2246$. The calculated lattice parameters for the tetragonal $\beta$-tin structure are $a_{\beta-tin} = 5.52870$, $c_{\beta-tin} = 2.95818$. These calculated lattice parameters clearly reveal the relationship suggested by the preservation of the $(200)_{\beta-tin}$ reflection where $b_{Mono} = \sqrt{a_{\beta-tin}^2 + b_{\beta-tin}^2}$. This allows the former $(200)_{\beta-tin}$ and $(020)_{\beta-tin}$ reflections of $\beta$-tin to retain the same d-spacing as they now define the $(\overline{1}01)_{Mono}$ plane in the monoclinic cell which remains rectangular no matter what values the monoclinic cell constants take. Further calculation for the monoclinic lattice parameters give $a_{Mono} \approx c_{Mono} = \sqrt{a_{\beta-tin}^2 + b_{\beta-tin}^2}$ and $\beta = 2 tan^{-1} \left[ \frac{3c_{\beta-tin}b_{\beta-tin}}{a_{\beta-tin}^2 \sqrt{3}} \right]$. Figure 4.7 shows the relationship between the tetragonal $\beta$-tin phase of Sr-III and the monoclinic superstructure of the Sr-IV phase. The relationship between the two unit
Table 4.1: The proposed indexing of the monoclinic structure with lattice parameters $a = 5.655(2)$, $b = 7.776(3)$, $c = 5.346(3)$ and $\beta = 97.11(6)$.

<table>
<thead>
<tr>
<th>h k l</th>
<th>observed $2\theta$</th>
<th>calculated $2\theta$</th>
<th>difference $2\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 0 0</td>
<td>9.511</td>
<td>9.515</td>
<td>-0.004</td>
</tr>
<tr>
<td>1 2 1</td>
<td>10.042</td>
<td>10.052</td>
<td>-0.010</td>
</tr>
<tr>
<td>2 1 $\bar{1}$</td>
<td>10.764</td>
<td>10.764</td>
<td>0.003</td>
</tr>
<tr>
<td>1 1 $\bar{2}$</td>
<td>11.133</td>
<td>11.134</td>
<td>-0.010</td>
</tr>
<tr>
<td>1 3 0</td>
<td>11.363</td>
<td>11.350</td>
<td>0.013</td>
</tr>
<tr>
<td>0 3 1</td>
<td>11.463</td>
<td>11.468</td>
<td>-0.005</td>
</tr>
<tr>
<td>2 2 0</td>
<td>11.736</td>
<td>11.741</td>
<td>-0.005</td>
</tr>
<tr>
<td>1 1 2</td>
<td>12.163</td>
<td>12.156</td>
<td>0.007</td>
</tr>
<tr>
<td>0 4 0</td>
<td>13.742</td>
<td>13.748</td>
<td>-0.006</td>
</tr>
<tr>
<td>2 3 $\bar{1}$</td>
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<td>14.516</td>
<td>0.001</td>
</tr>
<tr>
<td>3 1 0</td>
<td>14.706</td>
<td>14.703</td>
<td>0.003</td>
</tr>
<tr>
<td>1 3 $\bar{2}$</td>
<td>14.802</td>
<td>14.793</td>
<td>0.009</td>
</tr>
</tbody>
</table>
The volume of this conventional monoclinic cell, $abc \sin \beta$, is three times that of the tetragonal $\beta$-tin cell and it should, therefore, contain 12 atoms. In order to assign the appropriate space group for this monoclinic structure, the systematic absences of the reflections were investigated. Systematic absences occur when symmetry elements with translation components lead to the systematic cancelling (or absences) of classes of reflections. Therefore, by studying the absences of certain reflections, the symmetry of the structure can be implied. In order to establish the plausible cell, an attempt to obtain the symmetry was made by checking the systematic absences of a pattern where structure is strongly distorted from the tetragonal $\beta$-tin structure (i.e. new the peaks are well established).

From the observed profiles of Sr-IV, the pattern clearly exhibits compatibility with the I-centred symmetry where $h + k + l = 2n$ and hence a body-centred structure is expected. A further investigation of the systematic absences revealed the reflection conditions shown in table 4.2, which are compatible with only the space groups $Ia$ and
I2/a. However, it is not possible to distinguish between them by a study of systematic absences alone.

### 4.3.2 Structure Solution

In order to transform from one structure to another, it is necessary to express the vectors $a'$, $b'$ and $c'$ of the "new" structure, in term of vector sums of the vectors $a$, $b$, and $c$ representing the "old" structure. i.e.

\[
\begin{align*}
    a' &= p_1a + q_1b + r_1c \\
    b' &= p_2a + q_2b + r_2c \quad \text{or} \quad b' = p_2a + q_2b + r_2c \\
    c' &= p_3a + q_3b + r_3c
\end{align*}
\]

Where $p, q, r$ are integral or simple fractional coefficients. Such coefficients completely specify the relationship of the "new" to the "old" unit cell vectors. This matrix is called transformation matrix. In a similar manner, one can construct the transformation matrix which relates the "old" unit cell to the "new" unit cell.
From the relationship between the unit cells previously given, in terms of vectors, the matrix used to transform the atomic coordinates from one structure to another can be constructed. Since the crystal structure and its lattice are independent of the choice of unit cell, the lattice vector $t = Ua + Vb + Wc$ referred to the old axes becomes $t = U'a' + V'b' + W'c'$ referred to the new axes. These lattice vectors should, therefore, refer to the same point in space no matter which reference axes are used. Using this statement, the transformation matrix to transform the lattice vectors can be constructed.

\[
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
= \begin{pmatrix}
P_1 & Q_1 & R_1 \\
P_2 & Q_2 & R_2 \\
P_3 & Q_3 & R_3
\end{pmatrix}
\begin{pmatrix}
a' \\
b' \\
c'
\end{pmatrix}
\]

and

\[
\begin{pmatrix}
a' \\
b' \\
c'
\end{pmatrix}
= \begin{pmatrix}
P_1 & Q_1 & R_1 \\
P_2 & Q_2 & R_2 \\
P_3 & Q_3 & R_3
\end{pmatrix}
\begin{pmatrix}
u' \\
v' \\
w'
\end{pmatrix}
\]

therefore

\[
\begin{pmatrix}
u' \\
v' \\
w'
\end{pmatrix}
= \begin{pmatrix}
P_1 & Q_1 & R_1 \\
P_2 & Q_2 & R_2 \\
P_3 & Q_3 & R_3
\end{pmatrix}
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
\]

and by transposing
This transformation matrix for transforming the lattice vectors is the transpose of the reverse transformation ("new" to old" instead of "old" to "new"). In a similar manner, the distance of an atom from the origin of the coordinate system is \( r = xa + yb + zc \) where \( x, y, z \) are the coordinates of the atom in the "old" unit cell. In terms of the "new" unit cell the coordinates become \( r = x'a' + y'b' + z'c' \). Therefore, the transformation of atomic coordinates uses the same transformation matrix as that of the lattice vectors. From the relationship between the Sr-III and SrIV unit cells previously given, the transformation matrix for the atomic coordinates can be deduced as:

\[
\begin{pmatrix}
-\frac{1}{2} & \frac{1}{2} & \frac{1}{3} \\
\frac{1}{2} & \frac{1}{2} & 0 \\
-\frac{1}{2} & \frac{1}{2} & -\frac{1}{3}
\end{pmatrix}
\]

Using this transformation matrix, all the \( \beta \)-tin coordinates can be transformed from the Sr-III structure to the Sr-IV structure. The systematic absences suggest that the Sr-IV structure should be body-centred. The \( \beta \)-tin structure of Sr-III, previously described in chapter 3, is composed of 4 atoms in a unit cell generated by symmetry elements from an atom located on a special position of \( (0, \frac{1}{2}, \frac{1}{4}) \), giving atoms at \( (0,0,0), (0,\frac{1}{2},\frac{1}{4}) \), \( (\frac{1}{2},\frac{1}{2},\frac{1}{4}) \), \( (\frac{1}{2},0,\frac{3}{4}) \). With the same density, the Sr-IV structure should contain 12 atoms as the unit cell volume is 3 times larger than that of Sr-III. The related atoms used for the transformation are those clearly located in the Sr-IV structure from figure 4.7. The results of the transformation are shown in table 4.3 in which this relationship between atoms is clearly exhibited where every atom located at \( x, y, z \) has another atom related by \( x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2} \).

With the body-centred relationship, only 6 atoms are required to describe this structure. This monoclinic structure also reveals symmetry from \( a \)-glide planes perpendicular to
### Table 4.3: The transform coordinates from Sr-III β-tin to Sr-IV structure. The Sr-IV coordinates clearly exhibit the body-centred (I) relationship.

<table>
<thead>
<tr>
<th>β-tin coordinates</th>
<th>Sr-IV coordinates</th>
<th>Related by I</th>
<th>Related by a glide</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 1 0</td>
<td>1 1 1</td>
<td>1 1 1</td>
<td>1 1 1</td>
</tr>
<tr>
<td>0 0 0</td>
<td>0 0 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 1/2 - 3/4</td>
<td>0 1/4 1/2</td>
<td>0 1/4 1/2</td>
<td></td>
</tr>
<tr>
<td>1/2 1/4</td>
<td>1 3/4 1/4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1 1/2 - 1/2</td>
<td>1 0/3 1/3</td>
<td>1 0/3 1/3</td>
<td>1 0/3 1/3</td>
</tr>
<tr>
<td>0 1 1</td>
<td>5 1/2 1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 3/2 1/4</td>
<td>5 3/2 1/2</td>
<td>5 3/2 1/2</td>
<td></td>
</tr>
<tr>
<td>1/2 1/4</td>
<td>1 1/1 1/1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 -1/2 1/2</td>
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</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>1/2 -1/2</td>
<td>6 4/3 4/3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 -1/2</td>
<td>1 3/1 3/1</td>
<td>1 3/1 3/1</td>
<td></td>
</tr>
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</tr>
<tr>
<td>2/4</td>
<td>3 4/6 4/6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.8: The monoclinic structure with transformed coordinates. The red arrow indicates an example of atoms related by body-centred symmetry, the blue and green arrows show atoms related by an a-glide planes perpendicular to b at $\frac{3}{8}$ and $-\frac{1}{8}$ respectively.

$b$ at $y = \frac{3}{8}$ and $y = -\frac{1}{8}$ which are indicated by blue and green arrows in figure 4.8 respectively.

As previously suggested from the systematic absences, the Sr-IV pattern is compatible with both the $Ia$ and $I2/a$ space group. However, it is not possible to construct the $\beta$-tin like structure using $I2/a$ symmetry and therefore the proposed monoclinic structure with space group symmetry $Ia$ was used for subsequent data analysis.

In order to generate atoms in related by an a-glide, the origin must be shifted by $\frac{1}{8}$ along $y$: i.e. the $y$ values in the third and fourth column in table 4.3 need to be increased by an $\frac{1}{8}$. In other words, symmetry requires the origin to be located on the glide plane and thus atoms need to be shifted by an $\frac{1}{8}$ along $y$ before the refinement can be performed. Three refinable atoms, labeled as Sr1, Sr2 and Sr3, were initially placed on the 4a sites of $Ia$ at $(\frac{1}{2}, \frac{1}{8}, \frac{3}{8}), (\frac{1}{2}, \frac{5}{8}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{3}{8}, \frac{3}{8})$, respectively. The a glide will then generate atoms at $x +\frac{1}{2}, -y, z$ plus their $I$ related atoms with $3 \times 2 \times 2 = 12$ atoms per unit cell.
Figure 4.9: The Rietveld refinement with *Ia* structure shows the general good fit for all the main β-tin peaks at 37.8 GPa. Arrows indicate new growing Sr-IV peaks and the strongest peak from accompanying phase is indicated by a star.

The phase transition from Sr-III (β-tin) to Sr-IV at 37 GPa has now been confirmed and the structure of Sr-IV is proposed to be complex and monoclinic with space group *Ia*. This monoclinic structure has not been observed previously in elemental metals and it appears to develop as a continuous, increasing, distortion of the Sr-III β-tin structure. The transformation of the β-tin coordinates into the monoclinic unit cell, provided an initial structural model for subsequent Rietveld refinement. This provided a reasonably good fit to the strong peaks, shown in figure 4.9, with the structural coordinates fixed at their initial, transformed, values. The new weak reflections of Sr-IV are indicated by arrows and the star marks the strongest reflection from the accompanying phase which remains unchanged through the Sr-III to Sr-IV transition.

Given the geometrical relationship between the tetragonal Sr-III structure and that of the monoclinic Sr-IV phase, we expect that the “as transformed” coordinates will give a reasonable fit to the strongest lines of the powder diffraction patterns in the low-pressure stability range of Sr-IV. Indeed, this is seen to be the case for a fit of a diffraction pattern measured at 37.8 GPa where the cell parameters were refined but the atomic coordinates were fixed at their transformed values. As expected the weak peaks are given no calculated intensity though their 2θ positions are accounted for (as seen by the tick marks). The monoclinic *Ia* structure is, therefore, a very plausible candidate
for the high-pressure structure of Sr-IV. In order to understand this high pressure structure in greater detail, Rietveld refinement has been performed where the atomic coordinates were refined freely. In the subsequent Rietveld refinement (described as the "free" refinement) the atomic coordinates are refined as allowed by the \( Ia \) symmetry.

Free refinement of the structure from the transformed coordinates gives an excellent fit to the whole pattern at 41.7 GPa. The refined lattice parameters were \( a = 5.74562(16) \) Å, \( b = 7.80091(26) \) Å, \( c = 5.53704(29) \) Å and \( \beta = 96.9901(23)° \) with three refinable atoms in the asymmetric unit all on 4a positions (Sr1 (0.3039(13), 0.1574(11), 0.6322(21)), Sr2 (0.4787(17), 0.5784(7), 0.4645(36)) and Sr3 (0.6840(8), 0.1445(11), 0.3459(19)) with \( R_{wp} = 0.0237 \). Sr1, Sr2 and Sr3 displace in directions approximately 120° apart (to within about 5°) in layers parallel to the former \( \beta \)-tin a-b plane to form helical chains directed along the former \( \beta \)-tin c-axis, \([001]_{\beta-tin}\), see figure 4.10. The three low-angle \((110)_{\text{Mono}}, (011)_{\text{Mono}}\) and \((020)_{\text{Mono}}\) peaks are absent, or very weak, in all of the SRS data. However, these reflections cause some difficulties in structural refinement. These reflections are not required to be absent by the \( Ia \) symmetry and the intensities calculated for these reflections from the refined structure shows that they ought to be just detectable on the SRS data. This suggests that the structure is imposing geometrical constraints on the atoms that are not required by the space

Figure 4.10: The Rietveld free refinement with \( Ia \) structure shows an excellent fit for all peaks. The inset on the left shows calculated intensities for absent reflections and the inset on the right shows a helical distortion from \( \beta \)-tin structure.
Figure 4.11: The integrated profile of the Sr-IV phase collected from ESRF. The left inset reveals the weak reflections with the calculated positions indicated by tick marks. The right inset shows a close up region of two-dimensional data from ESRF showing evidence for the weak the 011 reflection.

group symmetry.

A further study of this behaviour has been undertaken at the ESRF, Grenoble. With the more intense beam at the ESRF, the patterns reveal a weak \((011)_\text{Mono}\) reflection although the \((110)_\text{Mono}\) and \((020)_\text{Mono}\) are still completely absent. The intensity for the overall pattern collected at the ESRF is, however, unreliable since the image-plate was deliberately over-exposed in an attempt to reveal these very weak reflections. Therefore, full Rietveld refinement can not be performed on the data. The results shown in figure 4.11 clearly confirm that there is a geometrical constraint applied to the atoms, in order to keep these reflections absent and/or very weak. In the unconstrained refinement of the SRS data, previously shown, the calculated intensities for the \((011)_\text{Mono}\), \((110)_\text{Mono}\) and \((020)_\text{Mono}\) reflections are consistently weak but, nevertheless, of an intensity that would be expected to allow them to become clearly observable. As the Rietveld procedure attempts to fit the entire pattern, the weights assigned to these reflections will be small compared to the more intense reflections despite their profound significance for the detailed nature of the structural distortions. The calculated positions for weak reflections are also given in the inset.
Given these apparent absences, three different structural models were introduced in order to explain them. These three models were tested, each based on the helical-rod structure previously observed from the free refinement, that would link the three-fold displacement of the three symmetrically unique atoms by a single refinable parameter, \( D \). The first constraint is based on the approximate 120° displacements observed in the free refinement which results in the absence of the \((020)^{M_0}\) reflection. In this constraint the three refinable atoms are constrained to displace in directions separated by 120°. The second constraint confines these displacement to the former a-b plane of the \( \beta \)-tin structure (which is \((I01)^{M_0}\) in the monoclinic structure) which is consistent with the apparent absence of both \((011)^{M_0}\) and \((110)^{M_0}\) reflections. This plane is, however, distorted with pressure and atoms are confined to displace only approximately in this plane. This model should certainly explain absences of all three weak reflections while it should still give an excellent fit to the whole diffraction pattern for the full pressure range of Sr-IV studied.

The three models used for the refinements were: (1) an atom is constrained to displace parallel to the monoclinic b-axis while the other two atoms are linked to displace in consecutive layers approximately parallel to \((I01)^{M_0}\) but in directions separated by 120° and 240° with respect to displacement direction of the first atom; (2) an atom is constrained to displace in a direction perpendicular to the monoclinic b-axis while the other two atoms are linked to displace in consecutive layers approximately parallel to \((I01)^{M_0}\) but in directions separated by 120° and 240° with respect to displacement direction of the first atom; (3) an atom is constrained to displace in a direction parallel to the \( \beta \)-tin a-axis while the other two atoms are linked to displace in consecutive layers approximately parallel to the \((I01)^{M_0}\) but in directions separated by 120° and 240° with respect to displacement direction of the first atom. The purpose for introducing these models is to understand the absence of the three low-angle reflections and also find a plausible relationship with the \( \beta \)-tin structure. In the three trial models used for the refinements all nine independent structural coordinates \((x, y, z)\) for Sr1, Sr2 and Sr3 were tied to a single constrained parameter, \( D \), as described below.

For the first model, one atom is confined to displace along the b-axis in consecutive layers approximately parallel to the \((I01)^{M_0}\) plane and the other two atoms are linked to this atom by 120° displacements. The relationship between the atoms as defined by
Figure 4.12: The displacement directions of the three refinable atoms in the first model. The green arrows indicate the displacements of the three atoms.

\( D \) is described below and figure 4.12 shows the direction of the helical displacements.

\[
\begin{align*}
\text{Sr1:} & \quad \Delta x = 0; \quad \Delta y = D; \quad \Delta z = 0 \\
\text{Sr2:} & \quad \Delta x = -\frac{D \cos \frac{\pi}{6}}{2 \cos \frac{\beta}{2}}; \quad \Delta y = -D \sin \frac{\pi}{6}; \quad \Delta z = -\frac{D \cos \frac{\pi}{6}}{2 \cos \frac{\beta}{2}} \\
\text{Sr3:} & \quad \Delta x = \frac{D \cos \frac{\pi}{6}}{2 \cos \frac{\beta}{2}}; \quad \Delta y = -D \sin \frac{\pi}{6}; \quad \Delta z = \frac{D \cos \frac{\pi}{6}}{2 \cos \frac{\beta}{2}}
\end{align*}
\]

In the second model, the three refinable atoms are allowed to displace in consecutive layers approximately parallel to the \((\overline{1}01)_{\text{mono}}\) plane but in directions separated by 90°, 210° and 330° with respect to the monoclinic b-axis. The relationship between the atom displacements defined by \( D \) is described below and figure 4.13 shows the corresponding displacement directions.

\[
\begin{align*}
\text{Sr1:} & \quad \Delta x = D; \quad \Delta y = 0; \quad \Delta z = D \\
\text{Sr2:} & \quad \Delta x = -D \cos \frac{\pi}{3}; \quad \Delta y = 2D \cos \frac{\beta}{2} \cos \frac{\pi}{6}; \quad \Delta z = -D \cos \frac{\pi}{3}
\end{align*}
\]
In the third case, the atoms are allowed to displace in consecutive layers approximately parallel to the $\{\overline{1}01\}_\text{Mon}o$ plane but in directions separated by $0^\circ$, $120^\circ$ and $240^\circ$ with respect to the $\beta$-tin $a$-axis. The relationship between the atom displacements defined by $D$ is described below and figure 4.14 shows the corresponding displacement directions.

**Sr3:** $\Delta x = -D \cos \frac{\pi}{3}; \Delta y = -2D \cos \frac{\beta}{2} \cos \frac{\pi}{6}; \Delta z = -D \cos \frac{\pi}{3}$

In all cases, the three refinable atoms will always displace approximately $120^\circ$ apart in consecutive layers approximately parallel to the $\{\overline{1}01\}_\text{Mon}o$ plane, and therefore, the $(020)_\text{Mon}o$ reflection should be calculated as absent in all the refinements. All the refinable atoms are constrained to displace in consecutive layers parallel to $(\overline{1}01)_\text{Mon}o$.
over the full pressure range. This ensures that the \((011)_{Mono}\) and \((110)_{Mono}\) reflections will remain absent or at least very weak while retaining an excellent fit to the entire powder pattern. Full Rietveld refinement has been performed with the three models on the data measured up to 49 GPa, the onset of the Sr-V transition. The results show good agreement with the weak reflections in all cases but the first two models fail to give a reasonable fit to the full pattern while only the third gives an extremely good fit. Figure 4.15 shows the result of a Rietveld refinement with the third model on the data collected at 41.7 GPa. Figure 4.16 shows the Sr-IV structure compared to the \(\beta\)-tin structure. The Sr-IV structure clearly shows a helical distortion from the Sr-III, \(\beta\)-tin structure.

The lattice parameters from the Rietveld refinement at 41.7 GPa, with the third case constraint, are \(a = 5.7463(2)\ \text{Å}, b = 7.8013(3)\ \text{Å}, c = 5.5360(4)\ \text{Å}\) and \(\beta = 96.986(3)^\circ\) with three refinable atoms Sr1 \((0.30678(15), 0.1602(2), 0.64012(15))\), Sr2 \((0.49028(5), 0.5769(2), 0.49028(5))\), Sr3 \((0.7029(2), 0.13788(7), 0.3696(2))\) with \(D = 0.02655(15)\) and \(R_{wp} = 0.0303\), comparable to those given by the unconstrained refinement on
Figure 4.15: Rietveld refinement of Sr-IV at 41.7 GPa. The dotted line shows the observed profile and the solid line shows the calculated profile. The tick marks below the profiles show the peak positions and the difference between the observed and calculated profiles is indicated under the tick marks. The smooth accompanying phase peaks are marked by stars. The inset shows a magnified low-angle region of the ESRF data collected at the same pressure and the tick marks show the calculated peak positions for the reflections $(110)_{Mono}$, $(011)_{Mono}$ and $(020)_{Mono}$.

the same data in section 4.3.2 previously shown. Using this single parameter model, Rietveld refinements have been performed for the full range of data up to the start of the transformation to Sr-V at 49 GPa, the model gives an excellent fit over the full pressure range of Sr-IV stability. From figure 4.17, it is apparent that $D$ varies smoothly with pressure and acts as an order-parameter for the transition. This also shows that the Sr-III to Sr-IV transition is obviously not first order in character.

However, this model cannot explain the patterns collected in the range $36.7(4)$ to $37.7(2)$ GPa where Sr-III starts to transform to the superstructure Sr-IV phase. In this pressure range, when the first new reflection just starts to grow, neither the monoclinic Sr-IV structure nor the Sr-III $\beta$-tin structure can account for the positions of the additional weak peaks observed in the powder pattern. The first weak peak exhibits anomalous behaviour in that it moves to a larger d-spacing with increasing pressure in the range $37.0(2)$-$37.7(2)$ GPa as shown in figure 4.18. The proposed monoclinic $Ia$ structure gives an excellent fit to the profiles above $37.7(2)$ GPa when the reflection splits into two peaks which both then shift to larger Bragg angles with increasing pressure. The behaviour of these weak peaks strongly suggests that there is an intermediate phase at
Figure 4.16: (a) The distorted \( \beta \)-tin structure of Sr-IV, compared with (b) the ideal \( \beta \)-tin structure. (c) A view parallel to \([\bar{1}01]_{Mono}\) compared to a c-axis projection of the ideal \( \beta \)-tin structure. (d) A view parallel to \([\bar{1}01]_{Mono}\) showing the helical distortion of the Sr-IV structure.
the transition from the Sr-III to the Sr-IV phase. This intermediate phase has not been previously reported and because of its similarity to Sr-III, this phase will be named Sr-III'. Attempts to determine the unit cell of this phase have been unsuccessful. Indeed, it is not clear whether the diffraction profiles collected between 36.7(4) GPa and 37.7(2) GPa are from a single phase of Sr-III', which has a diffraction pattern very similar to that of Sr-III, or form a mixture of (dominantly) Sr-III and Sr-III'. Figure 4.19 shows the behaviour of the weak peak over the full pressure range of this study. Apart from the 36.7(4) to 37.7(2) GPa pressure range, the proposed Sr-IV structure gives an excellent fit up to 49.0(7) GPa where it transforms to the Sr-V phase. The smooth accompanying phase remains unchanged through the Sr-IV to Sr-V phase transition. Table 4.4 shows results from the structure refinement using the third model for the full pressure range. All the refined patterns show an excellent fit up to the Sr-IV to Sr-V transition. Figure 4.20 shows the compressibility of Sr up to 49.0(7) GPa where it starts to transform to Sr-V.
Figure 4.18: The evolution of the Sr-III' into Sr-IV phase between 36.7(4)GPa and 37.7(2)GPa. The inset shows the development of weak peak which indicated the Sr-III' and G marks a gasket peak.
Figure 4.19: The measured Bragg angle $(2\theta)$ of the $(200)_{Mono}$ reflection as a function of pressure. $(200)_{\beta\text{-tin}}$ is calculated from the $\beta$-tin lattice parameter.
<table>
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<th>Pressure (GPa)</th>
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<th>$b$</th>
<th>$c$</th>
<th>$\beta$</th>
<th>Volume</th>
<th>$D$</th>
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<td>7.7599(4)</td>
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Table 4.4: Refined monoclinic structure with the third model constraint.

Figure 4.20: The relative volume of Sr showing a continuous compressibility from bcc to fcc, fcc to Sr-III and from Sr-III to the monoclinic $Ia$ structure.
4.4 Concluding Remarks

In conclusion, the transition from Sr-III to Sr-IV appears to be initiated by an intermediate phase which is stable between 36.7(4) GPa and 37.7(2) GPa. The transition from β-tin otherwise appears to be continuous in nature and the additional smooth accompanying phase remains unchanged through the phase IV to phase V transition. The structure of Sr-IV is monoclinic with spacegroup $Ia$ and it has 12 atoms in the unit cell. Three different models have been introduced for the purpose of confining the intensity of the lowest angle weak peaks. The constraint applied to the refinement restricts the direction of the atomic displacements and relates these displacements to only one refinable parameter. The structure can be considered as a helical distortion of the β-tin structure resulting in a unit cell 3 times larger in volume than the tetragonal β-tin phase. This complex monoclinic structure has not been observed previously in elemental metals.
Chapter 5

Sr-V: The Remarkable Self-hosting Structure

5.1 Introduction

Under further compression, Sr-TV transforms into another previously unknown structure (Sr-V) at 49.0(7) GPa. This structure has been previously observed by Olijnyk and Holzapfel from their original high pressure EDX experiments at 46 GPa [20]. The one-dimensional pattern from their EDX experiment reveals a strong similarity to the Ba-TV pattern [20]. However, the Ba-IV and Sr-V phases were reported to have relatively simple patterns compared to those of Sr-IV but they were still rather complicated and therefore the structure could not be successfully identified using their EDX data. Recently, however, the use of angle-dispersive diffraction techniques coupled with monochromatic synchrotron radiation has led to the successful determination of the high pressure structure of Li-III [62], RbIV and Rb-V [63], Cs-V [61], Sr-III [21], Sr-IV [22], and Ba-IV [64]. The structures of all these phases are remarkably complex, and this is particularly true for the Ba-IV structure where the structure is composed of two components — a host and a guest — that are incommensurate with each other in one direction. This self-hosting structure has not been observed before in an element [64]. A similar structure has also been reported recently for Rb-IV although the host has a different atomic arrangement and the guest appears to be commensurate, Schwarz et al. [63]. Based on the similarity between the diffraction patterns of Ba-IV and Sr-V,
a first attempt to fit the Sr-V diffraction patterns with a Ba-IV type model was carried out using the Rietveld refinement program MPROF [65] (which is used in preference to GSAS for reasons outlined later). The results suggested that the Sr-V structure was indeed similar to that observed in Ba-IV [66]. This chapter describes the author's involvement with this study where he performed all the experimental procedures. The author also performed the very detailed data analysis for the whole pressure range where Sr-V is stable. This work includes the study of the development of the accompanying phase, first observed with Sr-III, which appears to undergo a phase transition at 59.6(5) GPa. The Sr-V structure also shows a transformation in its guest structure at 67.2(4) GPa. A short introduction of the prototype Ba-IV structure will be given to provide a background for further discussion and comparison between the Sr-V and Ba-IV structures.

5.2 Experimental Details

The experimental procedures used for the investigation of Sr-V have been performed in essentially the same manner as previously described in chapter two. The samples used for the structural work on Sr-V were also obtained from Johnson Matthey and Aldrich Chemicals, the same supplier of Sr used in all prior experiments. The diffraction data were collected to 56 GPa on station 9.1 SRS, Daresbury, and to 75 GPa, the highest pressure obtained so far, on beamline ID9 at the European Synchrotron Radiation Facility (ESRF), Grenoble. Both studies used ADX techniques in conjunction with IP area detectors [60]. The incident wavelengths were 0.4654(1)Å, and 0.45115(4)Å at the SRS and the ESRF, respectively. The two dimensional patterns were then integrated in order to obtain conventional one dimensional profiles suitable for Rietveld refinement. The IP software, EDIPUS, developed by the Edinburgh group was used for the SRS data and FIT2D [67] was used for the ESRF data. The structures were refined using the Rietveld method on the integrated profiles with the program MPROF [65].
5.3 Result and Discussions

5.3.1 Nature of the Transition

The previous work on Sr that has mentioned the structural phase transition from Sr-IV to Sr-V was the EDX experiment reported by Olijnyk and Holzapfel at 46 GPa [20]. In their report, they mentioned a similarity between the EDX patterns of Ba-IV and Sr-V but the structures could not be identified using their EDX patterns. In our studies, using ADX techniques, the diffraction peaks from the Sr-V phase were observed on pressure increase at 49.0(7) GPa close to the previously reported transition pressure. Whereas the diffraction patterns from Sr-IV showed short arcs of intensity due to the highly textured powder sample, formerly illustrated in the previous chapter, the diffraction patterns from Sr-V consisted of many strong, quite sharp, spots, indicating that recrystallisation of the sample occurs at the IV-to-V transition. Similar recrystallisation effects were also observed in the Ba II-to-IV transition [64].

In the Ba-IV experiment performed by the Edinburgh group, the structure solution came from a powder sample which was pressurised through the II-IV transition very slowly which resulted in a sample with a small number of relatively large crystallites. Further effort produced a sample with only a single crystal of phase IV. This particular single crystal is an important key to the structure solution of this complex prototype Ba-IV structure as will be detailed in the next section. However, the highly textured and spotty diffraction pattern of the Ba-IV phase could also be smoothed by cycling the pressure up to ~25 GPa and back down to ~13 GPa. An integration of such a pattern can be used for structural refinement with standard powder techniques. In the Sr-V experiment, however, attempts to grow a single crystal of Sr-V by annealing a partially recrystallised sample at 373K for two hours were unsuccessful, and instead, resulted in a sample with a smoother diffraction pattern and was therefore, made more suitable for powder refinement. Data were collected from several samples that gave similar diffraction peaks, but data collected at 56 GPa from this annealed, smooth, sample was used for the first successful structural refinement. Figure 5.1 shows powder patterns of Sr-V before and after sample annealing.
Figure 5.1: (a) shows a powder pattern of Sr-V before heating and (b) a powder pattern taken at 56 GPa from the same sample after heating at 373K for two hours.

5.3.2 The Ba-IV Prototype Structure

The reported similarities in the EDX diffraction patterns of Ba-IV and Sr-V by Olijnyk and Holzapfel was also confirmed by our ADX patterns and has led to the re-examination of Sr-V based on the Ba-IV structure solution (which was recently undertaken by the Edinburgh group). The Sr-V phase is, indeed, found to have the Ba-IV type structure. In order to fully understand the transitions and behaviour of the Sr-V structure, the prototype structure of complex Ba-IV must be illustrated before any further discussion of the two structures can be made.

The recently reported structure solution of Ba-IV came from a single-crystal experiment. As previously mentioned, a single crystal of Ba-IV (which was grown in a pressure cell) has played a pivotally important role in the structural identification of this complex structure. Indeed, the structure solution could not be obtained using only powder methods as the information obtained from powder techniques is inadequate. The Ba-IV structure is found to have a remarkable self-hosting structure, comprising a tetragonal host with chains of guest atoms contained in channels running along the four
Figure 5.2: The powder pattern of Ba-IV reveals an unusual diffraction pattern with several lines of diffuse scattering.

fold axis of the host [64]. In the Ba-IV structure, the chain atoms form two different crystal structures and one of these was found to undergo a structural phase transition without any accompanying structural change in the host structure.

The initial study of Ba-IV was carried out using angle-dispersive powder diffraction techniques. The powder patterns recorded on image-plate area detectors revealed diffuse scattering which could not be understood at first. The diffuse scattering lines can also be clearly seen in other reports previously published elsewhere [20, 68] but their significance had been discounted. Figure 5.2 shows a powder pattern of Ba-IV recorded by the image-plate detector at SRS, Daresbury. This Ba-IV phase gives very strongly textured and spotty powder patterns. Several attempts to understand the powder diffraction patterns from the Ba-IV phase were unsuccessful. The most likely solution, proposed by Takemura, was a body-centred tetragonal structure where most of the strong reflections could be indexed. However, using this proposed structure many weak reflections remain unindexed [68]. Re-examination of the Ba-IV phase using powder diffraction techniques by the Edinburgh group was carried out and also showed that the pattern could not be completely explained using the cell proposed by Takemura.
The Ba sample was prepared in a similar manner to the methods used for Sr described previously in chapter 2. Pressure cells of the Merrill-Bassett design were used for the Ba experiment as they could provide a sufficient pressure. The powder patterns of Ba-IV were collected using the ordinary image plate setup at station 9.1, SRS, Daresbury Laboratory, as described previously in chapter 2. An attempt to index the powder pattern of Ba-IV at 12.9 GPa can explain all the strong reflections with a body-centred tetragonal unit cell with a = 8.35 Å and c = 4.70 Å. This cell is related to Takemura’s previously reported body-centred tetragonal cell (a' = b', c') by \( a = 2a' + \bar{b} \) and \( c = c' \) but this indexing still cannot explain a number of weak reflections. These weak unindexed reflections were also found to vary in intensity from sample to sample relative to the main indexed reflections. Moreover, many of them were observed to change on reducing pressure while the main reflections indexed by the body-centred tetragonal cell were unaltered. This transition in the weak peaks was also found to be reproducible in different samples at 12.5(2) GPa. The Ba-IV phase was thus labelled as Ba-IVa and Ba-IVb for the structure below and above this pressure respectively. As far as the powder diffraction techniques are concerned, this body-centred tetragonal structure is the most likely structure for Ba-IV that can be implied from the integrated diffraction patterns. Yet, this structure still left a number of weak reflections unindexed.

However, with the pressure cycling techniques mentioned earlier, the Ba sample was transformed into a single crystal and a structural investigation using single-crystal techniques could then be performed. Single-crystal data were collected on CAD4 diffractometers with both Synchrotron radiation at station 9.8 SRS, Daresbury, using a wavelength of 0.6891(1) Å and the in-house single-crystal diffraction kit with a conventional MoK\(_\alpha\) x-ray tube (\( \lambda = 0.71 \) Å). The two-dimensional image of this single crystal is shown in figure 5.3. As can be clearly seen this extraordinary pattern reveals an astonishing diffraction pattern. The observed reflections can be readily classified into three different groups: reflections that are not located on the diffuse lines; reflections on the diffuse lines; and satellite reflections which are grouped around the reflections on the diffuse lines.

Using relatively standard high-pressure single-crystal methods the full structure solution could then be obtained. The different groups of reflections can be indexed using three different unit cells which lead to a full understanding of the whole structure.
Figure 5.3: Two-dimensional image from a single crystal of Ba phase IVa showing lines of diffuse scattering. The inset enlarges the marked area, and the arrows indicate satellite peaks adjacent to (stronger) main reflections on the diffuse lines. The arrow in the two-dimensional image marks a line of main peaks which are not located on the diffuse lines.

Firstly, those reflections that are not located on the diffuse lines can be indexed as a body-centred tetragonal structure with lattice parameters $a_I = 8.408(6) \, \text{Å}$ and $c_I = 4.735(3) \, \text{Å}$ which will be called the $I$ structure. The strong reflections lying on the diffuse lines can be indexed as a $C$-face-centred tetragonal structure with $a_C = 8.400(5) \, \text{Å}$ and $c_C = 3.411(4) \, \text{Å}$ and will be referred to as the $C$ structure. Finally, the remaining satellite reflections can be indexed by a $C$-centred monoclinic structure with lattice parameters $a_M = 8.4513(4) \, \text{Å}$, $b_M = 8.414(3) \, \text{Å}$, $c_M = 3.4191(11) \, \text{Å}$ and $\beta_M = 95.96(4)^\circ$ which form four orthogonal domains. To the order of the accuracy in the measurements, one may readily see that $a_I = a_C = b_M$. Images were also recorded, as the sample was moved in $0.5^\circ$ steps around an axis perpendicular to the diffuse planes and these reveal the distribution of scattering in reciprocal space. The diagram illustrating the reciprocal lattice is shown in figure 5.4. The open blue circles mark reflections from the main body-centred tetragonal ($I$) unit cell ($a_I = b_I = 8.408(6) \, \text{Å}$, $c_I = 4.735(3) \, \text{Å}$). The large red crosses mark reflections that can be indexed on the $C$-centred tetragonal unit cell with the same dimension in the $a - b$ plane, but with $c_C = 3.411(4) \, \text{Å}$. The green circles mark reflections that can be indexed on four identical $C$-face-centred monoclinic unit cells, related by $90^\circ$ rotations around the tetragonal $c$ axis, with $a_M$.
Figure 5.4: Composite reciprocal lattice of the Ba-IVa phase, showing the $I$ (open blue circles), $C$ (red crosses), and $M$ (open green circles) reflections and planes of diffuse scattering. In phase IVb, the $M$ reflections are replaced by peaks at the positions of the small green crosses. The $hk0$ reflections are indicated by the superposition of all three components.

$$= 8.4513(4) \text{ Å}, \quad b_M = a_I, \quad c_M = 3.4191(11) \text{ Å} \quad \text{and} \quad \beta_M = 95.96(4)$. The $I$, $C$ and $M$ lattices are all commensurate with each other in the tetragonal $a - b$ plane. But, the $C$ and $M$ lattices — and the planes of diffuse scattering — are incommensurate with the $I$ lattice along the $c$ axis.

The reported structure solution of Ba-IV is shown in figure 5.5 where the diffraction patterns collected from the powder technique can also be understood using this structural model obtained from single crystal techniques. From the single crystal experiment, accurate $hkl$ reflection intensities could be measured for the body-centred tetragonal cell. The non-$hk0$ data could be fitted using the proposed body-centred tetragonal unit cell, $I$-lattice, with eight atoms in the unit cell occupying site $8h$ of space group $I4/mcm$, with coordinates $x = 0.1486(1), \quad y = x + 0.5 \quad \text{and} \quad z = 0$ at 12.1 GPa. Misfits of this structure to the $hk0$ intensities revealed that the octagonal channels of the $I$ structure or so called the “host” structure are occupied by “guest” chains atoms running along the tetragonal $c$ axis. These chains form a $C$-centred tetragonal structure and four orthogonal $C$-centred monoclinic structures, as shown in inset (i) and (ii) in figure 5.5,
and are labelled as the $C$ and $M$ (or "guest") structures respectively. All three lattice types ($I$, $C$ and $M$) have reciprocal lattices which overlap exactly in the $a^*$, $b^*$-plane and consequently the $hk0$ reflections have intensity contributions from the host and the guest: i.e. from the $I$-structure, the $C$-structure and all four components of the $M$-structure. With single-crystal techniques, reflections from all six lattices ($I$, $C$, $4 \times M$) can be collected separately and standard refinement techniques can be employed provided that the $hk0$ reflections are excluded. The $hk0$ reflections provide information on the projection of the complete structure (including all its components) and the relative proportions of the host and the guest can be refined to reveal the overall density. Since all the guest chains are identical in a $c$-axis projection, the relative occupancies of the host and guest parts can be obtained from a simultaneous fit to the $hk0$ reflections and the non-$hk0$ $I$-lattice reflections. At 12.1 GPa the "guest" structure of the Ba-IVa phase was refined to a 100% occupancy within a 1% error. There are then $c_I/CC,M = 1.388$ guest atoms in each channel in $I$ unit cell. The whole structure thus contains 10.776 atoms in the $I$ cell. For powder-diffraction methods, the $hk0$ reflections provide significant difficulties for Rietveld refinement techniques and the structural model must be constructed so that a guest component (which is "smeared" along $z$) is included in the host model structure — as will be described in section 5.3.3.

The refined unit cell dimensions for the composite Ba-IVa structure, using the powder
pattern collected at 12.0 GPa by Nelmes et al [64], are $a_C = b_C = b_M = a_I = 8.4207(13)$ Å, $c_I = 4.7369(4)$ Å, $a_M = 8.4623(35)$ Å, $\beta_M = 96.151(9)^\circ$, $c_C = 3.4117(5)$ Å and $c_M = 3.4269(7)$ Å. At 12.8 GPa, single crystal data were also collected for a sample in the Ba-IV phase. No change was found in the $C$ and $I$ structures in passing through the IVa/IVb transition. However, the reflections previously belonging to the $M$ structure can now be explained using an orthorhombic structure (denoted as the $O$ structure) which has two orthogonal domains. Refinement of the powder pattern at 12.9 GPa gives $a_C = b_C = a_I = 8.346(3)$ Å, $a_O = 11.802(3)$ Å, $b_O = 5.912(4)$ Å, $c_I = 4.6966(10)$ Å, $c_C = 3.4095(5)$ Å and $c_O = 3.4070(27)$ Å. Within error there is no difference between $c_C$ and $c_O$. This is clearly another arrangement of the $c$-axis chains while the main host structure remains unchanged. The diffuse scattering can also be understood as this type of structure is incommensurate along the $c$ axis resulting in the high positional disorder of the guest chains in this structure. However, as this structure is commensurate in the $a - b$ plane therefore no diffuse scattering in the $hk0$ layer.

This is the first time that this type of structure has been observed in an element. In the next section, the Sr-V structure studied by the author will be explained in comparison with this Ba-IV prototype structure. It is important to note that the structure solution of Sr-V could not have been completely understood without the structure solution of the Ba-IV structure obtained from single crystal methods.

5.3.3 The Structure Solution of Sr-V from the Prototype Ba-IV Structure

Based on the similarity between the Ba-IV and Sr-V patterns, a full structural study of the Sr-V phase has been carried out. In this section, the Sr-V phase is clearly shown to have a very complex structure, similar to that reported for the Ba-IV phase. The integrated ADX powder profiles of Sr-V and Ba-IV were compared in order to establish a connection between their structures. Figure 5.6 reveals a strong similarity between the integrated profile of Ba-IV collected at 13 GPa and the Sr-V pattern collected at 56 GPa. The relative intensites and spacings of the strongest peaks, labelled 1 to 8 in both patterns, bear a very close resemblance.

In Ba-IV, the main strong peaks labelled 1 to 8 in figure 5.6 arise from the body-centred tetragonal ($I$) or host structure. In Sr-V, these main strong peaks can be explained
Figure 5.6: The blue pattern is the integrated profile of Ba-IV collected at 13 GPa. The red pattern is the integrated profile of Sr-V collected at 56 GPa. The inset shows an enlarged view of part of the Sr-V profile. Peaks marked with asterisks are from the accompanying phase, peak G is from gasket and the peaks label 1 to 8 are correspond to each other which exhibit a strong similarity.

by the same body-centred tetragonal unit cell with lattice parameters $a_l = 6.958(2)$ Å and $c_l = 3.959(2)$ Å at 56 GPa, giving a $c_l/a_l$ of 0.569(1) compared with 0.563(1) in Ba at 12.9 GPa. The Rietveld refinement is shown in figure 5.7 where the body-centred tetragonal structure is used (space group $I4/mcm$ with eight atoms in the unit cell, occupying $8h$ sites at $x, y = x+0.5$ and $z = 0$ with $x \sim 0.15$). However, as for Ba-IV, this structure could not explain the whole diffraction pattern. This proposed body-centred tetragonal cell clearly exhibits intensity misfits for all the $hk0$ reflections and also leaves about 15 weak reflections unindexed, as shown in figure 5.7. The accompanying smooth reflections, which appear first at the Sr-II-to-III transition, are unchanged at the IV-V transition and remain relatively smooth compared to those of the Sr-V pattern, and can therefore be readily distinguished. The lines from the accompanying smooth phase are indicated by asterisks in figure 5.7.

The remaining unindexed peaks from this body-centred tetragonal structure can be explained by the $C$-face-centred tetragonal (C) "guest" phase alone, as also observed in Ba-IV [64]. In Ba-IV, this $C$ guest lattice is commensurate with the $I$ host lattice in the $a-b$ plane, but incommensurate with it along $c$. This is also the case for Sr-V where
Figure 5.7: The structural refinement using body-centred tetragonal unit cell, shown in the insets. The observed data is shown as a dotted line and the calculated pattern is shown as a solid line, tick marks indicate the calculated peak positions of the proposed tetragonal host structure. Below the tick marks is the difference between the observed and calculated profiles and G indicates a reflections from the tungsten gasket.
the whole pattern can be fully explained with this guest-host structure. As for Ba-IV, the $C$ structure is formed from chains of atoms running through the channels, along four-fold axis of the $I$ host structure, and therefore the intensities of the $hk0$ reflections have contributions from both the "host" and the "guest" components. The peaks that were not indexed by the $I$ phase can therefore be indexed as non-$hk0$ reflections from the $C$ phase. The measured peak positions of such peaks give the refined lattice parameters to be $a_C = 6.961(3)$ Å and $c_C = 2.820(1)$ Å at 56.0 GPa with $c_I/c_C = 1.404(1)$, similar to the refined value of 1.378(1) for Ba-IV at 12.9 GPa [64].

Before full Rietveld refinement of the structure can be undertaken careful consideration must be made of how intensity assignment is made to the $hk0$ reflections which have contributions from both the $I$ and $C$ structures. As the structures are commensurate in the $a$, $b$-plane both structures will contribute coherently in the $hk0$ layer and, therefore, a standard two-phase Rietveld refinement will not determine the intensities correctly for this layer. Considering only the $I$ "host" structure for now, we know that placing atoms on the $8h$ sites of $I4/mcm$ ($x(x = 0.1460(2)), y = x + 0.5, z = 0$) will fit the non-$hk0$ reflections extremely well (as can be seen in figure 5.7). To simulate the contribution for the $C$ "guest" atoms, rods of electron density must be placed at $(0,0,0)$ and $(, ,0)$ so that the full structure is reproduced in projection (thus satisfying the $hk0$ reflections) but the "smearing" of electron density along $z$ will result in no contribution to the non-$hk0$ reflections. This model is a realistic approximation to the diffraction process as the non-$hk0$ reflections provide observations of the $I$ lattice unit cell averaged over the whole crystal. As $c_I$ and $c_C$ are incommensurate, on average, the guest atoms will explore all positions along $z$ in the average host unit cell — hence the host atoms in the average unit cell "see" the guest atoms as being smeared into uniform rods of electron density. To produce a reasonable approximation to this model for Rietveld refinement, guest atoms were placed at $(0,0,0)$ and $(, ,0)$ with substantial thermal motion along $c$-axis.

The resulting Rietveld refinement fit produced by this model is shown in figure 5.8 where the intensities (and positions) of all the $hk0$ reflections are very well defined, leaving only the weak non-$hk0$ $C$-phase reflections. The refined coordinates of the $I$ "host" structure are $x = 0.1460(2), y = x + 0.5$ and $z = 0$. 
Figure 5.8: Structural refinement fit using the body-centred tetragonal unit cell with electron densities modelled as rods along the host channels. The observed data is shown as a dotted line and the calculated pattern is shown as a solid line, tick marks indicate the calculated peak positions of the tetragonal host structure. Below the tick marks is the difference between the observed and calculated profiles and G indicates a tungsten gasket reflection. The red arrow in the inset shows the first strongest reflections from the smooth accompanying phase. The asterisks in the integrated profile and the blue arrows mark the unindexed peaks from non-\(hk0\) C-phase.
Figure 5.9: Rietveld refinement of the Sr-V profile at 56 GPa. The tick marks below the profile show the peak positions from (upper set) the $I$ structure with $C$ rods to fit the $hk0$ reflections and (lower set) the $C$ structure with its $hk0$ reflections deleted. Below the tick marks is the difference between the observed and calculated profiles. Indices are also given for both $I$ and $C$ structure with the subscript $C$ for the $C$ structure. Asterisks indicate reflections from the smooth phase.

In order to perform Rietveld refinement of the full structure on the whole pattern, a full model for the $C$ structure is needed to model the non-$hk0$ reflections from $C$ structure. The non-$hk0$ $C$-phase reflections are fitted as a second separate phase, and the contribution of this phase to the $hk0$ reflections had to be deleted from the fit as they were already accounted for by the first composite phase model. The Rietveld refinement program must therefore allow the reflection list to be edited. The Rietveld refinement program used by the author for most of the refinements presented in this thesis, GSAS, does not allow the reflection list to be edited. An alternative Rietveld refinement program, MPROF [65] had to be used instead. The resulting fit to the whole pattern using the full structure is excellent, as can be seen in figure 5.9. The final full structure is shown in figure 5.10.

In the Ba-IV experiment, after many attempts, a sample was transformed to one single crystal of phase IV at 12.1 GPa. This sample therefore gave a strong single set of
Figure 5.10: The structure of Sr phase V. The “host” $I$ structure (green atoms) with guest chains (red atoms) is shown in a $c$-axis projection. The $I$ structure atoms are labelled with their $z$ coordinates. The inset shows the $C$ “guest” structure.

reflections and diffuse scattering lines previously shown in figure 5.3. This particular sample was a crucial key to the structure determination. In the single crystal case, the reflections from the $I$, $C$ and $M$ structures should form bright spots while the disordered arrangement of guest atoms along the octagonal channels should produce parallel sheets of diffuse scattering lying perpendicular to $l$ in reciprocal lattice (though not at $l = 0$).

The Sr-V diffraction patterns collected up to 56 GPa at SRS, Daresbury showed no evidence of either diffuse scattering or a transformation in the guest structure which were both observed in Ba-IV. However, a further study has been carried out at the ESRF in order to obtain increased sensitivity to weak diffraction features and to extend the pressure range explored. Figure 5.11 shows an image recorded at 70 GPa with the ESRF beamline equipment. Lines of diffuse scattering are clearly visible, revealing the presence of one large crystallite with its $c$ axis in the plane of the image. The positions of these lines correspond to sheets of diffuse scattering that are coplanar with the $hk1$, $hk2$, etc., reciprocal-lattice layers of the $C$ component, exactly as in Ba-IV. There is no plane of diffuse scattering for $l = 0$ because the chain displacements are along $c$. 

Figure 5.11: Two-dimensional image of Sr-V recorded at 70 GPa showing $l \neq 0$ lines of diffuse scattering, as marked by arrows. The streaks along AB direction are an artefact of the image-plate reader.
In fact, the ESRF data reveal diffuse scattering at the pressures of previous SRS data, but it becomes readily visible only at much higher pressures. This may be because of increasing disorder with increasing pressure, or because the crystallite giving the diffuse scattering grew larger with increasing pressure.

The diagram of the reciprocal lattice of this structure is shown in figure 5.12. The blue open circles mark reflections arising from the main body-centred tetragonal $I$ "host" structure (unit cell $a_I = 6.958(2)$ Å, $c_I = 3.959(2)$ Å) and the red crosses mark reflections that can be indexed on another tetragonal $C$ "guest" structure (unit cell with the same dimensions in the $a - b$ plane, but with a $C$-face-centred lattice and $c_C = 2.820(1)$ Å). The $I$ and $C$ lattice are commensurate with each other in the tetragonal $a - b$ plane but the $C$ lattice - and the planes of diffuse scattering - are incommensurate with the $I$ lattice along the $c$-axis.
Figure 5.13: The evolution of the \( I \) "host" and \( C \) "guest" structure are illustrated in (a) evolution of \( a \) for both guest and host structure (b) and (c) development of \( c \) in host and guest structure respectively and (d) the ratio of \( c_I/c_C \).

### 5.3.4 Minor Phase Transition in Sr-V

Rietveld refinements using the composite \( I \) "host" and \( C \) "guest" structural model have been performed over a wide pressure range up to 67.2(4) GPa where the patterns undergo a minor change which suggests an intra-structural phase transition. The evolution of the powder patterns indicates a structural transition in the "guest" structure at 67.2(4) GPa, similar to that observed in Ba-TV at 12.6(2) GPa. The main non-\( hko \) strong reflections from the \( I \) structure show no significant change while the \( hko \) and weak reflections indexed by the \( C \) structure are obviously changed. The whole structure, therefore, forms another structure similar to the previous phase but with a minor change in their "guest" structure. This phase is labelled Sr-Vb and the previous lower pressure phase is now called Sr-Va.

On pressure increase the cell dimensions of Sr-Va vary continuously up to and through the transition to Sr-Vb. Figure 5.13 shows the changes in the cell dimensions as a function of pressure obtained on pressure increase to \( \sim68 \) GPa. At a pressure of 67.2(4)
Figure 5.14: $V/V_0$ for the full pressure range up to Sr-Va. The calculated values from host structure only are shown to be offset.

GPa, the guest structure undergoes a structural phase transition as obviously shown in (d) in figure 5.13 while the host structure is unchanged.

In Ba-IV, the availability of accurate single-crystal data enabled the relative occupancy of the host and guest parts to be refined from a simultaneous fit to the $hk0$ reflections and the non-$hk0$ $I$-lattice reflections. This resulted in an occupancy of 100% within less than 1% error. In Sr-V, however, the transition takes place at much higher pressure and several attempts to grow a single crystal at such a high pressure were unsuccessful. At the same time, the strongly textured nature of the sample limits the accuracy with which the guest site occupancy can be refined from powder data, and it can only be shown to be 100% within only ~30%. However, the great similarity to Ba-IV in atomic coordinates, the unit cell ratios $c_I/c_C$ and $c_I/a_I$ as well as structural stability considerations, all strongly suggest that the occupancy is 100%. For this particular type of structure, even though the lattice parameters and atomic coordinates are known, the density cannot be determined with complete certainty. If 100% occupancy is assumed, one can calculate the number of guest atoms contained within the “host” structure from $c_I/c_C$. At 56 GPa, $c_I/c_C = 1.404(1)$ and therefore the structure should have 1.404 atoms in each of the two channels in the volume of the $I$ unit cell and hence it
should contain a total of \(8 + 2.808 = 10.808\) atoms. However, as previously illustrated, \(c_1/c_C\) decreases with pressure. Therefore, based on the assumption of 100% occupancy at all pressures, the measured \(c_1/c_C\) can be used to derive \(V/V_0\) values, as plotted in figure 5.14. There is no discernible \(V/V_0\) discontinuity at the Sr-IV-V transition and, therefore, the assumption of 100% of the guest site occupancy is shown to be required.

5.3.5 Phase Transition in the Guest Structure

On further compression, Sr-Va undergoes a minor structural phase transition to Sr-Vb at 67.2(4) GPa. The integrated profiles collected at 65.8(3) GPa and 72.3(3) GPa are shown in figure 5.15. In these data, oversaturation of the strong reflections has enhanced the apparent magnitude of the weaker reflections compared to the true relative \(I\) and \(C\) lattice intensities. All the non-\(hk0\) strong reflections from the \(I\) lattice reveal no changes. Most of the \(C\) reflections, apart from 001\(C\), are reduced in intensity while new relatively weak peaks emerge. These new weak reflections reveal no changes between 70.8(4) and 75.1(3) GPa suggesting that the transition is complete. As the \(C\) peaks are weakened with respect to the unaltered \(I\)-lattice peaks and the new weak reflections emerge at the same time, it can be interpreted that the previous \(C\) structure is transforming into another guest structure while there are no significant changes in host structure. A similar phenomenon is also observed in the Ba-IV structure where the \(M\) guest structure undergoes a structural phase transition but the host structure is unchanged. In Ba-IVa, there are two types of guest structures, a \(C\) structure and a monoclinic \(M\) structure [64]. Upon transforming into the Ba-IVb structure, the \(C\) guest structure remains the same while \(M\) structure transforms into an orthorhombic \(O\) structure.

Diffraction data for Sr-Vb were measured up to 75 GPa, the highest pressure obtained. At 75 GPa reflections from the \(C\) structure are markedly reduced but can still be detected suggesting that the sample retains the \(C\) guest structure while a significant fraction of the \(C\) guest has transformed into another structure. The 001\(C\) reflection from the \(C\) structure persists, sharp and strong, throughout the transition, as shown in figure 5.16, suggesting that the new guest structure should have some geometrical relationship with the \(C\) structure. A series of patterns showing the evolution of the
Figure 5.15: Diffraction profiles from Sr-Va at 65.8 GPa and Sr-Vb at 72.3 GPa. The C lattice reflections a, b and c are labeled in both profiles. Arrows in Sr-Vb pattern mark new non-I lattice reflections. The inset reveals a very spotty Sr-Vb pattern where smooth peaks from accompanying phase are still clearly distinguishable and the strongest peak is indicated by the red arrow.
Sr-Vb phase are shown in figure 5.16. The two-dimensional pattern in the inset shows the very spotty patterns of Sr-Vb. As previously mentioned, recrystallised Sr-V has spotty patterns which become increasingly spotty with pressure. This particular set of data had been annealed at lower pressure in order to acquire a smooth and refinable Sr-Va pattern. However, the pattern becomes spotty on pressure increase into the Sr-Vb phase. The inset on the left reveals the evolution of a new peak on the low-angle side of the first smooth phase peak, indicating the transition to the Sr-Vb phase. The middle inset shows the development of the pattern where all the strong \( I \) reflections show no sign of changing.

To obtain a complete structure solution of Sr-Vb, systematic attempts to index this new guest structure have been carried out using the widely available indexing programs DICVOL [52, 53] and CRYSFIRE [54]. As previously mentioned, the guest structure shares the \( hk0 \) reflections with the host structure and this information needs to be included in the attempted indexing. Several attempts to index the pattern using the \( hk0 \) host reflections and the new peaks failed. Later trials which also included the \( 001_c \) reflection and other weakened \( C \) reflections were also unsuccessful. The lack of success at indexing the new reflections was probably due to the very small number of observations — even when the \( C \) reflections were added.

Starting with an annealed Sr-Va sample which gave smooth powder patterns, pressure increase caused the diffraction rings to form discontinuous short arcs of intensity resulting in a more textured pattern. At the transition pressure from Sr-Va to Sr-Vb the patterns were very highly textured. This behaviour strongly suggests that the sample suffers from deviatoric stress arising from the fact that under such a high pressure, the pressure medium has solidified and thus fails to provide a quasi-hydrostatic environment to the sample. Uniaxial compression of a solid with finite strength causes pressure anisotropy. This leads to a variation of stress conditions at different points in the sample — so called deviatoric stress. The diffraction pattern from a powder sample under these conditions is generated from crystallites under non-uniform stress with each suffering quite different distortions. As a consequence, such patterns suffer from peak broadening and asymmetric peak shapes.

To establish whether or not recrystallised Sr-Vb has pronounced deviatoric stress and
Figure 5.16: Integrated profiles from Sr phase V collected from ESRF revealing the transition in guest structure. The first inset shows a close up region of the 001$_C$ reflection and first strong smooth accompanying phase, marked with an asterisk, with a newly growing Sr-Vb peak in the middle. The middle inset is an enlarged view of part of the Sr-V profile and the two-dimensional image shows a spotty Sr-Vb pattern collected at 72.3 GPa.
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Table 5.1: The comparison of calculated peak positions and measured peak positions. Indexing of these lines at 72.3 GPa given a calculated tetragonal structure with lattice parameters $a = 6.766(9)$ and $c = 3.856(6)$.

Therefore has anomalous peak displacement in its powder patterns, further attempts to study the host structure have been carried out. From the powder patterns, and from comparison studies with the Ba-IV structure, the host structure can be readily shown to be stable up to the highest pressure obtained at 75 GPa. Provided that the host structure is very well defined over this pressure range, lattice parameters can be calculated from the measured peak positions of $hk0$ and non- $hk0$ host reflections. This can then used to refine the structure using Unitcell [69] and the misfit of these reflections can be used to shows the degree of displacement from the expected peak positions. Table 5.1 shows the misfits of the measured structure to the calculated structure at 72.3 GPa. A misfit in $2\theta$ of up to 0.045° (compared to a FWHM of $\sim 0.12^\circ$) indicates significant displacements in peak positions especially for the $hk0$ reflections which also contribute directly to the guest structures. The Sr-Vb patterns therefore exhibit severe peak displacements and are consequently not suitable for indexing.
5.3.6 A Structural Phase Transition in the Smooth Accompanying Phase

The Sr-Va patterns appear to develop smoothly on compression along with the accompanying phase which remains reasonably smooth in texture compared to the Sr-V pattern. At 59.6(5) GPa this accompanying phase undergoes a structural phase transition. Figure 5.17 shows the development of the smooth accompanying phase (along with the Sr-Va phase) in the pressure range between 55.8(4) and 64.7(3) GPa from the ESRF data. The first two insets show close-up regions of the patterns revealing the continuous development of the smooth accompanying phase, indicated by asterisks. The first inset shows the intensity of the low-angle smooth peak (marked with a red asterisk) reduce with increasing pressure while the new smooth peak, marked with a black asterisk, grows (on the lower-angle side of the vanishing smooth peak). The 001 reflection from the C "guest" structure (001\textsubscript{C}) shows no obvious change. Patterns recorded from SRS, Daresbury, up to 56 GPa shows no sign of a phase transition in this accompanying smooth phase. The data collected from the ESRF are however collected over a higher pressure range and the smooth accompanying phase reveals a structural transformation at 59.6(5) GPa. The transition can be clearly observed through the first strong peak and other peaks previously marked with asterisks in figure 5.9. These reflections decrease in intensity while new reflections emerge. The transition is complete at 64.7(5) where only three reflections from the new structure of the smooth accompanying phase can be observed. With such limited data, structure solution is not possible. This accompanying phase persists up to 75 GPa, the highest pressure reached for a structural study of Sr so far. The smooth phase appears to evolve independently and is stable over a very wide pressure range, from 25 GPa up to 59 GPa, where it undergoes a phase transition to another smooth phase which persists to at least 75 GPa. On pressure decrease, the smooth phase also shows a reversible transition and completely disappears at \sim 10 GPa when Sr transforms back to the fcc structure. This phenomenon confirms that this accompanying smooth phase is not just a simple contamination but is possibly another high-pressure form of Sr.
Figure 5.17: Evolution of the smooth accompanying phase between 55.8(4) GPa and 64.7(3) GPa. The insets show expanded regions of the powder patterns. The red arrow in two-dimensional image indicates the strongest smooth peak which can be readily observed in the otherwise spotty pattern. The red and black asterisks in the insets indicate the reflections from the smooth phase before and after the transition respectively.
In conclusion, the structure and behaviour of Sr-V is shown to be very similar to that of Ba-IV in all its principal features. There are some differences in detail in the nature of the guest structure. The structure comprises a "host" structure which can be explained by $I4/mcm$ with atoms on $8h$ sites with a refined $x$ value of 0.1460(2). The second component of the structure is the "guest" structure which forms a $C$-centred tetragonal arrangement of atoms within the octagonal channels of the host structure. This structure is commensurate in the $a - b$ plane but not in the $c$ direction as $c_t/c_C$ is non-rational. The guest structure appears to undergo a phase transformation at 67.2(4) GPa while the host structure remains unchanged, a similar behaviour to that observed in Ba-IV but at much higher pressure. The structure solution for this second guest phase is however not possible with the currently available data.

It is interesting to note that this type of high-pressure structure, observed first in Ba-IV, can not be solved without single-crystal techniques. As previously mentioned, single-crystal techniques are ideal for very accurate structure determination and, in this case, they have been proven to be crucial for the structural solution of the guest chain in Ba-IV. However, with relatively high-pressure experiments where the samples usually pulverise after the first transition, the powder method is more appropriate. In Sr-V, the transition occurs at much higher pressure and therefore it is not possible to obtain a good quality single crystal suitable for single-crystal experiments. In fact, several attempts to grow a single crystal of Sr-V at such a high pressure using pressure cycling techniques, which were successfully performed in Ba-IV, failed. Image-plate techniques have been proven to be a crucial method for the high-pressure structure determination of Sr-V. Without texture information, the identification of the accompanying phase could not be clearly distinguished and therefore may lead to a misunderstanding of the evolution of the guest structure.

Along with Ba and Rb, Sr is one of the very first elements shown to have this type of structure. In Sr-V, the incommensurate self-hosting structure can be interpreted in the same way as the Ba-IV structure where the segregation of an element into two different electronic species is observed. A commensurate prototype of the Ba-IV structure can be found in $M_2M'$ intermetallics such as Al$_2$Cu and Na$_2$Au [70], in which the $M$ atoms
form the $I4/mcm$ host structure and the $M'$ atoms occupy the chain sites. The chain atoms are smaller in all cases. This suggest that the guest-host structure found in Sr-V and Ba-IV are formed by two different pressure induced electronic species of the same element. The chain atoms have an electronic configuration with a smaller radius than those forming the host structure. It is astonishing that a single element can form this type of structure but it is emerging as a stable phase over a very wide pressure range in Sr.
Chapter 6

Computational Work on the High-Pressure Phases of Strontium

6.1 Introduction

Pressure induced phase transformations have been an area of interest for both experimental and computational aspects for a long period of time. Recently, several high-pressure crystal structures have been discovered experimentally in elements and have been shown to be very complex in many cases. A theoretical understanding of such crystal structures is an important key to their properties at high pressure. Most of the physical properties are related to total energy or its derivatives, among them the lattice constants of a crystal. The desired lattice constant of a crystal is the lattice constant that minimizes the total energy. One may assume that by calculating a precise total energy of the system, many of these physical properties such as equilibrium lattice constant can be computationally determined. Quantum mechanics is then required for this situation where the total energy calculations involved are at the atomic level. In principle, the total energy of the structure can be calculated by solving the Schrödinger equation for a many-body problem. Given the many-body nature of the problem, this would of course involve many-body wavefunctions of the electrons in the solid and is
therefore a complicated calculation. In a real solid, there are a very large number of electrons which interact strongly with each other and with the nuclei. Therefore, a substantial level of approximation is required to solve the problem analytically.

This chapter will briefly describe the approximations and methodology used to perform the calculations in this thesis. A full presentation of the theory can be found elsewhere [71, 72, 73]. Later on, the total energy calculation of the high pressure structures of Sr will be presented. All the calculations presented in this thesis were performed by the author using the CAmbridge Serial Total Energy Package (CASTEP) [71].

6.2 Total Energy Calculations

6.2.1 Born-Oppenheimer Approximation

As previously mentioned, the total energy of the system is the important key to the understanding of the various physical properties. The obvious approach to this is the use of quantum-mechanical rules or Hamiltonians to calculate the total energy of a system. This involves trying to solve the many-body Schrödinger equation for a system of electrons and nuclei. The problem of solving the Schrödinger equation is to find the eigenfunctions, $\Psi$, and eigenvalues, $E$ from equation 6.1.

$$\mathcal{H}\Psi = E\Psi$$

(6.1)

Where $\mathcal{H}$ is the Hamiltonian for the system which is defined in (6.2) for non-interacting particles.

$$\mathcal{H} = \sum_i -\frac{\hbar^2}{2m_i} \nabla_i^2 + V(r_i)$$

(6.2)

Where $m_i$ is particle's mass and $V$ is the potential. Independent solutions can be obtained separately because the systems do not interact. However, for a system comprising $N$ electrons, the Coulomb interaction between ions and electrons needs to be included and the Schrödinger equation is therefore applied to a many-body wavefunc-
tion $\Psi(r_1, r_2, ... r_N)$ describing all electrons. The Hamiltonian then becomes:

$$H = \sum_i -\frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{Z^2 e^2}{4\pi \epsilon_0 |R_i - R_j|} + \sum_k -\frac{\hbar^2}{2m} \nabla_k^2 + \frac{1}{2} \sum_k \sum_{k \neq l} \frac{e^2}{4\pi \epsilon_0 |r_k - r_l|} + \sum_{k,i} \frac{Ze^2}{4\pi \epsilon_0 |r_k - R_i|} \tag{6.3}$$

where $M$ and $m$ are the mass of the nucleus and the electron respectively; $Z$ is the atomic number; $e$ is electronic charge; $\epsilon_0$ is the electric constant; and $R$ and $r$ are the relative coordinates of the nucleus and electrons respectively. The second term in the Hamiltonian is the Coulomb interaction between the nuclei (sometimes called the Ewald interaction), the fourth term is the Coulomb interaction between electrons (often called the Hartree term) and the fifth term is electron-nuclei coupling term. The system is thus dealing with two components, electrons and nuclei, interacting with themselves and each other. Since the electrons are much lighter than the nuclei they respond to any change in the system at a much faster rate. Based on this assumption, the nuclei are assumed to be stationary relative to the electrons. This assumption is called "The Born-Oppenheimer Approximation". This approximation is made throughout the work described here and therefore the Hamiltonian for a static external potential is:

$$H = \sum_k -\frac{\hbar^2}{2m} \nabla_k^2 + V_{ext} + \frac{1}{2} \sum_k \sum_{k \neq l} \frac{e^2}{4\pi \epsilon_0 |r_k - r_l|} \tag{6.4}$$

The first two terms are the kinetic energy and the external potential energy (i.e. the Coulomb interaction between the electron and the nucleus in the Born-Oppenheimer approximation) respectively and the third term is the Coulomb interaction between electrons. However the Schrödinger equation still cannot be solved $\Psi$ is still unknown therefore a number of approximations are required for the construction of $\Psi$ and therefore finding $E$. 
6.2.2 Density Functional Theory

The most important and probably the most difficult problem for electronic structure calculation is to take account of the effects from the electron-electron interaction. Approximation techniques required to make the many-body Schrödinger equation solvable are briefly described in this section. The very obvious complication is that the electrons repel each other due to the Coulomb interaction between their charges and therefore the potential term arising from electron-electron interaction (i.e. the third term in 6.4) depends on the position of all other electrons. To simplify this problem, we need to introduce a single particle model of the problem which can be explained as a function of the position of one electron. The electron-electron interaction is thus approximated by the interaction between the electron and the overall charge density of the remaining electrons and the solution to the Schrödinger equation therefore becomes a solution for a one-electron wavefunction, $\psi_i(r)$ for the $i^{th}$ electron.

Density functional theory (DFT), first introduced by Hohenberg and Kohn in 1964 [74], provides an efficient method to deal with the many-body problem. The core principle of this theory states that the total energy, including exchange and correlation, of a system is a unique functional of the electron density, $n(r)$, only. The minimum value of the total energy functional is the ground state energy of the system and the electronic charge density that gives this minimum energy is then the single particle ground state density. The electron charge density thus becomes a central variation for the solution of the Schrödinger equation with a given external potential. In other words, the theory allows us to reduce the problem of an interacting many-body problem to an effective one-body problem.

Consider an arbitrary number of electrons moving under the influence of an external potential $V_{\text{ext}}(r)$ and the Coulomb repulsion. The Hamiltonian takes the form:

$$\mathcal{H} = T + V + U$$  \hspace{1cm} (6.5)
\[ T = -\frac{\hbar^2}{2m} \int \nabla \psi^*(r) \nabla \psi(r) dr \]  
(6.6)

\[ V = \int V_{\text{ext}}(r) \psi^*(r) \psi(r) dr \]  
(6.7)

\[ U = \frac{e^2}{2} \int \frac{1}{4\pi\varepsilon_0 |r - r'|} \psi^*(r) \psi^*(r') \psi(r') \psi(r) dr dr' \]  
(6.8)

where \( T \) is kinetic energy, \( V \) is the external energy and \( U \) is the electron-electron interaction. The electronic charge density in the ground state \( \psi \) is defined by:

\[ n(r) = \psi^*(r) \psi(r) \]  
(6.9)

which is clearly a functional of \( V_{\text{ext}}(r) \) i.e. a given \( V_{\text{ext}}(r) \) will lead to a unique electronic charge density \( n(r) \). Conversely, \( V_{\text{ext}}(r) \) can also be proved to be a unique functional of \( n(r) \) [74].

The Schrödinger equation can then be written in the form of charge density instead of wavefunction and the exact expression for the ground state energy as a function of the charge density in an external potential \( V_{\text{ext}}(r) \) becomes:

\[ E[n(r)] = \int V_{\text{ext}}(r) n(r) dr + \frac{e^2}{2} \int \int \frac{n(r)n(r')}{4\pi\varepsilon_0 |r - r'|} dr dr' + G[n(r)] \]  
(6.10)

The first two terms are a classical Coulomb interaction between the electrons and the external potential and the interaction of the electrons with each other respectively. Both terms are clearly seen to be a function of electronic charge density, \( n(r) \). The third term, \( G[n(r)] \), is a universal function of the charge density which contains the kinetic energy and any many-body effects which include all the exchange and correlation effects due to the electron interactions. However, equation (6.10) still requires a many-body wavefunction and thus the problem is still relatively complicated.

In 1965, Kohn and Sham showed how it is possible to replace the many-electron problem by an exactly equivalent set of self-consistent one-electron equations [75], known as
Kohn-Sham equations. From equation (6.10), Kohn and Sham have re-written the third term, $G[n(r)]$, as:

$$G[n(r)] = T[n(r)] + E_{xc}[n(r)]$$

(6.11)

where $T[n(r)]$ is the kinetic energy of a system of non-interacting electrons with density $n(r)$, and $E_{xc}[n(r)]$ is the exchange and correlation energy of the interacting system with density $n(r)$ i.e. including all the electron-electron interaction effects. It is still impossible to give an exact expression of $E_{xc}[n(r)]$ for an arbitrary $n(r)$. However, if the $n(r)$ is varying slowly, the $E_{xc}[n(r)]$ term can be written as:

$$E_{xc}[n(r)] = \int n(r) \epsilon_{xc}(n(r)) dr$$

(6.12)

where $\epsilon_{xc}(n(r))$ is the exchange and correlation energy per electron of a uniform electron gas of density $n(r)$. This assumption will be shown to have a crucial role in the next section. The total energy function obtained from (6.10) is stationary with respect to variations in the ground state charge density and therefore:

$$\int \delta n(r) \left\{ V_{ext}(r) + \frac{e^2}{2} \int \frac{n(r')}{|r-r'|} dr' + \frac{\delta T[n]}{\delta n(r)} + \mu_{xc}(n(r)) \right\} dr = 0$$

(6.13)

where $\mu_{xc}(n(r))$ is the functional derivative of the exchange and correlation energy with respect to the electronic charge density:

$$\mu_{xc}(n(r)) = \frac{\delta[n(r)\epsilon_{xc}(n(r))]}{\delta n(r)}$$

(6.14)

Since the variation in charge density should leave the total number of particles unchanged i.e.:

$$N = \int n(r) dr$$

(6.15)

then, the condition:
\[ \int \delta n(r) dr = 0 \quad (6.16) \]

must also be observed. Applying equation (6.16), a constant number of particles condition, to equation (6.13) gives the result:

\[ \frac{\delta E[n(r)]}{\delta n(r)} = V_{\text{ext}}(r) + \frac{\epsilon^2}{2} \int \frac{n(r')}{4\pi\varepsilon_0 |r-r'|} dr' + \frac{\delta T[n(r)]}{\delta n(r)} + \mu_{\text{xc}}(n(r)) = \nu \quad (6.17) \]

where \( \nu \) is a constant. Comparing this to the corresponding equation for a system with an effective potential \( V_{\text{eff}}(r) \) but without the electron-electron interaction.

\[ \frac{\delta E[n(r)]}{\delta n(r)} = \frac{\delta T[n(r)]}{\delta n(r)} + V_{\text{eff}}(r) = \nu \quad (6.18) \]

It can be readily seen from (6.17) and (6.18) that:

\[ V_{\text{eff}}(r) = V_{\text{ext}}(r) + \frac{\epsilon^2}{2} \int \frac{n(r')}{4\pi\varepsilon_0 |r-r'|} dr' + \mu_{\text{xc}}(n(r)) \quad (6.19) \]

This equation for non-interacting electrons moving in an effective potential is identical to that of interacting electrons. Therefore, with a given potential, one obtains the \( n(r) \) which satisfies these equations by simply solving the one-electron Schrödinger equation. In other words, the N-body Schrödinger equation can be written as N one-body Schrödinger equations in terms of the charge density.

Kohn and Sham defined the electronic charge density as:

\[ n(r) = \sum_{i=1}^{N} \psi_i^*(r)\psi_i(r) \quad (6.20) \]

The kinetic energy operator can now be expressed in terms of a single particle as follows:

\[ T = \sum_{i=1}^{N} \frac{-\hbar^2}{2m} \int \psi_i^*(r) \nabla^2 \psi_i(r) \quad (6.21) \]
This leads to the Schrödinger equation for non-interacting particles moving under an effective potential $V_{\text{eff}}(r)$, the so called Kohn-Sham equation:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(r)\right\} \psi_i(r) = \epsilon_i \psi_i(r) \tag{6.22}$$

where $V_{\text{eff}}(r)$ can be written as:

$$V_{\text{eff}}(r) = V_{\text{ext}}(r) + \frac{e^2}{2} \int \frac{n(r')}{4\pi\varepsilon_0|r-r'|} dr' + \mu_{xc}(n(r)) \tag{6.23}$$

The interacting multi-electron system can now be simulated by non-interacting electrons under the influence of the effective potential, $V_{\text{eff}}$. Therefore, if this effective potential term is local, i.e. it depends on only one point in space, then this equation should not be too difficult to solve.

The Kohn-Sham equation, (6.22), can be solved iteratively. By making an initial guess of $\psi = \psi_{\text{in}}$ and calculating $V_{\text{eff}}$ from equation 6.23, then equation 6.22 can be solved to obtain a new $\psi = \psi_{\text{out}}$. Using this new $\psi$ to calculate $V_{\text{eff}}$ via (6.23) again, the calculation is then repeated until the convergence, $\psi_{\text{in}} = \psi_{\text{out}}$, is reached. This procedure is called self-consistency in which the calculation is performed until potentials and wavefunctions change infinitesimally from one iteration to the next. This technique is used to obtain the wavefunctions. The self-consistent solution, $\psi_i$, can thus be obtained for the Kohn-Sham equation.

The resulting $\psi_i$ represents a single particle moving in an effective potential, $V_{\text{eff}}$. This wavefunction, known as a Kohn-Sham orbital, has the corresponding Kohn-Sham eigenvalue $\epsilon_i$. The electronic charge density can then be obtained from $\psi_i$ using (6.20) and the total ground state energy can be calculated from (6.10) using the charge density.

In principle, density functional theory would give the correct ground state of a given system. However, the exact form of exchange and correlation, $\mu_{xc}(n(r))$ term in the effective potential is still unknown and more approximations to this term are thus required. The local density approximation is the simplest method as shown by Kohn and Sham [75].
6.2.3 Local Density Approximation

In practice, the Kohn-Sham equation, (6.22), cannot be solved without knowing the exact form of the exchange and correlation term, $\mu_{xc}(n(r))$, hidden in $V_{eff}$. The local density approximation assumes that the exchange and correlation energy per electron at point $r$ in the electron gas, $\epsilon_{xc}(n(r))$, is approximately equal to the exchange and correlation energy per electron in a homogeneous electron gas (jellium) that has the same electron density at point $r$. That is:

$$E_{xc}[n(r)] = \int n(r)\epsilon_{xc}(n(r))dr$$ \hspace{1cm} (6.24)

where we approximate:

$$\epsilon_{xc}(n(r)) = \epsilon_{xc}^{hom}(n(r))$$ \hspace{1cm} (6.25)

So that from equation (6.14), the exchange correlation potential is a functional derivative of the exchange correlation energy. We have:

$$\mu_{xc}(n(r)) = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} = \frac{\partial[n(r)\epsilon_{xc}^{hom}(n(r))]}{\partial n(r)}$$ \hspace{1cm} (6.26)

The exchange and correlation functional is then purely assumed to be a function of $n(r)$ for a homogeneous system. For a nonhomogeneous system, the value of the exchange correlation potential at the point $r$ depends not only on the value of the charge density but also on its variation close to the point $r$. The corrections to the exchange and correlation energy due to the inhomogeneities in the electronic charge density about $r$ are ignored in the local density approximation. The Kohn-Sham equation can now be solved iteratively. The local density approximation is valid when the spatial variation of the density is relatively slow.

Despite its simplicity, the local density approximation has been shown to work remarkably well [76, 77]. This is partially due to the fact that this approximation correctly excludes one electron worth of charge from the neighbourhood of the electron at $r$ and therefore satisfies the correct sum rule for the exchange and correlation hole [78]. In
other words, the local density approximation considers both exchange and correlation effects arising from electrons of the same and opposite spin. i.e. each electron excludes the right amount of negative charge around it.

Figure 6.1 shows a summary of the electron-electron interactions in N-electron systems for different approximation schemes and illustrates the probability distributions of \( n(r) \) for \( N - 1 \) electrons around an electron with any given spin situated at \( r = 0 \). Probabilities are normalised such that \( p(r) \to 1 \) as \( r \to \infty \). In the Hartree approximation (a), all electrons are treated as independent particles and therefore the probability of \( n(r) \), \( p(r) \), is structureless. The Hartree-Fock approximation (b), the many-electron wavefunction satisfies the Pauli exclusion principle. Thus around the electron at \( r = 0 \) (and around all other electrons as well), the exchange hole can be seen by electrons of the same spin resulting in the density of electrons with the same spin being reduced while electrons with opposite spins are unaffected and are still structureless. In the local density approximation (c), electrons of both spins are effected by the same exchange-correlation hole i.e. the spin states are degenerate. This can be regarded as the spin average of the local spin density approximation. The local spin density approximation (d), allows for different shaped holes in the distribution of electrons with same spin and electron with opposite spin i.e. the spin states are non-degenerate. Using the local spin density approximation is however more complicated in the sense that explicit calculation of all electrons in the system are required and hence it doubles the computational effort.

There are now further improvements to the local density approximation such as the generalised gradient approximation [80] in which the exchange and correlation are taken as a functional of the local electron density and its gradient (6.27). The generalised gradient approximation is not illustrated in figure 6.1 but would not qualitatively differ from the local density approximation. The calculations presented in this thesis are all performed with the generalised gradient approximation.

\[
\epsilon_{xc}[n(r)] = \epsilon_{xc}(n(r), \nabla n(r)) \tag{6.27}
\]

Several parameterisations exist for the exchange correlation energy and potential of a homogeneous gas system [76, 77, 81, 82, 83].
Figure 6.1: Effects of the different approximation schemes on the electron probability at a distance $r$ from an electron of some spin [79]
6.3 Periodicity: Boundary Conditions of the System

The Kohn-Sham system of equations correctly includes exchange and correlation effects and can now be solved for each electron in a solid. We have the Kohn-Sham equations, one for each electron, in a form that can be solved, but a real sample of materials contain an enormous number of electrons. Thus the calculations still remains formidable and requires further simplifications which can be made using the principle of periodicity in crystals.

A perfect crystal can be regarded as made up of an infinite number of periodically arranged cells. This periodic boundary condition greatly simplifies the problem as each of these cells contain only a few hundred electrons which can be solved easily. The translational symmetry in a crystal allows a simulation of an infinite periodic crystal to be performed by considering only one unit cell. For a perfect crystal, the external potential, $V_{ext}$, acting on the electrons depends on a periodic array of ions. Therefore the electrons charge density $\rho(r)$ must also have the periodic property such that:

$$\rho(r) = \rho(r + R_L)$$  \hspace{1cm} (6.28)

where $R_L$ is a lattice vector and the external potential felt by electrons is also periodic and can be expressed as $V_{ext}(r) = V_{ext}(r + R_L)$. This condition meets the requirement needed for the use of Bloch’s theorem which is described below.

6.3.1 Bloch’s Theorem

Bloch’s theorem [84] states that in a periodic solid each electronic wavefunction can be written as the product of a cell-periodic part, $f_j(r)$, and a wavelike part (with wavevector $k$), $e^{ik \cdot r}$. The $i^{th}$ electron wavefunction, labelled as $\psi_i$ so far, is now labelled with $j$ to avoid confusing with $i$, the complex quantity.

$$\psi_j(r) = e^{ik \cdot r} f_j(r)$$  \hspace{1cm} (6.29)

The cell-periodic part of the wave function can be expanded using a finite number of
plane waves whose wavevectors are reciprocal lattice vectors of the crystal.

\[ f_j(r) = \sum_G c_G e^{iG \cdot r} \]  
(6.30)

Where \( G \) are the reciprocal lattice vectors, defined as \( G \cdot R_L = 2\pi n \) for all \( R_L \) where \( R_L \) is a lattice vector and \( n \) is an integer. Thus, each electronic wave function can be written as a sum of plane waves:

\[ \psi_{j,k}(r) = \sum_G c_{j,k+G} e^{i(k+G) \cdot r} \] 
(6.31)

The wavefunctions which are labelled by \( j \) for the band and wavevector, \( k \), are now expressed in terms of a plane wave basis set.

### 6.3.2 k-point Sampling

The use of Bloch’s theorem in the periodic solid greatly reduces the complication of the problem. In a periodic crystal, only a set of \( k \) points within the first Brillouin zone in reciprocal space are required for electronic state calculations. However, in a bulk solid, the electronic potential is composed of the finite electronic states at each point of the infinite \( k \) points and hence the infinite plane wave expansion of the electron wavefunctions still remains. The problem is now reduced from calculating an infinite number of wavefunctions to one of calculating a finite number of wavefunctions for an infinite number of \( k \) points.

However, electronic wavefunctions are smoothly varying over \( k \) space. In other words, electronic wavefunctions at \( k \) points that are very close to each other are nearly identical and hence make equal contributions to the total energy. Therefore, it is possible to represent electronic wavefunctions in the vicinity of a \( k \) point by using only a wavefunction at a single \( k \) point. Based on this assumption, the Brillouin zone can be approximated by a finite set of \( k \) points with appropriate weights. Each \( k \) point is assigned a weight \( \alpha_i \) such that \( \sum_i \alpha_i = 1 \). The electron density averaged over these is then taken as representative for the whole Brillouin zone.
\[ n(r) = \sum_i \alpha_i \sum_{j=1}^m \psi_{j,k_i}^*(r) \psi_{j,k_i}(r) \] (6.32)

The problem is now further simplified to that of only calculating a finite number of wavefunctions over a finite number of \( k \) points, so called special \( k \) points, representing the whole infinite \( k \) space. Bloch’s theorem uses the periodicity of a crystal to replace the calculations for an infinite number of one-electron wavefunctions with only calculations for a finite number of electron in the unit cell of a crystal. If the unit cell contains \( 2N \) electrons and the states are assumed to be doubly occupied, i.e. spin degenerate, only \( N \) electrons are need to be calculated at each \( k \) point as they have different \( f_j(r) \).

The electronic states are now labelled with \( k \) and \( j \) which form a basic formalism for the bandstructure.

There are a number of techniques used to generate the special \( k \) points [85, 86, 87] all of which result in a set of special \( k \) points which are sufficient to describe the contribution from the occupied electronic states to the potential and hence to the total energy. The magnitude of the error arising in the total energy contributed by an inadequate sampling of \( k \) points can be systematically minimised by using a denser set of special \( k \) points but this would obviously cost more computing time. Provided sufficient computing time is available, a converged electronic potential and a total energy can always be obtained by calculating the wavefunction at an adequately dense set of special \( k \) points.

All of the \( k \) point sampling procedures are based on the same techniques: the use of point group symmetries of the crystal to find points that are the same and then only calculating them once but with an appropriate weighting factor proportional to how often they repeat. This is an important key to reducing the time spent by the calculation since the time scale largely depends on the number of \( k \) points actually calculated. All the results presented in this thesis are based on the special \( k \) points generated using the Monkhorst and Pack sampling scheme [86], which samples the minimum number of special \( k \) points reduced by the symmetry.
6.3.3 Plane Wave Basis Sets

At each special \( k \) point, an infinite number of plane wave basis sets are required to expand the electronic wavefunction and this would again make the calculation formidable. This problem can be solved by introducing the kinetic cutoff energy \( \epsilon_{\text{cutoff}} \). This technique is based on the fact that the coefficients \( c_{j,k+G} \) in equation (6.31) for the plane waves with higher kinetic energy, \( (\hbar^2/2m)|k + G|^2 \), are very small compared to those with lower kinetic energies. Thus, a cutoff energy is set such that only plane wave with a kinetic energy less than \( \epsilon_{\text{cutoff}} \) are used. The truncation of the plane wave basis set at a finite cutoff energy reduces the number of basis plane waves to manageable size but also leads to an error in the computed total energy. The magnitude of the error can again be systematically reduced by increasing the value of this plane wave cutoff energy, \( \epsilon_{\text{cutoff}} \), but this would certainly cost more computing time. In practice, the cutoff energy can be determined by increasing the cutoff until the calculated total energy has converged to the optimum point. The optimum point is where the error in the total energy is minimised to an acceptable value for the problem.

6.3.4 Representation of Kohn-Sham Equations Using Plane Waves

Introducing plane wave basis sets for the wave functions has several advantages for the implementation of density functional theory. One of the main advantages is that by substituting equation (6.31) into the Kohn-Sham equation (6.22) gives the Kohn-Sham equation in a simpler form:

\[
\sum_{G'} \left[ \frac{\hbar^2}{2m} |k + G|^2 \delta_{GG'} + V_{\text{eff}}(G - G') \right] c_{j,k+G} = \epsilon_j c_{i,k+G} \tag{6.33}
\]

where \( V_{\text{eff}} \) from equation (6.23) has now taken the form of their Fourier transforms or, in other words in the reciprocal expression of (6.23).

\[
V_{\text{eff}}(G - G') = V_{\text{ext}}(G - G') + V_H(G - G') + V_{\text{xc}}(G - G') \tag{6.34}
\]

Where \( V_H \) is the Hartree potential. The kinetic energy is then diagonal, since it is simply
the weighted sum of the plane wave and the potential terms depending only on \( \mathbf{G} - \mathbf{G}' \). This can be solved by matrix diagonalisation and iteration until the eigenvalues converge to their ground state. The size of the Hamiltonian matrix (in square brackets in equation 6.33) increases with increased cutoff energy, \( (\hbar^2/2m)|k + \mathbf{G}_{\text{cutoff}}|^2 \), therefore it still needs further simplification to make the cutoff energy as low as possible and still give less error to the calculated total energy. This problem can be overcome by the use of the pseudopotential approximation which describes the core and valence electrons and will be discussed in the next section.

It is important to point out before going on that the total energy of the system is now a multi-dimensional function of the plane wave coefficients, \( c_{i,k+G} \), which can be solved using minimisation techniques.

6.4 Pseudopotential Approximation: Ion-Electron Interactions

The plane wave basis set has provided a simpler approach to the problem. However, to expand the wavefunctions of the tightly bound core electrons requires a large number of plane waves. Similarly valence electrons, which oscillate rapidly in the core region also require a large number of plane wave basis sets. This would lead to a tremendous computing time and make the problem intractable.

The pseudopotential theory [88, 89, 90] provides a great simplification in modelling the interactions between electrons and ions (or nuclei) in solids. It has been long known that most physical and chemical properties of solids are largely governed by their valence electrons rather than the core electrons. Therefore, the explicit states of these inner core electrons are not required for the total energy calculation. Pseudopotential techniques exploit this fact by separating electrons into two categories: the inner electrons which are located in the core region; and the outer electrons which are located outside the core region. In fact, the pseudopotential approximation neglects the full description of the electronic wavefunctions within the core region and only considers the valence wavefunctions outside the core region. In other words, the pseudopotential technique replaces the true strong ionic potential and their corresponding electronic wavefunctions with a weaker and smoother pseudopotential acting on pseudo-electronic
Figure 6.2: Schematic illustration of all electron (solid lines) and pseudoelectron (dashed lines) potentials and their corresponding wavefunctions. The radius at which all electron and pseudoelectron values match is designated $r_c$ [71].

wavefunctions rather than the true valence electron wavefunctions. The true valence wavefunctions oscillate rapidly in the core region due to the strong potential. These oscillations maintain the orthogonality between the core wavefunctions and the valence wavefunctions, which are required by the exclusion principle. This leads to a large number of plane waves for inside the core region. By using the pseudopotential approximation, only valence electrons outside the core region are required for the calculation. This means that the number of plane waves required to expand the pseudo-electronic wavefunctions will be reduced since the core electron wavefunctions need not be included. A schematic diagram for the potential and their corresponding wavefunctions for all electrons and pseudoelectrons are illustrated in figure 6.2.

The pseudopotential is constructed to replace the real Coulomb potential with a much weaker potential inside the core region radius $r_c$. The true electron wavefunction $\psi(r)$ is replaced by the much smoother pseudoelectron wavefunction $\psi_{ps}(r)$. Outside the core region, $r_c$, the two types of potential and wavefunction are identical so that the behaviour of the valence electrons can be fully described in terms of pseudoelectron potentials and wavefunctions. Usually not only should $\psi_{ps}(r)$ and $\psi(r)$ smoothly match
at \( r_c \), but also their first and often second derivatives with respect to \( r \) are also constrained to be equal at \( r_c \). Inside the core region, however, the rapid oscillations of the true valence wavefunction are no longer present in the pseudo-electronic wavefunction and hence require a smaller number of plane wave basis sets to describe.

The pseudopotential is generated by using the results of full-potential calculations of the isolated atoms in which all electrons are included in the calculation. The results are then used to substitute back into the equation. By directly inverting the Schrödinger equation (or the so called Kohn-Sham equation for this particular problem) with the pseudo-electron wavefunction, the pseudopotential is yielded. Ideally, the pseudopotential should imitate all the properties of the full potential which include the scattering properties of electrons and the core. The scattering properties depend on the angular momentum component of the wavefunction. Therefore, in order to fully explain the scattering behaviour of the real system, the pseudopotential should have different components for different angular momenta. Pseudopotentials that use the same potential for all angular momentum components of the wave function are called local pseudopotentials which are only a function of the distance from the nucleus. Pseudopotentials that are dependent on angular momentum are called non-local pseudopotentials.

The combination of the plane wave basis set and the pseudopotential approximation has constructed very efficient techniques for the electronic structure calculations. The total energy calculated using this approximation is no longer the true binding energy of all electrons to the nucleus, but instead only refers to the valence electrons and the pseudocore which are given a similar value to those using true electron wavefunctions. The replacement of the true potential with pseudopotential not only allows a smaller number of plane wave basis sets to be used but also the removal of core electrons means that less electronic wavefunctions need to be calculated. Moreover, the total energy for the valence electron system is usually a thousand times smaller than that of the all electron system. Since the difference between the electronic energies of different ionic configurations appears almost totally in the energy of the valence electrons, using the pseudopotential approximation, the accuracy required to determine the energy differences between different ionic configurations is much smaller than that required for the all electron calculation.
6.5 Ewald Sum: Ion-Ion Interactions

In the previous section, the ion-electron interactions have been discussed and the pseudopotential approximation was used to simplify the problem. However, another important interaction in solids is the ion-ion interaction. Ewald has developed a method to calculate the Coulomb energy associated with long range ion-ion interactions in solids [91]. This technique performs a Coulomb summation over a periodic lattice. The Coulomb interactions between an ion at position $\mathbf{R}_2$ and an array of ions positioned at $\mathbf{R}_1 + \mathbf{l}$ is given by:

$$E_{\text{ion}} = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{l}} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 |\mathbf{R}_1 + \mathbf{l} - \mathbf{R}_2|} \quad (6.35)$$

where $\mathbf{l}$ are lattice vectors; and $Z_i$ and $Z_j$ are the valences of ions $i$ and $j$. The Coulomb interaction is a long range interaction and leads to an infinite sum for the infinite crystal. Ewald has spilt this sum into a two part infinite sum: one over real space vectors and one over reciprocal space vectors. Both sums converge rapidly and only need to be calculated over a small number of lattice, or reciprocal lattice, vectors. The infinite sum of Coulomb interactions is now simplified to only a small number of summations over both real and reciprocal spaces.

6.6 Computational Procedure

The procedure requires an initial step of guessing the electronic charge density from which the Hartree potential and the exchange and correlation potential can be calculated using (6.23). The Hamiltonian for each $\mathbf{k}$ point must then be constructed and the Kohn-Sham eigenstates obtained. The charge density generated by these eigenstates are usually different from those initially used to construct the electronic potentials. The new Hamiltonian is thus reconstructed using the new potentials obtained from the new eigenstates. The calculation is then repeated until the solutions are self-consistent. The new electronic potentials are usually generated using the combination of the old and new eigenstates since this speeds up the convergence to self-consistency.
From the previous sections, it has been demonstrated that the number of \( k \) points used and the plane wave kinetic energy cutoff also play an important role in the accuracy of the total energy calculations. These need to be determined for the first step before performing any further calculation. Usually a number of test calculations need to be performed in the beginning to ensure that enough \( k \) points are being used and that the cutoff energy for the plane wave basis set are sufficient. Once convergence has been confirmed the total energy calculation can then be performed using the appropriate values. However, for most calculations, the difference in energy between different ionic configurations are of interest not the absolute converged total energy of the individual configuration itself. Therefore, the total energy calculations are usually performed at the cutoff energy and the number of \( k \) points in which the energy differences have converged rather than when the absolute energies have converged. For the results presented in this thesis, the energy differences between different ionic configurations are used to determine the stable crystal structure over the studied pressure ranges.

### 6.7 Ionic Relaxation

All the computational procedures mentioned so far are for calculations in which the electronic configuration has been relaxed to its ground state while the ionic positions and the size and shape of the unit cell have been held fixed. However, in high pressure structural studies, the stabilities of various crystal structures under high pressure are of interest. Therefore, the calculated total energy of the structures in which the ionic positions are optimised to obtain the minimum energy should be used. Since at equilibrium there must be no net forces on any ions, the forces acting on ions must be calculated in order to adjust the ionic positions towards their equilibrium positions. In this way, a new minimum energy for new ionic positions can be calculated and used to compare different structures.

#### 6.7.1 The Hellmann-Feynman Theorem: Force Calculation

As previously stated, the force acting on the ions needs to be calculated in order to relax the structure towards its equilibrium and to hence obtain the minimum energy
for any given structure. The force on $i$ ion at position $R_i$ is given by:

$$ F_i = -\frac{dE}{dR_i} \quad (6.36) $$

If the Kohn-Sham energy functional is still to remain meaningful, the wavefunctions must evolve corresponding to the new position of the ion i.e. for the total energy to be minimised for the new ionic configuration. This effect must be taken into account by expanding

$$ F_i = -\frac{\partial E}{\partial R_i} - \frac{\partial E}{\partial \psi} \frac{d\psi}{dR_i} - \frac{\partial E}{\partial \psi^*} \frac{d\psi^*}{dR_i} \quad (6.37) $$

When the last wavefunction is the eigenstate of the Hamiltonian, the Hellmann-Feynman theorem [92] states that the last two terms will cancel each other since they are related to the derivative of the normalisation constant $< \psi^* | \psi >$ with respect to $R_i$. The force on each ion may then be obtained from simply taking the derivative of the total energy with respect to ionic position.

$$ F_i = -\frac{\partial E}{\partial R_i} \quad (6.38) $$

This calculated force is known as the Hellmann-Feynman force. In the density functional formalism, the total energy is a function of only the charge density, which can be calculated from the individual $\psi_i$. The force calculated using the Hellmann-Feynman theorem therefore requires only the charge density and not the individual wavefunctions.

The Hellmann-Feynman theorem is however only applicable when the electronic wavefunction is an eigenstate of the Kohn-Sham Hamiltonian. Therefore the force on the ion can not be calculated until the electronic configuration is near its ground state. Once the force has been calculated, the positions of the ions and size and shape of the unit cell can be adjusted. Every time that the positions of the ions or the unit cell are changed, it is important to ensure that the electrons are allowed to relax to the new ground states for the new ionic configuration before the forces can be recalculated.
This ensures that the error is sufficiently small and will not lead to instabilities in the calculation process.

### 6.7.2 Pulay Forces

In practice, equation (6.37) does not entirely represent the total force acting on an ion. The derivative of the basis set with respect to the position of the ion also needs to be included. This force arising from the derivative of the basis set with respect to the ionic position is called Pulay force [93]. If this Pulay force is not included a further error in the Hellmann-Feynman force would result.

If the wavefunctions are represented using a basis set such that \( \psi_i = \sum_j c_{ij} \phi_j \), then the energy calculated can be written as \( E(\{R_I\}, \{c_{ij}\}, \{\phi_j\}) \) [93]. The expansion should then include terms involving \( \Psi \).

\[
\frac{\partial E}{\partial \Psi} \frac{d\Psi}{dR_I} = \sum_{i,j} \frac{\partial E}{\partial c_{i,j}} \frac{dc_{i,j}}{dR_I} + \sum_{i,j} \frac{\partial E}{\partial \phi_j} \frac{d\phi_j}{dR_I} \tag{6.39}
\]

In the variational nature of the Kohn-Sham equations, if the wavefunction has completely converged, then \( \partial E / \partial c_{i,j} = 0 \) since the Kohn-Sham functional is at a minimum at the ground state. Thus the first term in the equation is zero. The second term gives rise to an effect known as the Pulay force. However, by using a plane wave basis set in the calculation a great simplification can be made. For a plane wave basis set, the derivatives of each basis state with respect to the position of an ion are zero (\( d\phi_j / dR_I = 0 \)) since the basis set is independent of the ionic positions and the Pulay force is thus also zero. The calculated Hellmann-Feynman force will then be exactly equal to the derivative of the total energy with respect to the position of the ion. The error arising in the calculation is hence only due to the convergence in the calculation procedure itself. On the other hand, if other basis sets are used, the forces acting on an ion can be found by a very complicated procedure involving the calculation of the Pulay force. This would require much more computing time and effort. While the Pulay force can be ignored in the calculation using the plane wave basis set, the Pulay stress cannot be ignored (as detailed in the next section).
6.7.3 Pulay Stresses: Unit Cell Optimisation

If a plane wave basis set is used in the total energy calculation, the Pulay force on an ion will be zero. However, the Pulay stress on the unit cell may be nonzero and in order to relax the unit cell accordingly this stress needs to be calculated. The size and shape of the unit cell can then be optimised by relaxing the cell under the corresponding stress until the calculated stress on the unit cell reduces to zero. However, the effect of changing the unit cell is to change the number of plane waves that are needed in the basis set. If the number of plane waves is fixed in the calculation, the cutoff energy for a given number of plane wave basis sets changes. As a result, the stress calculated by holding the cutoff energy constant is not precisely correct in general and the corresponding correction required to the stress is known as the Pulay stress. Only if the cutoff energy is large enough to achieve absolute convergence, will the change in the total energy be zero. However, for most calculations, lower cutoff energies are used only when the energy differences have converged. Therefore, if this correction is not included then the energy minimum does not occur when the stress is zero. Since an anisotropic stress causes shearing distortions which do not change the volume, only the effects due to isotropic stress are of significance here.

The strain matrix $\epsilon$ is used to explain any small changes in unit cell such that the new lattice represented by the matrix $h = a, b, c$ is related to the old lattice, $h_0$, by $h = (1 + \epsilon)h_0$. The stress can be defined as the derivative of the total energy per unit volume with respect to strain $\epsilon$.

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \frac{dE}{d\epsilon_{\alpha,\beta}}$$  \hspace{1cm} (6.40)

Where $\Omega = |h|$ is the volume of the unit cell. In practice, this equation can be split into two parts with respect to the constant number of basis functions ($N$) and the constant cutoff energy ($\epsilon_{\text{cutoff}}$). Equation (6.40) can now be written as:

$$\sigma_{\alpha\beta} = \frac{dE}{d\epsilon_{\alpha,\beta}} \bigg|_N + \frac{dE}{dN} \bigg|_{\epsilon_{\text{cutoff}}} \frac{dN}{d\epsilon_{\alpha,\beta}}$$  \hspace{1cm} (6.41)

$$\sigma_{\alpha\beta} = \sigma_N + \sigma_p$$  \hspace{1cm} (6.42)
The first term can be calculated simply for a constant number of plane waves [94, 95]. The second term is the calculated Pulay stress [96] which is needed for the correction for a constant energy cutoff and can be written as

$$\sigma_p = \frac{2}{3 \Omega} \frac{\partial E}{\partial \ln \varepsilon_{cutoff}}$$  \hspace{1cm} (6.43)

where $\varepsilon_{cutoff}$ is the cutoff energy. The finite basis set corrections (or so called Pulay corrections) and stresses can be calculated by determining the convergence gradients ($\partial E/\partial (\ln \varepsilon_{cutoff})$) from fitting a curve to several total energy calculations which have been relaxed at different energy cutoffs for a given volume (the same way as the cutoff energy is determined). Since increasing the number of plane waves (by increasing the cutoff energy) always decreases the total energy $E$, the Pulay stress is always negative and, therefore, the volume of the unit cell relaxed under uncorrected stress is always underestimated.

### 6.8 Computer Code

With the techniques discussed in the chapter so far, it is possible to perform pseudopotential total energy calculations where the electrons, ions and the cell can be converged to a self-consistent ground state. All the work presented in this thesis was performed using the widely available CAmbridge Serial Total Energy Package (CASTEP). This code uses plane wave basis sets for the wave functions based on the previously discussed techniques to find the ground state energy.

### 6.9 Determination of Equilibrium Structures

The relative stability of two structures can be predicted by comparing the calculated total energy per atom. The energies of both structures are calculated at a number of different volumes and, subsequently, energy versus volume relations can be plotted for both structures on the same axes. The pressure can be calculated using a common tangent method from the negative partial derivative of the energy with respect to the volume ($P = -\frac{\partial E}{\partial V}$). Transition pressures can also be obtained using the same
Figure 6.3: The diagram for a pressure induced structural phase transition. The transition pressure from phase I to phase II can be calculated from the common tangents of the energy volume curves of phase I and II.

principle by finding the common tangent to both curves as illustrated in figure 6.3. This convenient method for calculating the transition pressure, however, completely ignores kinetic effects and hysteresis. The kinetic effects are due to the energy barrier created by trying to deform one structure in to the other. Some structural properties of solids, such as bulk modulus $B$, can be obtained by fitting the total energy ($E_{\text{total}}$)-Volume($V$) to an equation of state. All energy curves subsequently presented in this thesis are fitted to the Murnaghan equation of state [97].

$$E_{\text{total}}(V) = \frac{BV}{B'(B' - 1)} \left[ B' \left( 1 - \frac{V_0}{V} \right) + \left( \frac{V_0}{V} \right)^{B'} - 1 \right] + E_{\text{total}}(V_0)$$

(6.44)

where $B = -V \frac{\partial^2 E}{\partial V^2}$ is the bulk modulus, $B'$ is its pressure derivative and $V_0$ is the equilibrium volume. The relative structural stability of different phases can then be determined by comparing the associated $E$ versus $V$ curves in which the structure with the lowest total energy corresponds to the equilibrium phase.
6.10 Computational Details

All the computational work on Sr has been performed using the pseudopotential method previously discussed. The controlled parameters have been tested in order to establish the calculation conditions which lead to the desired computational efficiency and precision. The two major parameters that govern the precision of the calculations are the plane wave kinetic energy cutoff and the number of k points used. Since an additional number of plane waves provide further variational freedom for the wavefunctions, the total energy decreases dramatically as the plane wave cutoff energy increases. All calculations were performed using a plane wave kinetic energy cutoff of 670 eV. This was found to be sufficient to converge the calculated total energy to 1 meV per atom. Another important factor for the precision of the total energy is the number of k points used in the calculation. As previously mentioned, calculations performed for metals require denser k points in order to define the Fermi surface precisely, as the Fermi surface varies rapidly in metals. Figure 6.4 shows the convergence of the calculated total energy of the bcc structure as a greater number of k points are used. The figure clearly illustrates that a convergence of 1 meV can be obtained if at least an 8 × 8 × 8 set is used. At the beginning of the calculation for each structure, the number of k points are tested for convergence. For the fcc and the bcc structure, 56 and 155 special k points (both using an 11 × 11 × 11 mesh) are used, respectively. In the β-tin and monoclinic structures, 208 and 13 k points are used, respectively. In all cases, the sets of k points were generated by the Monkhorst-Pack method [86]. In every calculation, Sr was treated as a metal.

6.11 Structural Results

6.11.1 FCC-BCC Structural Phase Transition

Calculations have been performed for both the fcc and bcc structures and the resulting structural parameters were compared with the experimental results in order to estimate the likely error in the calculated values near ambient pressure before calculations of the higher pressure phases were carried out. At ambient pressure the calculated lattice parameter of the fcc structure is 5.9877 Å. This is about 1.5% smaller than the
Figure 6.4: Variation of the calculated total energy with k points mesh for bcc structure using Monkhorst-Pack scheme. The convergence of less than 1 mev can be yielded if enough k points are used.

Experimental value of 6.0785 Å measured by the author using the diffraction experiment setup previously described in chapter 2. This value is also found to be in very good agreement with other previous experimental studies [13, 14]. The calculations were performed using a single-point energy calculation in which the total energies were calculated for a given set of lattice parameters. The results are fitted to the energy versus volume curve using the Murnagahan equation of state. The fcc structure is used as a reference as it is stable at ambient pressure. The bcc structure was also calculated in the same way and the transition pressure was obtained from the common tangent of both energy curves. The results are presented in figure 6.5 where both the fcc and bcc curves are shown and the transition pressure is determined. The density functional formalism takes no account of any kinetic barrier between the phases and hence the transition pressure obtained in this way from the common tangent ignores kinetic effects which may inhibit the transition. Therefore the calculated transition pressure is usually underestimated. The experimental value obtained by the author for the fcc to bcc transition is 3.5 GPa (see chapter 3) which is in very good agreement with previous studies [20]. The calculated transition pressure is 1.16 GPa which is about 2 GPa below the experimental value. Table 6.1 gives the fitted values of a fit of the Murnagahan equation of state (equation 6.44) to the data in figure 6.5. There are misfits of less than 0.5 meV for the fcc structure and less than 0.7 meV for the bcc structure to the
Table 6.1: The Murnaghan equation of state parameters for the fcc and bcc structures. The units are in eV and Å³.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>fcc structure</th>
<th>bcc structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>$9.2217 \times 10^{-2}$</td>
<td>$8.7278 \times 10^{-2}$</td>
</tr>
<tr>
<td>$B'$</td>
<td>1.9813</td>
<td>2.2478</td>
</tr>
<tr>
<td>$E(V_0)$</td>
<td>-838.3183</td>
<td>-838.3130</td>
</tr>
<tr>
<td>$V_0$</td>
<td>53.6601</td>
<td>52.9944</td>
</tr>
</tbody>
</table>

The transition pressures presented in this thesis were determined from curves fitted to the Murnaghan equation of state. The refined parameters for the Murnaghan equation of state were used to reproduce the energy versus volume curves which are in turn used for the common tangent determination. At the transition from fcc to bcc, the bcc structure is found to have a lattice parameter of $a = 4.4289$ Å which is only ~0.5% bigger than the experimental value, $a = 4.4069$ Å. Therefore, the structural phase transition from the fcc to the bcc structure can be predicted using the total energy pseudopotential calculation and the setup for the calculation procedure is now verified.

6.11.2 BCC-$\beta$-tin Structural Phase Transition

Further calculations have also been performed for the $\beta$-tin structure in order to investigate the bcc to $\beta$-tin structural phase transition. In chapter 3, the author has shown that the use of EDX techniques by other research groups had led to the misidentification of the Sr-III structure. The author subsequently re-identified the Sr-III phase as having the tetragonal $\beta$-tin structure with ADX techniques. In this section, total energy calculations were carried out by the author for this structure.

The calculations for the $\beta$-tin structure were performed using plane wave kinetic energy cutoffs of 670 eV and the $k$ point sampling used the Monkhorst-Pack scheme with parameters $(10 \times 10 \times 8)$ giving the total number of special $k$ points to be 208. The calculations were also performed using the unit cell optimisation mode in which the
Figure 6.5: The energy versus volume curves of the calculated fcc (black) and bcc (red) structures revealing that at higher pressure the bcc structure has a lower energy and hence more stable. The inset shows a close-up region of the common tangent used to calculate the transition pressure.

unit cell is optimised with the given isotropic pressure. Firstly, the pressure is used to calculate the stress acting on the given unit cell. The unit cell is relaxed to reduce the calculated stress and the stress is then recalculated. This procedure is repeated until the calculated stress is zero or falls within the desired tolerance. The total energy of the system is then calculated with the optimised unit cell. As previously mentioned in chapter 3, Sr is the first element outside group IV which has an “ideal” β-tin structure with a $c/a$ ratio of 0.54 which is similar to the value observed for group-IV elements such as Sn, Si and Ge. The computational work presented here also agrees with the data obtained from experiment. Over the wide pressure range of the calculations, the $c/a$ ratio remains 0.544(5) which is also found experimentally over the smaller pressure stability region of the β-tin structure. The optimised lattice parameters are compared with the experimental values in figure 6.6.

The optimised structures can be clearly seen to have a very good agreement with the experimental data. At 31 GPa, the optimised lattice parameters give $a = 5.5477\ \text{Å}$ and $c = 3.0278\ \text{Å}$ compared to the measured values of $a = 5.5629\ \text{Å}$ and $c = 2.9912\ \text{Å}$. The difference between the experimental and calculated values are found to be less than 1% between 25-36 GPa in which the β-tin structure is stable. The transition pressure can
Figure 6.6: Pressure dependence of the optimised lattice parameters compared with experimental data. Black squares and red circles are calculated $a$ and $c$ respectively. Green and blue triangles are represent experimentally measured lattice parameters. Solid lines are used as a guide to eyes only.

be predicted theoretically using the gradient of the total energy versus volume curves as previously used for the fcc to bcc transition. At higher pressure, however, the errors introduced by the steeper gradient lead to a relatively large error in calculating the transition pressure. In this case, the transition from the bcc to the $\beta$-tin structure was found to be 44 GPa whereas from experiment the transition appears to start at 24.4 GPa and is complete by 26.8 GPa. Table 6.2 shows the Murnaghan equation parameters fitted from calculated points with an average fitting error of less than 0.7 meV for the bcc structure and 0.6 meV for the $\beta$-tin structure.

<table>
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<tr>
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<th>$\beta$-tin structure</th>
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<td>$B$</td>
<td>$8.7278 \times 10^{-2}$</td>
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<td>$B'$</td>
<td>2.2478</td>
<td>2.1952</td>
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<td>$E(V_0)$</td>
<td>-838.3130</td>
<td>-837.8600</td>
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<tr>
<td>$V_0$</td>
<td>52.9944</td>
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Table 6.2: The Murnaghan equation of state parameters for the bcc and $\beta$-tin structures used for transition pressure calculation. The units are in eV and Å$^3$. 
Figure 6.7: The energy versus volume curves for the bcc (red) and β-tin (blue) structures fitted with the Murnaghan equation of state. Predicted transition pressure can be calculated using common tangent as previously done for bcc-fcc transition. The inset shows the region where phase transition is reported from experimental study. The bcc and β-tin structures show a very close calculated total energy.

Figure 6.7 shows the energy versus volume curves for the bcc and the β-tin structures. As already mentioned, the error in the predicted transition pressure can be explained by the increased gradient of the $E/V$ curve at higher pressure. The energy versus volume curves shown in the figure reveal clearly that at the experimental transition pressure of 25 GPa (or a volume/atom of $24 \text{ Å}^3$) the bcc and β-tin curves are very close together and the energy differences are very small $\sim 0.03$ eV. Therefore, the gradient used to calculate the transition pressure (the common tangent) is very difficult to determine and any small error in the calculated energy can be result in a very significant error in the pressure calculation. The free energy (enthalpy) can also be used to predict the stability of the high-pressure structure. Figure 6.8 illustrates the calculated enthalpy for the fcc and bcc structures. The bcc structure is undoubtedly a preferred structure beyond 1.16 GPa where it has a lower enthalpy. The pressure for the bcc to β-tin transition can also predicted from the point at which the calculated enthalpy for the β-tin structure falls below that calculated for bcc.

The calculated pressure dependence of the enthalpy difference between the β-tin and the bcc structure of Sr are shown in figure 6.9. The enthalpy difference curve for β-tin crosses over that for the bcc phase at a pressure of 44 GPa and consequently the cal-
Figure 6.8: The enthalpy of the bcc phase of Sr relative to enthalpy of the fcc phase as a function of pressure. The fcc to bcc transition pressure is predicted at 1.16 GPa.

Figure 6.9: The enthalpy of the bcc and $\beta$-tin phases Sr relative to enthalpy of the fcc phase as a function of pressure. The fcc structure stable at ambient pressure (the straight line at 0).
calculation predicts that the transition should occur at this pressure. Therefore, $\beta$-tin is calculated to be stable at a much higher pressure than that found experimentally (27 GPa). This error can be understood as the calculated energies for the bcc and $\beta$-tin structure are relatively close, as can be clearly seen in the inset to figure 6.7. Additionally, the calculations have been performed at zero kelvin conditions and, hence, the thermal energy is ignored in all the results presented. Therefore, if the enthalpy difference is relatively small compared to $k_B T$, the thermal energy will have a non-negligible effect on the system. The experiments have all been performed at room temperature at which $k_B T$ is about 0.025 eV. Thus an error in predicting the transition pressure can result if the enthalpy difference is less than 0.025 eV. This can be clearly seen in figure 6.9 where the enthalpy difference is close to 0.025 eV at pressures between 32 GPa and 38 GPa. Experimentally, therefore the thermal energy at room temperature might have a significant effect on the stability of the structures and make the higher energy, $\beta$-tin, structure stable over this lower pressure region. The relaxed $\beta$-tin structure however confirms the "ideal" $c/a$ ratio of 0.54 which is similar to those reported in the group IV elements.

6.11.3 The Complex Monoclinic Sr-IV Structure

The total energy calculations have been extended to study the structural stability of the monoclinic Sr-IV phase. The calculations performed for the Sr-IV phase used the same plane wave kinetic energy cut-off of 670 eV and the special $k$ points were generated using Monkhorst-Pack scheme with a $3 \times 3 \times 4$ mesh resulting in 13 special $k$ points. For this monoclinic structure, the coordinates were relaxed during the calculation as well as the lattice parameters. The total energy calculation has been carried out over a wide pressure range extending above and below the experimentally determined Sr-IV stability range. The results are shown in figure 6.10 where the total energy is compared with the fcc, bcc and $\beta$-tin structures. The calculated enthalpy between all four phases is also compared in figure 6.11. As before, the Murnaghan equation of state is used to fit the calculated values and the refined fitting parameters for the Sr-IV structure are given in table 6.3, where the average fitting errors are less than 0.3 meV.

The predicted stable structure should be the one that gives the lowest energy at any
Sr-IV monoclinic structure

<table>
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<tr>
<td>$B'$</td>
<td>2.0968</td>
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<td>$E(V_0)$</td>
<td>-837.9585</td>
</tr>
<tr>
<td>$V_0$</td>
<td>46.8717</td>
</tr>
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Table 6.3: Table shows Murnaghan equation of state parameters for the monoclinic Sr-IV structure used for transition pressure calculation. The units are in eV and Å³.

Figure 6.10: The energy versus volume curves of high pressure phases of Sr. The predicted transition pressure is simply a common tangent between two curves cross. The transition from fcc to bcc is calculated to be 1.16 GPa and the transition from bcc to Sr-IV is predicted to be 26.62 GPa (common tangent of the red and green curves).
Figure 6.11: The enthalpy differences of the bcc, β-tin and the monoclinic Sr-IV structure related to the fcc structure stable at ambient pressure (the straight line at 0).

given pressure. On increasing pressure (or decreasing the volume) the transition sequence is thus predicted to be: from fcc to bcc at 1.16 GPa; and the bcc phase then transforms to monoclinic Sr-IV at 26.62 GPa. The β-tin structure is not be predicted to be stable in this transition sequence. Interestingly, the predicted transition pressure from the bcc structure to the monoclinic structure is very close to that observed experimentally for bcc to β-tin. However, as previously mentioned, the difference in the calculated total energies between the β-tin structure and bcc are below the room temperature $k_B T$ of 0.025 eV between about 32 GPa and 38 GPa and hence the transition is likely to be observed experimentally. As previously demonstrated in chapter 4, the monoclinic Sr-IV structure can be viewed as a superstructure of the Sr-III β-tin structure. The structure of the Sr-IV phase obtained from the calculations will be studied in detail in the next section and compared with the experimental results.

6.11.4 Structural Results for the Monoclinic Structure

The calculations for the monoclinic Sr-IV phase have been performed with all the structural parameters relaxed. The results can then be compared with those from experiment over the pressure range where the structural parameters were measured ex-
Figure 6.12: The pressure dependence of the monoclinic structure for the calculated and measured structures. The results from both calculated and experimental are in a good agreement. As can be clearly seen in the inset, all the calculated points are well-aligned with the measured values.

Experimentally. The compressibilities are compared in figure 6.12 where the experimental results are shown between 38 GPa and 47 GPa (the full experimentally observed phase IV stability range). The calculated and the measured values can be clearly seen to be in good agreement. At 42 GPa the measured lattice parameters are $a = 5.7247(3)$ Å, $b = 7.8044(6)$ Å, $c = 5.4789(7)$ Å and $\beta = 96.958(5)^\circ$ compared to the calculated lattice parameters of $a = 5.7846$ Å, $b = 7.7416$ Å, $c = 5.4752$ Å and $\beta = 96.0651^\circ$. At this pressure, the difference between calculated and measured unit cell volume is less than 0.4%.

The monoclinic Sr-IV structure comprises three refinable atoms as previously detailed in chapter 4. Therefore, the calculated structure should allow the optimisation of these atomic coordinates in order to obtain a minimum total energy for a given pressure and hence the plausible stable structure. To compare the calculated structural coordinates directly with those obtained by experiment, the calculation has been performed using the lattice parameters found by experiment at a given pressure but with freely relaxed atomic coordinates from the starting values transformed from the $\beta$-tin coordinates. The relaxed structure agrees with the experimental data down to $\sim0.01$ in
<table>
<thead>
<tr>
<th>Atom label</th>
<th>coordinates</th>
<th>Calculation</th>
<th>Experiment</th>
<th>Differences</th>
</tr>
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<tr>
<td>Sr1</td>
<td>$x$</td>
<td>0.30036</td>
<td>0.30678(15)</td>
<td>-0.00642</td>
</tr>
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<td></td>
<td>$y$</td>
<td>0.165</td>
<td>0.16019(20)</td>
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<tr>
<td></td>
<td>$z$</td>
<td>0.62841</td>
<td>0.64012(15)</td>
<td>-0.01171</td>
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<tr>
<td>Sr2</td>
<td>$x$</td>
<td>0.4873</td>
<td>0.49028(5)</td>
<td>-0.00298</td>
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<td>$y$</td>
<td>0.56937</td>
<td>0.57693(27)</td>
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<td>$z$</td>
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<td>0.70294(20)</td>
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<tr>
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<td>$z$</td>
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<td>0.3696(20)</td>
<td>0.01328</td>
</tr>
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Table 6.4: Table shows relaxed atomic coordinates and the measured values at 41.7 GPa. The lattice parameters are $a = 5.7463(3)$ Å, $b = 7.8013(3)$ Å, $c = 5.5360(4)$ Å and $\beta = 96.987(3)^\circ$. 

terms of fractional coordinates. Table 6.4 shows the relaxed coordinates obtained from calculation in comparison with the refined experimental values at 41.7 GPa.

To within the accuracy of the computational process and the experimental measurement, one can conclude that the relaxed structure and the refined structure agree extremely well. It is important to note that the optimised structure also generates a similar diffraction pattern to that observed experimentally, as shown in figure 6.13 where the data previously shown in figure 4.16 are compared with a calculated profiles from the relaxed structure. In chapter 4, the author argued that this monoclinic structure gave an extremely good fit to the data especially for the weak reflections at low angle. The calculations confirm this by giving the same structure which accordingly also explains the whole diffraction pattern. The inset in figure 6.13 shows the data at low angle and it is clear that the calculated structure predicted that the low-angle peaks should have zero intensity or at least be very weak. This relaxed structure gives the same structure as the helical constraint in the structural refinement. As previously illustrated in chapter 4, the constraint is required in order to restrain these weak re-
Figure 6.13: The calculated diffraction pattern of the relaxed structure at 41.7 GPa reveals the same diffraction as previously shown for data collected in the phase IV. The inset shows a close up region for the weak reflections from the data collected at the same pressure.

... reflections while giving the general good fit to the whole pattern. The relaxed atomic coordinates provide strong confirmation to this model as they agree very well with the measured values. At 41.7 GPa the shortest bond length observed from experiment is 2.790(3) Å which compares well with the value of 2.755 Å obtained theoretically from the \textit{ab initio} calculations. The Sr-IV structure is found to be stable between 38 GPa and 49 GPa experimentally before it transforms into the self-hosting Sr-V structure.

6.12 Concluding Remarks

Total energy calculations on the high pressure structures of Sr have been performed and the structural phase transition sequence has been investigated. The fcc structure is found to be stable at ambient pressure up to 1.16 GPa where it transforms to the bcc structure which is stable to 26.62 GPa. At this stage experiment and calculation agree very well. However, at this pressure the phase transition to the tetragonal $\beta$-tin structure was observed experimentally while the computational studies found a phase transition from bcc to the monoclinic structure. The $\beta$-tin structure is however, very close in energy compared to the bcc structure at the transition region. Experimentally, the tetragonal $\beta$-tin structure therefore may be stable in preference to both the bcc and monoclinic phase at this pressure. Further investigation of the structural parameters...
of the Sr-IV phase shows that the optimised structure matches very closely with that found by experiment. In other words, the helical rod model previously proposed in chapter 4 for the purpose of refinement has been confirmed in the calculations. The monoclinic structure is therefore theoretically proven to be a stable structure at high pressure.
Chapter 7

Conclusions

As presented in the preceeding chapters, the author has performed a detailed investigation of the high-pressure behaviour of Sr using both computational and experimental techniques. This chapter summarises the results of these studies as well as suggesting possible further investigations.

The high-pressure crystal structures of Sr have been extensively studied from the ambient pressure fcc structure up to the remarkable self-hosting Sr-V phase. The Sr-V phase is stable over a very wide pressure range from 50 GPa up to 75 GPa, the highest pressure reached in these studies. All the data were collected with angle-dispersive powder-diffraction techniques using image-plate area detectors and synchrotron radiation \cite{46, 50, 60}. The author has introduced an alternative set up for the image-plate which results in a significant improvement in the resolution of the data collected. This proved to be a crucial step for the structure solution of the high pressure Sr-IV phase. The two-dimensional data collected with the area detector allows textural information to be obtained and has allowed the correct identification of the Sr-III phase \cite{21}.

At ambient pressure, Sr has the fcc structure which transforms to the bcc structure at 3.5 GPa. This transition pressure was found to be in very good agreement with previously reported values. The bcc structure is stable up to 26.8 GPa where it transforms into the Sr-III phase. For this high pressure phase, the two-dimensional diffraction patterns suggest a mixture of two different phases which can be clearly distinguished from the texture of their respective diffraction rings. The Sr-III phase forms a very
spotty powder pattern on recrystalisation from the bcc structure while the accompanying phase forms very smooth diffraction rings. This Sr-III phase was previously reported to have an orthorhombic structure with \textit{Imma} symmetry from an EDX study which could not record the difference in texture between the two phases. Consequently, the misidentification of the Sr-III structure was due to an indexing of the whole pattern with only one phase. The Sr-III phase has now been re-identified as having a tetragonal structure with $I4_1/amd$ symmetry which is conventionally referred to as the $\beta$-tin structure. Accompanying the Sr-III structure, a smooth phase is also found to be stable over a wide pressure range. The accompanying phase can not be identified with the available data but from its behaviour with pressure the author suggests that this phase is another form of Sr and not just a simple contamination. This accompanying phase is stable up to 57 GPa where it transforms into another accompanying phase which persists at higher pressure in the stability regime of Sr-V.

In previous work [20], Sr-III transforms into another high pressure phase at 35 GPa on pressure increase where the EDX powder patterns are relatively complex and could not be solved. The ADX study by the author reveals that the transition from Sr-III to Sr-IV appears to be initiated by an intermediate phase, Sr-III', which is stable between 36.7(4) GPa and 37.7(2) GPa. The transition from $\beta$-tin otherwise appears to be almost continuous in nature and the additional smooth accompanying phase remains unchanged through the phase IV into the phase V transition. The powder pattern of Sr-IV collected with the conventional ADX setup at SRS are composed of several reflections which are not resolved sufficiently for indexing. Modification of the existing image-plate set-up by the author has resulted in the collection of data with sufficient resolution to allow the indexing and subsequent structure solution of the Sr-IV. Using this newly introduced set up, Sr-IV was identified as having a monoclinic structure with \textit{Ia} symmetry and 12 atoms in the unit cell. The three lowest-angle peaks were found to have no intensity, or at least were extremely weak, over the full stability range of Sr-IV suggesting that the structure had additional constraints that were not imposed by the \textit{Ia} symmetry. Consequently, three different models have been introduced for the purpose of constraining the structure so that the intensity of the low-angle peaks are held close to zero. The atoms are constrained to displace in flat layers, parallel the former $\beta$-tin $a$-axis, and the displacement direction between consecutive layers is fixed.
at 120° so that a three-fold helical distortion is introduced to the structure [22]. This helical distortion results in a unit cell 3 times larger in volume than the tetragonal β-tin phase. This is the first time that this complex high-pressure monoclinic structure has been reported for an element.

At higher pressure, the monoclinic Sr-IV structure transforms into the extremely complex structure of Sr-V. This high-pressure phase has been previously reported to exist at 45 GPa but the structure had not been solved until the current work by the author. In the current study, Sr-V emerged with a strong and spotty pattern at 49.0(7) GPa. This pattern can be indexed using the self-hosting structure originally reported for the Ba-IV structure [64] as a preliminary model. The structure comprises a “host” structure which can be explained by the $I4/mcm$ space group with atoms on the 8$h$ sites and a refined $x$ value of 0.1460(2). The second component of the structure is a “guest” phase in which a $C$-centred tetragonal structure is formed which is composed of columns of atoms running through the octagonal channels of the host structure. Both structures are commensurate in the $a$-$b$ plane but are incommensurate along the $c$ direction, resulting in a non-integer value of $c_I/c_C$. The guest structure appears to undergo a phase transition at 67.2(4) GPa while the host structure remains unchange. The Sr-V phase is stable up to 75 GPa, the highest pressure reached in this experimental study.

Computational studies of the high pressure phases of Sr have also been undertaken. The calculations are based on the first principles approach using density functional theory and pseudopotential theory [88] within the generalised gradient approximation [74, 80]. This method allows an accurate procedure for solving the Schrödinger equation for a crystal structure. The structures can be relaxed according to the calculated stress and full structural optimisation can also be performed by calculating and minimising the total energies. The high-pressure structures were determined with fully optimised structural parameters including lattice parameters and atomic coordinates where applicable and they were found to be in a good agreement with those observed experimentally. The fcc structure was found to be stable at ambient pressure and the calculated fcc to bcc transition pressure is 1.16 GPa which is slightly less than the experimental value. The calculated lattice parameters for the Sr-III β-tin structure reveal the “ideal” value of 0.54 and is the same as those originally reported for group IV elements. This confirms that Sr is the first non-group IV element shown to have
the "ideal" $\beta$-tin structure. The only other non-group IV element which is reported to have this structure is Cs but with a different $c/a$ ratio. At higher pressure, the relaxed structure of Sr-IV is found to be in excellent agreement with the experimental data and found to be stable over a wide pressure range. This monoclinic structure may be a good prospective candidate for the high-pressure structures of other elemental metals.

In conclusion, structural investigations of Sr have been conducted up to 75 GPa experimentally. The Sr-III phase has been re-identified as having the $\beta$-tin structure and much effort has gone into the structure solution of Sr-IV which has shown to have a very complex monoclinic structure. The structure solution of Sr-IV required the development of an experimental set-up for data collection with improved resolution. Since Sr-V is stable over a very wide pressure range, between 50 GPa and at least 75 GPa, the experimental studies can be extend into the higher pressure region where further transitions are expected. The advent of area detectors such as the image-plate has permitted a significant increase in the accuracy of high-pressure structural studies. The data collected by the image-plate are now of sufficiently high quality that the accuracy of such studies are more likely to be limited by the quality of the sample itself rather than the method of data acquisition.

High temperature also plays an important role in high-pressure structural studies. The primary purpose of combined high-pressure high-temperature experiments is to extend the knowledge of new physics and structures that are likely to occur under extreme conditions. Most combined high-pressure and high-temperature investigations emulate the conditions relevant to materials that reside in planetary interiors. The application of simultaneous high-pressure and high-temperature to elements such as Sr allows us to understand their behaviour fully, under all conditions, so that eventually their physical properties can be predicted as well as measured. A fast-growing research area is materials synthesis under extreme conditions and for this work a detailed knowledge of the behaviour of elements and compounds under these conditions is vitally important. These combined techniques can also produce some beneficial effects on the sample for diffraction studies. Under very high pressure samples usually suffer from non-hydrostatic stresses which can be relieved using high temperature techniques: i.e. the application of temperature can soften the stressed materials so that they can no longer support large anisotropic stress. Recent studies by the Edinburgh group show
that it is even possible to grow single crystals at high pressure using high-pressure high-temperature techniques. Single crystal techniques are ideal for solving crystal structures especially those that are complicated — e.g. the intra-phase transitions observed in the guest component of Sr-V.

With the development of the new generation of brilliant synchrotron radiation sources, it is clear that a new era of high-pressure x-ray diffraction has begun. The obvious advantage of these very intense radiation sources for high pressure research is to allow the precise measurement of weak reflections from a very small sample volume. The decrease in sample volume offers the prospect of increasing the available pressure range that will be crucial for the study of currently inaccessible high-pressure structural phase transitions. For the Sr experiment, the incommensurate Sr-V phase has been observed to be a stable structure over a relatively wide pressure regime (from 49 GPa to 75 GPa). It is possible that at even higher pressure Sr could transform into a simpler structure as was observed in Ba. Provided with a very intense radiation source, not only can higher pressure structures be studied, but also new techniques can be introduced. The precise study of electron density is a clear possibility with these new sources. Although the coupling of x-rays to magnetic moments is considerably smaller than those for neutrons or electrons, the extremely high intensities available with the new sources may allow the development of high-pressure magnetic structure studies to compliment those performed with neutrons especially for very high pressure studies — which are not currently accessible with neutron diffraction due to the demands of a relatively large sample volume.

The rapid increase in computing power allows ever more sophisticated calculations to be performed on a reasonable time scale. More complicated or larger systems can therefore be studied computationally with less approximation, resulting in more precise structure predictions. In this case, the calculation of the high-pressure structures of Sr can be expanded into the incommensurate structure of the Sr-V phase. In order to clarify the stability range of the tetragonal, Sr-III, structure, a more sophisticated calculation could be performed where finite temperature effects are taken into account. The calculation results reported in this thesis are, however, the first attempt to understand these structural phase transitions using the readily available computational code, CASTEP.
Finally, the high pressure structural studies of Sr presented in this thesis show an extraordinary rich variety of crystal structures for this elemental metal. The high-pressure crystal structures of Sr have been fully explored up to 75 GPa, the highest pressure so far attained for structural studies of this metal. The high-pressure crystal structure of Sr-III has been revised and two wholly new structures of Sr-IV and Sr-V have now been identified. The computational work for Sr carried out by the author is also shown to be in good agreement with the experimental results.
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Published Work
Observation of a Simple-Cubic Phase of GaAs with a 16-Atom Basis (SC16)

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An SC16 phase of GaAs has been observed at high pressure. The phase is obtained by heating the high-pressure Cmcm phase to above ~400 K at ~14 GPa and is found to be stable on cooling back to room temperature. The detailed structure has been refined. On pressure decrease, the SC16 phase is found to be stable down to atmospheric pressure. From high-temperature studies, the equilibrium range for the SC16 structure is 13 to 14.5 GPa.

PACS numbers: 61.50.Ks, 62.50.+p

On pressure decrease from their high-pressure β-tin phases, Si and Ge transform back not to the diamond structure, but to more complex metastable structures denoted BC8 (body-centered cubic with an 8-atom basis), R8 (rhombohedral with an 8-atom basis) [1,2], and ST12 (simple tetragonal with a 12-atom basis) [3]. These phases have attracted considerable attention from theoreticians [4–10] both because of their intrinsic interest, and because the topology of the distorted-tetrahedral bonding is similar to that proposed for grain boundaries and surface reconstructions in Si [8]. These complex tetrahedral structures also provide computationally tractable models for studying how amorphous structures develop from increasing short-range disorder in the crystalline phase [5].

It would be of great interest if similar phases existed in III-V or II-VI systems, and, indeed, calculations using the binary equivalent of the BC8 structure in GaAs [11], denoted SC16 (simple cubic with a 16-atom basis), were performed over 20 years ago [12]. More recently, ab initio calculations have been used to consider the stability of the SC16 phase in a number of III-V systems. Crain et al. [13] reported that the SC16 structure is stable in GaAs, InAs, and InSb at high pressure, and calculated that the zinc blende (ZB) to SC16 transition in GaAs should occur at the surprisingly low pressure of 2.0 GPa [13]. Subsequent calculations by Mujica et al. [14] confirmed SC16 to be an equilibrium phase of GaAs, but reported a ZB-to-SC16 transition pressure of 11.5 GPa. They also found that SC16 itself would transform to the orthorhombic Cmcm structure at 12.7 GPa [14]. The higher value for the ZB-to-SC16 transition pressure in GaAs was supported in further calculations by Crain et al. [15], who, using more extensive k-point sampling than in their earlier study, obtained a transition pressure of 10.9 GPa.

However, despite these results, and further recent calculations which report that the SC16 structure should be stable also in GaP from 14.7 to 20.3 GPa [16], there has been no experimental evidence of the SC16 phase in any III-V or II-VI semiconductor to date. Crain et al. [13] suggested that transitions to the SC16 phase are kinetically inhibited by the requirement that no like-atom bonds are formed—a problem that does not arise in monatomic Si and Ge. Indeed, the SC16 structure has been observed in the more ionic I-VII systems CuCl and CuBr [17] where the kinetic barriers are lower [13].

As part of a systematic study of the high-pressure behavior of the III-V, II-VI, and group IV semiconductors, we have made high-temperature high-pressure diffraction studies of GaAs. We find that the SC16 phase can be obtained by moderate heating of the Cmcm phase at pressures of ~14 GPa. The SC16 phase is stable on reducing temperature back to ambient and can be recovered to ambient pressure.

The samples of GaAs were a finely ground powder obtained from starting material of 99.9999% purity. Diffraction data were collected on station 9.1 at the SPring-8 Synchrotron Radiation Source, Daresbury Laboratory, using an image-plate area detector [18]. The incident wavelength was 0.4654 Å. The samples were loaded into Merrill-Bassett and Diacell DXR5 diamond-anvil cells (DACs) with 4:1 methanol:ethanol as a pressure transmitting medium and chips of ruby for pressure measurement. In situ high-temperature measurements were made by resistively heating the entire pressure cell. The sample temperature was obtained from a thermocouple attached to the gasket and is accurate to better than ±5 K. Structural information was obtained from Rietveld refinement of the integrated profiles using the program MPcOF.

Evidence for SC16 was first observed during attempts to sharpen Cmcm-phase profiles by heating. Figure 1 shows a series of diffraction profiles obtained on heating to 448 K in a Merrill-Bassett DAC, starting with Cmcm-GaAs at a pressure of 18 GPa. Heating below 373 K produced only a drop in sample pressure. Slightly higher temperatures—profiles (d) and (e)—produced the considerably sharper Cmcm-phase diffraction patterns that were sought. However, further heating to 423 K resulted in the appearance of new reflections, as marked by dots below profile (f). These additional peaks were found to remain on reducing the sample temperature back to ambient—as marked by arrows in profile (h)—but the cooling of the pressure cell produced a further reduction in sample pressure to 10.5 GPa. Because this pressure is below that at which the Cmcm phase transforms to ZB and cinnabar [19], profile...
The inset shows an enlargement of the low-angle region of profile (h), with the most intense reflections from the zincblende (Z) and cinnabar (Cinn) phases indexed.

(h) is a mixture of SC16 with both these phases—as shown in the inset. From the peak positions of the Cmcm phase in profiles (e) and (f), we can estimate that the sample pressure was 13.5(5) GPa when SC16 first appeared, at an estimated temperature of 410(13) K.

Subtraction of the ZB- and cinnabar-phase peaks from profile (h) in Fig. 1 yielded a simple diffraction profile very similar to that we have observed previously from the BC8 phases of Si and Ge [20]. Refinements showed that all the peaks from the new phase could indeed be indexed on a cubic unit cell and that the peak intensities were consistent with those expected from the SC16 structure. However, these refinements revealed that the three-phase nature of the profile hampered detailed refinement of the SC16 structure, and that better quality diffraction profiles were required.

As the SC16 phase is stable at ambient temperature, all further diffraction studies of the SC16 phase were made at room temperature (RT) on samples that had previously been heated in an off-line furnace. As the Merrill-Bassett DAC used in the in situ study lost considerable pressure on heating, these further studies were made in Dia-cell DXR5 DACs which lost only ~0.2 GPa on heating. Results showed that if the sample pressure remains above 14.5 GPa at high temperature (HT), the only effect of heating is to sharpen the diffraction profiles from the Cmcm phase. If the pressure at HT is below 14.5 GPa but above 13 GPa, samples transform to the SC16 phase. If the sample pressure at HT falls below 13 GPa, the diffraction profiles are dominated by peaks from the cinnabar and ZB phases, with only a small proportion of the SC16 phase being present. The highest-quality SC16 profiles were obtained by heating Cmcm samples at 13.8(4) GPa to ~460 K, the maximum temperature available using the Dia-cell DAC. Such profiles still contain (weak) peaks from the Cmcm phase, and it is likely that single-phase SC16 profiles could be obtained by heating the Cmcm phase to temperatures above that obtainable using the beryllium-seat DACs employed in this study.

Before presenting a detailed analysis of the diffraction data for the SC16 phase, some discussion of the symmetry of the BC8 and SC16 structures is required. Since the initial discovery of the BC8 structure in Si, the structure has been described using spacegroup Ia3 with an atom on the 16c position at (x, x, x) with x = 0.1 [1]. However, an identical structure is obtained with x = 0.15. In both cases the structure has centers of inversion symmetry at (0, 0, 0) and (1/4, 1/4, 1/4). With the x = 0.1 description, the inversion center at (0, 0, 0) must disappear in the SC16 structure to enable the bonded atoms at (0.1, 0.1, 0.1) and (0.1, 0.1, 0.1) to be of different atomic species; this appears to have misled Crain et al. [13] into concluding that the SC16 structure has the noncentrosymmetric spacegroup P2_3. In fact, the SC16 structure still contains a center of inversion at (1/4, 1/4, 1/4) and the true symmetry is Pa3. This second set of inversion centers was noted by Mujica et al. [14] and the Pa3 symmetry is supported experimentally by Hull and Keen [17]. In spacegroup Pa3 one atomic species is on the 8(c) position at (u, u, u) with u = 0.15 while the other is on another 8(c) site at (v, v, v) with v = 0.65. Although the x = 0.1 and x = 0.15 descriptions of the BC8 structure are identical, the relationship between the BC8 and SC16 structures is greatly simplified if the x = 0.15 description of BC8 is used, because this allows both structures to be described with respect to a common origin. The transition from BC8 to SC16 then results in the loss of the inversion center at (1/4, 1/4, 1/4) and the atoms at (0.15, 0.15, 0.15) and (0.35, 0.35, 0.35) are bonded to each other in both structures.

Figure 2 shows a mixed SC16/Cmcm profile obtained by heating Cmcm GaAs at 13.8 GPa and 453 K for 48 min before cooling to RT and raising the pressure to 18.9 GPa [21]. The SC16 profile comprises strong h + k + l = even reflections and much weaker h + k + l = odd reflections which are absent in profiles from the body-centered BC8 structure. This second class of reflections, the strongest of which are enlarged and indexed in the inset to Fig. 2, shows the SC16 structure to be site ordered, and provides critical information on the values of u and v: if v = u = 1/2 then the SC16 structure is pseudo body-centered and the intensity of the h + k + l = odd reflections depends only on the difference in scattering power of the Ga and As atoms, while if v = u = 1/2 there will be an additional structural component. As shown in Fig. 2, the Rietveld fit to the SC16/Cmcm profile is excellent, with Rl = 2.50% and Rwp = 4.72%. The best fit to the low-angle weak reflections is shown enlarged in profile (b) of the inset. Trial refinements with v = u constrained to be equal to 1/2 gave significantly less intense

FIG. 1. Diffraction profiles obtained on heating a sample of Cmcm GaAs to 448 K starting at a pressure of 18 GPa. The dots below profile (f) mark the positions of new reflections appearing at 423 K. These reflections remain on cooling back to ambient temperature—as marked by arrows in profile (h). The inset shows an enlargement of the low-angle region of profile (h), with the most intense reflections from the zincblende (Z) and cinnabar (Cinn) phases indexed.
The best fit to the low-angle weak reflections is shown enlarged in profile at 18.9 GPa and 298 K. The upper (lower) tick marks confirm directly that the refined lattice parameter (from the experimental value) is 0.844 [22], and thus the SC16 structure has the same bonding arrangement with respect to nearest neighbors at 2.313 Å and three so-called B-B bonds are shown.

$\text{h} + k + l = \text{odd reflections [profile (a) in the inset], confirming directly that } v - u \neq \frac{1}{2}.$

The refined lattice parameters are $a = 5.017(1) \AA$, $b = 5.325(1) \AA$, and $c = 4.862(3) \AA$ for Cmcm [V/V0 = 0.719(1)] and $a = 6.594(1) \AA$ for SC16 [V/V0 = 0.793(1)]. The relative volume of the ZB phase at the same pressure is 0.844 [22], and thus the SC16 phase is 5.1(1)% denser than ZB, and 7.4(1)% less dense than Cmcm at 18.9 GPa. The theoretical relative volume of the SC16 phase at 18.9 GPa—obtained from the calculated values of $B_0$ and $B'$ [14]—is 0.776, giving a calculated lattice parameter (from the experimental value of V0) of 6.546 Å, only 0.7% smaller than that observed.

The atomic coordinates for the SC16 phase at 18.9 GPa are $u(Ga) = 0.152(1)$ and $v(As) = 0.640(1)$, so that $v - u = 0.488(1)$. The recent calculations on SC16-GaAs have used a different description of the structure from that used here [13,14], and a linear extrapolation of the results of Mujica et al. [14] to $V/V_0 = 0.793$ gives (in their notation) $x_1(Ga) = 0.0952$ and $x_2(As) = 0.1115$. In our notation, these are equivalent to $u(Ga) = 0.1548$ and $v(As) = 0.6385$, in excellent agreement with the experimental values.

The refined SC16 structure is shown in Fig. 3. As in the BC8 structure, each atom has one so-called A bond along the (111) axis and three so-called B bonds. In SC16-GaAs at 18.9 GPa, the A bondlength is 2.376(9) Å and the B bondlength is 2.365(9) Å. This compares with 4 unlike nearest neighbors at 2.313 Å in the zincblende structure at the same pressure [22]. Although each atomic species in the SC16 structure has the same bonding arrangement to its unlike nearest neighbors, the distances to the like-atom next-nearest neighbors (nnn) are different—3.472(9) Å for Ga and 3.198(9) Å for As. In the BC8 structure, these distances are the same and become the so-called $R_5$ bond at the transition to R8 [13]. This difference in the nnn distances arises as a consequence of $v - u = \frac{1}{2}$, and means that interchange of the atomic species—such that $u(Ga) = 0.640$ and $v(As) = 0.152$—results in a different structure where the nnn distance for As is longer than that for Ga. Because $v - u = \frac{1}{2}$ and because of the very similar scattering power of Ga and As, the two different structures produce diffraction patterns too similar to distinguish decisively. This problem was also noted in CuCl and CuBr by Hull and Keen [17], and in that case the distinction between the two structures was made on the basis that one results in unphysically short Cl-Cl and Br-Br distances. Trial refinements of SC16-GaAs using the second possible atomic arrangement—with As-As > Ga-Ga—did give a slightly poorer overall fit to the diffraction data ($R_f = 2.55%$ and $R_{wp} = 4.74%$), and, in particular, a poorer fit to the weak $h + k + l = \text{odd reflections at low angles. Furthermore, Ga-Ga is expected to be greater than As-As because the structure is covalently bonded and Ga has the larger covalent radius [23]. This is supported by the calculations of Crain et al. [13] and Mujica et al. [14] which both find Ga-Ga > As-As. In both calculations, the other configuration was explicitly tested and found to have a higher energy [23].

We have also studied the apparent stability range of SC16-GaAs at room temperature (RT). We observe no transition from the SC16 phase down to ambient pressure (AP), where refinements of the SC16 structure give $a = 6.934(2) \AA$ [$V/V_0 = 0.923(1)$] with $u(Ga) = 0.157(2)$ and $v(As) = 0.643(2)$, so that $v - u = 0.486(3)$. The theoretical SC16 structure at AP has $u(Ga) = 0.1583$ and $v(As) = 0.6398$, and a calculated volume (per molecule) of 40.549 [14]. This volume equates to a lattice parameter of 6.871 Å, some ~1% smaller than that observed.

![FIG. 2. Rietveld refinement fit to a mixed SC16/Cmcm profile at 18.9 GPa and 298 K. The upper (lower) tick marks show the positions of all reflections allowed by symmetry in the SC16 (Cmcm) phase. The difference between the observed and calculated profiles is shown below the tick marks. The strongest Cmcm phase peaks are indexed in the main profile. The best fit to the low-angle weak reflections is shown enlarged in profile (b) of the inset, while profile (a) shows the best-fitting profile with $v - u$ constrained to be equal to $\frac{1}{2}$.](image1)

![FIG. 3. The SC16 structure of GaAs, shown in projection down the z axis. Ga is at $(u = 0.15, v, u)$ and As is at $(v = 0.64, v, v)$. The numbers on each atom give the z coordinate in units of 0.01. Some of the short nearest-neighbor A and B bonds are shown.](image2)
On pressure increase at RT, we observe no change until 22.0(7) GPa when the SC16 phase begins to transform to the Cmcm phase. This suggests a stability field of the order of 20 GPa, which is much larger that calculated by Mujica et al. [14]. However, the true equilibrium stability range of the SC16 phase is likely to be smaller than that suggested by the RT results, where large kinetic barriers almost certainly inhibit the phase transitions to the ZB and Cmcm phases. This is borne out by the present high-temperature results which show that SC16 is not the equilibrium phase above 14.5 GPa, nor below 13 GPa. This range of only —1.5 GPa is closely similar to the 1.2 GPa calculated by Mujica et al. [14] suggesting that the true equilibrium range at RT is of this magnitude. The large difference from the experimental results at RT graphically illustrates the influence of kinetic effects in determining experimental transition pressures in this system.

The observation of both the SC16 and cinnabar structures means that GaAs is now unique among the III-V and II-VI semiconductors in having two strongly distorted tetrahedral phases at high pressure. It is interesting to compare their degrees of distortion. At 8.3 GPa, \(a(\text{SC16}) = 6.739(2) \text{Å} \) \(V/V_0 = 0.847(1)\) and \(u = 0.155(2)\) and \(v = 0.642(2)\). At the same pressure, cinnabar-GaAs has \(V/V_0 = 0.834(1)\) [19] and is thus 1.3(1)% denser than the SC16 phase. This greater density is accompanied by only a slightly greater distortion of the tetrahedra: SC16 has nearest-neighbor (nn) bondlengths of 2.369(19) and 2.426(19) Å, while in cinnabar the bondlengths are 2.371(8) and 2.477(8) Å [19,24]. But the nn bondangles in SC16 are \(\sim 100°\) and \(\sim 118°\), while in cinnabar they vary much more, from 91° to 141° [24]. In this sense cinnabar is the more distorted. However, since the distortion arises mostly from a simple twisting of the tetrahedra [25], cinnabar can also be seen as the less distorted. In any case, the existence of two quite differently distorted tetrahedral forms makes GaAs a particularly promising model system for studies of more complex and amorphous structures in binary materials.

In conclusion, we have found an SC16 phase of GaAs, the first observation of such a structure in a III-V semiconductor. The observation of SC16-GaAs realizes the earlier predictions of such a phase using \textit{ab initio} calculations, and supports suggestions that the same structure may also be stable in other III-V systems [13,14,16]. The present results, along with the earlier determination of the SC16 structure in the copper halides, now invite experimental and computational study of the II-VI systems, where the more ionic bonding should facilitate the formation of SC16.

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[11] The ST12 structure is unlikely to possess a binary equivalent, since its 5- and 7-fold rings of atoms would require bonding between like-atoms and would thus be energetically unfavorable.
[21] This was done to prevent any possible transformation to cinnabar if a sample went below 14 GPa for any extended period. This was later found not to happen, but the profile in Fig. 2 was the best quality data obtained (an 8 h exposure) and so is used in structure analysis.
[23] G. J. Ackland (private communication); A. Mujica (private communication).
[24] In cinnabar-GaAs (Ref. [19]) we could not explicitly rule out \(u = v = 0.52(1)\). If \(u = v\), then all four nn bondlengths in cinnabar-GaAs would be the same. However, the nn bondangles would still vary from \(-91°\) to \(-140°\).
Structures and Transitions in Strontium

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The structural pressure dependence of strontium has been studied using angle-dispersive powder diffraction techniques with the image plate detector system. The two-dimensional diffraction data has allowed the clear identification of an accompanying minor phase in the Sr-III stability range which has enabled the structure of Sr-III to be assigned correctly as that of β-tin. The structural conformation and atomic coordination are very similar to those of β-Sn and of the high-pressure β-tin phases of Si and Ge. Sr is the first non group-IV element to be shown to have the "ideal" β-tin structure.

strontium, crystal structure, synchrotron, image plate, angle-dispersive

The rich variety of high-pressure crystal structures found in the heavier alkaline-earth metals Sr, Ba and Ca has stimulated substantial experimental and theoretical studies of the transition mechanisms. In their original high-pressure energy-dispersive powder diffraction study, Olijnyk and Holzapfel [1] found the unusual sequence fcc – bcc – simple cubic in Ca, with evidence of a further transition at 42 GPa; in Ba, they found the sequence bcc – hcp – Ba-III with a possible hcp-superlattice structure at 7.5 GPa – the complex Ba-IV structure at 12.2 GPa; and in Sr they found the sequence fcc – bcc – a relatively simple, but unsolved Sr-III phase at 26 GPa – a more complex Sr-IV phase at 35 GPa – a Sr-V phase that appears to be the same as Ba-IV at 46 GPa. A more recent study by Winzemck and Holzapfel [2] at 31.3 GPa has identified Sr-III as having an orthorhombic structure with Imma symmetry, similar to that of the high-pressure phase of Si [3] and Ge [4]. We have now repeated this study of Sr with angle-dispersive x-ray diffraction techniques with the image plate area detector system, and report a revised structure for Sr-III.

The samples, of 99.95 % purity, were obtained from Johnson Matthey in the form of large granules stored in sealed glass ampoules under argon. The granules were removed from the ampoules prior to use and subsequently stored in mineral oil. Suitably sized samples for loading into the diamond-anvil cells were cut from the granules under mineral oil so that any residual surface oxide was carefully removed. Diamond-anvil cells of the Diacell DXR-5 design and the Mao-Bell design were used as each type offers full conical x-ray apertures with 50° and 40° half angles respectively. The diamond anvils had either 400 μm or 300 μm culets and the preindented tungsten gaskets had spark-eroded holes of 100 μm diameter. Samples were loaded with mineral oil as a pressure-transmitting medium to prevent oxidation, and the pressure was measured to ±0.1 GPa using the ruby-fluorescence technique.

Diffraction data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury, at a wavelength of 0.4654 Å. The incident beam was collimated by a platinum pinhole to a diameter of 75 μm. The two dimensional powder patterns collected on the image plates were read on a Molecular Dynamics 400A PhosphorImager and then integrated to give conventional one-dimensional diffraction profiles. Details of our experimental setup and pattern integration software have been reported previously [5].

Fig. 1. Part of the two dimensional diffraction pattern of Sr-III. One of the smooth lines from the additional phase has been indicated by an arrow.

On compression, the Sr-II (bcc) phase was first observed in a mixed-phase sample with Sr-I (fcc) at 3.5 GPa, in excellent agreement with the transition pressure of 3.5 GPa observed by Olijnyk and Holzapfel [1]. The crystallisation from Sr-II to Sr-III initially appeared at approximately 24.4 GPa and manifested itself by the formation of bright spots on the two-dimensional diffraction patterns. On subsequent pressure increase a larger number of spots appeared as more Sr-II transformed to Sr-III with an accompanying decrease in the intensity of the bcc contribution to the diffraction pattern. Recrystallisation of Sr-II to Sr-III was complete at 26.8 GPa, which is in good agreement with the pressure of 26 GPa determined by Olijnyk and Holzapfel [1]. The two-dimensional images also revealed smooth lines from the formation of an additional phase accompanying the Sr-II to Sr-III transition.
Figure 1 shows an example collected at 32.6 GPa and the strongest of the smooth lines from the additional phase has been indicated by an arrow.

Attempts were first made to fit the pattern with the Imma structure of Winzenick and Holzapfel. Figure 2 shows a comparison of the calculated pattern, using the cell of Winzenick and Holzapfel, with the observed powder pattern, from the same sample at 34.8 GPa, and indicates clear discrepancies between the observed and calculated splittings of the peaks corresponding to the (0 3 1) and (3 0 1) reflections. Moreover the (2 0 0) reflection of the orthorhombic Imma cell does not correspond with the spotty lines of the recrystallised phase but most closely coincides with the strongest smooth line from the accompanying phase. This indicates that the Imma structure proposed by Olijnyk and Holzapfel [1] is based on a mixed-phase pattern which is also suggested by a number of un-indexed peaks in their original powder patterns that can now be identified with the accompanying smooth phase.

Fig. 2. A comparison of the observed Sr-III powder diffraction data, at 34.8 GPa, with the profile calculated using the orthorhombic Imma cell of Winzenick and Holzapfel [2].

Subsequent unit-cell indexing of only the spotty lines, using DICVOL, determined that they could be indexed on a body-centred tetragonal cell with dimensions a = 5.504 Å, c = 2.960 Å at 34.8 GPa. The systematic absences were consistent with the I 41/a m d spacegroup of the β-tin structure (Sr at 0, 1/4, Δ = 1/2) and so a full Rietveld refinement of the pattern was then undertaken, assuming this structural model, with a correction for preferred orientation. The result is shown in Figure 3 and it is apparent that, apart from the extra peaks from the additional 'smooth' phase, the β-tin structure gives an excellent fit to the data. The slight intensity mismatches are expected to be related to small inadequacies of the preferred orientation model. Any shift away from the ideal β-tin coordinates so that Δ is increased from its ideal value of 0.25 [3,4], places intensity into systematically absent reflections. This may also explain why the Imma structure of Olijnyk and Holzapfel [1] has Δ equal the ideal β-tin value as otherwise significant intensities would have been predicted for reflections at positions where no diffraction peaks were observed in their data.

Fig. 3. Rietveld refinement of Sr-III at 34.8 GPa with the β-tin structure. The principal smooth lines have been indicated by arrows.

The c/a ratio for β-tin Sr is 0.6007 at 28.4 GPa which is similar to the values observed in Sn (c/a = 0.5455 at ambient pressure [6]), Si (c/a = 0.5498 at 11.7 GPa [3]) and Ge (c/a = 0.5575 at 12.6 GPa [4]). The only other known high-pressure structure with the β-tin spacegroup and coordinates outside the group-IV elements is that of Cs-IV, which has an elongated unit cell with a c/a ratio of 3.728 at 8.0 GPa [7]. The marked discrepancy in the c/a ratio for Cs is also reflected in the structural conformation where each atom is 8-fold-coordinated rather than the 6-fold-coordination of Sn, Si, Ge and Sr. We conclude, therefore, that Sr is the first non-group-IV element to be shown to have the "ideal" β-tin structure. Additional support for this conclusion comes from the observation that the proportion of the smooth component varies considerably from sample to sample, and it is sometimes almost absent as shown in Figure 4.

Fig. 4. Rietveld refinement of Sr-III sample with almost no smooth phase present.

The sequence of phase transitions with increasing pressure, fcc → bcc → β-tin, reduces the coordination number from 12 to 8 to 6. This decrease in the number of neighbours is a well
known behaviour in the group I and II metals attributed to s→d electron band transfer [8]. The preferred structure will be the one which gives the greatest broadening of the d-band (and hence the lowest energy for the band edge). At still higher pressures the overlap between the core electrons will dominate, and a close packed structure is expected. Detailed total energy pseudo-potential calculations are now in progress to establish the electronic configuration of the Sr-III structure and the mechanisms of the fcc → bcc → β-tin phase transitions.

Work is continuing to identify the smooth accompanying phase and its possible relationship with the β-tin phase. The smooth phase first appears close to the bcc → β-tin transition from a contaminant-free bcc pattern. As the pressure is increased the smooth phase appears to have a similar compressibility to Sr-III and it persists up to and through the Sr-III → Sr-IV transition. On pressure decrease the additional smooth phase appears to undergo a structural phase transition at a pressure of 23.1 GPa which is somewhat below the β-tin → bcc transition on download at 26 GPa. On further pressure decrease the diffraction pattern from the low-pressure smooth form progressively weakens until, at about 10 GPa, only a clean bcc pattern remains. This behaviour strongly suggests that the smooth phase is another structural form of Sr, rather than simply a contaminant, and we are currently working towards the identification of its “low pressure” and “high pressure” structures.

Finally, it is interesting to note the key role of the two-dimensional image-plate data in distinguishing the smooth diffraction pattern of the additional phase from the spotty pattern of Sr-III. This additional information proved crucial in determining conclusively that Sr-III has the β-tin structure.

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References

Observation of the incommensurate barium-IV structure in strontium phase V

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A previously unknown type of elemental structure has been discovered recently in barium, phase IV. The structure is composed of a “host” and two or more “guest” components made up of chains that lie in channels in the host, and form structures that are incommensurate with the host. This implies a segregation into different electronic species. The same structure has now been found in phase V of Sr above 45 GPa.

Under pressure, Sr transforms from the ambient-pressure face-centred cubic (fcc) phase, to a body-centred cubic (bcc) structure at 3.5 GPa. This phase is stable up to 24 GPa, where there is a transition to Sr-III. On further compression, there are transitions to Sr-IV at 35 GPa, and to Sr-V at 46 GPa. There is a long established interest in these phases of Sr and other alkaline earth metals as a manifestation of the electron transfer under pressure. 3 However, attempts to grow a single crystal of Sr-V by annealing a partially recrystallised sample at 373 K for 2 h were unsuccessful, and resulted, instead, in a sample with smoother diffraction rings. Data were collected from several other samples that gave the same diffraction peaks, but this annealed, smooth sample was used for structure refinement.

Recently, we have found Ba-IV to have a remarkable self-hosting structure, comprising a tetragonal host with chains of guest atoms contained in channels running along the fourfold axis of the host. 4 The chains form two different structures, both of which are incommensurate with the host, and one of which is disordered and gives rise to strong diffuse scattering. One of the guest structures was also found to undergo a structural phase transition without any accompanying structural change in the host structure. The reported similarities in the diffraction patterns of Ba-IV and Sr-V have led us to reexamine Sr-V, and indeed we find it to have the Ba-IV-type structure. This is thus emerging as a radically new type of elemental structure, stable over wide pressure ranges in both barium and strontium, that may be found in other elements.

The samples of Sr were small pieces cut from starting material of 99.95% purity purchased from the Aldrich Chemical Company. To prevent oxidation, the samples were cut while completely immersed in dry mineral oil. Then, still enveloped in oil, they were loaded into Diacell DXR5 and DXR6 diamond-anvil pressure cells, with a small chip of ruby for pressure measurement. The mineral oil also provided a quasi-hydrostatic pressure transmitting medium. Diffraction patterns collected after loading revealed no peaks from SrO. Data were collected to 56 GPa on station 9.1 at SRS Daresbury, and to 74 GPa on beamline ID9 at the European Synchrotron Radiation Facility (ESRF), Grenoble, using image-plate area detectors. 5, 6 The incident wavelengths were 0.46541 Å and 0.45115 Å, at SRS and ESRF, respectively. Structural information was obtained from Rietveld refinement of the integrated profiles using the program MPROF. 7

Diffraction peaks from Sr-V were observed on pressure increase at 49.0(7) GPa. Whereas the diffraction pattern from Sr-IV was that of a highly textured powder sample, with short arcs of intensity, the diffraction patterns from Sr-V consisted of many strong, quite sharp, spots, indicating that recrystallisation of the sample occurs at the IV-to-V transition. Similar recrystallisation effects were observed at the Ba II-to-IV transition. 8 However, attempts to grow a single crystal of Sr-V by annealing a partially recrystallised sample at 733 K for 2 h were unsuccessful, and resulted, instead, in a sample with smoother diffraction rings. Data were collected from several other samples that gave the same diffraction peaks, but this annealed, smooth sample was used for structure refinement.

Figure 1 shows the integrated diffraction profile obtained from Sr-V at 56 GPa, compared with a profile from Ba-IV at 12.9 GPa. The relative intensities and spacings of the strongest peaks in each pattern (numbered 1 to 8) are clearly very similar, as was rather less certainly apparent before. 9 In Ba-IV, these peaks arise principally from the body-centred tetragonal (I) host structure. They can be interpreted in the same way in Sr-V, with lattice parameters a 1 = 6.958(2) Å and c 1 = 3.959(2) Å, giving a c 1 /a 1 ratio of 0.569(1) compared with 0.563(1) in Ba-IV at 12.9 GPa. However, as in Ba-IV, this cell could not index all the reflections; some 15 weak reflections remained unindexed, of which the ten lowest-angle ones are marked in the inset to Fig. 1. Of these, one (labeled G) arises from the tungsten gasket, and five—those marked with asterisks—are from the unidentified contaminant phase discussed above. This phase appears at the II-to-III transition, and produces very smooth diffraction rings—see Fig. 1 of Ref. 1— which are thus readily distinguishable from the textured diffraction rings of Sr-III, IV and V. The contaminant phase is unchanged at the III-IV and IV-V transitions, and the peaks marked with asterisks in Fig. 1 are the same as those marked with arrows in Fig. 3 of Ref. 1. (The strongest contaminant peak, at 10.5° in the inset to
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the Sr-V profile. Peaks marked with asterisks are from a contaminated phase, peak G is from the gasket, and the peaks marked a to d are from the guest component. The lowest-angle peaks from the C and O structures in Ba-IV are labeled. The first of these corresponds to peak a in the Sr-V profile.

Fig. 1, is the one that led Winzenick and Holzapfel to misassign the structure of Sr-III as orthorhombic Imma,4 as already discussed.)

The remaining weak peaks unaccounted for by the f lattice (a, b, c, and d in Fig. 1 and others at higher angles) are clearly in the same relative positions as reflections from the C-face-centred tetragonal (C) guest phase observed in Ba-IV.5 From the measured positions of 7 such peaks, the refined lattice parameters are \( a_C = 6.961(3) \) Å and \( c_C = 2.820(1) \) Å at 56.0 GPa. As in the case of Ba-IV, the C lattice is commensurate with the host f lattice in the ab plane, but incommensurate with it along c. The \( c_f/c_C \) ratio is 1.404(1), similar to the value of 1.378(1) in Ba-IV at 12.9 GPa.

The host f structure is shown by the dark colored symbols in Fig. 2, in a c-axis projection. The C structure formed by the (light colored) guest chains at \( x,y = (0,0) \) and \( (\frac{1}{2},\frac{1}{2}) \) is shown in inset (i). Figure 3 shows a Rietveld refinement fit with these structures to the diffraction pattern in Fig. 1. The non-\( hk0 \) f-lattice reflections can be fitted with atoms in the \( 8h \) sites of spacegroup \( I4/mcm \), at \( x,y = x+0.5 \) and \( z = 0 \), with \( x \approx 0.15 \). To fit the \( hk0 \) reflections, which include contributions from both f and C components, guest atoms were placed at \( (0,0,0) \) and \( (\frac{1}{2},\frac{1}{2},0) \) with very large thermal motion along c so that they model uniform rods of density and contribute only to the \( hk0 \) reflections. The non-\( hk0 \) C-phase reflections were fitted as a second separate “phase,” the contributions of which to the \( hk0 \) reflections had to be deleted from the fit as they were already given by the first composite “phase.” The fit can be seen to be very good. There are some small displacements in peak positions of a magnitude to be expected with a solidified pressure medium at such a high pressure. Significant preferred orientation is included in the fit, in accord with the evidently strong texturing of the sample. The refined value of the \( f \)-structure \( z \) coordinate was 0.1460(2), compared with 0.1484(3) in Ba-IV at 12.9 GPa.

In Ba-IV, the availability of accurate single-crystal data enabled the occupancy of the guest sites to be refined as 100% within less than 1%.5 We do not have a sample of Sr-V that is sufficiently well recrystallised to obtain single crystal data. At the same time, the strongly textured nature of the sample limits the accuracy with which the guest site occupancy can be refined from the powder data, and it can be shown to be 100% within only \( \sim 30\% \). However, the great similarity to Ba-IV in atomic coordinates, \( c_f/c_C \) and \( c_f/a_f \), as well as considerations of structural stability, all strongly suggest that the occupancy is 100%. (It is a curious feature of this type of structure that the density thus cannot be determined with complete certainty even though the lattice parameters and atomic coordinates are known.) If 100% occupancy is assumed, there are then \( c_f/c_C = 1.404 \) guest atoms in each of the two channels in the host f unit cell at 56 GPa,
and hence a total of 10.808 atoms in the volume of the I cell.

In Ba-IV, we identified three different guest structures C, as in Fig. 2(i), a monoclinic distortion of it (M), and an orthorhombic distortion of it (O). C and M coexist from 12.0 to 12.6 GPa (Ba-Wa); M transforms to O at 12.6 GPa (Ba-IVb); and there is a further transformation in the guest structure at 18 GPa (Ba-IVc)—and maybe yet further transformations occur at higher pressures beyond the range of our studies. \textsuperscript{5} Forms Iva, IVb, and IVc all have the same (14/mcm) host structure, which can be identified in data from earlier work\textsuperscript{5,10} across the whole range of phase IV to 45 GPa. In addition, we observed strong diffuse scattering, in at least forms Iva and Ivb, that signal a degree of random positional disordering of the guest chains along the c axis in the C structure. The Sr-V diffraction patterns collected up to 56 GPa at SRS showed no evidence of either diffuse scattering or transformations in the guest structure. We therefore conducted a detailed study of Sr-V to 74 GPa at the ESRF, to obtain increased sensitivity to weak diffraction features and extend the pressure range explored. The samples were prepared and loaded as already described.

Figure 4 shows an image recorded at 70 GPa, and lines of diffuse scattering are plainly visible, revealing the presence of one larger crystallite with its c axis in the plane of the image. The positions of these lines correspond to sheets of diffuse scattering that are coplanar with the hkl, hk2, etc., reciprocal-lattice layers of the C component, exactly as in Ba-IV. (There is no plane of diffuse scattering for l=0 because the chain displacements are along c.) In fact, the ESRF data reveal diffuse scattering at the pressures of the SRS data, but it becomes readily visible only at much higher pressures. This may be because of increasing disorder with increasing pressure, or because the crystallite giving the diffuse scattering in Fig. 4 grew larger with increasing pressure.

Figure 5 shows integrated profiles collected at 69 and 74 GPa, the highest pressure reached. The C peaks a, b, and d (see Fig. 1; peak c has become too weak to detect) can be seen to have reduced markedly in intensity between 69 and 74 GPa, and several new weak diffraction peaks have appeared, as marked. But there is no discernible change in the I-lattice peaks. Because the C peaks are all weakened with respect to the (unaltered) I-lattice peaks, the most probable interpretation is that, like Ba-IV, Sr-V shows a transformation in its guest component—at 71(1) GPa. However, we cannot completely rule out the possibility that the weak new peaks mark the start of a transition to another phase, Sr-Vl. So, we label the form below 71 GPa as Sr-Va, and that above 71 GPa as Sr-Vb, but only provisionally. Again, as with Ba-IV, the C form of the guest is associated with significant disorder of the chains in their positions along c. As said, it is impossible to compare the degree of this disorder with Ba because the strength of the diffuse scattering depends on crystallite size, and this is not known for the Sr sample.

We thus conclude that the structure and behavior of Sr-V is very similar to that of Ba-IV in all its principal features. There are some differences in detail in the nature of the guest component: Sr-Va has only the disordered C structure. The Sr-Vb form (in the samples we have studied to date), whereas Ba-Iva and Ba-Ivb, and probably Ba-Ivc, have two forms; and Sr-Vb, if that is its correct designation, gives a guest-structure pattern unlike any of the Ba forms observed so far. However, the key characteristic of having an incommensurably self-hosting structure is the same, and suggests that there is a segregation into two different electronic species. This state is surprisingly stable in both metals; Ba-IV exists from 12 to 45 GPa and Sr-V from 48 to at least 74 GPa (the highest pressure yet reached in studies of Sr). In the host structure of Sr at 56 GPa, each Sr atom has four nearest neighbors at 2.837(1) Å, two at 2.847(1) Å, and one at 2.873(2) Å.
The atoms in the chains are separated along \( c \) by a similar distance of 2.82 Å. However, on the assumption that the chains are 100% occupied, as in Ba-IV, the chain atoms have a significantly shorter minimum approach to the host atoms of 2.664(1) Å, with a maximum distance from them of 2.842(1) Å. There is a commensurate prototype of the Ba-IV structure formed by \( M_2M' \) intermetallics such as Al\(_2\)Cu and Na\(_2\)Au, in which the \( M \) atoms form the 14\( \alpha \)mcm host structure and the \( M' \) atoms occupy the chain sites. The \( M' \) atoms are the smaller in all cases. This and the close chain-host approach in Ba-IV and Sr-V suggest that the Ba and Sr atoms in the chains have an electronic configuration with a smaller radius than those forming the host structure.

As discussed in Ref. 5, there are also interesting parallels to pursue with the remarkably similar phenomenology of organic inclusion compounds such as is formed by \( \alpha, \omega \)-dibromoalkane guest molecules in the channels of a urea host, and with the disordered incommensurate Hg chains in Hg\(_{5-}\)\(_x\)As\(_6\). However, these and the commensurate \( M_2M' \) prototype are all two-component systems; an incommensurate host-guest structure is very surprising in an element. But its emergence as a phase stable over 25 GPa or more in already two elements suggests that it may prove to be a ubiquitous new phenomenon.

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