High-Pressure High-Temperature
Structural Studies of Binary Semiconductors

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“The most important thing in science is not so much to obtain new facts as to discover new ways of thinking about them.”

Sir William Henry Bragg (1862-1942)
Abstract

The last decade has seen a tremendous improvement in high-pressure diffraction techniques. Among other things, this has led to a completely new understanding of the structural systematics of the group IV, III-V and II-VI semiconductors. Many phases have been shown to have more complex, lower-symmetry, high-pressure structures than previously thought. One of the most surprising discoveries has been the non-existence of the diatomic $\beta$-tin structure, long believed to be one of the principal high-pressure phases of the III-V and II-VI systems. However, most of the work to date has been performed at room temperature and in fact, very little is yet known about the high-pressure phases of these systems above room temperature.

The work presented in this thesis centres on the use of high temperature under pressure to investigate further the absence of the diatomic, site-ordered, $\beta$-tin structure in both GaSb and InSb, where the $\beta$-tin or $\beta$-tin-like phases have been found but appear to be site-disordered. Additionally, the P-T phase diagrams of these systems are explored above room temperature. This work has required the development of the existing high-pressure facilities on the SRS synchrotron source at Daresbury Laboratory to allow routine high-pressure high-temperature (hp/ht) experiments. These technical developments are described.

High-temperature studies of GaSb under pressure reveal a new, previously unknown phase. A detailed study of the structural ordering in the hp/ht phases of GaSb is performed by combining two different experimental techniques. It is shown, by x-ray powder-diffraction, that all the hp and hp/ht phases of GaSb are site-disordered over about two unit cells or less. A complementary high-pressure EXAFS study demonstrates the absence of complete order over nearest-neighbour distances. This unique
behaviour among the III-V and II-VI systems suggests that GaSb, under high pressure and high temperature, becomes similar to a metallic alloy.

A high-pressure/high-temperature structural study of InSb is also presented. It shows that the most recently accepted version of the P-T phase diagram is incorrect. The new results reveal a very complex behaviour, where the site-disordered β-tin structure is found to be stable at high temperature. Strong evidence for sample decomposition has been obtained by combining x-ray powder-diffraction and TEM techniques. Two different interpretations of this phenomenon are given and a revised version of the P-T phase diagram is presented.

Finally, it is concluded that the presence of the site-disordered β-tin structure in both GaSb and InSb appears to be a sign of a transition, at high pressure and high temperature, to disordered alloyed states. The observation of various site-disordered structures in other binary semiconductors indicates that this behaviour may occur in other III-V and II-VI systems.
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Chapter 1

General Introduction

1.1 Historical Background

Pressure and temperature are the two fundamental thermodynamic variables. Researchers have studied and observed that extreme conditions of both pressure and temperature cause matter to change in spectacular ways. Temperature effects have been known for centuries. From near absolute zero to the heat generated by intense laser beams, temperature has been widely exploited by scientists and has led to remarkable discoveries such as nuclear fusion or superconductivity. Liquid water transforms to ice if cooled and boils to a gas when heated. These changes of state can be reproduced at room temperature by using pressure: water freezes to ice at high pressure, and has led to the discovery of many high pressure phases, and can be transformed into a gas in vacuum. Pressure has the ability to transform liquids into perfect crystals or ordinary gases into exotic dense metals. For example, fluid molecular hydrogen has been found, experimentally, to be metallic at $1.4 \times 10^4$ GPa and 3000 K (Weir et al. (1996) and Nellis et al. (1999)). In fact most of the matter in the universe is maintained at very high pressures over a wide range of temperature. The greatest depths in oceans sustain pressure in the range of ~ 10 GPa while the pressure at the centre of a neutron star reaches ~ $10^{27}$ GPa. Temperature varies from the cold surface of Triton, a satellite of Neptune known for being the coldest body found so far in the Solar System (~ 38 K), to the hottest temperatures existing at the centers of planetary nebulae (~ $2 \times 10^5$ K).
The effects of pressure and temperature have long captivated scientists. In the last few decades substantial technical developments have been made to achieve these extreme conditions in laboratories.

In the context of physical crystallography, pressure has the most impressive effect on the structure of materials. Pressure reduces interatomic distances and therefore forces atoms to adopt more densely packed arrangements. As pressure increases, volume decreases. This volume reduction is accompanied by a change in the atomic bonds that alters the physical and chemical properties of the compressed materials. For example semiconductors become metallic under pressure as the band gap energy is reduced. Temperature, on the other hand, can change the thermal energy of atoms within a crystal but has a minimal effect on interatomic distances compared to pressure. Changing the nature of chemical bonding provides an efficient way of creating new substances that cannot be found at ambient conditions, making high-pressure science the extraordinary “new alchemy” at the edge of the new millenium.

Structural studies of materials at high pressure and high temperature have been conducted with the aim of constantly pushing the limits accessible in the pressure and temperature (P-T) range. The XXth century has seen the remarkable competition to achieve the necessary P-T conditions to synthesise diamond from graphite (Hazen, (1999)). This has led to a fast-growing technique development period, when the major contribution was brought by P.W. Bridgman who studied nearly one thousand different substances at high pressure and high temperature. However, prior to these developments, researchers were already investigating crystal structures at ambient conditions. Since W.L. Bragg, in collaboration with his father, solved the structure of NaCl in 1913, a considerable interest for structure determination emerged among scientists and the structures of thousands of crystals have been determined. The information acquired by the knowledge of crystal structure is of fundamental importance in such fields as crystal chemistry, solid state physics and biological sciences because structure determines properties and the properties of a substance cannot be fully understood until its structure is known. For example, in metallurgy, the knowledge of crystal structure is necessary to understand phenomena such as alloy formation or phase transformations.

Today, for accurate crystal structure determination at extreme conditions, various tech-
niques using x-rays or neutrons can be used. Single-crystal diffraction methods have
the advantage over powder techniques to produce patterns with all reflections sepa-
rated in space (no overlap) offering more accurate data analysis. Neutron diffraction
techniques, on the other hand, allow the determination of intensities at small values of
d-spacing with better accuracy than x-ray methods since the nuclear form factor does
not decrease as a function of scattering angle. However single crystals often do not
survive the abrupt change in density when passing through a first-order high-pressure
phase transition and the low flux of neutron sources requires the use of large sample vol-
umes limiting the maximum pressure accessible. Therefore much high-pressure work,
including that in this thesis, has been performed using x-ray powder diffraction.

With the invention of the diamond-anvil cell (DAC) in 1959 (Jamieson et al. (1959)),
small samples could be pressurised well above 10 GPa. Over the years, the maximum
pressure limit was extended to 40 GPa (Jayaraman, (1972)) and reached 100 GPa in
1978 (Mao et al. (1978)). Simultaneously, attempts were made to achieve combined
high-pressure high-temperature (hp/ht) conditions. The first DAC used for hp/ht stud-
ies was developed in 1965 to carry out studies on silver iodide polymorphs to a maximum
temperature of $300^\circ\text{C}$ (Bassett and Takahashi, (1965)). Later the temperature limit was
pushed to $600^\circ\text{C}$ (Sung, (1976)). Unfortunately the use of very small sample volumes
in DACs produces a very weak signal. This problem was only overcome with the advent
of synchrotron radiation sources. The first experiments using a DAC with synchrotron
radiation were performed in 1977 at the Deutsches Elektronen-Synchrotron, DESY,
in Germany using energy-dispersive techniques (Buras et al. (1977)). The energy-
dispersive diffraction (EDX) technique used the full white beam of the synchrotron
and allowed diffraction patterns to be recorded as a function of x-ray energy at a fixed
scattering angle. This new technique extended the accessible pressure range and en-
abled more weakly scattering systems to be studied. However EDX methods present
various known disadvantages such as poor resolution, contaminant fluorescence peaks
and unreliable peak intensities from poor powder averaging. Although EDX techniques
made a major impact in high-pressure science, they presented clear limitations that
needed to be overcome to achieve accurate structure determination.

In the late 1980s, an outstanding breakthrough in technique development was achieved
by scientists at the Photon Factory in Japan. They introduced the novel use of the 2-d
image-plate detector for high-pressure angle-dispersive x-ray powder diffraction (ADX) (Shimomura et al. (1992)). Image plates offer the advantage of recording a large part of 2-d patterns and when combined with ADX, using a monochromatic beam, more accurate data collection can be achieved (higher resolution, reliable peak intensities and high sensitivity to weak reflections). However, the Japanese used slot-aperture pressure cells where only a strip of the diffraction pattern could be collected and the data were not used for full structural refinement. In 1991, these techniques were implemented by members of the High-Pressure Group of the University of Edinburgh on Station 9.1 at SRS Daresbury, where substantial technique developments were made (Nelmes et al. (1992), Nelmes and McMahon (1994)). Diamond-anvil cells with wide conical apertures ($2\theta \sim 40^\circ$), traditionally used for single-crystal studies, were more adapted for ADX work so that full 2-d patterns could be recorded. Data analysis software (Piltz et al. (1992)) was then developed to integrate the 2-d images into 1-d powder profiles, which were used in Rietveld refinement packages.

The advent of these optimised image-plate techniques has allowed the access to full 2-d data that has brought additional benefits. For example it became possible to detect and characterize sample microstructure effects, such as preferred orientation, non-hydrostatic stress and stacking faults. Therefore new approaches to tackle these problems had to be developed to contribute to a better accuracy in crystal structure determination (Wright (1994), Wright et al. (1996) and Belmonte (1998)).

The use of the image-plate technique has also allowed the visualisation of different phases distinguishable by their appearance: e.g. one displaying spotty lines and the other giving smooth lines (Nelmes et al. (1993)). Consequently it became possible to observe dramatic changes in powder patterns when samples recrystallise on heating, as illustrated in Fig. 1.1.

All these new and substantial technique developments and improvements in data quality have had a considerable impact on the structural systematics of the group IV, III-V and II-VI semiconductors. Previous experimental work on semiconductors is summarised in the next section.
Figure 1.1: Recrystallisation of InSb at 3.8 GPa on heating, (a) shows sample taken at room temperature and (b) illustrates one effect of temperature on the sample.
1.2 Previous Work on Semiconductors

Following the development of ADX techniques coupled with the image-plate detector at SRS Daresbury, structural studies of group IV, III-V and II-VI semiconductors have shown that most of the previously accepted structural systematics in these systems were incorrect. For example, many phases have been shown to have more complex, lower-symmetry high-pressure structures than previously thought and various new phenomena, such as intermediate phases as observed in InSb, have been found (Nelmes and McMahon (1998)). In one of the most surprising discoveries, one major phase in the previously accepted systematics has been shown not to exist at all - namely, the diatomic $\beta$-tin structure (Nelmes et al. (1997)). The absence of this structure was completely unexpected as it had apparently been identified experimentally in many systems and as theoretical calculations had shown it to have the lowest energy configuration in cases such as GaAs and GaP (Mujica et al. (1995), Mujica and Needs (1997)). As yet there is no example of a site-ordered tetragonal structure in any of the III-V or II-VI systems, with the possible exception of the $I4/mmm$ phase of HgO (Zhou et al. (1998)).

This matter of structural site-ordering is one of the key issues examined in the work reported in this thesis, along with investigations of the behaviour of III-V and II-VI systems at high temperature and pressure. Much has been done recently to clarify site-ordering in these systems, but there is still relatively little known about their high-pressure, high-temperature behaviour.

The work conducted in the past few years has shown that most of the known high-pressure phases are site-ordered but there remain some exceptions to this such as the $Cmcm$ phase of GaP (Nelmes et al. (1997)), the $Imma$ phases of GaSb (McMahon et al. (1994)) and InSb (Nelmes and McMahon (1996)), the $\beta$-tin-like P2 phase of InSb (Nelmes et al. (1993)) and the bcc phases of InSb and HgTe (Nelmes et al. (1995)). Unfortunately, diffraction studies cannot determine the length scale of site-ordering over nearest-neighbour distances and therefore other techniques are necessary to investigate the matter of ordering over a short-range scale. The most appropriate method to overcome this limitation is an x-ray absorption spectroscopic technique such as EXAFS, used to extract short-range structural information in crystalline and amorphous materials (Sayers et al. (1971)). The experimental challenge to elucidate this prob-
lem make these exceptional cases interesting. They raise several questions such as the reasons why site-disordered phases are formed in these particular systems, the length scale of ordering and the significance of a quasi-monatomic behaviour. Clearly, more work needs to be done.

Nearly all the phases found so far in the high-pressure studies of group IV, III-V and II-VI systems have been obtained at room temperature with the usual pressure-transmitting medium (methanol:ethanol, water, etc) or without a medium. More recently, work in which samples have been heated or have been compressed under highly hydrostatic conditions with a gas medium has shown different behaviour. Heating samples under pressure has the effect of sharpening diffraction peaks and therefore enhancing data quality by annealing microstructure effects: non-hydrostatic stresses are relieved on heating because temperature reduces stress gradients across the sample. This effect is illustrated in Fig. 1.2. The use of sample heating opens a vast new area that is now required to fully explore the P-T structural systematics. Very little is known about these high-pressure phases above room temperature. Only a very few systems have been investigated at high temperature, e.g. GaAs, InSb, GaSb, ZnTe, CdTe and HgTe.

For example, due to its technological importance, the high-pressure behaviour of GaAs has long attracted attention among the III-V systems (e.g.: Minomura and Drickamer (1962), Yu et al. (1978a), Shimomura et al. (1980), Baublitz and Ruoff (1982) and Weir et al. (1989)). Recent work (McMahon et al. (1998)) has revealed a new site-ordered structure, a simple cubic phase called SC16, that has been obtained by heating the high-pressure phase $Cmcm$ to above $\sim 400$ K at $\sim 14$ GPa and was found to be stable on recovering back to room temperature.

InSb has been one of the most extensively studied of the III-V semiconductors at high pressure and high temperature (e.g. Gebbie et al. (1960), Kasper and Brandhorst (1964), Banus and Lavine (1967), Yu et al. (1978b)). Due to its extremely complex behaviour, many hp and hp/ht structures and phase transitions have been misinterpreted and have subsequently been revised by Nelmes et al. (1993). The long-accepted phase diagram by Banus and Lavine (1969) has been reexamined by Nelmes and McMahon (1996) and a new version was given by Mezouar et al. (1996), which was then slightly
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modified by Mezouar et al. (1999b). The full story of InSb will be given in Chapter 6.

The phase diagram of GaSb has also attracted the attention for showing some unusual characteristics, such as the presence of two liquid phases in the melt (Umnov (1994)). Very recent EDX work up to 7 GPa and 973 K has been performed to establish accurately the P-T phase diagram (Martinez-Garcia et al. (1999a)). More details about the hp/ht behaviour of GaSb will be given in Chapter 4.

Among the II-VI semiconductor compounds, the XTe (where X = Zn, Cd and Hg) have been investigated above room temperature. ZnTe is one of the few systems among the II-VI semiconductors in having no NaCl phase at room temperature. This peculiarity might have motivated Shimomura et al. (1997) to perform in situ hp/ht measurements using EDX techniques. They found a transition to an NaCl phase (ZnTe-TV) at high pressure and elevated temperatures. The triple point between this phase and the two other known high-pressure phases, the cinnabar and Cmcm structures, has been determined at 13 GPa and 453 K.

Recent hp/ht work has been carried out also on CdTe, the binary compound isoelectronic with InSb and Sn, by Martinez-Garcia et al. (1999b). By using the EDX method, they have mapped its P-T phase diagram up to 5 GPa and 1173 K. They found that the pressure range of the cinnabar structure (the intermediate phase between zincblende and NaCl) decreases with temperature until the triple point is reached at 2.6(1) GPa and 735(2) K.

And finally, the high-pressure behaviour of HgTe, has been investigated above room temperature. This compound has been found to transform from the ambient pressure zincblende phase to the cinnabar phase via a "hidden" intermediate orthorhombic phase C2221 as observed in HgSe (McMahon et al. (1996)). The presence of this previously unknown phase may be related to the unusual behaviour in the pressure dependence of the thermal expansion in its zincblende phase found by Besson et al. (1996). They measured the equation of state of HgTe under pressure in the zincblende and cinnabar phases up to 800 K by x-ray diffraction with a large volume cell.

These high-temperature studies under pressure have revealed, among other phenomena, new phase transitions and raise, now, interesting matters such as what the true equilib-
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Figure 1.2: Effect of temperature on sample of GaSb at 22.5 GPa before and after heating where the pattern displays a much sharper profile.

...rium phases are or what the kinetic effects are at phase transitions or on site-ordering. Once again, more work needs to be done.

The objectives of the work presented in this thesis have been to address both of these questions mentioned above. The main goal was to elucidate the nature of site-ordering in the few exceptional cases described earlier while simultaneously developing the techniques needed for combined high-pressure high-temperature (hp/ht) studies on Station 9.1 at the Synchrotron Radiation Source, Daresbury. This thesis presents the author’s contribution towards this aim. The development work consisted of installing new experimental equipment and upgrading the existing equipment to perform routine hp/ht experiments. A new type of DAC has been used and improved for this purpose.

Combined hp/ht work has been performed to study the structural phase transitions of GaSb. This method has been applied successfully and new phase transitions have been found. The site-ordering behaviour has been clarified.

Besides the diffraction work, an extended x-ray absorption fine structure (EXAFS)
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study has been successfully carried out on the various phases of GaSb. This has revealed some answers to previously unsolved questions about the length scale of site-ordering. The possible significance of such behaviour is presented.

Additionally, the hp/ht behaviour of InSb has been investigated. A revised version of the P-T phase diagram is presented along with some additional information about site-ordering. New phases have been found and are discussed.

1.3 Thesis Outline

This thesis is organised as follows:

Chapter 2 introduces the experimental methods used to perform high-pressure powder diffraction experiments at room temperature. The author has not been involved in the development of these techniques, but they are presented here as they form the foundation of further development work described and used in the following chapters.

Chapter 3 presents the experimental methods and technique developments to achieve simultaneous high-pressure high-temperature conditions. A review of hp/ht techniques is given. The development of high-temperature equipment and the upgrade of existing equipment to allow high-temperature experiments under pressure, are described.

Chapter 4 describes a detailed structural study of GaSb at high pressure and high temperature. It includes a brief review of previous work on GaSb and an introduction on order-disorder transformations. It presents the new phase transitions and shows experimental evidence of the absence of long-range order in all the phases discovered so far.

Chapter 5 focuses on the EXAFS studies of the three hp and hp/ht phases of GaSb. The basic theory of the EXAFS method and analysis procedure are given. It is shown how the EXAFS data have been used to demonstrate the absence of complete short-range order in all the hp and hp/ht phases studied in GaSb.

Chapter 6 presents a detailed study of the structural hp/ht phase transitions in InSb. It summarises the complex behaviour of InSb and then describes the new phase tran-
sitions discovered at high temperatures. A revised version of the P-T phase diagram is presented along with discussions about site-ordering and sample decomposition.

Chapter 7 concludes the thesis, summarises the achievements to date and discusses potential future developments for combined high-pressure and high-temperature studies.
Chapter 2

High-Pressure Powder Diffraction Techniques

2.1 Introduction

This chapter introduces the basic theory of powder diffraction techniques and outlines the important factors for completion of a successful experiment using powder samples. It then provides a description of the high-pressure cells, beamline equipment and techniques at the Synchrotron Radiation Source at Daresbury for performing high-pressure experiments. The experimental set-up has been implemented by the members of the High Pressure Group of the University of Edinburgh. Although the author was not directly involved in these developments, it is important to detail them at this stage as they are the core element of the experimental data collection procedure described in this thesis. They also provide the basis to further development work presented in the next chapter.

2.2 Basic Theory of Powder Diffraction

X-ray powder diffraction techniques were first developed by P.J.W. Debye and P.H. Scherrer and independently by A.W Hull in the period 1914-1919. However the theory of x-ray diffraction was explained by W.L. Bragg who was the first, in 1913, to describe
the mechanism of diffraction. He considered crystals in terms of layers of atoms behaving as reflecting planes. The angle of incidence equals the angle of reflection, giving rise to constructive interferences, when the path difference between rays reflected from successive planes is equal to an integer number of wavelengths. This formulation led him to an elegantly simple expression:

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

where $\lambda$ is the wavelength of the incident beam, $d_{hkl}$ is the $(hkl)$ lattice planes spacing, $n$ is the order of diffraction and $\theta$ is the angle between the diffracted beam and the lattice plane. It is known as Bragg’s law and is illustrated in Fig. 2.1.

Detailed structural information can be extracted from the relative intensities of the Bragg reflection peaks through the structure factor $F$. The intensity of each reflection is proportional to $F^2$, where $F$ is defined by

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

where $N$ is the number of atoms in the unit cell, $f_n$ is the scattering factor of the $n^{th}$ atom and $x_n, y_n, z_n$ represent the fractional coordinates of the $n^{th}$ atom. The size and shape of the unit cell can be deduced from the d-spacings of each reflection, calculated
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using the Bragg's law (equation 2.1) and the atomic positions within the unit cell can be determined from the intensities of the reflections using equation 2.2. This forms the basis for all diffraction structural studies.

Crystal diffraction techniques can be classified into two groups depending on which of the two variables - $\theta$ and $\lambda$ - is maintained constant to satisfy the Bragg's law experimentally. When the incident radiation is monochromatic, fixed $\lambda$, diffraction occurs at $\theta$ angles that satisfy the Bragg condition. Data are then collected as a function of the angle $\theta$ and the technique is therefore known as angle-dispersive diffraction (ADX). When a polychromatic beam is used, diffraction data are collected from a fixed $\theta$ angle where each reflection is recorded from a different wavelength (or energy) of radiation. This technique takes advantage of the full white beam. Different wavelengths are diffracted by the appropriate crystal plane, according to Bragg's law, and signals are recorded into the detector. The intensities of each individual reflections can be determined by analysing the energy distribution of the detected radiation. It is known as energy-dispersive diffraction (EDX).

A powder sample consists, ideally, of many tiny ($\sim 1 \mu m$ across) crystallites randomly oriented with respect to the incident beam. Therefore the reflected beam from all the planes of a given $d_{hkl}$-spacing lie on a cone with half-angle $2\theta$ about the incident beam. If these diffraction cones are intercepted by a flat area detector, such as an image-plate (IP), perpendicular to the incident beam, the recorded pattern will display sharp, smooth and concentric powder rings, as shown in Fig. 2.2. However samples are generally far from a perfect powder. They may contain some large crystallites that will affect the diffracted intensities. Such data are said to contain “poor powder averaging”. Sometimes crystallites are not randomly arranged, for example, if they are “needles”, they may align along a particular axis and therefore the orientation of the powder sample is no longer statistically random. Consequently, the number of crystallites contributing to each reflection will be different, affecting the relative diffracted intensities. In this case, the powder sample is said to have preferred orientation.

The effect of pressure on the samples produces other imperfections that will affect the diffraction profiles. Applying pressure to a powder can create a stress gradient over the sample displacing the diffraction peaks. Properties of the sample such as elasticity
or crystallite morphology or intrinsic imperfections such as crystal lattice defects or stacking faults produce anisotropic strains that also displace the diffraction peaks. For accurate structure determination with powder diffraction techniques, it is important to take these effects into account.

The quality of the data depends largely on the choice of the diffraction method techniques. The ADX approach is the most successful method for crystal structure determination at ambient pressure and has been widely used since it can be used for structural refinement with the method developed by Rietveld (1969). However the EDX method became more popular than the ADX approach with the advent of synchrotron radiation sources in the early 1980s. But these methods suffered from major limitations. Due to the poor resolution of the powder patterns, limited to that of the detectors, EDX diffraction techniques were rarely used for structural refinement. The patterns were contaminated with fluorescence lines from the sample and escape peaks from the detector and the highly collimated beam required to define the scattering angle led to poor powder averaging. Therefore this technique is not the most suitable method for accurate structure determination.
2.3 Criteria for Accurate Data Collection

To optimise the conditions of any experiment, the following factors must be applied for accurate structure analysis using powder diffraction techniques.

(a) As much of the powder pattern as possible needs to be collected with the highest resolution possible.

(b) The background should be as low as possible and also isotropic about the incident beam to prevent intensity variations around the powder rings and therefore allows accurate Rietveld refinement. The diffraction pattern should also be free from contamination.

(c) The powder should contain small randomly oriented crystallites to avoid effects as peak broadening or preferred orientation.

(d) Absorption from the sample and its environment cannot be ignored, as well as other effect such as incident beam polarisation to avoid intensity variations round the powder rings.

In order to satisfy these criteria, experimental techniques have been developed for high-pressure powder diffraction. They are discussed in the following sections.

2.4 High-Pressure Cells: Design and Operation

Since the pioneering work of P.W. Bridgman in the high-pressure field in 1940's (Bridgman, (1940)), various types of high-pressure cells have been built for x-ray diffraction studies. The first pressure cells used were designed with a hydraulic mechanism where pressure was generated by a piston-cylinder. They were large and heavy, so practically inconvenient. Their use was restricted to specialised laboratories. The advent of the diamond-anvil cell (DAC) in 1959 has revolutionised the techniques for producing high pressure and has opened new horizons in this area of science. They were small, light and compact. The sample was contained within a sheet of gasket material and pressure was applied with bolts to two opposed diamond anvils. The DAC was first designed.
Figure 2.3: (a) Schematic illustration of the mechanism of a diamond-anvil cell, (b) the "brilliant" cut design of the diamond anvil.

by Jamieson et al. (1959) for high-pressure x-ray powder diffraction work and independently by Weir et al. (1959) for infrared absorption measurements. Since then, the DAC has been developed for powder (Piermarini and Weir (1962)) and single-crystal x-ray diffraction (Block et al. (1965), Weir et al. (1965)). The use of the metal gasket (Van Valkenburg, (1965)) and pressure transmitting media (Piermarini et al. (1973) pushed back the accessible limit of pressure and extended the pressure range for hydrostatic conditions. The DAC has been universally adopted as an invaluable tool for high pressure studies and is now widely used in various laboratories around the world.

The basic mechanism of a diamond-anvil cell is very simple. The sample, contained in a hole drilled in a metal gasket, is compressed by pushing together two flat parallel diamond faces (or culets) aligned along a single axis, as shown in Fig. 2.3(a). Diamonds are cut to form an anvil (diamonds used here follow the so-called “brilliant” cut design) with a small culet face, as illustrated in Fig. 2.3(b).

Diamond-anvil cells differ from one another by the way pressure is applied and by the way the diamonds culets are aligned and supported. Many types of DAC are described and presented along with results in the review by Jayaraman (1983). Since the advent of synchrotron radiation sources, the EDX technique was often preferably chosen for high-pressure studies to take advantage of the full polychromatic beam. The pressure cells designed for EDX work required only small beam entry and exit holes, therefore
the anvils could be highly supported. The strength of the cells was then optimised and higher pressures could be reached. However this method presents major disadvantages, mentioned earlier, and therefore does not offer the optimal conditions required to satisfy the criteria described in Section 2.3. Additionally the difficulties of working with a white beam, for example, the energy dependence of detector sensitivity and the need for energy-dependent absorption corrections with EDX techniques made accurate high-pressure structure determination extremely difficult. To overcome these limitations, it was necessary to develop the high pressure cells for angle-dispersive studies. Cells used for angle-dispersive studies need to allow a wide opening angle of the diffraction cone to leave the cell. For that reason at least one diamond must be mounted on a material of low x-ray absorption. The most convenient material that combines high strength and low x-ray absorption is beryllium. However, it has the disadvantage of being a highly toxic material and difficult to machine.

As the work presented in this thesis is mainly concerned with high-pressure high-temperature studies, a specific type of cell has been used by the author and will be described in detail in the following chapter. However, two types of full conical-aperture DACs will be described here: a cell designed by Mao and Bell (1980) and the Merrill-Bassett pressure cell (Merrill and Bassett, 1974)). The first cell has been used for generating high pressure before heating and the second one has been used with the Mao-Bell-type cell to perform high-pressure EXAFS experiments. As this type of study is explained in Chapter 5, it is therefore necessary to present its design.

The cell designed by Mao and Bell (1980) is illustrated in Fig. 2.4(a). The diamond anvils are mounted on beryllium backing discs. Optical access is ensured by a 0.8 mm diameter hole, drilled through the discs, to enable the sample to be viewed through the diamonds. The backing discs are enclosed in a steel body. The top half is driven down with the help of four guide pins located on the bottom half that can slide down through the four holes when closing the cell. Pressure is applied by tightening two pairs of left- and right-handed Allen screws. One of the diamonds can be horizontally translated by using three small screws but there is no provision to allow the correction of relative tilt between the diamond culets. Fig. 2.4(b) gives a schematic diagram of a Merrill-Bassett cell, which is a smaller version of the Mao-Bell cell. Its original design was made for single-crystal experiments, but their small size and wide angular access make them very
convenient for angle-dispersive powder diffraction studies. In this cell design, pressure is applied with the three Allen screws and diamond alignment is maintained by three guide pins. The translational alignment of the diamond culets can be set by adjusting the position of the Be disc with three small screws but as with the Mao-Bell cell, a tilt correction cannot be applied.

The maximum pressure accessible by these cells depends on the diameter of the diamond culets (the smaller the size, the greater the pressure that can be achieved), the design of the cell body and the opening angle of the conical aperture in the cell body.

Three different culet sizes have been used in these cells: 600 μm, 400 μm and 300 μm. The Mao-Bell cell has an opening angle of 40° and with 400 μm culet diamonds ~ 35 GPa can be reached. The Merrill-Bassett cell has a wider opening angle of 45°, allowing up to 45° 2θ angle of diffraction to exit the cell. A limit of ~ 15-18 GPa is reached with the use of a 600 μm culet diamonds but 400 μm culet size allows pressure of ~ 25 GPa to be obtained. The difference in the pressure limit between both cells comes from the fact that the Mao-Bell cell has a stronger cell body and a higher diamond alignment stability under pressure variations. However the Merrill-Bassett cell has the advantage of allowing finer control over changes in sample pressure.

Loading a pressure cell is a process that can be divided into different stages. The first stage is the preparation of the gasket. The gasket material used for high-pressure
experiments was a 250 μm thick tungsten foil. Its hardness makes it suitable to support high pressure conditions and its high absorption serves as a good shield for background scattering. Other materials, such as rhenium or stainless-steel can be used in DAC as explained by Spain and Dustan (1989). The tungsten foil is carefully placed on the top of one diamond and fixed to the cell body with Blu-Tack. After closing the cell, pressure is applied by pushing the two diamonds together to indent the gasket. The cell is then opened and the foil is removed. A hole, usually between 50-200 μm in diameter, is spark-eroded in the centre of the indent. Spark-erosion techniques are usually preferred to those of mechanical drilling and are essential for hard materials such as tungsten or rhenium.

The second stage is sample loading. Once the gasket has been replaced on the top of the first diamond, the hole is filled with the powder sample using a fine needle. To pack the sample into the hole, the cell is closed and slight pressure is applied by hand. The cell is then opened and any residual sample on the second diamond is cleaned off with ethanol. At this stage, the cell is ready to collect an ambient pressure pattern, if need be, for calibration purposes, as detailed in Section 2.6.3.

The final step is to add a ruby chip for pressure measurement, as described in Section 3.2.3. The cell is re-opened and the second diamond face is covered with a thin film of vaseline. A single-crystal ruby sphere (~ 10 μm in diameter) is placed in the centre of the diamond culet. The indent of the gasket is then filled with a 4:1 mixture of methanol:ethanol as a pressure transmitting medium. The cell is closed quickly and pressure is applied immediately to avoid the evaporation of the methanol:ethanol mixture. This mixture is used to ensure hydrostatic conditions in the sample. Studies of hydrostatic limits of various pressure transmitting media were made by Piermarini et al. (1973). The mixture described here freezes at 10.4 GPa. An investigation of different condensed gases as pressure transmitting media has been made by Mao et al. (1982) and Liebenberg (1979) but these require special loading techniques are rather inconvenient.
CHAPTER 2. HIGH-PRESSURE POWDER DIFFRACTION TECHNIQUES

2.5 Accurate Sample Alignment

The sample alignment techniques are based on an optical method which was first used by the Japanese group at the Photon Factory (Shimomura et al., 1992). These techniques were then developed considerably by the Edinburgh Group in the following years. They allow samples to be accurately aligned to the incident beam without the beam hitting the gasket. This was a great improvement since sample sizes (around 50-200 μm in diameter) and the beam diameter (around 50-100 μm) have almost the same dimensions.

To ensure accurate sample alignment, each cell has its own collar that is inserted into a universal mount. The collar is firmly held in place by two spring-loaded brass clamps. The cell is therefore always placed back to the same position in the holder and can be rotated about its own cylinder axis.

To align the sample with the x-ray beam, the pressure cell is put on the sample stage and the microscope is focused on the sample through the back face of the diamond. The pressure cell is removed and replaced by a mount holding a piece of x-ray sensitive paper along the incident beam direction. The surface of the paper is then focused onto the microscope by a micrometer located on the paper mount. After being exposed to the x-ray beam for a few minutes, the dark mark left by the beam is centered on the microscope's crosshair by moving the microscope vertically and horizontally perpendicular to the beam direction. The paper holder is removed and the pressure cell is put back on the sample stage. The sample is then centered to the crosshair by adjusting the position of the sample stage. The whole process takes approximately ten minutes. A beam diameter of 75 μm passing through a sample 100 μm will not strike the gasket. The microscope is removed before data collection.

The optical axis of the microscope also needs to be aligned with the x-ray beam. This step is necessary due to the high refractive index of diamond, the apparent position of the sample is shifted from its actual position if (i) the face of the diamond is not perpendicular to the optical axis of the microscope and (ii) the optical axis of the microscope is not parallel to the incident beam (Allan, 1993). This alignment is performed by screwing a mirror into the objective end of the microscope, the eyepiece
and objective lenses being removed. The optical axis of the microscope will be aligned when the laser spot, reflected from the mirror, coincides with the aperture of the laser.

For accurate sample alignment, it is necessary to align the pressure cell parallel to the x-ray beam. The alignment laser is used for that purpose. The laser is aligned with the x-ray beam by using two pieces of x-ray sensitive paper. Therefore the pressure cell holder can be "shimmed" until the back face of the diamond reflects the laser beam along its original path. This procedure needs to be done once for each pressure cell, at the beginning of the run as each cell has its own mount.

2.6 Image-Plate Set-Up on Station 9.1

The use of an image-plate detector enabled to move from EDX techniques to ADX techniques. The combination of both ADX mode and IP detector has brought a major improvement in data quality, satisfying the first two criteria in Section 2.3: higher resolution, freedom from contamination, reliable peak intensities and higher sensitivity to weaker reflections.

Inspired by the design of the Japanese image-plate set-up (Shimomura et. al., (1992)), the Edinburgh Group developed an image-plate set-up for high-pressure angle-dispersive powder diffraction on Station 9.1 at SRS Daresbury. The first main developments consisted of using full-conical aperture DACs described in Section 2.4 and a 2-D image-plate area detector, which is detailed in the present section. The beamline set-up is illustrated in Fig. 2.5.

Station 9.1 is located at about 15m from a 5T superconducting wiggler magnet. The wavelength of the incident beam $\lambda$ is selected by the Si(111) double-bounce channel-cut monochromator, leaving a certain amount of $\lambda/3$ diffraction from the (333) planes of the monochromator. The beam dimensions are reduced to $0.5 \times 0.5 \text{ mm}^2$ when passing through a pair of tungsten carbide slits. The beam then goes through a lead shielding tube before being collimated to a circular beam of 50-100 $\mu$m diameter by a platinum pinhole. Platinum is known for its good absorption properties and therefore is used to reduce the $\lambda/3$ contribution of the incident beam. It is attenuated by the platinum K-absorption edge at 0.1582 Å for wavelengths shorter than 0.4745 Å. All the diffraction
HIGH-PRESSURE POWDER-DIFFRACTION EXPERIMENTS PRIOR TO THE UPGRADE DESCRIBED IN CHAPTER 3.

Figure 2.5: A schematic illustration of the beamline set-up on Station 9.1 at SRS.
data presented in this thesis were collected at 0.4654 Å.

2.6.1 2-D Image-Plate Area Detector

The use of an image-plate detector has revolutionised the high-pressure powder diffraction techniques by collecting a significant portion of the 2-D pattern, allowing accurate structural studies with a monochromatic beam. The main advantage of the image-plates is their high sensitivity to the short wavelengths (< 0.7 Å). In this energy range, the IP can detect less than ten photons per pixel. Image-plates have also a large dynamic range of \( \sim 10^5 \) and a low intrinsic noise.

The image-plate (IP) detector, used in this thesis, is a flat aluminium plate, onto which is bonded an x-ray sensitive phosphor material \( \text{BaFBr : Eu}^{2+} \) protected by a layer of plastic. It has the dimensions of 20 cm \( \times \) 25 cm. When the x-ray photons strike the phosphor surface, it produces excited electron states, which decay emitting visible light when stimulated by a He-Ne laser. While exposed to x-rays, the IP is enclosed in a light-tight cassette inserted in a “frame-type” holder situated approximately 300 mm from the sample. It allows the IP to collect up to 30° \( 2\theta \) of the diffraction on the set-up on Station 9.1 at SRS. The intense \( \lambda \) component of the beam passing through the sample is attenuated by a piece of lead located on the cassette. The lead is partially transparent to the weaker \( \lambda/3 \) component of the beam, which produces a beam spot that marks the centre of the powder pattern. This is particularly useful for further data analysis (see Section 2.5.1). Once the cassette has been removed, the IP is taken out and quickly inserted into the image-plate reader. The image-plate system used by the author was a Molecular Dynamics 400A Phosphor Imager.

The image-plate is scanned by mechanically tracking the plate over a He-Ne laser. This tracking is achieved by pulling the IP in its carriage perpendicular to the laser direction by a wire attached to a stepper motor. The photoluminescence travels through a fiber-optic guide until it reaches a photomultiplier tube. The intensity is converted there into a voltage and then a digital signal. The image dimensions from 20 cm \( \times \) 25 cm IP is 2816 \( \times \) 2052 pixels, the size of a pixel is approximately 88 \( \mu \text{m} \times 88 \mu \text{m} \).

The scan-process of the image-plate produces intensity and spatial distortions that
need to be calibrated before any data analysis. The intensity distortions come from the non-uniform sensitivity of the reader optics and the non-linear intensity response of the reader. They are calibrated periodically by the manufacturer. Two sources of spatial distortion are introduced by the reader. During the mechanical tracking of the plate, the wrapping of the wires is not even and therefore the motion of the IP is not constant. This creates a small spatial distortion in the direction perpendicular to the laser scanning direction. The second source of distortion is related to the laser. Due to its fixed position and the fact that the IP is flat, the distance from the source to the plate varies as the beam scans from side to side across the plate. This effect produces a change in the laser spot size across the plate, which means that the true size and separation of the pixels differ across the plate. However, due to mechanical stability, the scan is largely reproducible. The image file from the reader gives only the intensity of each pixel. Due to the non-uniformity of the pixel separation, the pixel positions have to be calibrated. This calibration is performed by placing a grid of holes (the separation distance (2 mm) and diameter (200 μm) are accurately known) in a nickel sheet over the IP. The grid is then exposed to the source of parallel x-ray covering an area at least as large as the IP (Stanton et al. (1992)). If the x-ray energy is not too high, the beam will be absorbed by the nickel leaving an image of uniformly spaced spots on the plate. The plate is then read, but due to spatial distortion, the grid spots are not uniformly spaced. The location in pixels of the centre of the spots are calculated by fitting a function to each spot. Since the pixel positions of the grid spots are known, the spatial distortion at the position of each spot can be determined by interpolation.

It is important to note that for accurate structural determination, the IP should ideally be perpendicular to the incident beam to distinguish non-circular powder rings due to sample microstructure from the tilt of the IP to the incident beam. A holder and a cassette have been designed to accurately align the IP with respect to the incident beam (Belmonte (1998)). The holder allows the cassette to be inserted from behind and with raised edges around the inside of the frame the cassette can be inserted accurately and reproducibly. Two spring-loaded clamps hold the cassette firmly against the frame of the holder. The back face of the cassette has a hole to allow the alignment laser to reflect from the back surface of the IP. Therefore the image-plate is perpendicular to the x-ray beam when the laser beam is reflected back onto itself.
2.6.2 Shielding

As the second criterion states in Section 2.3, it is important to keep the background radiation as low as possible during experiments. High background arises from the fluorescence caused when x-rays scatter from the floor and other components in the hutch. Since the image-plate is very sensitive to a wide range of radiation, it has to be shielded. The experimental set-up on Station 9.1 is enclosed completely from each side by a removable panels of lead-lined aluminium. The front panel is made from a lead-loaded perspex door. The advantage of such an enclosure makes the background isotropic around the beam.

Other sources of background arise from within the enclosure: the Compton scattering from the diamonds in the pressure cell and the radiation scattered by the incident beam when it travels through the air between the cell and the IP. Contributions from Compton scattering and air scatter and contributions from Compton scattering alone have been determined by Belmonte (1998). He has shown that the air scatter can be significantly reduced by using a "beamstop" to capture the straight-through beam. The beamstop consists of a lead cup, mounted on a sheet of mylar, and it is placed on the same clamp as the alignment microscope. The lead cup is situated approximately 6 cm from the sample during exposure. From that distance, it only obscures about 2°20 of the diffraction pattern. The sheet of mylar is attached to an aluminium frame, which is large enough to allow up to 45° 2θ of diffraction pattern to pass through.

2.6.3 Software for Processing the Image-Plate Data

This section describes the operation of the main processing software, called EDIPUS (EDinburgh Image-Plate User Software), an upgraded version of PLATYPUS, the original program for image-plate data integration (Piltz et al. (1992)). The upgrade (Belmonte (1998)) consists of the addition of a facility for 2-d data analysis. It is then followed by a description of the method used to calibrate the data.

PLATYPUS is used on a 'X Windows System' with a graphical-user-interface, which allows the IP data and integrated 1-d profiles to be displayed simultaneously. The interface provides an easy accessible environment where all the functions for integrating
the data can be reached from pull-down menus.

The main function of the software is to produce a 1-d integrated profile from the 2-d powder image after applying corrections for IP tilts, spatial distortion and incident beam polarisation. Due to the fact that the image-plate is rarely exactly perpendicular to the incident beam, corrections for the IP tilt needs to be calculated. This step is necessary to avoid peak splitting or peak broadening in the integrated pattern. The method consists of "sectoring" the image into 60 azimuthal sectors about the centre of the pattern, obtained by fitting a two-dimensional gaussian function to the incident beam spot. This process, then produces sixty 1-d powder patterns. If the IP is tilted with respect to the incident beam, the peaks in the 60 powder patterns will not all line up. This can be easily understood by the fact that the non-perpendicularity of the IP relative to the beam causes the circular powder rings to be recorded as ellipses. Therefore the image needs to be "sharpened" to calculate the tilt parameters. This final adjustment is performed by a routine called "sharpen", which modifies the effective radial position of the data points in each sector until all the sectors line-up. The next step of the pattern integration is called the "rebinning" process. It calculates for each pixel in the image an effective radius from the centre of the pattern, taking into account IP tilts and spatial distortion. The intensity of the pixel is then added to the appropriate bin. Very often the pixel will overlap two bins so the intensity is partitioned and assigned to the appropriate bin. For a pixel located at a radius \( r \) lying between two radial bins \( r_1 \) and \( r_2 \), its intensity \( I \) is partitioned such that \( (r - r_1)I \) is added for \( r_1 \) and \( (1 - (r - r_1))I \) is added to \( r_2 \). An array of corrections to the intensity is also calculated to correct the effects of incident beam polarisation. The array of rebinned intensity is divided by the array of rebinned corrections at the end of the "rebinning" process. The output is written to a file containing the integrated 1-d profile. The PLATYPUS source code has been extended (Belmonte (1998)) to allow facilities for the analysis of intensity and position variations around the powder rings.

Once the data have been integrated with EDIPUS, the next stage is to convert the 1-d profile expressed in the form of intensity vs. pixel radius to the form of intensity vs. \( 2\theta \). For each pressure cell, a diffraction pattern from a sample with known lattice parameters, usually at ambient pressure, needs to be collected to calibrate the data obtained with that pressure cell. The conversion from pixels to \( 2\theta \) is done by a poly-
nominal function that has been fitted to the measured pixel positions of the observed reflections. However, due to the spatial distortion and plate-tilt corrections in EDIPUS, this conversion produces unequal $2\theta$ steps. A single program has been written by Belmonte (1998) that overcomes the problem. It includes the interpolation of the powder pattern into equally spaced $2\theta$ correcting these deviations (from the linear ($\tan\theta$)-dependence relationship between the radius in pixels, from the centre of the pattern, and the sample-to-plate distance). It is this program that has been used by the author to calibrate the powder diffraction data whose analysis is presented in this thesis.

2.7 Concluding Notes

This chapter has described the basic theory of powder diffraction and has provided an overview of the high-pressure powder diffraction devices and techniques developed by the High Pressure Group of the University of Edinburgh at SRS at Daresbury in the last decade. These developments have considerably improved the high-pressure data quality thanks to the use of an image-plate area detector combined with angle-dispersive diffraction techniques, which have optimised the conditions for accurate structure determination. However almost all high-pressure studies, prior to the work presented in this thesis, have been performed at room temperature. The experimental methods and developments necessary to combine high-pressure high-temperature work is the subject of the next chapter.
Chapter 3

High-Pressure High-Temperature Experimental Methods and Technique Development

3.1 Introduction

The work presented in this chapter focuses on the developments of high-pressure high-temperature techniques. It is divided into two sections. The first section presents a detailed review of the experimental methods and techniques developed to achieve simultaneously high-pressure and high-temperature, from the first attempts to the currently available methods used in both x-ray laboratories and synchrotron facilities. The review illustrates in detail the difficulties that arise when trying to extend high-pressure techniques to combined high-pressure high-temperatures studies from the pioneering work thirty-five years ago to the present. It is presented here to provide an overview of all the experimental techniques developed in these fields of research up to date, for both completeness and clarity prior to the work presented in this thesis. It is then followed by the second section of this chapter. It describes the new project, where the author has been closely involved, of developing high-pressure high-temperature techniques on Station 9.1 at Daresbury Laboratory, with the purpose of being able to determine accurately crystal structures under these extreme conditions.
3.2 Experimental Methods for High-Pressure High-Temperature Studies: A Review

The introduction of the diamond-anvil cell (DAC) has made a significant contribution to the development of the study of various physical, optical and crystal structure properties under high pressure (Jayaraman (1983), Bassett (1979)). When used with x-ray diffraction equipment, the DAC is the most useful tool for structural investigations at nonambient pressures. Its basic principles have been explained in the previous chapter.

Combining high-temperature with high-pressure studies in conjunction with the DAC offers a wide range of new and attractive possibilities but which are, unfortunately, not straightforward. Various difficulties arise depending on the techniques chosen to generate high temperatures.

The following sections explore different methods attempted to achieve high temperatures under high pressure. They describe the necessary modifications (material, design and operation) made in the DACs to produce, simultaneously, such extreme conditions. To overcome the limitations imposed by HP/HT techniques, it is important first to reconsider the choice of materials used to adapt the DACs for high-temperature work. These preliminary requirements are explained below.

3.2.1 Materials for High-Pressure High-Temperature DACs

When the diamond-anvil cell is heated, special care needs to be taken with regard to the choice of the materials used for the different parts of the cell. A short review of the constraints, imposed by HT operation on the materials used in cell construction, is given below. Experimental investigations on these materials have been done by Schiferl (1987), Schiferl et al. (1987) and Adams and Christy (1992).

Anvils

At room temperature, diamond is the ideal anvil material due to its exceptional compressive strength. Its transparency to electromagnetic radiation over a wide spectral
range, from infrared to hard x-rays, makes its use suitable with synchrotron radiation.

When a diamond is heated in air above 600°C for a long period of time (several days), its surface becomes frosted (Sung, (1976)). Heating above 800°C may cause the anvil surface to become undulated due to the inhomogeneity of the thermal expansion. This may produce pressure release on the sample. To prevent diamond oxidation, it is therefore essential that a DAC subjected to temperatures over 600°C should be operated in vacuo or in an inert atmosphere. However, under these conditions, when a diamond is heated above approximately 1700°C, it will convert to graphite (Seal (1963)). Additionally, the mechanical and chemical properties of diamond change quite dramatically under high temperatures. For example, the strength of diamond considerably decreases with temperature, a phenomenon that occurs in other superhard materials as illustrated in Fig. 3.1.

Another important property of diamond is that the rigidity of its structure makes it a very good thermal conductor. At ambient temperature, diamond is four times as thermally conductive as copper. However diamond is not electrically conductive (Harlow, (1998)).

Apart from diamond, alumina (sapphire) and Y-stabilised cubic zirconia have been used as anvil materials due to their good infrared transmission (Patterson and Margrave (1990)). Unfortunately, these oxides weaken above 1000°C (Schaffer (1964), Lynch et al. (1966)) and therefore their high-temperature applicability is limited.
In conclusion, diamond remains the best anvil material for HP/HT work, despite its high thermal conductivity. However extra care needs to be taken and thus additional features have to be added to make DACs suitable for HT studies, as described in Section 3.2.2.

**Anvil Supports**

The diamond anvils must be supported by a strong material to allow high pressures to be reached. In a DAC, the diamonds are usually mounted on beryllium backing discs (see Chapter 2). Unfortunately beryllium softens above 200°C and remains highly toxic. It is therefore no longer suitable for high-temperature work.

Alternative materials that sustain high temperature without changing their required mechanical properties have to be used. Intrinsically high-strength materials suitable for HT work appear to be the high melting-temperature metals such as tungsten (W), tantalum (Ta), rhenium (Re), molybdenum (Mo) and their alloys, and carbide ceramics (Schaffer (1964), Lynch et al. (1966)). However due to the risk of corrosion by formation of volatile oxides, the metals need to be protected from the air above a few hundreds degrees Celsius. Silicon carbide (SiC) and Boron Carbide (B₄C) are air resistant to high temperatures and are therefore convenient for HT work. For x-ray diffraction studies, the most suitable support material is B₄C due to its x-ray transparency.

**Gasket Materials**

As described in the previous chapter, a gasket is used in a DAC to provide mechanical support to the anvils at high pressure. At room temperature, materials such as tungsten, rhenium, hardened stainless-steel or alloys such as inconel are generally used for their hardness.

For high-temperature work, suitable materials should ideally be ductile, machinable, maintain its strength at high temperature and not react with either the sample or with the diamond anvils (Schiferl (1987), Kikegawa and Iwasaki (1983)). Materials, mentioned earlier, such as W, Ta, Re, Mo and their alloys and carbide ceramics satisfy these criteria.
Investigations have been made in the search for the most suitable gasket materials for HT work and it seems that rhenium is the best gasket material at elevated temperatures (Schiferl et al. (1987), Pottlacher et al. (1986)). However Zinn et al. (1987) reported that rhenium reacts with nitrogen at temperatures above 800°C.

Nevertheless, it seems that a rhenium gasket remains durable at high temperatures to support the diamond anvils. The thermal conductivity of rhenium is $43 \text{ W m}^{-1}\text{K}^{-1}$ at 300 K and $76 \text{ W m}^{-1}\text{K}^{-1}$ at 2000 K (Andreeva et al. (1976)).

**Other Construction Materials**

The other components of the diamond-anvil cell do not experience the same amount of stress as the one sustained by the anvils, anvil-supports or gasket. However it is important that the whole cell assembly maintains its alignment at high temperatures. Several limitations need to be overcome to accomplish this. The materials must not be subjected to creep deformation and at the same time, the elastic moduli and thermal expansion of the components must be such that the force on the diamond anvils remains constant under high temperature. Most metals and alloys have a low temperature limit. For example, the strength of Fe and Ni alloys declines rapidly above 500°C (tool steels), 700 – 850°C (stainless steel), 800 – 1200°C (inconels, incolloys, nimonics) (Rothmans ed. (1988)). It is also important to take into account the compatibility of different materials at high temperature. For example, SiC reacts with many metals and oxides above 1200°C (GIAC (1986)), but $\text{B}_4\text{C}$ and $\text{Si}_3\text{Ni}_4$ are more inert. In some cases, good electrical insulating materials are required depending on the method used to generate high temperatures (see Section 3.2.2).

This section has focused on the additional constraints imposed by HP/HT technology. All these limitations must be taken into account while developing the existing diamond-anvil cells. The first cells modified for HP/HT work were not initially designed with the appropriate materials simply because scientists were not aware of these additional problems or did not know how to solve them or did not have the right technology, therefore the high-temperature limit was relatively low. A review of HP/HT cells used with different techniques is presented in the next section.
CHAPTER 3. HIGH-PRESSURE HIGH-TEMPERATURE EXPERIMENTAL ...

3.2.2 High-Pressure High-Temperature Cells: Design and Operation

Introduction

Since the advent of the diamond-anvil cell, various attempts have been made in the development of new cell designs to extend high-pressure work to simultaneous HP/HT studies. Several methods of sample heating in the DAC have been proposed. The simplest way to raise the sample temperature is directly heating the cell without the need of a heating element. This is usually done off-line, and therefore is not suitable for in-situ x-ray diffraction experiments. This basic technique allows temperatures of approximately 200°C to be reached, which is very limited. A more elaborate way of increasing the temperature of the sample is to heat the cell with the help of a heating device attached to the DAC. There are different configurations in which a heater can be placed in the cell. In one kind of design, the heater can be placed outside of the cylinder containing the diamond anvils, mounting plate and the piston (Weir et al. (1965), Barnett et al. (1973)) or outside the press body (Asaumi et al. (1980)). This method, known as external resistive heating, provides a uniform temperature distribution over the whole sample and allows temperatures of 900°C – 1300°C to be achieved. Alternatively, the gasket may serve as the heater element (Moore et al. (1970)), and in a more sophisticated design a resistance wire wound around the diamonds can be used as the heater (Sung (1976), Hazen and Finger (1981), Ming et al. (1983), Bassett et al. (1985)) or a wire can be inserted in the sample chamber and used as the heater element (Boehler et al. (1986)). This heating method, called internal resistive heating, leads to inhomogeneous temperatures over the sample but enables temperatures of approximately 2000°C to be reached. A more direct way of heating the sample is to irradiate it through the diamonds with a laser beam (Ming and Bassett (1974), Jeanloz and Heinz (1984)). The highest temperature reached (~ 5000°C) was obtained by this technique, however it is extremely difficult to perform in situ experiments by laser heating due to the complexity of the optical equipment involved. This method presents the inconvenience of producing an extremely large thermal gradient across the sample and depends also on its optical and electrical properties.

The following sections describe in detail the various cell designs and operation developed to achieve simultaneous HP/HT along with the different techniques that have been
External Resistive Heating

Among the first and simplest attempts of achieving high temperature was simply to heat the whole DAC externally. Such experiments have been conducted at the United States National Bureau of Standards. A cell, containing a pressurised sample, was placed on a hot plate and warmed up to approximately 200°C. The behaviour of the sample was then observed on cooling under a microscope.

This very basic technique has also been applied to ADX powder diffraction studies where DACs were heated up to 200°C in an off-line furnace to explore the stability conditions of the high-pressure phases of binary semiconductors and simple elements (for example, McMahon and Nelmes (1997), Nelmes et al. (1993)). Despite the fact that this simple technique has shown to be fruitful to find new high-pressure phases, this method presents obvious inconveniences. Without the necessary modifications (materials or design) discussed earlier, the DAC cannot be heated above 200°C. Also critical information about the high-temperature behaviour of the sample is lost and it is therefore not possible to map P-T phase diagrams or determine equations of state.

The first diamond-anvil cell used for in situ HP/HT studies was developed by Basset and Takahashi (1965) to carry out x-ray and optical observations on silver iodide polymorphs under pressure to about 300°C. Later, Sung (1976) modified the original design of this cell by using a new alignment technique and a new heating element to study the kinetics of the olivine to spinel transition in Fe2SiO4 to 30 GPa and 600°C. In this design, heating was achieved by placing a resistance coil immediately around the two diamond anvils. The detailed assembly of the cell is illustrated in Fig. 3.2.

Before the advent of synchrotron radiation, the only available x-ray sources were monochromatic radiation from x-ray tubes in in-house laboratories. Therefore the cell was designed for ADX experiments where the slot allowed the passage of x-rays up to $2\theta = 35^\circ$.

As shown in Fig. 3.2, the two diamonds (A) are mounted on the two pistons (B,C). The upper piston (B) is driven by the gimbal (D) and guided by the cylindrical sleeve (E).
Both pistons and cylindrical sleeve are made of Inconel metal. Pressure is applied by squeezing the screw (F) on the spring (G), which transmits the force to the sample held between the two diamond anvils. The x-ray source is collimated by a lead dispersed glass capillary tube (H), which can be adjusted by the three screws (I) on the collimator holder (J). The data are collected with the help of an x-ray camera (K) on a curved film (L) where the centre of the radius coincides with the sample. The camera is attached to the cell by four legs (M) that allows the sample-to-film distance to be adjusted before the heater (N) is placed around the diamonds. The whole cell can be connected to a sample fixture (O) attached to the track on the x-ray generator. The heater is made of a fired pyrophyllite disc wound with a Pt-13%Rh thermocouple wire (0.4 mm diam, 1 m long). The two holes, penetrating the heater horizontally, allow access for two thermocouples that can be used simultaneously to measure temperature inside the heater. Diamond alignment is achieved by translational and rotational adjustments of the lower diamond, respectively with three equally spaced screws (P) and (Q). Circulating cooling water through the hose fitting (R) is required to prevent pressure loss on high temperature heating (800°C) due to the decrease of the elastic constant of the spring (G). Using this facility is necessary to keep the spring end and the hose end (S) cold during heating.
Even if, technically, this cell could reach temperatures up to 1000°C, Sung was constrained to heat up to only 600°C as the diamonds were not protected from the air and therefore could oxidize during prolonged heating.

Later, Kikegawa and Iwasaki (1983) introduced their own modifications to that cell to conduct x-ray diffraction experiments on polycrystalline materials. They studied phase transitions of phosphorus at 30 GPa and elevated temperatures. Various improvements were made in heating efficiency, uniformity of temperature, diamond alignment and the elimination of preferred orientation effects. The new DAC design was made to meet the following criteria: (i) the sample must be heated as efficiently and uniformly as possible (ii) diamond alignment must be easily made from outside without dismantling the whole assembly (iii) the cell must be small and compact (for easy manipulation), for example easy orientation adjustment. Two vertical truncated cross sections of the cell are illustrated schematically in Fig. 3.3.

The diamond-anvil cell proposed by Kikegawa and Iwasaki is a modified version of the cell developed by Sung. Its principle mechanism is therefore similar. Before synchrotron radiation became available for general use, the cells were designed for ADX studies to use the monochromatic source available in in-house laboratories. The improved design allowed a maximum opening angle of $2\theta = 45^\circ$. The cell mechanism is briefly described below, see Fig. 3.3.

The two diamonds (1) are mounted on the disk-shape plate (2) and hemispherical plate (3). Translational adjustment of the lower plate can be done with the alignment screws (13) and rotational adjustment of the upper plate can be achieved with the aid of an annular disk (4) and vertical screws (5). It can be seen from Fig. 3.3 that the criterium (ii) is satisfied since the adjustment screws can be turned from outside thanks to the holes drilled in the upper stationary piston (6). The lower plate is placed on the lower sliding piston (7) that can be guided into the cylindrical sleeve (8). Pressure is applied by turning the screw (9) that drives the lower piston upwards which then transmits force to the diamond anvils. The choice of the material has been carefully taken: anvil supports (2) and (3) are made of sintered tungsten carbide that does not soften until 700°C. The pistons (6,7), the screw (9) and the press body are made of a hardened steel, SKH-9, that remains unchanged up to 700°C. The gasket material
Figure 3.3: Mechanism of the improved high-pressure high-temperature diamond-anvil cell from its original design (After Kikegawa and Iwasaki (1983)).
used is high-strength Inconel.

Between the anvil supports, a ring (11) made of pyrophyllite, holding a heating element, is placed. It consists of a Pt-13%Rh alloy wire in the form of a spiral wound around the ring. Additionally, there is an external heater (12) fixed to the corners of the cell body. To ensure heating efficiency and uniformity in temperature, an input of AC power (50 W each is necessary to reach 500°C) is provided simultaneously to both heaters. Criterium (i) is therefore satisfied. The whole assembly of the DAC can be attached to an x-y-z translational and rotational stage. This facility meets criterium (iii) and reduces preferred orientation.

Despite the improvements made on the HP/HT cell, long-time heating above 800°C caused pressure release due to thermal expansion of the different components of the cell. This limitation could be overcome by reducing the time of exposure, which was not possible until the advent of more intense x-ray beams from synchrotron radiation.

When high-energy sources became available for general use, the resistively heated DAC was then developed for EDX studies and were successfully used to about 20 GPa and 600°C by Ming et al. (1983), Furnish and Bassett (1983), Ming et al. (1984) and Manghnani et al. (1985). Being aware of the necessary requirements described earlier, Ming et al. (1987) made a number of improvements to enable sample heating to about 1000°C. This cell was used to study the high-pressure high-temperature phase...
transitions of two $\gamma - (\text{Mg, Fe})_2\text{SiO}_4$ samples.

Fig. 3.4 illustrates the mechanism of the DAC used for these EDX studies. The two plates are brought together by a pivot pin at one end and a spring-loading mechanism at the other end. The piston-cylinder assembly is located at the centre of the cell and its details are shown in Fig. 3.5. This cell is a modified version of the one developed initially by Sung (1976), described earlier in this section. The improvements made to increase HP/HT performance are also shown in Fig. 3.5. To overcome the major problem of deformation of the piston and the cylinder due to prolonged heating, it was necessary to replace the previously used stainless steel by a more suitable material. The material chosen was a high-temperature alloy, Inconel 718. At the same time, the length of the moving upper piston was increased to improve stability.

The diamond anvil supports, located on the upper and lower pistons, are made of tungsten carbide. The hole of the lower piston (150 $\mu$m size) serves as a collimator while the beam can exit the cell through a conical slot of 30° angle. Additional Inconel sleeves are added around the rocker-seats and the anvils to strengthen diamond alignment. The sample is heated with the help of a miniheater, as shown in Fig. 3.6.
Figure 3.6: Miniheater used for heating the sample in the diamond-anvil cell (After Ming et al. (1987)).

The heating element is wired through the base, which is made of heat-treated talc, with Pt-13%Rh. It has been found to be very efficient over prolonged heating (several days) at temperatures up to 600°C. However, to prevent the tungsten carbide anvil supports from oxidising, it is necessary to heat the sample in vacuo or in an inert atmosphere. Tests made in a vacuum chamber have shown that not only can oxidation be avoided but also heat efficiency inside the cell can be improved (Ming et al. (1987)), see Section 3.2.3. These developments allowed samples to be heated up to approximately 1000°C. A great step forward had been made.

Since then, many other type of cells for in situ HP/HT EDX experiments using synchrotron radiation were developed around the world. For example, accurate studies on the phase diagram of iron were successfully made with the use of a cubic-anvil cell, that could reach \( \sim 800°C \) under 12.5 GPa (Akimoto et al. (1987)) at the Photon Factory, Japan. Later, new technique developments have made it possible to conduct high-pressure melting experiments, which were of great interest particularly among earth scientists. For example, it was possible to sustain 20 GPa above 2000°C (Ohtani et al. (1982)) and therefore obtain new information about the earth mantle composition.

Significant improvements have been made since the first attempts of heating the DACs. However despite the fact that the external resistive heating method made a major impact in HP/HT technique development, the maximum pressure achievable by this
technique was still limited due to the decrease in the diamond and support strength and the maximum temperature reached was still low. This problem was only overcome in 1986 when Boehler et al. presented a new technique for internally heating the diamond-anvil cell. This new method is described below.

**Internal Resistive Heating**

The new technique of internal heating in DACs proposed by Boehler et al. (1986) is relatively simple. Its principle is based on passing a current through a small filament in the sample chamber, as illustrated in Fig. 3.7.

It was first used to study the various phase transitions in the P-T phase diagram of iron. This method combines two other techniques used independently for measurements of electrical resistivity with a sandwiched-gasket arrangement (Block et al., (1977)) and measurements of melting of a resistively-heated iron wire between two diamonds (Liu and Bassett, (1975)).

As shown in Fig. 3.7, the gasket consists of two discs of stainless steel with 0.2 mm thickness, electrically insulated by an alumina base cement of 0.05 mm thickness. An iron (or tungsten) wire is mechanically connected to the two gasket halves acting as electrical leads. Alumina is used as a pressure transmitting medium and was shown not to react with the wire (Boehler, (1986)). The high thermal conductivity of diamond prevents the two ends of the wire, in close contact with the diamonds, from heating leaving a hot spot (~20 µm x 20 µm area) in the centre of the cell.

The hot part of the wire is therefore thermally insulated from the diamonds. Temperature stability can be maintained for long periods of time due to the low power requirements (only ~9 W is required to maintain the sample at 2400 K and 40 GPa). With this simple arrangement, it was possible to reach temperatures above 2000°C at ~43 GPa. However it was relying on the use of the iron wire acting simultaneously as both the heater and the sample.

The intensive studies on the P-T phase diagram of iron has led Mao et al. (1987) to improve slightly Boehler’s original idea. The modified version of the internally-resistive heated DAC is illustrated in Fig. 3.8.
The mechanism for heating the sample remains the same. The modification consists of combining an iron foil electrode of 10 \( \mu \text{m} \) in thickness with iron sample/resistance element. The diamond anvils and the gasket are insulated from the iron foil by a layer of alumina powder. In both designs, a current flow from a D.C. power supply is sent to the iron sample. Measurements of applied voltage and current can be used to calculate resistance and power in the circuit. Therefore a resistance-power curve can be determined to monitor the temperature of the sample. A change in the slope indicates a phase transition. This method presents, therefore, the advantage of monitoring \textit{in situ} phase transitions.

Since then progress has been made to combine this method with synchrotron radiation. Simultaneously studies of phase transitions of iron were made by laser heating technique (Williams \textit{et al.} (1987)), as discussed later. Ten years later, a novel technique was introduced successfully by Dubrovinsky \textit{et al.} (1997 and 1998a) who modified the original design by adding two layers of mica between the gaskets. The heating wire was then completely isolated from the gaskets by being sandwiched between the two mica sheets. A detailed illustration of this new arrangement is shown in Fig. 3.9.

The two gaskets are made of inconel steel with 200 \( \mu \text{m} \) thickness. They are isolated from each other and from the cell body with thin layers of mica (20-50 \( \mu \text{m} \)) and high-temperature cement. A thin iron foil (5 \( \mu \text{m} \)) is placed between the two gaskets and is connected with two Teflon covered copper wires. The foil is isolated from the gaskets with the mica plates and epoxy. A wire (Pt 0.5 mm, Re 0.3 mm or W 0.35 mm) with a
Figure 3.8: Cross-sections of the improved internally-heated diamond-anvil cell and the iron sample acting also as the heater element (After Mao et al. (1987)).

hole is used as the heater. The diameter of the hole (25-100 μm) is always smaller than the diameter of the corresponding holes in the gaskets (125-300 μm). This arrangement allows both electrically conducting materials and insulators to be heated.

The thermocouple is a Pt/Pt13%Rh wire with a junction diameter of 25-60 μm. The junction is placed between the diamond anvils in contact with the sample and is isolated from the gaskets by high-temperature glue. The double gasket design prevents the foil from bending, reducing the risk of the diamond cutting off the wire or touching the hot wire. The whole cell is placed in liquid argon to prevent cell oxidation. Argon is also used as pressure transmitting medium. The wire is heated by sending a current from a D.C. power supply. A typical power output is about 60 W for pressure-temperature conditions of 50 GPa and 1800 K in a Mao-Bell type cell.

This new design has proved to be very efficient in the study of the phase diagram of iron (Dubrovinsky et al. (2000)). It has also been used for pressure-volume-temperature measurements on corundum Al₂O₃ and Fe. There is now a need to extend the use of this technique to the study of a wider range of materials.
Laser Heating

This technique offers a direct way of heating the sample in a DAC by focusing a laser beam onto the sample to create a hot spot that can exceed 4000°C. The highest temperatures ever reached was achieved by this method. The methodology behind this technique is very different than the one proposed in the resistive heating methods described above. Its basic principles are summarised here.

The first developments of laser heating techniques were carried out to provide a method for heating pressurized samples to sufficiently high temperatures to induce phase transitions with high kinetic barriers. The initial interest was to observe phase transitions in silicates. The first studies made with laser heating were performed by Bassett and Ming (1972). They reported experiments up to 26 GPa at 3000°C (Ming and Bassett (1974)). More than a decade later, melting experiments on carbon up to 30 GPa were made successfully with the use of the laser heating technique (Weathers and Bassett (1987)). The experimental procedure used in that specific experiment is described here to illustrate the principles of this technique. A schematic diagram of the apparatus is shown in Fig. 3.10.
A Nd doped YAG laser, equipped with a very fast shutter placed inside the laser cavity (Q-switch), is used to heat the samples. The laser beam is reflected down through an objective lens that focuses it through the upper diamond anvil onto the sample to create a hot spot ($\sim 10 \mu m$). Samples are maintained under pressure between the diamond anvils. The laser produces infrared radiation with a wavelength of $1.06 \mu m$ and can be used continuously or rapidly pulsed with the Q-switch. The Q-switch can provide individual pulses of 100-200 nsec duration that can heat sample to very high temperatures. The power of each pulse is controlled from zero to a few thousands watts with the help of an attenuator. A beam splitter mirror is then used to divert a portion of the light onto the television camera to monitor the sample during the experiment. The incandescent light from the heated sample is guided to the grating spectrometer and photodiode array. The photodiode array collects the spectra, which are stored in the “optical multichannel analyser” (OMA) to be processed for temperature determination. Details on temperature and pressure measurement and serious difficulties arising when using this technique are explained in the next section.

The power of the Q-switch allows very high temperatures in the range of 3500 K to 10,000 K to be reached (Bassett and Weathers (1987)). However one of the various inconveniences of this technique is the large temperature gradients within the sample due to the small region heated (up to $400^\circ C$ per micron). Also the sophisticated optical
Other Cells

In order to increase the temperature range accessible, further progress has been made in the 1990's on the development of cell design and choices of material for simultaneous high-pressure and high-temperature studies. Two main examples are given here for completeness.

In 1993, a new style of diamond-anvil cell was designed for conducting research in fluids at pressures to 2.5 GPa and temperatures from -190 °C to 200 °C (Bassett et al. (1993)). A schematic illustration of the cell is given in Fig. 3.11.
The two diamond-anvil cells (A) are mounted on two platens (E and F). Pressure is applied, via belleville springs (K), by tightening nuts (J) on the threaded ends of three posts (I) to draw the two platens together. The diamond anvils can be aligned by adjusting the lower anvil with the ball joint (B) and the upper anvil with a sliding disk (C). Visual and optical access to the sample is provided by the holes on the centres of the platens. The holes are covered with (glass or mica) windows (H). The diamond anvils are supported by tungsten carbide seats, wrapped by molybdenum wires that serve as heaters. Uniform heat can be applied to the anvils up to 1200°C. Electrical leads for the heaters and thermocouples can be inserted through the cell. The whole assembly is enclosed and completely surrounded with a gas to prevent diamond oxidation. The base is made of brass and is equipped with a cooling chamber (G).

This cell design has been optimised according to the following criteria:

(i) Stability of the DAC: the tensile stress is supported only by the three posts (I) that are isolated from the heat sources. To minimize the effects of heating, the posts have been designed with hollow centres for air cooling.

(ii) Heating efficiency: heat is transmitted by thermal conduction to the seats and then to the diamonds anvils through molybdenum heater wires wound around the tungsten carbide seats.

(iii) Protection of the anvils: the HT metal parts are enclosed in a chamber where an inert gas can be introduced. The diamonds are therefore protected from oxidation. A continuous flow of Ar gas (with 1% of H₂) is used for that purpose.

This cell has been designed especially for combined high-pressure high-temperature work for hydrothermal studies up to 1200°C, however its high-pressure range is limited to less than 5 GPa.

In an effort to overcome the difficulties caused by simultaneous HP/HT conditions, a new DAC design has been proposed in 1996 by Le Toullec et al. (1996). The two main improvements consists of the use of a ceramic body and a heated gasket. It has been designed to provide good optical access, good mechanical stability and fast temperature stabilisation. A schematic illustration of the cell is given in Fig. 3.12.
The cell body is made of alumina and is inserted inside a steel jacket equipped with a gas membrane to generate force on the piston. The diamonds are mounted on zirconia seats. The cell is placed in a vacuum chamber to protect the diamonds at high temperatures. To minimize the effects of heating, heat is applied directly to the gasket. The material chosen for the gasket was rhenium. A pair of heater coils, made from kanthal (FeCrAl alloy), is connected in series on each side of the gasket.

Temperature homogeneity in the sample region is ensured by the spiral shapes of the heaters. A thin alumina layer deposited on the heater coils provides electrical insulation. In addition mica screens are mounted on each side of the gasket to stop radiative heating from the surrounding cell components. The resulting thickness of the gasket is 2.6 mm. Heat is then transmitted to the cell by conduction through the diamonds. Pressure can be maintained by adjusting the gas pressure on the membrane at any temperature. This cell has been used to measure the melting curve of argon up to 620 K.

**Conclusion**

Since the first attempts of adapting the existing diamond-anvil cells to combined HP/HT work, a lot of progress has been made in cell designs and techniques development. Pressure cells were first designed for ADX studies and were subsequently
modified for EDX work with the advent of synchrotron radiation sources. Evolution to miniaturization has led to the development of an internal resistive heating method while simultaneously the laser heating technique was in progress. In the 1990s new cells were especially designed for HP/HT work.

It is clear that despite the standardisation of the DAC to generate high-pressure, there is no standard method to produce high temperature under high pressure. Various methods have been described here and each of them presents both advantages and inconveniences. Since the way of generating high temperature is very different for each technique, the methods for calibrating and measuring pressure and temperature are subsequently different.

The next section gives a review of the various methods to measure and calibrate pressure at room temperature and then both pressure and temperature under non-ambient conditions.

3.2.3 Pressure-Temperature Calibration and Measurement

**Pressure Calibration and Measurement at Room Temperature**

Due to the design of most pressure cells, it would be extremely difficult to estimate the pressure by measuring directly the ratio force over area sustained by the sample and often it is simply not possible. To overcome this limitation, pressure calibration techniques have been used. A simple method requires the use of a reference material, mixed with the sample, whose equation of state is well known. For x-ray diffraction experiments, NaCl has been often chosen as a suitable calibrant and its equation of state has been calculated theoretically up to \( \sim 29 \) GPa by Decker et al. (1972). With this technique pressure is deduced from the equation of state according to the unit cell volume calculated from the shift of the diffraction peaks on pressure increase. However, this method suffers from a major problem: the diffraction patterns are inevitably contaminated by peaks from the reference material that may strongly affect the quality of the data and therefore reduce the accuracy of subsequent analysis (e.g. by Rietveld refinement).
Another method for pressure measurement was required to avoid this contamination problem. That was found in 1972 when a completely different method based on a ruby fluorescence technique was introduced by Forman et al. (1972). The basic principle behind this technique is very simple: a chip of ruby, Cr$^{3+}$ doped Al$_2$O$_3$, fluoresces when the light from a He-Cd laser is focused on it. This process gives rise to two intense ruby lines, the $R$ lines, producing a doublet $R_1$ and $R_2$ with wavelengths of 692.7 and 694.2 nm, respectively, at ambient pressure. Piermarini and Block (1975) showed that pressure varies linearly with the shift of the ruby lines and therefore the pressure can be deduced from a simple linear equation. They determined this expression quantitatively using the equation of state of NaCl up to 29 GPa. Later Mao et al. (1978) observed a slight deviation from the linearity in the shift of the ruby line which can be seen above 30 GPa. They derived the following equation:

$$P = 380.8[(\Delta \lambda/694.2 + 1)^5 - 1]$$  \hspace{1cm} (3.1)

The ruby fluorescence system, used at Daresbury, is manufactured by Instruments S.A. and uses a He-Cd Class III-b 12mW laser to stimulate the ruby fluorescence and a spectrometer to measure the wavelength shift. The spectrum is recorded and displayed on a PC where the wavelength of the $R_1$ line is measured. Pressure is deduced from the value of the wavelength shift using the equation (3.1).

Unfortunately this system presents two main disadvantages. It has not been built to be set up on the beamline, each pressure measurement can only be made before and after data collection introducing some inaccuracies in the pressure determination. And the other constraint comes from the fact that the ruby fluorescence technique is limited to, mainly, room temperature measurements, which makes it inconvenient for high temperature studies. This problem is explored below. However it has been necessary to detail the present system here since it has been used by the author for all room temperature measurements.
Pressure Calibration and Measurement at High Temperature

One of the most difficult problems encountered while using HP/HT diamond-anvil cells is the calibration of pressure and temperature. Despite the intensive use of the ruby fluorescence technique (Mao et al. (1986), Vos and Schouten (1991), Dong-ping et al. (1995)), this method is no longer suitable at elevated temperatures. Thermal line broadening causes $R_1$ and $R_2$ to overlap and therefore creates a large uncertainty in the determination of the ruby peak wavelength (Bi et al. (1990)). Additionally, the fluorescence intensity decreases quickly with temperature and becomes difficult to detect from the background above 500 °C (Hess and Schiferl (1990)). Also the $R_1$ line shows a large wavelength shift with temperature therefore any error in the temperature measurement will affect the pressure determination. To minimize these errors, various empirical models have been developed (Munro and Piermarini (1985), Sorensen (1987)). However, little is known about the temperature-induced shift of ruby fluorescence lines at high pressure and other methods need to be used to overcome this problem.

An alternative technique for pressure measurements at high temperature is the use of Yttrium aluminium garnet (YAG) doped with rare earth elements. Sm:YAG, for example, presents nearly temperature-independent electronic transitions and can be used up to 700 °C at 10 GPa (Hess and Schiferl (1992), Liu and Vohra (1993)) or up to ultrahigh pressures at room temperature (Liu and Vohra (1996)). However the Sm:YAG spectrum displays many peaks, which strongly overlap at high pressure and/or high temperature. Another inconvenience is that the relative intensity of the different lines varies dramatically with pressure. Another family of compounds, Sm:BaFCl or Sm:SrFCl was found attractive due to the simplicity of their fluorescence spectra (a single and sharp line with a large pressure shift). However the increased coupling of the different electronic states of Sm$^{2+}$ limits the use of these compounds below 20 GPa.

Simultaneously, another fluorescence method using SrB$_4$O$_7$:Sm$^{2+}$ as a new optical sensor was developed by Lacam and Chateau (1989) and Leger et al. (1990). It uses the fact that the negligible temperature dependence of the $^7D_0 - ^5F_0$ fluorescence line of SrB$_4$O$_7$:Sm$^{2+}$ and its small line broadening make this compound very convenient for HP/HT studies in diamond-anvil cells.
A few years later, revised spectroscopic studies on this compound have shown that the $^7D_0 - ^5F_0$ line can be used for pressure calibration up to 124 GPa in a hydrostatic medium (helium) and up to 130 GPa in nonhydrostatic medium ($H_2O$) and temperatures up to 900 K. By combining both SrB$_4$O$_7$ : Sm$^{2+}$ and ruby sensors, it was also possible to calibrate the ruby $R_1$ line up to 800 K. A non-linear expression for the wavelength pressure shift of the $^7D_0 - ^5F_0$ line of SrB$_4$O$_7$ : Sm$^{2+}$ was proposed:

$$P = 4.032\Delta\lambda(1 + 9.29 \times 10^{-3}\Delta\lambda)/(1 + 2.32 \times 10^{-2}\Delta\lambda) \quad (3.2)$$

A more traditional technique for P-T calibration is the application of the P-V-T equations with the use of internal pressure calibrants. A review of the suitability of various pressure calibrants in HP/HT diffraction studies and key results of in situ P-V-T equation of state measurements of different materials have been presented by Manghnani et al. (1984). When it is not possible to obtain accurate temperature measurements, optical pyrometry is used instead.

The next section describes how these methods were used to calibrate pressure and temperature to obtain the best data quality possible along with details on temperature measurements for each different technique described in Section 3.2.2.

**P-T Calibration and Measurement For Resistive and Laser Heating Techniques**

One of the first pressure cells used to generate high temperature was designed by Sung (1976) as illustrated in Fig. 3.2. High temperature was achieved with the use of a resistance coil placed around the diamond anvils. The heater was wound with a Pt-13%Rh thermocouple wire and allowed access for two extra thermocouples to measure temperatures inside the heater. The temperature distribution inside the heater is reasonably homogeneous without the diamonds. However when the two diamonds are closed up, horizontal and vertical temperature gradients inside the heater can be both very large, especially at high temperature. The temperature profile across the heater at a sample temperature of 600°C is shown in Fig. 3.13.

Sample temperature measurements can exceed 50°C from the true sample temperature.
Figure 3.13: Temperature profile across the heater used in one of the first pressure cells adapted for HT studies. The temperature distribution along the horizontal line passing through the centre of the sample is illustrated when the diamonds are closed together (C) and open (O). Numbers are temperatures in °C (After Sung (1976)).

The true temperature of the sample can be measured by inserting the head of an ultrafine thermocouple (25 μm wire diameter) at one edge between the two diamonds. The advantage is that because of the high thermal conductivity of the diamond and the small volume of the sample, the temperature gradient inside the sample is not very large.

When Kikegawa and Iwasaki (1983) brought their own modification to that cell, they aimed for improvements in heating efficiency and uniformity in temperature. They placed an external heater in the cell body in addition to the heater disc around the anvils, see Fig. 3.3. Combining two sets of heaters greatly improved heating homogeneity by reducing temperature gradient across the anvils and the cell body.

The sample temperature is measured with an alumel-chromel thermocouple (0.1 mm in diameter) whose head is placed in contact with the gasket. Once again the measured temperature is not necessarily the true sample temperature, therefore calibration must be made either with calibrant materials with known transitions temperatures or, as previously done by Sung, by clamping the head of another thermocouple in the sample. With this arrangement, temperature can be maintained with ± 3 °C over a day.

In terms of pressure measurement, a pressure calibrant, mixed with the sample, is used at high temperatures. Here the lattice parameters of sodium chloride were measured and pressure was determined with the known equation of state. Due to the thermal
expansion of the various components of the cell, pressure release is often observed upon heating, therefore it is important to be able to measure P-T simultaneously.

Later Ming et al. (1987) developed a pressure cell for EDX studies for HP/HT experiments with synchrotron radiation. This cell allowed samples to be heated up to \( \sim 1000 \, ^\circ C \). The heating assemblage is shown in Fig. 3.5. The sample is heated by using a miniheater (see Fig. 3.6). The miniheater is composed of two parts: (i) the heat-treated base made from talc and (ii) the heating element, wired through the base with 0.254 mm diameter Pt-13%Rh wire. This system provides efficient heating for several days up to 600 \( ^\circ C \). Higher temperatures can be achieved by heating the sample, for example, in a vacuum chamber. Fig. 3.14. shows a comparison in the temperatures attained while heating sample in air or in vacuo.

At a given output power, heating in vacuo reaches much higher temperatures than heating in air. The advantage is the high efficiency of the vacuum heating allows temperature up to \( \sim 1000 \, ^\circ C \) to be achieved.

Temperature was calibrated by using the thermal expansivity data of NaCl. The x-ray diffraction pattern of NaCl was recorded for each temperature step when thermal equilibrium was reached. The calibration was made up to \( \sim 450^\circ C \) by plotting the temperature of NaCl, from diffraction data and published data (American Physics Handbook, 1972), against the thermocouple temperature values. The results obtained by Ming et al. (1987) based on two separate runs shows clearly the linear relationship
between the two temperatures, as illustrated in Fig. 3.15.

The accuracy in sample temperature was estimated within ± 5°C. This calibration was in a good agreement with that obtained with a previous study (Ming et al. (1983)).

In conclusion, the external resistive heating method provides a good temperature homogeneity across the sample and temperature can be measured with the use of one or several thermocouples. Pressure and temperature calibration are made by using the P-V-T equation of state of internal calibrants.

The radically novel technique introduced by Boehler et al. (1986), based on resistance heating of Fe and W wires in gasketed DACs, has led to use more sophisticated methods to measure temperature. A schematic arrangement of an internally heated diamond-anvil cell is illustrated in Fig. 3.7. The wire inside the sample chamber is electrically heated, leaving a hot spot in the centre of the cell. It thus creates inhomogeneity in temperature across the sample, and therefore, the use of internal calibrant is no longer accurate. Optical pyrometry was used instead.

Temperature is measured by collecting blackbody emission spectra from the hot wire in the OMA by using a diode-array detector attached to a monochromator with a diffraction grating. A schematic diagram of the optical arrangement used to measure
temperature is shown in Fig. 3.16.

The spectra are calibrated against a standard emission source and then fitted to a black-body radiation function. Temperatures are determined by a least-square program. Errors in temperature are typically ±20 K at 1000 K and ±8 K at 2300 K. No information on the emissivity of the sample is required since the DAC is not calibrated and whole spectral regions are collected.

Pressure is measured by the ruby fluorescence technique. Ruby chips are placed near the "cool" diamond, see Fig. 3.7. Pressure is determined from the shift of the ruby fluorescence spectrum using the conversion factor 0.36 nm/GPa (Boehler et al. (1987)).

The same technique was used for temperature measurement and calibration by Mao et al. on his improved internally-heated DAC, shown in Fig. 3.8. Pressure was measured by the ruby fluorescence technique at room temperature and the ruby scale was calibrated against the equation of state of NaCl to correct errors in pressure measurements at high temperatures. With this technique, phase transitions can be determined by discontinuities in the resistance-temperature curve of the heated wire, therefore temperature can be monitored in situ.

The double gasket cell assemblage created by Dubrovinsky et al. (1997), see Fig. 3.9, is equipped with a Pt/Pt13%Rh thermocouple. Heat is provided by a D.C. power supply.
The temperature variation is monitored by connecting a thermocouple to the Pt wire and another thermocouple touching the cell. Temperature was then estimated from the cell constants of the sample, used as a calibrant, assuming that the pressure did not change upon heating. Errors were estimated as ~ 20%. More accurate studies on pressure-temperature variation using different P-T calibrants were made to test the behaviour of the double gasket assemblage at HP/HT (Dubrovinsky et al. (1998b)).

In conclusion, the inhomogeneity in temperature produced by the internal resistive heating method requires the use of more suitable methods for temperature measurement. Optical pyrometry and resistance measurement have been used to estimate T and both pressure calibrants and ruby fluorescence technique to measure the pressure. However the ruby scale needs to be properly calibrated if used at elevated temperatures but as explained earlier, it is not the best method to measure the pressure at high temperature.

The laser-heating method used to generate high temperature is by far the most complex and sophisticated technique, especially in terms of temperature measurement. It is beyond the scope of this thesis to explain these problems in details, therefore only the basic ideas are given here for completeness.

The optical arrangement used by Weathers and Bassett (1987) is illustrated in Fig. 3.10. Temperature is determined by optical pyrometry since heating is confined to the sample itself, it is not possible to use thermocouples. The spectrometer produces a spectrum received by a photodiode array and recorded in the multichannel analyser. Temperature is then estimated by fitting the spectrum to a calculated blackbody curve. Pressure was measured at room temperature with the ruby fluorescence method using the green light from the frequency-doubled light of the YAG laser.

The effect of laser heating on the pressure is not clearly understood. It is believed to be a minor factor because the heating is very local and the pulse durations are long relative to the time required for sound to travel across the sample.

Since the introduction of the laser-heating method, no accurate technique for measuring the temperature has yet been established. The reason for this is that temperatures produced in high pressure samples by a pulse ruby laser are extremely difficult to measure. The small heated area in the sample and the high thermal conductivity of diamond
produce large thermal gradients and represent one of the main obstacles to quantify experimental conditions at these extreme conditions. Laser heating also creates thermal stress in the sample and the non-uniformity of each laser pulse produces considerable temperatures fluctuations. A review about temperature measurement techniques from thermal radiation is given by Heinz and Jeanloz (1987).

In comparison, the internal heating method presents several advantages over the laser heating technique:

(i) resistive heating of fine wires in a DAC offers a larger heated area with a more uniform temperature distribution, even though temperature gradients within the wire cannot be ignored

(ii) resistive heating allows *in situ* monitoring of phase transitions

(iii) temperature fluctuations are minimal

A more detailed comparison between those two methods for the studies of phase transitions in Fe have been made by Boehler *et al.* (1990).
The constant effort to produce improvements in the P-T range attainable by a DAC has led Bassett et al. (1993) to design a new type of cell for hydrothermal studies. The cell is illustrated in Fig. 3.11 and has been designed for accurate temperature measurement, as shown in Fig. 3.17.

The thermocouples are cemented to the diamond anvils and are isolated from the heaters and other parts of the cell. Temperature can be measured within ± 0.1°C accuracy from -110°C to 380°C. Above 380°C the accuracy is ± 1.5°C. Temperature balance is ensured by controlling the electrical power to the upper and lower heaters individually. They are both connected in parallel so the current is the same for both heaters and temperature difference between the heaters can be corrected within ± 0.1°C from -100°C to 380°C and ± 0.5°C beyond that range. The equation of state of H₂O was used to determine pressure with an accuracy of ± 1% in the aqueous samples studied.

The gas-membrane cell proposed by Le Toullec et al. (1996) uses a heating gasket to reduce the effects of thermal expansion. A cross-section of the cell is shown in Fig. 3.12. A K-type thermocouple is inserted at a distance of 1 mm away from the sample chamber to control the gasket temperature. Temperature was measured at the centre of the gasket and plotted against the input power. This study has shown that the simple mechanical and electrical arrangement in the cell does not need much power to achieve high temperature, e.g. 15 W is enough to reach 1000 K. Pressure was determined with the SrB₄O₇ : Sm²⁺ fluorescence technique.

### 3.3 Technique Development

#### 3.3.1 Introduction

This section describes the technique developments necessary to adapt the existing high-pressure equipment, presented in Chapter 2, to perform simultaneous high-pressure high-temperature experiments on Station 9.1 at Daresbury Laboratory.

Among the various heating methods described in the previous section, the simplest one is the basic external resistive heating technique where the whole DAC is heated externally in an off-line furnace. This direct method has been used, initially, by the
3.3.2 The Dynocell

The Dynocell is a piston-cylinder lever-arm diamond-anvil cell, an improved design, by Diacell Products Ltd., of the original DAC created by Piermarini and Block (1975) for energy-dispersive studies, as illustrated Fig. 3.18.

Diamonds are mounted on two stainless steel backing plates as shown in Fig. 3.19(a).
One is stationary and is located in the bottom of the cylinder, where translational adjustments can be made, while the other one is mounted to the piston, with screws for parallel alignment. The main body of the cell consists of a rectangular hardened steel plate and has an aperture at one end to slide the piston-cylinder press body, which is approximately 5 cm in length and 3 cm diameter. Pressure is applied when compressing the Belleville spring washers by rotation of a screw, as illustrated in Fig 3.18 and 3.19(b). The spring lever-arm mechanism generates a continuously varying force as the screw is rotated. The applied pressure is transmitted via the lever-arm to the piston containing one of the diamond anvils, while the other anvil is in a fixed position in the cylinder. The Dynocell can reach pressures in the Mbar range and has an opening angle of $2\theta \sim 18^\circ$. The whole assembly is screwed to a metallic L-shaped base that maintains the cell perpendicular to the incident beam.

The cell is made from hardened stainless steel, suitable for high-temperature work. A resistive heater can be placed around the piston-cylinder cell. The heater used was a thinband nozzle 240 W heater manufactured by Watlow that could operate to temperatures of $\sim 673$ K. A schematic diagram is given in Fig. 3.20. The heater is connected to a microprocessor type temperature controller. Temperature was measured with an external chromel-alumel K-type thermocouple, with $\pm 2^\circ$ C accuracy, connected to a microprocessor-based digital thermometer.

As described in the previous section, extra care needs to be taken when heating a diamond-anvil cell. Diamonds must be protected from the air to avoid oxidation at high temperature. The cell was therefore connected to a gas cylinder containing a mixture of argon (98 %) and hydrogen (2 %). The back and front apertures of the cell were covered with a mica window to enclose the diamonds from the air. However, a hole ($\sim 2$ mm) in the mica window is necessary to allow optical access and exit for the gas.

The most difficult problem encountered while installing this new equipment on the beamline was to stop the heat propagating through the cell environment and therefore damaging the surrounding equipment. As illustrated in Fig. 3.21, a “metal-metal” contact between the base and the cell highly favours heat conduction resulting in an unwanted hot area.
Figure 3.19: (a) The piston-cylinder and (b) lever-arm mechanism of the Dynocell.
Figure 3.20: External resistive heating for the Dynocell.
Figure 3.21: The propagation of the heat through the Dynocell and its base.
The lack of thermal insulation was a serious problem that needed to be overcome. The base was consequently modified. A new water-cooled system was successfully installed. It consists of S-shaped channels machined through the metallic base that allows the circulation of cold water during heating. Additionally, a thin insulating sheet was inserted as an extra layer in the base to prevent water leaking. The sheet was "sandwiched" between the channels and the bottom of the base and firmly closed by a series of screws along the edges. The size of the base was also adapted to allow an air gap and thus reduce the "metal-metal" contact area. These modifications are illustrated in Fig. 3.22. The cell is then connected to a water supply. The temperature of the water circulating through the base was approximately 10°C and was found to provide excellent thermal insulation. A schematic diagram of all the new high-temperature equipment installed on Station 9.1 is shown in Fig. 3.23.
Figure 3.23: A schematic illustration of Station 9.1 with the new equipment for combined high-pressure and high-temperature studies.
3.3.3 Concluding Notes

As it can be seen from the technical developments described above, the critical step to perform high-pressure experiments from room temperature to high temperature is not straightforward. The same limitations as encountered from the earliest work had to be overcome: protection of diamond anvils from the air, appropriate thermal insulation, use of materials suitable for high-pressure high-temperature work, etc.

The developmental work described in this thesis has consisted of implementing new equipment for high-temperature experiments that could be used in combination with the 2-D image-plate set-up on Station 9.1, already in place before the present work. When using the Dynocell, the two major difficulties have been the protection of the surrounding equipment from the heat and the accommodation of additional devices (gas bottle, temperature controller and water supply) in the space provided in the experimental hutch.

The successful use of the Dynocell on Station 9.1 has allowed a series of new high-pressure high-temperature experiments to be carried out. The external resistive heating method used with the Dynocell has provided temperatures of $673 \text{ K}$ at pressures up to $\sim 15 \text{ GPa}$ and new phase transitions have been observed. This cell has been extensively used by the author for combined hp/ht studies of InSb and GaSb. These studies are presented in the following chapters.
Chapter 4

High-Pressure High-Temperature Diffraction Studies of GaSb

4.1 Introduction

GaSb is the most covalent of the III-V semiconductors and it is therefore expected to be the closest to germanium and silicon in its high-pressure behaviour. At ambient pressure and room temperature it has the cubic site-ordered zincblende structure with \( a = 6.0959 \) Å. The space group is \( F\bar{4}3m \) with one atomic species on the 4(a) site at \((0,0,0)\) and the other on the 4(c) site at \((1/4,1/4,1/4)\). Each atom is tetrahedrally coordinated with four “unlike” nearest neighbours.

At 7 GPa and room temperature, it transforms to a site-disordered orthorhombic structure with the space group \( I\bar{m}a \) (McMahon et al., (1994)), previously misinterpreted as the tetragonal \( \beta \)-tin structure (Jamieson, (1963), Yu et al., (1978a) and Weir et al., (1987)). The \( I\bar{m}a \) structure is an orthorhombic distortion of both tetragonal \( \beta \)-tin and simple hexagonal structure. It has also been found in Si (McMahon and Nelmes (1993)), Ge (Nelmes et al. (1996)) and InSb (Nelmes and McMahon (1996)). All the atoms are located on the 4(e) sites at \((0,1/4,\Delta/2)\), as illustrated in Figure 4.1. The structure is centrosymmetric and the origin is usually chosen at a centre of inversion symmetry. However, the structure is sometimes described with the origin shifted to \((0,1/4,\Delta/2)\) to facilitate comparison with the \( \beta \)-tin structure. The atoms are then at
(0,0,0), (0,1/2,Δ), etc. When a = b and Δ = 0.25, the Imma structure becomes the same as the tetragonal β-tin structure and if b = \sqrt{3}c and Δ = 0.5, the structure is then simple hexagonal. The Imma structure remains stable to at least 50 GPa. Further measurements at higher pressures have shown a transition between 63 and 71 GPa to a phase not yet fully characterised but that appears to be site-disordered body-centered cubic. This may be the transition reported by Weir et al. (1987) at 61.0(7) GPa.

More recent work (Mezouar et al., 1999a) has shown that the Imma phase is only stabilised under non-hydrostatic conditions and that rather the zincblende phase transforms to a site-disordered β-tin structure. Mezouar et al. (1999a) made a comparative study of GaSb samples compressed with and without nitrogen gas as a pressure-transmitting medium and heated under pressure in a large-volume pressure cell. They have shown that the width and the shape of the diffraction peaks are affected by the pressure medium and therefore could lead to inaccurate structure determination. Also energy-dispersive x-ray diffraction experiments up to 7 GPa and 973 K have been made to determine accurately the melting curves, phase boundaries and triple points of the pressure-temperature phase diagram (Martinez-Garcia et al., 1999a). They confirmed the existence of two liquid phases in the melt, previously reported by Umnov (1994), and a strong hysteresis (> 4 GPa) at room temperature between the zincblende structure (GaSb-I) and the β-tin-like structure (GaSb-II). The most recent version of the P-T phase diagram is illustrated in Fig. 4.2

This chapter presents a detailed structural high-pressure high-temperature study of GaSb up to 25 GPa and 673 K. By using the techniques described in Chapter 3, it has been possible to explore further the P-T phase diagram. Simultaneously, the matter of site-ordering has been clarified and before presenting the results of this study, it is necessary, at this stage, to introduce the concept of order-disorder transformations.
4.2 Order-Disorder Transformations

When an order-disorder transformation occurs in a solid solution its structural atomic arrangement is affected and therefore changes in physical and chemical properties take place. Experimental evidence for such phase transitions can be obtained from x-ray diffraction. It was first observed, in 1923, by the American metallurgist Bain in the gold-copper solid solution AuCu₃ (Bain (1923)). Since then, this phenomenon has been discovered in other alloy systems.

This section explains how crystal structures are affected by this kind of transformation and how it can be detected by x-ray diffraction. The basic idea can be easily understood by considering, for example, a binary alloy composed of equal numbers of two types of metallic atoms A and B. When the two different metals are mixed with each other in the molten state, they form homogeneous solutions. The solid solution, or alloy, AB is obtained by quenching from the liquid state. When A and B atoms have a regular periodic arrangement along the lattice sites, the alloy is said to be ordered. If this arrangement persists over large distances in the lattice, the crystal structure is said to be long-range ordered, but if the periodicity remains only over a nearest-neighbour range, then the structure is known to be short-range ordered. In contrast, the alloy is said to be disordered if A and B are randomly distributed within the crystal network.

The tendency to form solid solution depends on the chemical relationship between the
metals and the relative size of their atoms (Hume-Rothery (1947)). For example, silver and gold form disordered alloys of arbitrary composition since they are chemically related and have atoms of similar size. Related metals, such as those from the same group of the periodic table, generally form solid solutions of any composition if their atomic radii do not differ by more than \( \sim 15\% \) (e.g. Mo/W, K/Cs but not NaCs). If the metals are chemically different or the atoms differ in size, ordered structures are energetically favoured. An ordered distribution of atoms of different sizes also allows a better space filling and often requires a definite chemical composition (Müller (1993)). For example, copper and gold form ordered alloys with the stoichiometric ratios AuCu and AuCu\(_3\) but are disordered in any other compositions. However, on temperature increase, these ordered alloys transforms to disordered structures in which all atomic positions are equally occupied by the Cu and Au atoms.

This is a general effect in any alloy. The long-range order disappears above a certain temperature, called the critical temperature, and the atomic distribution becomes more or less random. In some cases, depending on the stoichiometric composition, as for AB\(_3\) alloys, some short-range order may persist above the critical temperature (Nix and Shockley (1938)). In this kind of ordering, there is a great tendency for “unlike” atoms (A-B) to be nearest neighbours. Short-range order has been observed in AuCu\(_3\) at 65°C above the critical temperature. The other possibility is to have a tendency of “like” atoms (A-A or B-B) to be close neighbours. This effect is called clustering and has been observed in aluminium-silver and aluminium-zinc alloys. In fact, it is more likely that solid solutions exhibit either short-range ordering or clustering rather than perfectly random disordering, simply because they are composed of unlike atoms with particular forces of attraction or repulsion acting between them. Theory of ordering has been explained in terms of thermodynamics and bond energy by Pauling (1960), Lupis (1983) and Gurman (1992).

The long-range order or disorder of a crystal can be detected by x-ray diffraction. From a crystallographic point of view, there is a fundamental difference between an ordered or disordered structure. This important point is illustrated in Fig. 4.3(a) for a binary AB alloy with a cubic unit cell. In the ordered situation, the cell corners are occupied by one type of atom, for example atom A, and the cell centre by the other type, atom B. The ordered alloy AB has therefore the CsCl structure and the lattice is simple cubic.
Figure 4.3: (a) Unit cells of ordered and disordered structure of a binary alloy AB (b) with their respective powder patterns showing the difference reflection peaks.
On temperature increase the alloy becomes disordered and each lattice site is randomly occupied by atom A and atom B. The structure becomes body-centered cubic. This particular order-disorder transformation has been observed in CuZn alloy at \( \sim 465 \, ^\circ C \) (Kittel (1976)).

In the x-ray diffraction pattern, the disordered structure displays Bragg peaks at the same positions as if the lattice sites were all occupied by only one type of atom, while the ordered structure has extra diffraction peaks due to the difference in the scattering power between A and B. These extra lines are called the difference reflection peaks, or superstructure (or superlattice) lines, as shown highlighted in Fig. 4.3(b).

In the CsCl-type structure, the basis has one A atom at \((0,0,0)\) and one B atom at \((1/2,1/2,1/2)\). The structure factor is given by

\[
F = f_A + f_B e^{-i\pi(k+k+l)}
\]  

(4.1)

where \(f_A\) and \(f_B\) are the atomic scattering factor for respectively the atom A and B. Therefore all reflections of the simple cubic structure are present. In the disordered situation when the structure is body-centered cubic, the basis is equally likely to have either A or B at \((0,0,0)\) and either A or B at \((1/2,1/2,1/2)\). The average structure factor is then

\[
\langle F \rangle = \langle f \rangle + \langle f \rangle e^{-i\pi(k+k+l)}
\]  

(4.2)

where \(\langle f \rangle = \frac{1}{2}\langle f_A + f_B \rangle\), therefore the reflections when \(h + k + l\) is odd are absent.

It is important to note that these difference reflection peaks are much weaker than the main Bragg peaks, simply because their intensities are proportional to the square of the difference, rather than the sum, of the atomic scattering factors. Since both \(f_A\) and \(f_B\) decrease as \((\sin \theta)/\lambda\) increases, so does their difference, and therefore their intensities decrease as \(2\theta\) increases. Consequently, it becomes particularly difficult to detect such peaks when the elements A and B only differ in atomic number of one or two units. However, it is possible to increase the intensity of the difference reflection peaks, when the two atoms involved have almost the same atomic numbers, by an appropriate choice.
of the incident wavelength $\lambda$. When $\lambda$ is close to the wavelength of the K-absorption edge $\lambda_K$ of the scattering element, the atomic scattering factor of that element is lower than its usual value when $\lambda$ is very much shorter than $\lambda_K$. By taking advantage of this effect, the intensity of a difference reflection peak can be brought above its normal value. Another technique for the detection of order in alloys of elements of nearly the same atomic number is neutron diffraction, as the neutron scattering factor varies irregularly with increasing atomic number $Z$.

Since this chapter is concerned with the diffraction study of GaSb, in which the difference in scattering strength between the two atomic species is large (as the atomic number for Ga and Sb are respectively 31 and 51), x-ray diffraction provides an appropriate tool to investigate the long-range order in this binary compound. By using the intense monochromatic radiation from a synchrotron radiation source, it has been possible to demonstrate the complete absence of long-range order in the three high-pressure and high-pressure/high-temperature phases of GaSb. However the x-ray diffraction technique can only determine the ordering over a long-range scale and other techniques need to be used to extract information over nearest neighbours distances. This will be the subject of the next chapter.

The results of the diffraction study are given in the following section.

### 4.3 Results and Discussion

Data were collected on Station 9.1 at SRS, Daresbury Laboratory, using the image-plate set-up described in Chapter 2. Most of the high-temperature work was performed using the Mao-Bell type DAC that was heated in an off-line furnace for about two hours at $\sim 473$ K. Within the time allowed for the work presented in this thesis, only one experiment has been made using the Dynocell. Consequently, detailed information about phase transition boundaries and high-pressure behaviour at high temperature, could not be obtained. The sample material was a finely ground powder of 99.99 % purity from Aldrich Company.

This section is divided into two parts. The first one presents a new high-temperature phase and the second part presents the diffraction results about the site-ordering.
4.3.1 HP/HT Phase Transitions

As explained in Section 3.3.1, heating the whole DAC off-line has been shown to be very efficient to find new high-pressure phases despite its obvious limitations. It has been possible in this work, by using this basic technique, to identify a new phase transition, not observed at room temperature. Samples were loaded into the Mao-Bell-type DAC, then pressure was applied beyond the transition to the \textit{Imma} phase (i.e. above 7 GPa). Diffraction patterns were collected before and after heating. Pressure was also measured before and after heating, with the ruby fluorescence technique (see Chapter 3), and a pressure drop was always observed on recovering back to room temperature.

Two different behaviours were observed: for samples taken at \textasciitilde 13 GPa, the \textit{Imma} phase transforms to the \textit{\beta}-tin structure, while for samples taken above \textasciitilde 16 GPa, it transforms to a new orthorhombic phase with the spacegroup \textit{Ammm}, as discussed below. Between \textasciitilde 13 GPa and \textasciitilde 16 GPa, a mixture of the \textit{\beta}-tin and \textit{Ammm} phases was observed. The sequence of these phase transitions is illustrated in Fig. 4.4. Each of the four profiles has been collected from a different sample of the \textit{Imma} phase heated at the pressures shown.

It can be seen that profiles observed after sample heating are much sharper than is obtained at room temperature. Data quality is therefore enhanced and a more accurate data analysis can be made.

The new orthorhombic \textit{Ammm} phase was first observed with a small amount of the \textit{\beta}-tin phase present, as can be seen in the profile (d) in Fig. 4.4. This profile bears some striking similarities to a profile of InSb obtained at 2.1 GPa, which has been identified as a mixture of the \textit{Immm} and \textit{\beta}-tin phase (Nelmes et al. (1993)). Details on the phase transitions in InSb are given in Chapter 6. The profiles of InSb and GaSb are illustrated in Fig. 4.5.

One of the characteristics of the \textit{Immm} profile of InSb is the presence of the low-angle (110) peak, which is a difference reflection peak indicating that the structure is site-ordered, as explained in Section 4.2. Details on site-ordering in GaSb will be given in the following section, however it is important to note this point, at this stage, since it gives critical information about the structure. The profile of GaSb in Fig. 4.5 does
Figure 4.4: Sequence of phase transitions observed in GaSb after heating samples taken from the Imma phase (profile (a)) at four different pressures: (b) β-tin profile obtained at 10.5 GPa, (c) first appearance of the Ammm phase as indicated by the emergence of the (100) peak in the profile at 12.7 GPa, (d) profile of mostly the Ammm phase at 17.1 GPa with the remaining (200) peak of the β-tin phase shown by the arrow, (e) the Ammm profile obtained at 22.5 GPa. The peaks marked by an asterisk are discussed in the text.
CHAPTER 4. HP/HT DIFFRACTION STUDIES OF GASB

Figure 4.5: Similarities between a profile of InSb at 2.1 GPa and a profile of GaSb at 22.5 GPa. The presence of the (200) β-tin peak is indicated in both profiles. The presence of the (110) peak in the InSb profile is also shown. The peaks marked by an asterisk are discussed in the text.

not show the presence of the (110) peak. It is therefore concluded that the structure of GaSb is site-disordered, which means that each lattice site has an average of Ga and Sb atoms. The “monatomic equivalent” of the Immm structure gives a A-face-centered orthorhombic structure, as illustrated in Fig. 4.6.

The profile has been indexed as an orthorhombic structure where \( k+l = \) even, indicated that it is A-face centered, with spacegroup Ammm. The unit cell contains two atoms located at (0,0,0) and (0,1/2,1/2). This phase has been fitted at 22.5 GPa with \( a = 2.6432(1) \) Å, \( b = 4.8813(7) \) Å and \( c = 2.9583(2) \) Å. A Rietveld refinement of the Ammm phase is shown in Fig. 4.7. A table showing the comparison between the calculated \( (d_c) \) and observed \( (d_o) \) d-spacings is given in Table 4.1

Besides the discovery of the Ammm phase, some important remarks need to be made about the β-tin structure. The profile (b) in Fig. 4.4 shows a β-tin profile obtained after sample heating. This phase has not been observed before at room temperature
Figure 4.6: The unit cell of the *Immm* structure, a site-ordered phase compared to (b) a unit cell (doubled along the a-axis to facilitate comparison) of the *Ammm* structure, a site-disordered phase.

Figure 4.7: Rietveld refinement fit and indexing of the *Ammm* structure to a profile of GaSb at 22.5 GPa. The asterisks are discussed in the text.
Table 4.1: Comparison of the observed and calculated d-spacings of the Ammm structure of GaSb at 22.5 GPa.

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<td>2 1 1</td>
<td>1.1721</td>
<td>1.1714</td>
</tr>
<tr>
<td>2 2 0</td>
<td>1.1634</td>
<td>1.1622</td>
</tr>
<tr>
<td>1 2 2</td>
<td>1.1408</td>
<td>1.1411</td>
</tr>
<tr>
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<td>1.1086</td>
<td>1.1079</td>
</tr>
<tr>
<td>2 0 2</td>
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</tr>
<tr>
<td>2 3 1</td>
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</tr>
<tr>
<td>0 4 2</td>
<td>0.9410</td>
<td>0.9413</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison of the observed and calculated d-spacings of the Ammm structure of GaSb at 22.5 GPa.

(without heating). However, work performed by Mezouar et al. (1999a) shows that the β-tin phase is observed at room temperature under hydrostratic conditions, as mentioned in Section 4.1. The experiments presented in this thesis have been made using a mixture of methanol:ethanol (4:1 in volume) pressure transmitting medium where perfect hydrostaticity cannot be assured.

However, for the purpose of obtaining more information about the Imma and β-tin phases, an in situ hp/ht experiment has been made, using the Dynocell, to observe the transition between Imma and β-tin. A sample at 15.2 GPa in the Imma phase has been heated to 673 K. The changes in the profiles as temperature increases is illustrated in Fig. 4.8. The lattice parameters obtained from the Rietveld refinement of these phases are grouped in Table 4.2.

It can be seen from the data collected at 373 K that the orthorhombic Imma phase tends to transform to a tetragonal structure as Δ value decreases and the ratio b/a increases towards 1. The increase in the lattice parameters, clearly, indicates that the sample is expanding as the temperature increases. The thermal expansion effects have also been observed with a drop in the sample pressure. From the data collected in this work, it has been estimated, from the shift of the peak positions, that the pressure in
Figure 4.8: Transition from the $Imma$ phase to the $\beta$-tin phase in GaSb taken at 15.2 GPa as temperature increases to 673 K. The asterisks are discussed in the text.
GaSb decreases by ~0.5 GPa for each temperature increment of 100 K, when using the Dynocell. It can be deduced that the transition from the Imma to β-tin phase occurs between 373 K and 473 K.

Heating powder samples releases non-hydrostatic stresses, making the peak profiles much sharper. In these conditions the β-tin phase has been obtained, which is in agreement with the work performed by Mezouar et al. (1999a) at room temperature. Very recent theoretical work (Libotte et al. (2000)) has shown that the Imma phase is stabilised under the influence of non-hydrostatic compression, confirming the experimental work of Mezouar et al. (1999a). However, it cannot be concluded that the Imma structure is simply a consequence of non-hydrostatic conditions.

Finally, it has been noted that every profile obtained after heating contains some additional peaks, marked by an asterisk, over a range of pressures. The origin of these peaks is not clear. Data have been collected with and without the pressure-transmitting medium and with different gasket materials (W and Re) to investigate possible contamination due to sample environment on heating. The patterns subsequently collected were still exhibiting these additional weak peaks. Sample contamination (by the gasket or pressure-transmitting medium) is therefore excluded. The other possibility is that these extra peaks are related to the intrinsic behaviour of GaSb. It could be the presence of an additional phase, only formed at high temperature, but the weak intensities of the peaks make it very difficult to solve. This additional phase always accompanies the β-tin and Ammm phases. From the in situ hp/ht study, it can be seen that these peaks are present from the pattern obtained at 473 K and grow and sharpen on temperature increase. In fact, they always seem to appear at about the same temperature (i.e. 473 K) for all the patterns collected to date. The powder rings in the pattern

<table>
<thead>
<tr>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>b/a</th>
<th>Δ</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2547(4)</td>
<td>5.1931(1)</td>
<td>2.8795(2)</td>
<td>0.9882</td>
<td>0.3727(1)</td>
<td>RT</td>
</tr>
<tr>
<td>5.2611(3)</td>
<td>5.2076(6)</td>
<td>2.8952(2)</td>
<td>0.9898</td>
<td>0.3142(1)</td>
<td>373</td>
</tr>
<tr>
<td>5.2264(1)</td>
<td>5.2264(1)</td>
<td>2.8991(1)</td>
<td>1.0000</td>
<td>0.2500</td>
<td>473</td>
</tr>
<tr>
<td>5.2383(1)</td>
<td>5.2383(1)</td>
<td>2.9524(1)</td>
<td>1.0000</td>
<td>0.2500</td>
<td>578</td>
</tr>
<tr>
<td>5.3620(1)</td>
<td>5.3620(1)</td>
<td>2.9963(1)</td>
<td>1.0000</td>
<td>0.2500</td>
<td>673</td>
</tr>
</tbody>
</table>

Table 4.2: Lattice parameters from the Rietveld refinement of the Imma (at RT and 373K) and β-tin structures of GaSb taken from 15.2 GPa as temperature increases.
obtained above 573 K are very "spotty", including the one corresponding to the extra phase. This is an indication that the sample had started to recrystallize, suggesting that these unknown peaks are characteristic of the sample.

Despite the uncertain nature of these peaks, it is clear that they are not in the correct 2θ-position to be the difference reflection peaks, necessary for a site-ordered structure. The matter of site-ordering is discussed below.

### 4.3.2 Site-Ordering

A characteristic of all the hp and hp/ht phases, found so far, in GaSb is that they appear to be long-range site-disordered. Diffraction profiles of the Imma, β-tin and Ammm structures clearly show the complete absence of the difference reflection peaks. The length scale of ordering has been estimated to be about two unit cells for each phase. If the domain size of ordering was larger, it would then be possible to detect the difference reflection peaks.

Fig. 4.9(a) illustrates a Rietveld refinement fit of the Imma structure at 15.8 GPa. The two insets show the absence of the strongest difference reflections peaks ((110), (310) and (130)). The Rietveld refinement fits to the calculated profiles of an ordered and disordered structure produce respectively $\chi^2_{ord} = 0.1884$ and $\chi^2_{dis} = 0.0959$. Similar fits have been made for the β-tin ($\chi^2_{ord} = 0.3057$ and $\chi^2_{dis} = 0.1774$) and Ammm structures ($\chi^2_{ord} = 1.181$ and $\chi^2_{dis} = 0.8423$). In both cases, the difference reflection peaks are completely absent, as it can be seen in Fig. 4.9(b) and Fig. 4.9(c). The profile in Fig. 4.9(b) has been obtained at 673K, where the complete absence of the difference reflection peaks suggests that kinetic effects are not responsible for site-disordering.

GaSb is, so far, the only semiconductor compound to have all its different hp and hp/ht phases site-disordered. However, in order to get information about the site-ordering over nearest-neighbour distances, it is necessary to use other experimental techniques to complement the x-ray diffraction method (e.g. EXAFS). Therefore a complete characterisation is not possible without such a study.
CHAPTER 4. HP/HT DIFFRACTION STUDIES OF GaSb

Figure 4.9: Rietveld refinement fit of the site-disordered (a) Imma structure to a profile of GaSb collected at 15.8 GPa, (b) $\beta$-tin structure at 15.2 GPa and 673 K and (c) Ammm structure at 22.5 GPa. The two insets show the complete absence of the strongest difference peaks (110), (310) and (130) in the Imma profile and (110) and (310) in the $\beta$-tin and Ammm fits.
4.4 Conclusions

By using a very basic heating technique, it has been possible to discover and identify a new phase of GaSb, not observed at room temperature. This phase, like the \( \beta \)-tin structure, appears to be stable on cooling back to room temperature. It is interesting to note that the "diatomic equivalent" of this site-disordered phase in GaSb has been observed in InSb at much lower pressure (see Chapter 6). Both phases are related to the \( \text{Imma} \) structure, described in Section 4.1. The \( \text{Immm} \) structure is obtained from the diatomic "equivalent" of \( \text{Imma} \) when \( \Delta = 0.5 \), while the \( \text{Ammm} \) phase is simply a "monatomic equivalent" of that structure.

The effect of temperature on the body-centered \( \text{Imma} \) structure has been to increase the symmetry by transforming it into a tetragonal structure and, at higher pressure, to change into a lower-symmetry face-centered structure. The discovery of the \( \text{Ammm} \) phase, not previously observed at room temperature, suggests that the most recent P-T phase diagram of GaSb is not complete and should be, at least, extended above 8 GPa. However, no information about transition boundaries between the \( \beta \)-tin and \( \text{Ammm} \) phases could be obtained.

Simultaneously, it has been shown that all the hp and hp/ht phases, found so far, are site-disordered at least over a long-range scale. An interesting point comes from the \( \beta \)-tin structure. As mentioned earlier, none of the binary compounds form the diatomic \( \beta \)-tin structure. Even under hydrostatic conditions, this phase appears to be site-disordered. It seems that the \( \beta \)-tin structure is characteristic of monatomic systems and the observation of this phase in GaSb (as well as in InSb) suggests that any ordering should occur over a very short length scale. It is, therefore, of considerable interest to show on which length scale this behaviour occurs. However, different experimental techniques, such as x-ray spectroscopy, need to be used to extract structural information on a local scale. A complete study of the structural short-range order in the different phases of GaSb, using an absorption spectroscopy technique, has been made and is presented in the following chapter.
Chapter 5

Structural Ordering in GaSb: an EXAFS study

5.1 Introduction

The need to explore further the structural ordering of GaSb over a short-range scale has led the author to conduct high-pressure experiments using a completely different experimental method, i.e. the Extended X-ray Absorption Fine Structure (EXAFS) technique. This chapter describes the basic theory, the experimental set-up on Station 9.3 at SRS and the standard data analysis procedure of this specific experimental method. This work has been carried out in collaboration with the members of the Solid State Physics Group from De Monfort University in Leicester. The author has been partially involved in the experimental data collection and some aspects of the data analysis. The second part of the chapter presents the results and conclusions of this study.
CHAPTER 5. STRUCTURAL ORDERING IN GASB: AN EXAFS STUDY

5.2 An Extended X-ray Absorption Fine Structure Study

5.2.1 Basic Theory

When x-rays pass through matter, they can be absorbed, for example, by a photoelectric process — the excitation of the core electrons to unoccupied levels. If the absorption coefficient is measured as a function of energy, sudden increases in absorption (the absorption edges) at specific photon energies are observed. X-ray Absorption Fine Structure (XAFS) refers to variations in the x-ray absorption coefficient close to an x-ray absorption edge.

This phenomenon was observed experimentally by Kronig in 1931, who was one of the first to attempt to explain these changes in x-ray absorption (Kronig (1931)). However, despite the fact that the basic explanation of this effect in terms of quantum mechanics was known at that time, the nature of the phenomenon remained unclear until 1971 when Sayers et al. (1971) derived an equation that could explain the essential physics of the process along with a simple method for data analysis. Later, when high-energy sources became available for general use, the number of XAFS experiments started to grow. Today x-ray absorption fine structure spectroscopy is considered as an essential tool for the investigation of the local structure around selected atomic species in solids, liquids and molecular gases (Hasnain (1991)).

The level of structural information given by a single XAFS spectrum is small compared to that provided by x-ray diffraction. However a “well-chosen” experiment can deliver unique information not accessible by other techniques. For example XAFS, a “short-range order technique”, is particularly useful when combined with complementary techniques such as x-ray diffraction, a “long-range order technique” (Bunker (1997)).

To understand the XAFS phenomenon, it is convenient to illustrate how an absorption spectrum is collected during a typical experiment at a synchrotron radiation source. A double crystal monochromator selects the wavelength of the polychromatic x-rays. The monochromatic beam then passes through the sample which absorbs the incident x-rays. The incident flux and transmitted x-ray flux are measured simultaneously with
Figure 5.1: Schematic illustration of an x-ray absorption experimental set-up at a synchrotron radiation source.

gas ionization chambers. An overview of a XAFS experimental set-up is shown in Fig. 5.1.

The absorption coefficient $\mu(E)$ can be calculated from the transmitted ($I_t$) and the incident ($I_0$) fluxes by the expression

$$\frac{I_t}{I_0} = e^{-\mu(E)x}$$

(5.1)

where $x$ corresponds to the thickness of a homogeneous sample. The absorption coefficient decreases as the energy $E$ increases except at particular values of energy, characteristic of the elements within the sample, where the absorption coefficient suddenly increases rapidly. The sudden rise in absorption is called the absorption edge, as mentioned earlier, and the oscillating part of the high-energy side of the edge is known as the fine structure. A XAFS spectrum of cubic ZnS is illustrated in Fig. 5.2.

A sudden increase in absorption occurs when an incident x-ray photon has just enough energy to produce a transition of an electron from the $1s$ state (K-edge) of some element in the sample (in this case Zn) to an unfilled state of p-character (corresponding to an angular momentum $l = 1$ with respect to the absorbing atom). The near post-edge region usually refers to X-ray Absorption Near Edge Structure (XANES) transitions ($E \leq 30eV$) as opposed to the “well-above” absorption edge region ($E \geq 30eV$) called the extended x-ray absorption fine structure (EXAFS), where the oscillations are ob-
served. It is the EXAFS region that provides information on the local neighbourhood of the absorbing atom. Edges from less deeply bound levels also occur at lower energies. The so-called L-edges are used for higher atomic number elements when the K-edge energies are experimentally difficult to reach. For simplicity, only K-edge absorption will be considered.

The absorption probability can be derived from time-dependent perturbation theory. A detailed quantum mechanical treatment has been made by Lee et al. (1975) and Stern (1974). Only the underlying principles will be described here for simplicity and clarity.

The mechanism that causes the variations in the spectrum can be understood by considering the following situation, shown in Fig. 5.3.

If there are no atoms surrounding the excited atom, the final state wavefunction would only consist of a wave emerging from the central absorbing atom, illustrated in Fig. 5.3 as the outgoing solid lines. Therefore the x-ray absorption coefficient would vary monotonically with energy. If the excited atom is surrounded by other atoms as in a solid or a molecule, the outgoing wave scatters from the surrounding atoms producing ingoing waves as shown with the dotted lines in Fig. 5.3. The outgoing and ingoing parts of the final state wavefunction can interfere either constructively or destructively, depending on the electron wavelength and the distance to the neighbouring atom. As
the incident energy $E$ is scanned above the threshold energy of the absorption edge $E_0$, the kinetic energy of the photoelectron $E - E_0$ changes. Therefore its momentum $\hbar k$ and wavelength $2\pi/k$ also vary since they are related by conservation of energy by the expression $\hbar^2 k^2/(2m) = E - E_0$. This interference effect modulates the absorption probability, giving rise to oscillations in the absorption coefficient. It is in this way that the absorption coefficient vs energy records a spectrum of the spatial distribution of neighbouring atoms. Using quantum mechanical considerations, a simple expression for EXAFS can be deduced.

The absorption coefficient $\mu$ can be considered as the isolated atom absorption coefficient $\mu_0$ times a correction factor $\chi$:

$$\mu = \mu_0 (1 + \chi)$$  \hspace{1cm} (5.2)

where $\chi$ is the fractional change in absorption coefficient induced by surrounding atoms. Using various approximations, described below, Sayers et al. ((1970) and (1971)) were able to derive a simple expression that became the so-called EXAFS equation. They considered the surrounding atoms in terms of a system of point scatterers where $\chi(k)$ can be written as a sum of contributions corresponding to increasing numbers of scattering events. Therefore, for a K-edge excitation, an atom $i$ at relative distance $r_i$ from the central atom contributes to the EXAFS
CHAPTER 5. STRUCTURAL ORDERING IN GASB: AN EXAFS STUDY

\[ \chi(k) = -S(k) \sum_i \frac{1}{kr_i^2} |f_i(k)| e^{-2r_i/\lambda_e} \sin(2kr_i + 2\delta_i(k) + \theta_i) \]  

(5.3)

where

\[ k = \sqrt{2m(E - E_0)/\hbar^2} \]  

(5.4)

and \(|f_i(k)|\) and \(\theta_i\) are respectively the backscattering amplitude and the phaseshift of the surrounding atom \(i\); \(\delta_i(k)\) is the phase shift of the photoelectron caused by the potential of the excited central atom and \(kr_i\) is the phase shift gained when arriving at the atom \(i\) located at \(r_i\) from the central atom; the total phaseshift experienced by the photoelectron is \(2kr_i + 2\delta_i(k) + \theta_i\) as it travels to the atom \(i\) and back from it while undergoing the central atom phaseshift twice (leaving and entering again) and also undergoes a phaseshift of \(\theta_i\) at the neighbouring atom \(i\); \(S(k)\) is the amplitude reduction factor to account for energy loss due to multiple excitations at the central atom; and \(e^{-2r_i/\lambda_e}\) is a damping factor depending on the ratio of the distance travelled \(2r_i\) to the electron mean free path \(\lambda_e\). \(S(k)\) and \(e^{-2r_i/\lambda_e}\) approximate the amplitude lost due to inelastic scattering. The factor \(1/r_i^2\) can be regarded as the product \(1/r_i \cdot 1/r_i\) accounting for the decrease in intensity of the wave propagating out to the scatterer \(i\) and then back to the central atom.

It is important to note that several approximations have been made to produce this simple theory:

(i) the potential energy of the photoelectron propagating through the sample is considered within the “muffin-tin” approximation, a simple model where a solid is defined as an array of touching spheres using a regular lattice and in which the potential inside each sphere is equivalent to the potential of a single atom with spherical symmetry

(ii) it is assumed that only a single electron is excited directly

(iii) only backscattering from each neighbouring atom is considered, multiple scattering is neglected

(iv) the incident photoelectron wavefunction is approximated as a plane wave, since
the interatomic distance is larger than the atomic radius

Modern theory now takes into account the effects due to the plane wave and single scattering approximations (Rher et al. (1991)). Also without a multiple scattering factor, $\chi(k)$ is approximated as a simple linear sum of contributions from backscattering atoms. Equation (5.3) is a sum of damped sine waves, which means that each atom contributes a sinusoidal signal that, when plotted versus $k$, oscillates more rapidly the larger the distance. The stronger the scattering amplitude the larger the signal.

Experimentally data are averaged over the whole sample but the instantaneous atomic positions may vary due to thermal motion and structural inhomogeneity. An x-ray absorption fine structure experiment takes a “picture” of the instantaneous configurations of atoms since the lifetime of the excited state is limited by the lifetime of the core hole (the vacancy in the initial 1s state). The core hole level widths $\Delta(E)$ are larger than 1 eV and correspond to time scales of $\tau = \hbar/\Delta(E) \leq 10^{-15}\text{s}$, which is approximately $10^{3}$ times shorter than the periods of interatomic vibration. For randomly oriented polycrystalline samples, an isotropic average around the central atom must be made. The contributions from atoms of the same atomic number and at similar distances from the absorbing atom may not be distinguishable from each other. It is therefore convenient to conceptually group the atoms together into “coordination shells”. For small distance variations within a shell, when the effects of static disorder are negligible, equation (5.3) becomes

$$
\chi(k) = -S(k) \sum_j \frac{N_j}{k R_j^2} |f_j(k)| e^{-2R_j/\lambda} e^{-2k^2\sigma_j^2} \sin(2kR_j + 2\delta_j(k) + \theta_j) \tag{5.5}
$$

where $N_j$ is the number of atoms in the coordination shell $j$, and $\sigma_j^2$ is the mean square variation of distances (or the Debye-Waller factor) around $R_j$ to atoms in the $j^{th}$ shell. Equation (5.5) is the classic EXAFS equation. More advanced theories include multiple scattering corrections and take into account the effect of static disorder (Rher et al. (1990)).
CHAPTER 5. STRUCTURAL ORDERING IN GASB: AN EXAFS STUDY

5.2.2 The Experiment

The high-pressure EXAFS experiments were performed on Station 9.3 at Daresbury Laboratory using the HI-PREXX facility, implemented by members of the Solid State Physics Group of De Montfort University in Leicester (Sapelkin et al. (2000)).

Station 9.3 is located approximately 20 m from the 5T superconducting wiggler. The wavelength is selected by a double-bounced water-cooled channel cut Si(111) scanning monochromator to smoothly vary the energy of the beam. Harmonic rejection is ensured by offsetting the second crystal of the monochromator from the parallel initial position. The collection scan time was approximately ten minutes. All the data were collected at the Ga K-edge (E ~ 10.7 keV) and at room temperature (for practical reasons). A schematic diagram of the experimental set-up required for EXAFS experiments with synchrotron radiation is illustrated in Fig. 5.1.

Samples were loaded into diamond-anvil cells (Mao-Bell and Merill-Bassett cell type) and heated off-line in furnace to obtain the hp/ht phases. The same samples prepared for the diffraction experiments have been used for the present study. Pressure was measured at room temperature with the ruby fluorescence technique described in Chapter 3.

The use of the diamond-anvil cell for high-pressure EXAFS studies presents serious difficulties, compared to ambient pressure experiments (Shinomura et al. (1978)). Since the diamonds are single crystals, Bragg reflections occur at specific energies producing significant contamination peaks in the spectra, known as "diamond glitches". To overcome this problem Ingalls et al. (1980) used a B₄C anvil cell that could reach pressures of 10 GPa. Later Werner and Hochheimer (1982) developed a new cell for EXAFS measurements that could be used, though only up to 0.8 GPa. Further progress was reported by Sueno et al. (1986) who were able to collect EXAFS data near the Ni K-edge with a diamond-anvil cell without the contamination peaks from the anvils.

The HI-PREXX apparatus used for the data collection presented in this thesis has been designed to minimize this effect. This facility is described below.

HI-PREXX can be used for in situ, x-ray diffraction and photoluminescence experiments. The apparatus consists of a large breadboard equipped with He-Cd laser and
Figure 5.4: Schematic diagram of the HI-PREXX facility for high-pressure EXAFS data collection on Station 9.3 (Sapelkin et al. (2000)).
a spectrometer, as shown in Fig. 5.4. A Huber stage is mounted on the breadboard and supports a smaller breadboard where the optical system is arranged. The optical set-up consists of two lenses and a beamsplitter located at 90° from the direction of the beam. A mirror, positioned at 45° from the direction of the incident x-rays, diverts light to the optical system. A hole in the mirror allows the x-rays to go through the diamond-anvil cell. The confocal geometry of the system makes optical alignment straightforward. Also with this arrangement the DAC alignment does not interfere with the optical alignment. To align the sample with the x-ray beam, it is necessary to allow translational and rotational motions of the cell. Translations can be made manually. And as the cell is also mounted on a rotation table, which can be controlled remotely from outside the experimental hutch, careful rotations can be performed to find the best position of the DAC to obtain high quality data without contaminant peaks. The HI-PREXX facility allows contaminant-free EXAFS spectra to be collected up to ~1000 eV above the absorption edge.

5.2.3 Data Analysis Procedure

The EXAFS equation (5.5) contains the following structural parameters: the coordination number $N$, the interatomic distances $R$ and the thermal disorder parameter $\sigma^2$. It also includes functions that are characteristic of atoms in the sample: the backscattering amplitude of each surrounding atom $j$, $f_j(k)$, and the phase shift due to the central excited atom, $\delta_1(k)$.

The purpose of data analysis is to extract these structural and physical parameters as accurately as possible. Various mathematical and computational methods have been used to analyse EXAFS data (Koningsberger (1988)). This section concentrates on the standard methods, which have been used for the data analysis presented in this chapter.

The whole procedure can be divided into two main steps: (i) initial data processing or data reduction (including calibration, normalisation and background subtraction) and (ii) data analysis (model fitting and Fourier analysis) to extract structural information. Description of a simple method for data analysis has been made by Lytle et al. (1975) and Stern et al. (1975).
The first stage of data reduction consists of calibrating the data. A data set collected on Station 9.3 contains the number of counts from the various detectors recorded at each point in the spectrum. These points are defined by the position of the monochromator expressed in millidegrees. The calibration program EXCALIB converts the millidegree scale (x-scale) into an energy scale in eV. Then it is necessary to determine the position of the absorption edge to estimate the energy point where the EXAFS oscillations begin. The usual method consists of fitting the data within a few hundred electron-volts both below the edge and after the edge with low-order polynomials (linear in this case), and subsequently extrapolating them to the edge itself. The difference between the pre-edge and the post-edge fits extrapolated to the edge energy is called the edge step. Data are then divided by the size of the edge step. The y-scale is converted into the absorption scale by taking the logarithmic value of the ratio between the reference reading $I_0$ and the signal reading $I$. Once the spectrum has been calibrated and normalised (absorption vs energy), it is ready for background subtraction.

Background subtraction is essential so that the oscillatory EXAFS signal from the atomic part of the absorption $\mu(E)$ is accurately extracted from the background absorption. It is accomplished by linear least-squares fitting using cubic spline functions. This is achieved by using the program EXBACK and SPLINE. The program performs a pre-edge fit by using a straight line and a post-edge fit with multiple polynomials. After this process, the EXAFS oscillations can be extracted by subtracting the pre- and post-edge polynomials and converting the x-axis from energy to k-space. The spectrum is weighted by multiplying the EXAFS amplitude by $k^2$ or $k^3$ to enlarge the oscillations at large $k$. Once the EXAFS oscillations have been isolated, the program calculates the Fourier transform of the spectrum, which can be used as a guideline to check if the background subtraction is satisfactory and provides a first estimation of the position of the first coordination shell. Background subtraction is a critical step in the data analysis procedure since it directly affects the quality and the amount of information that can be extracted from the spectrum. It is a difficult problem to remove the background without altering the data. The spectrum amplitude is reduced and distorted if the background subtraction is too strict. If too little background is removed erroneous contributions appear in the Fourier transform, which might overlap and interfere with the first shell signal.
The last step of the data analysis procedure is to fit the data to a simulated model to extract structural information. This has been undertaken using the program EXCURV98 (Binsted (1998)). The program calculates the potentials and phase shifts of the studied system and fits the model created by the least-squares calculations to the experimental data.

It is important to note, at this stage, one of the main limitation of the EXAFS model fitting compared to x-ray diffraction simulations. An EXAFS spectrum is a 1-dimensional curve derived from a 3-dimensional material. Therefore the system is underdetermined and there may be several models that give a “good” fit. It is important, therefore, to use all the information known about the system to reduce the number of variables as much as possible. For example, lattice parameters and coordination numbers can be extracted easily from structural x-ray diffraction refinement, for crystalline materials, and subsequently used in the EXAFS analysis. The information contained in EXAFS data is limited by the fact that the spectrum extends over a finite range in \( k \)-space (\( \Delta k \)) and \( r \)-space (\( \Delta R \)). According to the Nyquist’s sampling theorem, the number of independent data points are:

\[
N_{\text{ind}} = 2\Delta k \Delta R / \pi \quad (5.6)
\]

The degree of determinacy in the system is given by \( N_{\text{ind}} / p \), where \( p \) is the number of parameters. EXCURV98 can make an estimate of \( N_{\text{ind}} \) and \( p \). The program gives an indication of the quality of the fit to the EXAFS data in \( k \)-space with the \( \chi^2 \) parameter:

\[
\chi^2 = \frac{N_{\text{ind}}}{N(N_{\text{ind}} - p)} \sum_i^N w_i (\chi_{\text{exp}}^i(k) - \chi_{\text{th}}^i(k))^2 \quad (5.7)
\]

where \( N \) is the number of data points in the spectrum and \( w_i \) is a weighting factor for each data point \( i \), which contains both statistical noise and experimental instrumentation noise. Also systematic errors, such as thickness effect, inaccurate theory or non-ideal background subtraction, remain present. Therefore \( \chi^2 \) cannot be estimated accurately but it can be used for comparison.

In recent years, substantial progress has been made in the development of accurate
computational codes for the theoretical calculation of EXAFS spectra which include, for example, multiple scattering factors (Rher and Albers (2000)). Despite these recent advances in the theory and simulation, the inherent problem of limited information content in the EXAFS data remains unresolved so the determination of a complete 3-d structure is not possible. However, combining information available from other sources into EXAFS modeling allows new information to be obtained, which may not be accessible by any other technique. The data collected here have been analysed by using the information given by x-ray diffraction. The results are presented in the following section.

5.3 Results and Analysis

This section presents the results and analysis of the EXAFS study on the structural ordering in GaSb. The three high-pressure phases of GaSb, described in the previous chapter, were investigated: the room temperature Imma phase and the high-temperature β-tin and Ammm structures.

The samples of GaSb were a finely ground powder obtained from a starting material of 99.99 % purity from Aldrich Company. Data were collected on Station 9.3 at SRS, Daresbury Laboratory, using the HI-PREXX facility. Experimental details have been given in Section 5.2.2.

A diffraction pattern of each phase was recorded prior to the EXAFS data collection in order to determine accurately the nearest-neighbour distances around the central Ga atom (bond lengths) from the known lattice parameters. The values were then kept fixed during refinement. For each phase, the fractional occupancy of Ga and Sb around the Ga atom was refined for each coordination shell. For example, in the β-tin structure, the first coordination shell contains four atoms (= four first-nearest neighbours), all Sb-type in the ordered case or "average of Ga and Sb" (50:50 occupancy) in the randomly disordered situation. The second coordination shell has two atoms, the two second-nearest neighbours located on the c-axis. They are both Ga-type if the structure is site-ordered or an average of Ga and Sb types in a disordered structure. The fractional occupancy of both types of atom has been refined in each coordination shell for the
three structures investigated. The sum of the partial fractional occupancy of each type of atom was constrained to be constant (i.e. 100 %).

The fractional occupancy of the first-nearest neighbour atoms around the Ga atom was first determined for the known site-ordered zincblende structure (the ambient pressure phase) to estimate the reliability of the refinement. As the structure is completely ordered, it is expected that 100 % occupancy of Sb will be obtained (four atoms in the first coordination shell) around Ga. The refined value was 92 ± 10 % of Sb-type atoms around Ga, showing a good estimation of the expected value.

The Imma Phase

GaSb transforms to a site-disordered orthorhombic structure, with the spacegroup Imma, at 7.0 GPa and room temperature (see Section 4.1). The diffraction profile, as illustrated in Fig 4.9(a), shows clearly the complete absence of the difference reflection peaks. As explained in the previous chapter, this indicates that the structure is site-disordered and that any ordering can only occur over approximately two unit cells or less.

The EXAFS data were collected at 15.8 GPa. The refined lattice parameters obtained from the diffraction pattern were \( a = 5.2784(4) \) Å, \( b = 5.156(1) \) Å, \( c = 2.8859(3) \) Å and \( \Delta = 0.360(1) \). Being an orthorhombic distortion of the \( \beta \)-tin structure, the Imma phase has its nearest-neighbour atoms located on three, rather than two, coordination shells. The first shell, as described earlier for the \( \beta \)-tin structure, is split into two shells, each of them containing two atoms. From the lattice parameters, the first-, second- and third-nearest neighbour distances from the central Ga atom were deduced as \( r_1 = 2.6698(0) \) Å, \( r_2 = 2.6771(3) \) Å and \( r_3 = 2.8859(3) \) Å, as shown in Fig. 5.5 and were maintained constant during refinement. Every site in each coordination shell around the central atom was assigned, initially, a 50:50 fractional occupancy of Ga and Sb. However, the accuracy of the EXAFS analysis did not allow the distinction of the first two coordination shells due to their proximity, their respective radii, \( r_1 \) and \( r_2 \), being very close. The refined spectrum is illustrated in Fig 5.5.

The fractional occupancies in the first two shells were 70 ± 10 % of Sb (30 ± 10 % of
Figure 5.5: Least squares refinement of $k^2 \chi(k)$ function profile from the *Imma* structure of GaSb at 15.8 GPa. The atoms marked by 1, 2 and 3 are respectively the first-, second- and third-nearest neighbours of the central atom.

Ga) around Ga and 45 ± 16 % of Sb (55 ± 16 % of Ga) in the third coordination shell. The Debye-Waller factor was equal to 0.014(2) Å² for the first two shells and 0.006(4) Å² for the third shell, showing that the mean square variations of atomic positions from the central atom are small. The increase in the error in the fractional occupancy values above the first coordination shell is due to multiple scattering contributions between parameters (*Joyner et al. (1987)*). The values obtained here are considered as acceptable.

The β-tin Phase

The transition to a site-disordered β-tin structure was observed above room temperature. Details have been given in the previous chapter, where the diffraction patterns showed, once again, the complete absence of the difference reflection peaks (see Fig. 4.9(b). As for the *Imma* phase, the structure appears to be site-disordered and any ordering can only take place over the range of about two unit cells or less.

The sample used for the *Imma* study was then heated to produce the β-tin sample. On heating the pressure reduced to 8.6 GPa. The refined parameters obtained from the diffraction data were $a = 5.3119(1)$ Å and $c = 2.9548(1)$ Å. The first- and second-nearest neighbours were located at $r_1 = 2.7568(0)$ Å and $r_2 = 2.9548(1)$ Å from the
Figure 5.6: Least squares refinement of the $k^2 \chi(k)$ function profile from the $\beta$-tin structure of a GaSb sample at 8.6 GPa. The first and second coordination shells contain the atoms marked, respectively, by 1 and 2.

central atom, as shown in Fig. 5.6. The fractional occupancy was set up as 50:50 for both types of atoms on each site before refinement. The refined spectrum is shown in Figure 5.6.

The results give a fractional occupancy of $75 \pm 10\%$ of Sb ($25 \pm 10\%$ of Ga) in the first shell and $41 \pm 12\%$ of Sb ($59 \pm 12\%$ of Ga) in the second shell. The respective Debye-Waller factors were $0.016(3) \, \text{Å}^2$ and $0.001(4) \, \text{Å}^2$.

The $\beta$-tin structure obtained with another GaSb sample has also been investigated at the higher pressure of 11.2 GPa. The refined values of the fractional occupancy of neighbouring atomic species were closer to those required for a randomly disordered structure. The results gave $62 \pm 10\%$ of Sb ($38 \pm 10\%$ of Ga) in the first shell and $55 \pm 12\%$ of Sb ($45 \pm 12\%$ of Ga) in the second shell. The spectrum collected at that pressure was very similar to the one obtained at lower pressure.

**The Ammm Phase**

On heating samples taken from the Imma phase above 20 GPa, GaSb transforms to a site-disordered A-face centered orthorhombic structure with spacegroup Ammm. Details about this structure have been given in Chapter 4. The absence of the difference
reflection peaks show that the phase is site-disordered (see Fig. 4.9(c)) and that any ordering only occurs over a range of about two unit cells or less.

The EXAFS data were collected at 22.5 GPa, where the refined lattice parameters were $a = 2.6432(1) \text{ Å}$, $b = 4.8813(1) \text{ Å}$ and $c = 2.9583(2) \text{ Å}$. Due to the mirror symmetry of the structure, the neighbouring atoms around the central Ga atom are located on three distinct coordination shells with radii $r_1 = 2.6432(1) \text{ Å}$, $r_2 = 2.8539(1) \text{ Å}$ and $r_3 = 2.9583(2) \text{ Å}$, as shown in Fig. 5.9. The final refinement, illustrated in Fig. 5.7, gives 65 ± 10 % of Sb (35 ± 10 % of Ga) in the first shell, 58 ± 12 % of Sb (42 ± 12 % of Ga) in the second shell and 36 ± 18 % of Sb (64 ± 18 % of Ga) in the third shell. The Debye-Waller factors for each shell were 0.005(8) Å$^2$, 0.001(4) Å$^2$ and 0.003(5) Å$^2$ respectively.

The EXAFS results show, clearly, that there is no complete order over one unit cell (first coordination shell). However it is difficult to determine whether or not there is a significant departure from the complete random disorder 50:50. The refinements reveal that each structure tends to be slightly “more” ordered within the first coordination shell. It could be an indication that “some” short-range order exists over one unit cell, perhaps due to the fact that the data were collected at room temperature after heating. The results also show, for the β-tin phase, that the structure is “more” disordered at
the higher pressure of 11.2 GPa than at 8.6 GPa. This could be related to the fact that the lower pressure of 8.6 GPa is closer to the transition pressure to the site-ordered zincblende phase. However, it is important to note that the values obtained for the fractional occupancy lie within the standard deviation ($\sigma$ or $2\sigma$) of a 50:50 distribution. In addition, since the EXAFS refinement program EXCURV98, as mentioned in Section 5.2, is not able to give a good estimation of the statistical errors (Dent (2000)), the $\sigma$ values quoted in the analysis, are thus underestimated by a certain amount. It is therefore difficult to demonstrate whether or not complete random disorder is present.

### 5.4 Discussion and Conclusions

The EXAFS results have illuminated the previously unanswered question about the length scale of structural ordering in GaSb. The diffraction work has shown that all the hp and hp/ht phases, found so far, are site-disordered and it is now apparent that complete order does not even exist over nearest-neighbour distances, at least at room temperature.

Several interpretations can be drawn from this combined study. One of them is related to the $\beta$-tin structure. It has been reported by Nelmes et al. (1997) that this structure has never been observed in any site-ordered binary systems. The absence of the diatomic $\beta$-tin structure in the binary semiconductor compounds has been confirmed by local density approximation pseudopotential calculations (Ozolins and Zunger (1999)). The phase has been found to be unstable (at room temperature). More recently, ab initio density functional pseudopotential calculations (Ackland (2000a)), taking into account temperature as a thermodynamic variable, have confirmed this and have given an interpretation of the absence of the diatomic $\beta$-tin structure based on bond energy fluctuations with temperature. These simulations have shown that the $\beta$-tin structure has a phase diagram (bond energy vs. temperature) with three distinct phases: order, "frustrated" order (low temperature) and disorder (high temperature). The energy calculations based on the Ising model suggest that all the III-V semiconductor materials should have the ordered $\beta$-tin structure at sufficiently low temperature and some of these compounds should show both low temperature "frustrated" order and high-temperature entropic disorder, passing therefore through two temperature-induced
phase transitions. According to this model, GaSb has a transition from an order to a “frustrated” order type at 62 K and from “frustrated” order to disorder at 92 K. If this is true, the β-tin structure of GaSb is expected to be disordered at ambient conditions and above. Since these simulations allow lattice parameters to relax, breaking pure tetrahedral symmetry in some cases, these results are valid for the Imma structure as well.

The three high-pressure phases of GaSb have been found to be site-disordered, both at room temperature (Imma) and high-temperature (β-tin and Ammm) up to 673 K. These phases can also be explained by simulations (Ackland (2000a)) to be the high-temperature entropic site-disordered phases, as those observed in metallic alloys (solid solutions). As described in Section 4.2, the ability to form a binary solid solution is highly favoured when, for example, the atomic sizes of both type of atoms do not differ more than ~15%. This is the case in GaSb where the atomic radii for Ga and Sb are, respectively, 1.36 Å and 1.33 Å. The pseudopotential calculations, based on a model that takes into account size mismatch, ionicity of atomic species and temperature, have shown that GaSb is a good candidate for disordering, which is in excellent agreement with the experimental results (Ackland (2000b)).

The observation of site-disorder at any length scale in all the high-pressure phases of GaSb, found so far, interpreted as a tendency of GaSb to behave as a quasi-monatomic system, can now be understood if GaSb is regarded as behaving like a metallic alloy.

The combination of both diffraction and EXAFS techniques has given the first experimental observation of the absence of site-ordering in the three high-pressure and high-pressure/high-temperature phases of GaSb. It is, so far, the only binary semiconductor that presents such a behaviour over all its phases studied to date. The lack of complete order over such a short lengthscale as one unit cell reveals an unusual behaviour for a binary system.

The presence of the site-disordered phases in other binary semiconductors suggests that a similar behaviour could occur in these systems. For example, the site-disordered β-tin phase has been observed in diffraction patterns of InSb and, for that particular reason, this compound has been investigated by the author. A complete high-pressure high-temperature diffraction study of InSb is presented in the following chapter.
Chapter 6

High-Pressure High-Temperature Diffraction Studies of InSb

6.1 Introduction

This chapter presents a detailed high-pressure high-temperature structural study of InSb up to 7 GPa and 633 K. It is divided into two main sections. The first half of this chapter gives an overview of the previous high-pressure high-temperature work on InSb and illustrates how numerous inconsistencies and doubts about the structure determination and phase transitions have led to the establishment of a phase diagram that was thought to be correct for more than thirty years. This section provides an account of all the work, performed in the last four decades, prior to the study described in this thesis, including the latest accepted version of the phase diagram. The second half of this chapter presents the author's contribution towards an accurate mapping of the P-T phase diagram and the accurate determination of the structures of the various phases of this binary semiconductor compound. As it will be shown, InSb has one of the most complex high-pressure high-temperature behaviours among the III-V and II-VI systems.
CHAPTER 6. HP/HT DIFFRACTION STUDIES OF INSB

6.2 Previous work

The behaviour of InSb under high pressure and high temperature has been investigated for nearly forty years and it is now recognised to be exceptionally complex. It has been, therefore, one of the most extensively studied of the III-V semiconductors under pressure. The experimental work performed in the first thirty years of these studies reveals significant uncertainties about the crystal structures at high pressure and major misinterpretations about the equilibrium phases above room temperature. The advent of the image-plate area detector used with ADX techniques in the early 1990s has allowed further investigations of the structural phase transitions of InSb that has led to a complete revision of the long-accepted P-T phase diagram.

A summary of these numerous structural studies, prior to the work presented in this thesis, is described below, covering various aspects such as the exploration of the P-T phase diagram, the matter of site-ordering and the effects of sample composition variations. It is necessary to present them, at this stage, to fully understand the results obtained by the author’s work.

At ambient conditions, InSb has the cubic site-ordered zincblende structure with $a = 6.4794$ Å. A phase transition under pressure was first reported at $\sim 3$ GPa by Gebbie et al. (1960) and was attributed to melting. A year later, the zincblende structure was shown to transform to a solid phase with a volume decrease of about 20% near 2 GPa at room temperature (Jayaraman et al. (1961)). This high pressure phase was called phase II and it was proposed that it had the diatomic equivalent of the $\beta$-tin structure, by analogy with the isoelectronic element tin. Further diffraction studies, then, confirmed this by observing a transition at 2.3 GPa and determining, at 2.5 GPa, the tetragonal unit cell dimensions $a = b = 5.79$ Å and $c = 3.11$ Å (Smith et al. (1962), Jamieson (1963), Banus et al. (1963) and Hanneman et al. (1964)). While this tetragonal phase seemed to be accepted, it did not take more than three years, since its first determination, to find a different behaviour. Kasper and Branhorst (1964) did not observe a transition before reaching the higher pressure of $\sim 3$ GPa, where the cubic phase transforms to a simple orthorhombic structure with $a = 2.92$ Å, $b = 5.56$ Å and $c = 3.06$ Å. The unit cell of this phase contains two atoms located at $(0,0,0)$ and $(0,1/2, \alpha \sim 1/2)$ and the density was found to be the same as phase II within
experimental errors. This new phase was called phase IV and the question as to which was the equilibrium high-pressure phase was then open.

Two years later, McWhan and Marezio (1966) observed that InSb-II was obtained on rapid pressure increase through the transition, while InSb-IV was found if pressure is raised gradually. This was explained by Banus and Lavine (1969), who found InSb-II to be stable just above room temperature, provided that pressure increase causes the sample temperature to rise above the II-IV boundary; and then the transition from phase II to the true room-temperature equilibrium phase (InSb-IV) takes place very slowly.

By combining their own high-temperature work with other high-temperature studies (Jayaraman et al. (1961), Banus et al. (1963), Hanneman et al. (1964), Kato et al. (1966) and Banus et al. (1967)), Banus and Lavine established the boundaries between phases II and IV and made further studies to find boundaries between both phases and the phase designated as III, a proposed hexagonal structure found two years earlier (Banus and Lavine (1967)) at high temperatures (above 575 K and 3 GPa) and at high pressures (above 9 GPa at room temperature). They established what became the long-accepted P-T phase diagram of InSb, illustrated in Fig. 6.1.

The II-III-IV triple point was determined at 6.5 GPa and 450 K. The data were collected on recovered phases, obtained by quenching to \( \sim 80 \) K before releasing the pressure.
A few years earlier, Darnell and Libby (1963) had found that this sample preparation procedure, starting from 2.5 GPa and 370 K, produces a hard, machinable metal which remains stable for weeks if kept below 210 K. Data analysis showed that the structure of this material was very close to that of the $\beta$-tin structure. Further work reproduced and confirmed these results (Darnell and Libby (1964), Hanneman et al. (1964), Kasper and Brandhorst (1964), McWhan and Marezio (1966), Geller et al. (1963) and Stromberg and Swenson (1964)) and it was generally accepted that the recovered phase (i.e. the $\beta$-tin structure) corresponded to InSb-II, as drawn by Banus and Lavine (1969), despite the doubts from Kasper and Brandhorst (1964) about $\beta$-tin being the correct structure for InSb-II and McWhan and Marezio (1966) showing that InSb-IV also recovers to the $\beta$-tin phase at ambient pressure and 77 K.

Nearly ten years later, further work has been carried out in the attempt to obtain a more accurate structure determination of InSb-II,-III and -IV (Yu et al. (1978b)). The orthorhombic structure, found by Kasper and Brandhorst (1964), was confirmed for InSb-IV with $\alpha$ (the $z$ variable coordinate of the second atomic site) being $\sim 1/4$ rather than $1/2$. The spacegroup was determined to be $Pmm2$. Following the phase diagram of Banus and Lavine (see Fig. 6.1), they tried to obtain InSb-II by heating the sample but failed to index the observed pattern. They also reported a better fit of InSb-III obtained at 11.5 GPa with a primitive orthorhombic unit cell, twice the volume of that of phase IV.

A few years later, Degtyareva et al. (1983) studied the effects of small composition variations on the phases found in quenched samples. For samples with equiatomic composition 50:50, starting from 3.8 GPa and 175°C, they also found InSb-IV to have the orthorhombic structure $Pmm2$, with $\alpha \sim 1/3$, rather than $\beta$-tin. The tetragonal $\beta$-tin structure was obtained with a sample containing more Sb than In, in In$_{65}$Sb$_{35}$, starting from 7 GPa and 350°C. Further studies on the In-Sb and other binary systems, in quenched samples of different stoichiometric compositions, have shown that increasing pressure leads to the dissociation of the compound and to the formation of new metallic intermediate phases (Degtyareva et al. (1983), Degtyareva et al. (1979), Degtyareva et al. (1981), Ponyatovskii and Degtyareva (1988)).

Later, in the late 1980s, energy-dispersive synchrotron experiments were carried out on
InSb up to 66 GPa at room temperature by Vanderborgh et al. (1989). They observed the transition from the cubic zincblende structure to InSb-IV at 2.8 GPa. The structure was fitted with the $Pmm2$ symmetry, in agreement with Yu et al. (1978b) but with $\alpha = 0.38$. However, as they noted, theoretical calculations had shown that this structure was energetically unfavorable (Zhang and Cohen (1987)) because each atom has four "like" atoms (out of six) nearest-neighbours, provided that the structure is site-ordered. As in all the previous work, they could not determine whether the structure was site-ordered or not, but they assumed that it was and therefore described the true unit cell doubled along the $a$- and $c$-axis of the $Pmm2$ cell. In this configuration, each atom has six "unlike" nearest-neighbours. Above 6 GPa, they observed a transition to a phase they could not identify. This new unknown phase was called InSb-V and was noted to become more hexagonal on pressure increase until the transition to InSb-III is complete at 17.5 GPa. This phase transforms to a bcc structure (CsCl-type if ordered) at 28 GPa, which remains stable up to 66 GPa, the highest pressure yet reached (Vanderborgh et al. (1989)).

With the discovery of InSb-V in the presumably well-established region of InSb-IV, the inability of Yu et al. (1978b) to find InSb-II and the uncertainty as to whether the structure of InSb-III is orthorhombic or hexagonal (Yu et al. (1978b), Vanderborgh et al. (1989)), there was an urgent need to reexamine the crystal structures of these high pressure phases. In addition, there was a clear evidence in the published work that InSb-II does not correspond to the $\beta$-tin structure. The second strongest doublet in the profile of the $\beta$-tin phase, (220) and (211), has a separation in 2$\theta$ scattering angle of about 2/3 of that of the first doublet, (200) and (101). All the reported patterns (Smith and Martin (1962), Banus et al. (1963), Kasper and Branhorst (1964), McWhan and Marezio (1966)) do not display the (200) reflection as noted by Kasper and Branhorst (1964). Further discrepancies at higher angles were shown by McWhan and Marezio (1966) who noted the poor fit and Banus and Lavine (1969), whose misfits were hidden because they indexed half their lines as reflections not allowed by the $\beta$-tin structure.

In the early 1990s, with the development of angle-dispersive powder-diffraction techniques at SRS using an image-plate area detector, by the Edinburgh Group, a complete reexamination of the structural phase transitions in InSb up to 5 GPa was carried out and has led to the discovery of a much more complex behaviour than previously re-
Two different phase transition sequences have been found as pressure is gradually increased. They involve the cubic zincblende phase (P1) and three high-pressure phases that have been labelled P2, P3 and P4. Either (i) the cubic phase (P1) transforms at ~2.1 GPa to a mixture of a site-disordered \( \beta \)-tin-like phase (P2) and an orthorhombic phase (P3). It then transforms to the nearly-single phase P3 before recrystallizing to a different orthorhombic phase (P4) over time (several hours), or (ii) P1 transforms directly to P4 at the higher pressure of ~3 GPa.

P2 has been identified as a site-disordered \( \beta \)-tin-like structure with \( a = 5.697(1) \) Å and \( c = 3.104(1) \) Å at 2.1 GPa. This phase has been observed only as a component in mixed-phase samples, therefore the possibility that it has a small orthorhombic distortion to \( Imma \) cannot be excluded. However, it is likely to be the same phase as the true \( \beta \)-tin structure obtained previously on recovery from 2.5 GPa to ambient pressure at low temperature (Darnell and Libby (1963)), or, at least, the transition occurs on pressure decrease to ambient pressure. It was the first time that P2 had been observed at high pressure. The conclusion was that this phase is not InSb-II, which is clearly not tetragonal, as explained below. The volume change \( (\Delta V/V_0) \) at the P1-to-P2 transition was determined to be 20.5(2) %.

P3 was indexed on an orthorhombic unit cell with \( a = 5.847(1) \) Å, \( b = 5.388(1) \) Å and \( c = 3.181(1) \) Å at ~2.3 GPa. Initially P3 was thought to have the \( Imm2 \) symmetry (a diatomic equivalent of \( Imma \), see Fig. 4.1) with \( \Delta = 0.47 \) (Guo et al. (1993)) but accurate measurement of peak intensities indicated that the true structure has a spacegroup \( Immm \) — which is equivalent to \( Imm2 \) when \( \Delta = 0.50 \) (Nelmes and McMahon (1996)). Distinguishing the two structures when \( \Delta \) is close to 0.50 is extremely difficult and can only be made by the comparison of difference reflection peaks for both structures. In \( Immm \) these reflections are the ones indexed as \((hk0)\) with \( h = \text{odd} \), such as \((110)\), \((310)\) and \((130)\), whose intensities do not depend on \( \Delta \) and \((hkl)\) with \( k + l = \text{odd} \), such as \((101)\), \((301)\) and \((031)\). In \( Imm2 \), the difference reflection peaks are only those with \( h = \text{odd} \) in \((hk0)\). Therefore the two structures can be distinguished by accurate measurement of the relative intensities of groups of peaks such as \((110)/(101)\) and \((310)/(130)/(301)\). Since \( \Delta \neq 0.50 \) in \( Imm2 \), the reflections
with \( l \neq 0 \) are more intense due to an additional component in the structure factor. Data have been subsequently collected near and far from the In K-absorption-edge. Due to the effects of anomalous dispersion, mentioned in Section 4.2, the intensities of the (310), (130) and (301) reflections were greatly enhanced near the edge and reduced away from the edge, suggesting that \( \Delta = 0.50 \). It was, then, concluded that P3 is the InSb-II phase and has the site-ordered orthorhombic structure with spacegroup \( \text{Immm} \), with In at \((0,0,0)\) and Sb at \((0,1/2,1/2)\), as illustrated in Fig. 4.6(a). The volume change \( (\Delta V/V_0) \) at the P1-to-P3 transition at 2.1 GPa is 21.0(2) \% and P3 is thus 0.5(3) \% denser than P2 at the same pressure.

P4 corresponds to the phase designated as InSb-IV. All the visible peaks in the pattern could be fitted well by the \( Pmm2 \) structure, as first suggested by Yu et al. (1978b), but with \( c = 0.387(1) \) (Nelmes and McMahon (1995)) in close agreement with Vanderborgh et al. (1989). However the high sensitivity of the image-plate area detector and the effects of anomalous dispersion have revealed the presence of a large number of super-lattice reflections and the true structure was identified to have the \( Cmcm \) symmetry. This structure is a site-ordered superstructure of the site-disordered \( Pmm2 \) subcell. The indexing was made based on a unit cell with \( a = a_p, b = 2c_p \) and \( c = 3b_p \), where \( a_p \times b_p \times c_p \) corresponds to the \( Pmm2 \)-subcell (with the b- and c-axis interchanged to give a standard spacegroup setting). At 5.1 GPa, the unit cell parameters were \( a = 5.847(1) \) Å, \( b = 6.140(1) \) Å and \( c = 16.791(1) \) Å, in which 12 In and 12 Sb atoms are located in two different 4(c) positions at \((0, 0.120(1), 0.25)\) and \((0, 0.620(1), 0.25)\) respectively and two different 8(f) positions at \((0, 0.410(1), 0.089(1))\) and \((0, 0.910(1), 0.081(1))\) respectively. The volume change \( (\Delta V/V_0) \) at the P1-to-P4 transition at 3 GPa is 19.5(1) \%. P3 is thus 0.5 \% denser than P4 at the same pressure.

The InSb-IV superstructure has 24 atoms in the unit cell arranged in six NaCl-like planes. They are stacked along the c-axis and are alternatively displaced approximately by \( \pm 0.1 \) b. This proposed structure by Nelmes and McMahon (1995) is illustrated in Fig. 6.2. The tripling of the subcell \( (c = 3b_p) \) along the z-axis illustrates the site-ordering in that direction as the sequence [Sb, Sb, In] Sb, Sb, In ...

As mentioned earlier, Vanderborgh et al. (1989) proposed that the true unit cell of InSb-IV was twice the size of \( Pmm2 \) cell along x and y (in the setting in Fig. 6.2) and
Figure 6.2: The $Cmcm$ superstructure of InSb-IV. The mirror planes at $z = 1/4$ and $3/4$ are indicated by the arrows. The $Pmm2$-like subcell is outlined in red.
has an ordered atomic arrangement in NaCl-like planes alternatively displayed along the y-axis by $\alpha/2 \sim 0.2$. This configuration would give a structure in which each atom has six unlike nearest neighbours that would agree with the total-energy calculations made by Zhang and Cohen ((1987), (1989)). The superstructure proposed by Nelmes and McMahon (1995) is similar to this arrangement but more complex. As shown in Fig. 6.2, only two of the six NaCl-like planes are flat. They are situated at the 4(c) positions marked by the arrows in Fig. 6.2. The four other planes are free to pucker, giving rise to significant distortions of the structure. At the flat planes planes $z = 1/4$ and $3/4$, both the In and Sb atoms have six nearest unlike neighbours at $\sim 3$ Å and two like neighbours at $\sim 3.3$ Å. The atoms in the puckered planes are surrounded by five nearest unlike neighbours at $\sim 3$ Å, with a sixth one further away at $\sim 3.5$ Å.

P4 was found to be stable up to 9 GPa, where a transition to an unknown phase occurs. This unknown phase was previously reported as hexagonal (Banus and Lavine (1967)) or orthorhombic (Yu et al. (1978b)). Using the ADX techniques, Nelmes and McMahon (1996) have shown that the transition goes through a previously undetected site-disordered intermediate phase, P5, which they found to be orthorhombic with spacegroup $I2am$ (the same structure as GaSb-II). The volume change at 9.8 GPa is $-0.3(2)$ %, which means that P5 is slightly less dense than the P4 phase. The lattice parameters of P5 were determined at 14.5 GPa to be $a = 5.661(1)$ Å, $b = 5.399(1)$ Å and $c = 3.003(1)$ Å with $\Delta = 0.392(1)$. They also observed that on moderate heating or with time, P5 transforms into InSb-III, which has the same $Immm$ structure as P3. At the P5-to-P3 transition, the volume change ($\Delta V/V_0$) is reduced by 1.8(2) %. It was then concluded that the distinct InSb-II and InSb-III phases of the phase diagram in Fig. 6.1 were one and the same phase (Nelmes and McMahon (1996)).

The work performed by Nelmes and McMahon ((1993), (1995) and (1996)) has clarified previous uncertainties but has given rise to new questions about the phase transitions and the P-T phase diagram of InSb.

**P2-P3**: as the cubic phase transforms to P2 and P3, it was noted that P2 was always accompanied by the same amount of P3 ($\sim 30$ % in this case). This could be explained by the fact that (i) if the transition goes from P1 to P2 and then P3, the pressure range of stability must be less than the pressure variation across the sample, therefore
the two phases transitions overlap, or (ii) if P1 changes directly to P3, some of the phase then transforms to P2 with a decrease in pressure due to the volume collapse at the P1-to-P3 transition. It was also observed that the peaks of P2 are significantly broader than those of P3 and do not show a strong 2θ-dependence, suggesting that the transition P2-to-P3 (then P4) is accompanied by an increase in crystallite size. Finally the δ-tin-like P2 phase appeared to be site-disordered (as observed in GaSb) and raised the question of the role of such a structure as an intermediate phase from ordered P1 to ordered P3.

**P3-P4:** the recrystallisation of P3 to P4 was observed at a pressure just above P1-to-P3 transition, indicating that the pressure range of stability of P3 is very narrow. Some evidence was found for P3 starting to change to P4 before all the zincblende phase has transformed, suggesting that there may be no stability field for P3, at least, at room temperature. Refinements of the P3-P4 pattern have shown that P4 is less dense (~ 5 %) than P3. This could explain why the recrystallisation to P4 is reduced as pressure increases and the P3-to-P4 transition does not even occur above ~ 3 GPa. In other words, if a sample of P3 is taken above ~ 3 GPa and its temperature increase above room temperature, it will remain in the P3 phase indefinitely. If the pressure is increased gradually to ~ 3 GPa, it seems that InSb (P1) transforms directly to P4 (second phase transition sequence). The observed values for the transition pressure were reported to be 3.0 GPa (Kapser and Brandhorst (1964)), 2.5 ± 0.2 GPa in Yu et al. (1978b), 3.05 GPa in Turusbekov and Estrin (1982), 2.8 GPa in Vanderborgh et al. (1989) and around 3.0 GPa in Nelmes et al. (1993). If the transitions reported at ~ 3.0 GPa are to P4, it is very interesting to remark that the first high-pressure phase transition in InSb reported by Gebbie et al. (1960) was then a transition to P4 rather than P3, four years before the discovery of P4 by Kapser and Brandhorst (1964).

**P2-P3-P4:** detailed structural analysis has shown that the shape of the P4 orthorhombic unit cell is slightly different when the phase is obtained directly from P1 as compared to that obtained from P3, even though the volume collapse (19.5 %) is the same for both transitions. However, once the transition to P4 is completed, both unit cells are identical. It can be said that, in general, fast pressure increase under strained or non-hydrostatic conditions favours the transition from P1 to P2-P3, while a slow increase in pressure under more hydrostatic conditions favours the transition from P1 to P4.
Nelmes et al. (1993) have found no obvious difference in behaviour between samples loaded with or without methanol:ethanol. Additionally, they have shown that a P2-P3-P4 mixture accounts for the pattern reported by Vanderborgh et al. (1989) to be InSb-V.

To summarize, in the range up to \(~5\) GPa, Nelmes et al. (1993) found no pressure range in which P3 is the equilibrium phase at room temperature. P4 is thus the equilibrium phase. Additionally, an intermediate narrow field may exist between P1 and P3, where P2 is the equilibrium phase or P2 could be a metastable phase which appears only on pressure decrease. Some preliminary high-temperature experiments have been carried out where samples were heated up to \(50^\circ\)C in phase P1, and after subsequent compression the product was found to be a mixture of P2 and P3. The same procedure at \(100^\circ\)C gave a clean P4 pattern, which was interpreted as having being reached via P3 and indicated (i) a boundary between P3 and P4 at approximately constant pressure and (ii) a transition from P4 to P3 on heating in the range of \(~3\) GPa to at least \(100^\circ\)C. This was not expected and therefore disagrees with the phase diagram of Banns and Lavine (1969). A sample composed of a mixture of P2 and P3 phases was found to transform to only P3 on heating up to \(60^\circ\)C and with time a further transformation occurred to P4. Another sample in the P3 and P4 phases at higher pressure was converted to P4 with some P3 remaining after ten hours at \(75-100^\circ\)C. These results showed that the equilibrium field of P4 extended well above room temperature at pressures up to \(~3\) GPa contrary to the phase diagram of Banns and Lavine (1969). Additionally, work performed by Yu et al. (1978b) described a transition from InSb-IV (P4) at \(4.6\) GPa and \(100^\circ\)C to a phase that they could not identify. It was demonstrated that the long-accepted phase diagram was incorrect and needed to be revised, especially regarding the transition from P4 (InSb-IV) to P3 (InSb-II) that was no longer found up to \(~3\) GPa and \(100^\circ\)C. Substantial high-pressure high-temperature work has been performed by the author to investigate the P4-P3 transition and will be presented in the next Section.

P3-P4-P5: in 1996, an intermediate phase was detected in the transition from InSb-IV to InSb-III at \(~10\) GPa (Nelmes and McMahon (1996)), as described earlier. They showed that P4 starts to transform to P5 at \(9.3(5)\) GPa, which was observed in all samples, then the transition from P5 to P3 could occur over a range of pressures up
to $\sim 17$ GPa or not occur at all at room temperature. Samples left for many hours (or heated) at pressures just above 10 GPa have provided the evidence that P3 is the stable phase above 10 GPa at room temperature (and up to at least 100°C). P3 then recrystallises back to P4 between 4 and 2.5 GPa on pressure decrease. It was then assumed that P3 is the equilibrium phase above a minimum pressure of $\sim 7$ GPa but this was not confirmed since the stability range of P5 could not be established.

On pressure increase, all P3 samples transform to another intermediate phase at $\sim 17$ GPa, that has not yet been characterised, and then to a site-disordered body-centered cubic structure at 21(1) GPa (Nelmes and McMahon (1996)). The lattice parameter of the bcc phase was determined at 36.7 GPa to be $a = 3.364(1) \AA$ and the volume change ($\Delta V/V_0$) was estimated to be 3.0(2) % at the P3-to-bcc transition. This phase transition was previously reported at 28 GPa by Vanderborgh et al. (1989), who found that the bcc structure was stable to at least 66 GPa.

After more than 35 years, it appears now obvious that the long-accepted InSb phase diagram by Banus and Lavine (1969) was misdirected by (i) the conviction that InSb-II and the phase recovered to ambient pressure at low temperature were the same and (ii) the appearance of InSb-II (P3) at pressures well below its equilibrium field. Despite the major revision of the phase diagram, there remained a lot to be understood about the high-pressure high-temperature phases of InSb, such as the transitions between the P3 and P4 phases, the roles played by the intermediate P2 and P5 phases and the mapping out of the true phase diagram.

In 1996, high-pressure high-temperature studies using EDX methods have been carried out to redetermine the P-T phase diagram up to 8 GPa and 800 K (Mezouar et al. (1996)). The new phase diagram to 8 GPa confirms and extends the ADX work by Nelmes and McMahon (1996). It establishes P4 as the stable phase below $\sim 8$ GPa at room temperature. P3 is the stable phase above $\sim 8$ GPa at room temperature and below $\sim 8$ GPa at high temperature. This phase diagram and, currently, the latest published version, is illustrated in Fig. 6.3.
In 1999, a new set-up for collecting data at high pressure and high temperature was developed at the European Synchrotron Radiation Facility (Mezouar et al. (1999b)). The use of the high-energies of a third-generation source combined with a new fast image-plate detector with a large-volume press has greatly enhanced the quality of the data and allowed, therefore, better structural refinement.

To illustrate the potential of this new set-up, they investigated the hp/ht behaviour of two compounds. One of them, coincidently, was InSb. They reexamined the structure of InSb-III at high temperature and found a \(\beta\)-tin-like-type tetragonal phase with space-group \(\text{I}m\text{2}\). The refined lattice parameters at 4.7 GPa and 603 K were \(a = 5.7462(2)\) Å and \(c = 3.1434(3)\) Å. The phase was obtained following the path illustrated in Fig. 6.4: pressure was slowly increased at room temperature from InSb-I to InSb-IV up to 4.7 GPa then temperature was gradually increased to InSb-III up to 603 K.

This latest work has boosted the problem of misinterpretation of the hp/ht structures of InSb and whether or not InSb-III is really tetragonal at high temperature, despite the fact that they reported previously (Mezouar et al. (1996)) that InSb-III corresponded to P3 as temperature is increased from InSb-IV at 3.7 GPa. These simple considerations have motivated the author to reproduce this simple experiment to check the validity of the results obtained by Mezouar et al. (1999b). The results of these experiments have shown that the latest P-T phase diagram is incorrect and the field of InSb-III above
Figure 6.4: The latest pressure-temperature study of the phase diagram of InSb, where the structure of InSb-III has been reexamined. The arrows indicate the path followed (After Mezouar et al. (1999b)).

room temperature needs to be revised. In addition two new high-symmetry phases have been observed, giving strong evidence of sample decomposition. The interpretation of this surprising behaviour will be discussed. What was thought initially to be a simple experiment has revealed that the latest P-T phase diagram of InSb, shown in Fig. 6.3, is incorrect and even more complex than previously reported. The results of these studies are presented below.

6.3 Results and Discussion

All data were collected on Station 9.1 at SRS, Daresbury, using the image-plate set-up described in Chapter 2 at a wavelength of 0.4654 Å. Samples from two different sources were investigated: a finely ground powder of 99.99 % purity from the Aldrich Company and a powder obtained from a In_{50}Sb_{50} single crystal to ensure purity and stoichiometry, supplied by Dr. Valentina Degtyareva from the Institute of Solid State Physics in Moscow.

In situ high-temperature work was performed using the Dynocell, as described in Chapter 3, up to 633 K. The path taken to study the different structures in the phase diagram always consisted of applying pressure to the appropriate value followed by temperature
The first part of this section describes in detail the high-pressure high-temperature phase transitions observed while reproducing the experiment performed by Mezouar et al. (1999b). It shows how the pattern they obtained can be related to the present work and how further structural investigations, by the author, can explain why and how their pattern has been misinterpreted. The matter of site-ordering and sample decomposition are discussed and finally a new version of the P-T phase diagram is presented.

6.3.1 HP/HT Phase Transitions

In an attempt to obtain the $\beta$-tin phase by heating InSb from InSb-IV, as claimed by Mezouar et al. (1999b), transitions from P4 to P3 have been investigated at three different starting pressures, as illustrated in Fig. 6.5.

Before presenting the phase transitions, it is necessary to describe, briefly, how the sample was prepared to reach the phase IV state (P4). This preparation was necessary to make sure that the sample reaches the equilibrium state, as P1 sometimes transforms into a P3-P2 mixture at room temperature. To obtain this phase, pressure is slowly increased from ambient pressure to $\sim$1.4 GPa at room temperature. Then the tem-
Figure 6.6: The path followed in the P-T phase diagram to obtain a sample in the single-phase P4. The dashed line shows an alternative route, on cooling to room temperature, to obtain P4.

Temperature is raised up to ~373 K and while at that temperature, pressure is applied to ~7.0 GPa then released to ~3.5 GPa. Samples were left at ~373 K for approximately 90 minutes. On temperature decrease to room temperature, pressure is decreased to ~2.5 GPa then increased again at ~303 K up to ~3.5 GPa. The path followed in this preparation is shown in Fig. 6.6. After a few hours, when the sample is completely back to room temperature conditions, the pressure was measured and was always found to remain stable from the value recorded at ~303 K. In this example, it is ~3.5 GPa. After this procedure, an x-ray powder pattern is collected at room temperature to verify that the sample has actually reached the pure single-phase P4. The pressure is then raised to the appropriate value.

For the experiments presented here, this sample preparation has been undertaken off-line, using the Dynocell, where pressure and temperature were measured by the techniques described in Chapter 3.

Path A

The transition from P4 to P3 was first investigated at 5.2 GPa. According to the phase diagram in Fig. 6.5, the transition occurs at 473 K. Temperature was increased slowly up to 593 K. The sequence of phase transitions observed is shown in Fig. 6.7. Each
colour indicates a different phase: red represents P4, blue P3, green P2 (β-tin phase), violet and pink represents the new phases that are labelled, for now, the "violet phase" and the "pink phase" respectively. At that time, these two new phases were unknown and details on how they have been indexed will be given later. The phase labelled "extra" corresponds to the peaks marked by the asterisks and will be discussed later.

Firstly, it can be seen from profile (a) in Fig. 6.7 that the P4 phase contained a small residue of P3, as indicated by the arrow (labelled 1), despite careful preparation. Little change is observed at 373 K. As temperature is increased to 473 K, a transition takes place where two distinct changes are observed, as shown in the profile (c):

(i) the changes in the intensities of the peaks labelled 1 and 2 indicate that P3 has grown up while P4 started to disappear

(ii) the single peak, labelled 3, shows the presence of the β-tin phase P2, which is clearly a very minor component when a comparison is made to the P3 peak labelled 4

Despite the presence of a residue of P2, the transition observed at 473 K agrees with the phase diagram. However, as temperature is increased above the transition, three unexpected features appear in the pattern, as shown in the profile (d) and subsequently in the profiles (e), (f) and (g) of Fig. 6.7:

(i) P2 is growing at the expense of P3 and becomes dominant, relative to P3, as temperature increases

(ii) a new phase appears, as indicated by the peak marked in pink and the first peak labelled 5 splits on further temperature increase as seen in profile (g), and

(iii) extra peaks, marked by an asterisk, are observed

Points (ii) and (iii) will be discussed later.

As far as the transition from P4 to P3 is concerned, it can be clearly seen from the data that this transition does occur at ~473 K, as predicted by the phase diagram, but P3 decreases quite rapidly as temperature increases. P2 seems to be the dominant phase at high temperature. In all the data collected around 5.0 GPa, this phenomenon has been observed for the samples provided from the two different sources. P2 appears
Figure 6.7: The sequence of phase transitions starting from a sample of P4 at 5.2 GPa as temperature is raised up to 593 K. The asterisks and arrows in the various profiles are discussed in the text. The peaks marked by “G” are from the gasket.
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to be the stable phase at elevated temperatures. The observation β-tin phase at high
temperature is quite surprising as this phase was previously obtained on recovery to
ambient pressure at low temperature (Banus and Lavine (1969)) in the region of InSb-
II in Fig. 6.1. Later, Nelmes et al. (1993) observed this phase at room temperature.
The P-T region reached following path A corresponds to the area of InSb-III where
the β-tin phase is not expected (Mezouar et al. (1996)), according to the latest version
of the phase diagram. However, the presence of the β-tin phase in this work can be
related to what has been observed by Mezouar et al. (1999b).

They studied the P4-to-P3 transition for samples at 4.7 GPa and heated from ambient
temperature to 603 K. The pattern has been refined with the β-tin structure with
spacegroup $I4m2$, as shown in Fig. 6.8. However, from their analysis, three main
important factors remain unclear:

(i) the powder pattern in their paper, corresponding to the step 2 in Fig. 6.4, clearly
indicates that their sample was not in the P4 state before heating but in the P3-P2
mixed state,

(ii) the presence of weak peaks marked by an asterisk are attributed to contamination
from the sample environment, but their powder pattern clearly reveals the presence of
extra lines, below the first β-tin doublet, that has not been included in their refinement
(Fig. 6.8 shows that the data have been truncated below 3°). These extra lines could,
possibly, correspond to the strongest peak of the "pink" and unknown phases, and
finally,

(iii) the refinement has been made with the spacegroup $I4m2$, which corresponds to an
ordered β-tin structure, and not the site-disordered phase, as they claim, which has the
spacegroup $I4_{1}/amd$ and no discussion about the difference reflection peaks has been
attempted.

In order to clarify these three points, further data have been collected by the author
at high temperature starting with a mixed P3-P2 sample to satisfy (i) and understand
(ii) and discussion about site-ordering of the β-tin phase has been made to clarify (iii).
The work performed to verify the first two points has led to the characterization of
the new phases, labelled in violet and pink, as will be described below. The matter of
site-ordering will be discussed in Section 6.3.2.

The path A, shown in Fig. 6.5, was followed with samples taken from the P3-P2 mixed state. This state can be reached when pressure is applied quickly from the P1 phase at room temperature, as explained in Section 6.2. Samples were taken to 5.0 GPa and then heated to 608 K. The phase transitions obtained by increasing temperature to 473 K, 573 K and 608 K are illustrated in Fig. 6.9.

A behaviour similar to the one observed in Fig. 6.7, where the sample of P4 is heated, takes place. As temperature increases, the β-tin structure grows at the expense of P3, and this transformation is almost complete at 573 K as shown in profile (c) of Fig. 6.9. Once again, above the transition temperature (473 K at ~5.0 GPa), additional peaks appeared: the peaks marked in violet and pink and the ones marked by an asterisk. And above 573 K, as indicated in profile (d) of Fig. 6.9, the “violet phase” and the “pink phase” are clearly dominant, with the intensities of the additional peaks having grown up slightly. The d-spacings of the four peaks marked in violet have been measured.

The exact ratios between these values (\(\sqrt{2}, \sqrt{3}/\sqrt{2}\), etc) indicated that the lattice was cubic. The structure was then refined with the spacegroup \(Pm\bar{3}m\). The unit cell size at ~5.0 GPa was \(a = 3.038(4) \, \text{Å}\) and it contains one atom at (0,0,0). The “violet phase” is therefore simple cubic. The difference between the observed and calculated d-spacings, \((d_0)\) and \((d_c)\) respectively are given in Table 6.1.
Figure 6.9: The sequence of phase transitions of a P3-P2 mixed sample of InSb at 5.0 GPa as the temperature is increased up to 608 K. The asterisks and arrows are discussed in the text.
Table 6.1: The indexing and comparison of the observed and calculated d-spacings of the simple cubic phase \(Pm\bar{3}m\) observed at \(\sim5\) GPa and 608 K.

<table>
<thead>
<tr>
<th>h k l</th>
<th>(d_\text{o}) (Å)</th>
<th>(d_\text{c}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>3.0386</td>
<td>3.0380</td>
</tr>
<tr>
<td>1 1 0</td>
<td>2.1474</td>
<td>2.1482</td>
</tr>
<tr>
<td>1 1 1</td>
<td>1.7527</td>
<td>1.7540</td>
</tr>
<tr>
<td>2 0 0</td>
<td>1.5218</td>
<td>1.5190</td>
</tr>
</tbody>
</table>

As shown in profile (d) of Fig. 6.9, the cubic phase appears to be mixed with another phase marked in pink. At \(\sim5.0\) GPa and above 573 K, this new phase seems to grow simultaneously with the cubic phase. The splitting of the (100) peak, as shown in profile (g) of Fig. 6.7 and even more clearly in profile (c) of Fig. 6.9, is an indication that the cubic phase was "hiding" another structure that appears to be structurally related to the cubic lattice. A slight distortion of a cubic structure can be obtained by "pulling the corners" aligned with the body diagonal of the cube (i.e. the [111] direction). This deformation would give rise to a rhombohedral lattice where \(\alpha\) is close to 90° (\(\alpha\) is the angle between the edges of the lattice along the x, y and z directions, and when \(\alpha = 90°\) the lattice becomes cubic).

The structure was then refined with the space group \(R\bar{3}m\) and lattice parameters \(a = 3.082(1)\) Å and \(\alpha = 88.013(1)°\). As will be explained in Section 6.3.3, the structure is better described with the hexagonal axes, where \(a = 4.283(1)\) Å, \(c = 11.042(4)\) Å and the variable coordinate \(z = 0.239(1)\), as illustrated in Fig. 6.14 in Section 6.3.3. The unit cell has, therefore, 6(c) atoms located at (0,0,z). The "pink phase" was then determined as being rhombohedral. The difference between the observed and calculated d-spacings of the rhombohedral structure, \((d_0)\) and \((d_c)\) respectively, are shown in Table 6.2. The remaining extra peaks, marked by an asterisk, will be discussed in Section 6.3.3.

The mixture of cubic and rhombohedral phases has appeared on heating above 473 K in all the data collected to date and in different relative proportions. Profile (d) in Fig. 6.9 gives an example of a profile dominated by the cubic phase, but it is not always the case. Sometimes, in similar P-T conditions, the rhombohedral phase appears more dominant compared to the cubic phase, as illustrated in Fig. 6.10. This pattern was collected at \(\sim3.2\) GPa and 633 K. The significance and possible interpretations of this
Table 6.2: The indexing and the values of the observed and calculated d-spacings of the rhombohedral phase $R\bar{3}m$ at ~5.0 GPa and 608 K.

<table>
<thead>
<tr>
<th>h k l</th>
<th>$d_o$ (Å)</th>
<th>$d_c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>3.0774</td>
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<td>2.2151</td>
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</tr>
<tr>
<td>1 0-1</td>
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<td>1 1 1</td>
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<td>1.8401</td>
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<tr>
<td>1 1-1</td>
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<td>1.7578</td>
</tr>
<tr>
<td>2 0 0</td>
<td>1.5404</td>
<td>1.5392</td>
</tr>
</tbody>
</table>

In all the data collected at around 5.0 GPa, InSb appears to behave in a similar way no matter what the initial state (single P4 or mixed P3-P2) of the sample before heating. One of the main characteristics of these phase transitions, as shown in both Fig. 6.7 and Fig. 6.9, is the dominance of P2 over P3 as temperature increases. This can explain, as mentioned earlier, the reason why the work performed by Mezouar et al. (1999b) shows a pattern of "nearly" pure P2. It could well be that with the path followed in pressure and temperature, a specific region of the phase diagram, where almost only P2 is stable, has been hit. Data collected in this work always display the presence of the cubic, rhombohedral and extra peaks, in various proportions, and P2 as a single phase has not been observed. However, as shown in Fig. 6.8, the pattern published by Mezouar et al. (1999b) indicates the presence of extra peaks, marked by an asterisk, attributed to contamination. These peaks could reveal the presence of an additional phase, as observed in this work, where the strongest peaks would appear at an angle lower than 3°, as shown by the extra lines in their powder pattern. Coincidently, their published profile has been truncated and does not show the low angle region.

Some important points can be drawn as a conclusion from the phase transitions observed around 5.0 GPa. It seems that the transition from P4 to P3 does occur at the temperature predicted by the phase boundary in the P-T phase diagram, but as soon as the temperature is increased above the transition, P3, initially containing a small residue of P2, decreases to give mostly P2. P2 appears to be the stable phase in this pressure and temperature range, relatively to P3. Therefore the interpretation given by Mezouar et al. (1999b) of considering InSb-III, at ~5 GPa and above 473 K, as a $\beta$-tin structure (P2) should be corrected. It seems more appropriate to conclude that
InSb-III, in this region of the phase diagram, has indeed the structure of P3 ($Immm$), as they claimed a few years earlier (Mezouar et al. (1996)), but the stability field in the high-temperature region should be revised. It seems that around 5.0 GPa the transition goes from P4 to P3 and on further temperature increase, P3 transforms to P2. The transition boundary at 5.0 GPa appears to be confirmed.

With the discovery of the further transition to P2 on heating and with the characterization of two new phases, the question as to whether this behaviour occurs at different starting pressures is raised. It was hoped to find out more about the cubic and rhombohedral phases and the unusual behaviour of the additional peaks. These questions have been partially answered by investigating further the P4 to P3 transitions following the paths B and C in Fig. 6.5. The possible interpretations of the cubic, rhombohedral and “extra” phases will be given in Section 6.3.3.

Path B

The transition from P4 to P3 has been investigated at 7.0 GPa. According to the phase diagram, the transition should occur near 373 K. Samples have been prepared following the procedure described earlier to reach the P4 state. Phase transitions have been observed in situ as the temperature was raised up to 633 K. The recorded sequence
The profile (a) shows the pattern of a pure P4 sample at room temperature and little change was observed to 333 K in profile (b). As the temperature is increased towards the transition, the first appearance of P3, as indicated by the emergence of the (011) and (211) peaks in profile (c), was observed at 366 K. On further temperature increase, P4 transforms progressively to P3, as shown by the relative intensities of the (011) P3-peak and the (023) P4-peak in profile (d), and the first appearance of the (200) P2-peak was observed accompanying the growth of P3. At 398 K, the transition from P4 to P3 seems to take place, as predicted by the phase diagram, and as was observed in path A, P3 is accompanied by a small residue of P2. At 483 K, the transition appeared to be complete and a mixture of P3 and P2, similar to the one observed at \( \sim 5 \) GPa at 473 K in profile (c) of Fig. 6.7, was recorded. Once again, P2 started to grow and additional peaks, marked by an asterisk, appeared, at the same temperature observed in path A of Fig. 6.5. However, there was no sign of the new cubic or rhombohedral phases. Temperature was then increased to 573 K. The profile (f) shows that P2 dominates as P3 disappears. The additional peaks also appear to have grown slightly.

As the temperature was raised to 633 K, the maximum temperature that could be reached technically, a dramatic change occurred, as a completely new profile appears. It seems that the new phase, characterized by the extra peaks present from 473 K, has suddenly grown into sharp distinct peaks. Despite some residue of P2 and P3, as seen in profile (g), InSb appears to have transformed to a new state, as the doublet at \( \sim 14^\circ \) and \( 18^\circ \) vanishes. This could possibly be attributed to the proximity of the liquid state. It was the first time, and the only time, that such a high temperature has been reached at that pressure, for the data collected in the present work. It is therefore not surprising that new changes were observed. This new phase has not been identified, however possible interpretations for such behaviour will be discussed in Section 6.3.3.

A similar study has been made starting with a mixed P3-P2 sample at 7.0 GPa. The transitions observed were close to those observed following path A in Fig. 6.7. The behaviour observed in path B with a P4 sample and the one starting with a mixed P3-P2 sample were not the same. A definite explanation of this behaviour cannot be made and much more data are required to verify which is the reproducible behaviour.
Figure 6.11: The sequence of phase transitions observed when heating a sample of P4 at 7.0 GPa. The asterisks and arrows are discussed in the text. The peaks marked by “G” are contaminations peaks from the gasket.
It could well be that both, and perhaps more, situations are “equally” produced. In fact, another high-temperature study has been performed at the lower pressure of 5.6 GPa with a mixed P3-P2 sample. The pattern collected at 593 K was a mixture of P2, P3, cubic, rhombohedral, the extra peaks seen in profile (g) of Fig. 6.11 and some more additional peaks. The co-existence of six phases suggests that the sample decomposes at high pressure on heating, however this phenomenon is very surprising as such a behaviour had never been observed in previous in situ hp/ht studies. It appears that the sample “breaks down” above ~473 K to give extremely complex patterns, which were not reported in Mezouar et al. (1996 and 1999b). More details about this behaviour will be given in Section 6.3.3.

It can be concluded, from the P4-to-P3 transition following path B, that, once again, the transition does occur at the temperature predicted by the phase diagram and P3 appears with a small residue of P2 that grows at the expense of P3 as temperature increases further. In the particular sequence shown here, there was no sign of the cubic or rhombohedral phase but a similar study, performed with a mixed P3-P2 sample, shows that the cubic and rhombohedral phases are present in the same pressure range, even though they did not appear to be dominant. P2 seems to be the most stable phase in this P-T range. As mentioned above, it is interesting to note that the extra peaks, marked by an asterisk, appeared at the same temperature (~473 K) in both path A and B, with all the patterns studied to date.

Path C

Finally, the P4-to-P3 transition was studied at the much lower pressure of 3.2 GPa where P4 is believed to be the stable phase until ~573 K, according to the phase diagram. A sample of P4 at 3.2 GPa and was heated to ~633 K. The observed phase transitions are illustrated in Fig. 6.12.

The profile (a) shows the pattern of the P4 sample at room temperature and, as expected, little change was observed at 423 K. On temperature increase up to 488 K, the profile (c) in Fig. 6.12 changes quite radically. Three main factors seem to have occurred, all simultaneously:
Figure 6.12: The phase transitions observed in a sample of P4 at 3.2 GPa as the temperature is raised up to 633 K. The asterisks and arrows are discussed in the text.
(i) the (100) peaks of both the cubic and rhombohedral phase, as shown by the doublets marked in pink and violet, appear

(ii) the (200) and (101) P2-peaks have grown up, as shown by the arrows, with perhaps P2-peaks overlapping the usually visible (011) P3 peak, and

(iii) the extra peaks, marked by an asterisk, become visible

At this transition, InSb seems to have 5 phases coexisting: P4/P2, cubic/rhombohedral and an extra unknown phase. As temperature is raised by 65 K from 423 K, the cubic and rhombohedral phases grow up while P4 and P2 started to disappear, as seen in profile (d) of Fig. 6.12. No clear changes are observed in the extra peaks. At the transition temperature (~573 K), a very small amount of P4 and P2 remains while the cubic and rhombohedral phases dominate the profile (e). These two phases seem to be stable at elevated temperatures at these pressures. On further temperature increase to ~633 K, there are no more P4 or P2 peaks and the cubic and rhombohedral phases remain present. The additional unknown phase reveals, clearly, a much sharper peak, at ~9°, as indicated by the arrow in profile (f), among other broad peaks. Once again, the presence of the various phases in the pattern was rather unexpected, since similar P-T studies (e.g. Mezouar et al. (1996)) did not report such obvious changes in the diffraction pattern. This phenomenon has been investigated further and will be presented in Section 6.3.3.

In conclusion, the sequence of phase transitions, studied here at 3.2 GPa following the path C, shows a very different behaviour from what is predicted by the phase diagram. P4 does actually disappear at ~573 K but the transition to a mixture of various phases, where P3 does not seem to be present, occurs at the temperature of ~473 K, much lower than the boundary transition drawn in the phase diagram. The region around 3.2 GPa and 473 K contains at least five different phases coexisting at approximately the same proportions: P4 with a certain amount of P2, the growing cubic and rhombohedral phase and the additional unknown phase that becomes visible at ~473 K, the same temperature observed in both path A and B.

To summarize, the studies of the phase transitions in the phase diagram of InSb have revealed three main new features:
(i) the transitions from P4 to P3 do occur at and above ~5.0 GPa but the small residue of P2, which is always present with P3, grows up on further temperature increase. P2 is therefore stable at elevated temperatures in the region of InSb-III

(ii) the unexpected observation of two new high-symmetry phases, simple cubic and rhombohedral

(iii) the unexplained presence of additional peaks that appear in all the samples studied so far, at the same temperature over the whole pressure range covered (up to ~7.0 GPa)

Points (ii) and (iii) will be discussed in Section 6.3.3. A brief discussion about (i) is given below.

**P2-P3:** as noted in the previous work, described in Section 6.2, the P3 phase was always observed with a small amount of P2. This is also seen in the present study and it is now clear that the hexagonal phase emerges as a stable phase on temperature increase (as seen in GaSb) while P3 disappears gradually. In path A and B, P3 has been observed at the transition temperature (~473 K in path A and ~373 K in path B) and was still present up to ~593 K in both cases and appeared in larger proportions relative to P2 at higher pressure (path B). At the transition in path C, at ~3.2 GPa, P3 did not seem to appear and if there was any P3 in the multiphase state at ~473 K, the peaks were hidden by the other phases. The dominance of P2 over P3 at high temperature might explain the results obtained by Mezouar et al. (1999b), where an almost single P2 phase was observed. However it is not correct to attribute the structure of P2 as InSb-III, in a region where P3 seems absent. It now appears obvious that is the field of stability that needs to be revised rather than its structure. Above ~5.0 GPa and ~473 K, P2 is more stable than P3, therefore the area covered by P3 in the phase diagram (Fig. 6.4) is much smaller.

**P2-P4:** from the results obtained in the present work, it appears that the well-established P4-to-P3 transition is actually correct. P4 is the stable phase below the boundary traced in the phase diagram in Fig. 6.4, but transforms to P3 and then P2 at high temperature above the transition boundary, where first P3 and then P2 is the stable phase. The transition from P4-to-P3-to-P2 corresponds to an “order-
disorder" transformation, similar to those observed in metallic alloys. This point will be discussed in the following section. The transition recorded at 3.2 GPa also shows a profile containing a certain amount of P2 on temperature increase but the pattern seems dominated by the cubic and rhombohedral phases as temperature increases.

6.3.2 Site-Ordering

As explained in Chapter 4, a site-ordered and a site-disordered structure can be distinguished using diffraction by the presence (or the absence) of difference reflection peaks. The detection of these peaks in InSb patterns is extremely difficult due to the similar scattering power of In (Z = 49) and Sb (Z = 51). However, by using the effects of anomalous dispersion at the In K-edge, as explained in Chapter 4, it is possible to detect the difference superlattice reflections. Previous work has been able to determine that P3 and P4 are site-ordered while P2 and P5 are site-disordered at room temperature (Nelmes et al. (1993), Nelmes and McMahon (1996)).

No discussion about the difference reflection peaks has been made by Mezouar et al. (1999b) to determine whether or not P2 is site-disordered at high temperature. In the data collected in this work, no experimental evidence has been provided to check if P2 is still site-disordered at high temperature. However, the β-tin structure has been predicted to be site-disordered at high temperature, as explained below.

At ambient conditions, most of the III-V semiconductor compounds exhibit a tetrahedrally coordinated structure (zincblende) with covalent bonds. Applying pressure reduces the bandgap and in most cases the first high-pressure phase transition transforms the zincblende structure into a metallic phase. Total-energy calculations have shown that the driving force underlying the transition to a more densely packed structure in InSb is greater than that for ordering (Ackland (2000b)). At high temperature, the large entropy associated with the disordered structure allows a thermodynamic order-disorder transition. In other words, the site-disordered β-tin structure is energetically favoured at high temperatures, as explained in Section 5.4. This type of transformation has been observed in metallic alloys (see Chapter 4). Due to the similar atomic radii of In (= 1.56 Å) and Sb (= 1.33 Å), InSb can form a solid solution at any composition.
The ability to form a solid solution (= alloy) at high-pressure high-temperature raises the question of which composition of InSb would give rise to the equilibrium phase and which proportions may produce an ordered structure. As observed experimentally (Nelmes et al. (1993)), the β-tin structure of InSb is site-disordered at least over a long-range scale. No attempt to measure the composition of InSb at hp/ht has been made, prior to the work presented in this thesis and it was always assumed that InSb retains its stoichiometric 50:50 composition from the ordered zincblende structure (P1) before P-T treatment. Previous work performed by Degtyareva et al. (1983) on the phases obtained in quenched samples showed that the 13-tin structure is found in samples of In143Sb57, a small deviation from the equicomposition. It was therefore of considerable interest to find out if sample dissociation occurs which could explain the presence of intermediate phases.

However, if the InSb samples dissociate at high pressure and high temperature, as shown by the coexistence of various phases in the patterns shown in Section 6.3.1, two main factors remain rather intriguing:

(i) the extra peaks, which are often associated with the cubic and rhombohedral phases, always appear at the same temperature (i.e. ~473 K) over the entire pressure range studied, and

(ii) similar \textit{in situ} hp/ht work (Mezouar et al. (1996 and 1999b)) has not reported such a phenomenon.

These simple facts have led the author to investigate further the matter of sample decomposition, by analysing the cubic, rhombohedral and unknown phases recovered at ambient conditions. The results of this study are presented below.

### 6.3.3 Decomposition

The detection for sample decomposition in patterns obtained by x-ray diffraction at high-pressure and high-temperature is quite complex. The appearance of new peaks at a phase transition is often readily visible but the determination of sample composition requires either the knowledge of the atomic positions of each type of atom in the true structure, i.e. the structure has to be known, or the possibility of referring to hp/ht data.
on known compositions for comparison. In the present work, only samples with initial stoichiometric composition 50:50 have been investigated. Therefore, the only way to get more information about the possible dissociation using x-ray diffraction methods was to investigate the patterns obtained on recovering back to ambient pressure and room temperature. These studies have revealed that the rhombohedral phase, recovered at ambient conditions, corresponds to the phase-I of elemental Sb. The observation of Sb-I in a sample of InSb came as an additional surprising factor, as, again, no previous work had reported such a behaviour. The presence of pure Sb was subsequently confirmed when a sample of InSb, recovered back to ambient conditions, was scanned under a transmission electron microscope (TEM). The results of these combined studies, with x-ray diffraction and TEM techniques, are presented below.

The first evidence that InSb might have decomposed at high pressure and high temperature came from the fact that samples did not recover, or not totally, to the site-ordered zincblende structure (P1) at ambient conditions. After pressurization and heating, the samples were allowed to cool to room temperature over approximately 12 hours. Pressure increase was always observed after this process. The sample pressure was then brought back to ambient pressure rapidly (in a few seconds). Patterns obtained from samples quenched this way showed varying proportions of the different phases observed at high-pressure and high-temperature and occasionally the ambient-pressure zincblende phase was present. Three examples of profiles from recovered InSb samples at ambient conditions are illustrated in Fig. 6.13.

The profile (a) shows a small amount of the zincblende structure, as indicated by the "ZB" symbols. The pattern is mainly dominated by the cubic and rhombohedral mixture. Peaks marked in pink are indexed by the rhombohedral phase $R3m$, with the refined lattice parameters of $a = 4.3032(9)$ Å and $c = 11.170(5)$ Å with $z = 0.2352(3)$ giving a volume per atom ($V_{at}$) of $29.85(5)$ Å$^3$, while the peaks in violet are indexed with the simple cubic phase $Pm3m$ with $a = 3.0349(3)$ Å and $V_{at} = 27.95(1)$ Å$^3$, showing that the rhombohedral phase is less dense than the cubic phase at the same pressure (i.e. ambient pressure). The asterisks mark the presence of the unknown phase, which is still present at ambient conditions. The pattern also shows a small amount of the $\beta$-tin phase, with the refined lattice parameters $a = 5.8227(2)$ Å and $c = 3.1794(7)$ Å with $V_{at} = 26.95(4)$ Å$^3$, more dense than the cubic and rhombohedral phase. This
Figure 6.13: The profiles of three InSb samples recovered at ambient conditions after three different pressure-temperature treatments. The asterisks are discussed in the text.
sample had been heated at 4.8 GPa up to 633 K starting from a mixed P3-P2 sample with a small amount of P4.

Profile (b) in Fig. 6.13 corresponds to the sample that has been treated following path B in the phase diagram, as shown in Fig. 6.5. The pattern is dominated by the rhombohedral phase with \( a = 4.2941(5) \) Å, \( c = 11.264(3) \) Å and \( z = 0.2349(1) \) with a \( V_{at} = 29.98(3) \) Å\(^3\), and the unknown phase, whose peak intensities have increased and sharpened, as seen in profile (g) of Fig. 6.11. A possible indexing has been attempted and will be discussed later. A small amount of the cubic phase, with a volume per atom of \( 27.96(4) \) Å\(^3\), is visible as shown by the arrows in Fig. 6.13. No zincblende peaks were found.

The profile (c) shows a pattern of a mixed P3-P2 sample that has been heated at 5.0 GPa to 623 K. It is surprisingly similar to the profile (b). Once again the zincblende phase was not found and the absence of the weak peak on the high-angle side of the (100) rhombohedral peak, as shown by the arrow, suggests that, in this case, there is no cubic structure recovered at ambient conditions. The profile is mainly dominated by two phases: the rhombohedral structure with the refined lattice parameters \( a = 4.3014(4) \) Å, \( c = 11.266(2) \) Å and \( z = 0.2353(1) \) giving a volume per atom of \( 30.08(2) \) Å\(^3\), and the unknown phase.

By quenching samples of InSb alloys under pressure, Degtyareva et al. (1983) have found six intermediate phases with different compositions. Starting from 7.0 GPa and 623 K, they obtained a sample of \( \text{In}_{40}\text{Sb}_{60} \) with the simple cubic structure, with \( a = 3.047 \) Å, the same structure found in the present work. Similarly, after another P-T treatment (1.8 GPa and 573 K), they found another intermediate phase that has the rhombohedral structure with lattice parameters \( a = 3.056 \) Å and \( \alpha = 89.2^\circ \) corresponding to a sample of \( \text{In}_{42.5}\text{Sb}_{57.5} \) (in hexagonal axes, the lattice parameters become \( a = 4.29156 \) Å and \( c = 10.73308 \) Å). Those values are slightly different to the ones obtained for the rhombohedral structure in the present study, but the P-T treatment and the sample preparations were also different. According to their work, both the cubic and rhombohedral phases are Sb-rich.

In fact, the refined lattice parameters obtained for the rhombohedral structure in the profile (a), (b) and (c) in Fig. 6.13 for samples recovered at ambient conditions are
surprisingly close to the size of the unit cell of pure Sb. At ambient conditions, Sb has the rhombohedral structure $R\bar{3}m$ with $a = 4.307$ Å, $c = 11.273$ Å with $z = 0.233$ and $V_{at} = 30.18$ Å$^3$. This structure is illustrated in Fig. 6.14.

Therefore the "pink phase" was refined with the structure of pure Sb with 6 atoms in the unit cell. Consequently, if InSb dissociates into pure Sb, the cubic and the unknown phases, it is deduced that at least one of the phases has to be In-rich since they do not correspond to the pure ambient pressure In phase, which has a body-centered tetragonal structure with $I4/mmm$ symmetry with the lattice parameters $a = 3.2523$ Å and $c = 4.9461$ Å.

Two different possible indexings have been found for the peaks of the unknown phase of in profile (c) (Fig. 6.13) and are shown in Fig. 6.15. The strongest reflections, except the peak marked by a question mark in the profiles (b) and (c) in Fig. 6.13 and profile (f) in Fig. 6.12, fit a body-centered orthorhombic unit cell with spacegroup $Immm$ where $h + k + l = \text{even}$, as illustrated in Fig. 6.15(a) ($\chi^2 = 1.516$). Some of the weak reflections fit the difference reflections peaks of an "ordered equivalent" of $Immm$, the spacegroup $Pmmm$, where $h + k + l = \text{odd}$ as shown in Fig. 6.15(b) ($\chi^2 = 0.7603$). This structure seems to be a good candidate for a site-ordered primitive orthorhombic
phase containing more In than Sb.

This is only a preliminary result as the pattern shown in Fig. 6.15 was the only one obtained where such a difference is obvious. If the structure has 2 atoms in the unit cell, one type at (0,0,0) and the other type at (1/2,1/2,1/2), the volume per atom in this phase would be $\sim 150\%$ bigger than it is for the rhombohedral phase. Also from the lattice parameters obtained, the interatomic distance between the atom at (0,0,0) and (1/2,1/2,1/2) was determined to be 5.1185(1) Å, which is very large compared to 2.8056(1) Å for the zincblende structure at ambient pressure. This large distance In(Sb)-In(Sb) suggests that an additional atom could be accommodated giving a more reasonable bondlength of 2.559 Å. With 3 atoms in the unit cell, the volume per atom would be approximately the same as that of the rhombohedral structure (i.e. 29.85(5) Å$^3$).

Among these new observations, the most surprising one is the fact that the $R\bar{3}m$ phase appears to be composed of pure Sb. From the x-ray diffraction pattern shown in Fig. 6.15, only the weak peaks in the rhombohedral structure marked by the arrows indicate that the structure is the same as Sb-I, rather than any other rhombohedral structure. However, with the presence of the unknown weak peaks, marked by asterisks, it cannot be guaranteed that the weak peaks marked by the arrows correspond to the structure of Sb-I (with the rhombohedral cell shown in Fig. 6.14).

In order to obtain definite evidence of the presence of pure Sb, the sample recovered at ambient conditions as shown in Fig. 6.15 has been analysed with a high-resolution transmission electron microscope (TEM) at the Bayerisches Geoinstitut in Germany. This analysis has been made in collaboration with Dr. Falko Langenhorst. The results of this single experiment are presented below.

The electrons of a TEM are focused by electromagnetic lenses producing an electron beam that can illuminate a very small area of the sample. The diffracted beams are then recombined to form a 2-D image, representing the density of the scattering material in the sample studied. This high-resolution imaging technique is particularly useful to study defects in mineral structures (Putnis (1992)).

The high-resolution image of a small area of the InSb sample is illustrated in Fig.
Figure 6.15: (a) A multiphase refinement of an InSb sample recovered at ambient conditions. The upper tick marks are the reflections allowed by the *Immm* structure. (b) Similar refinement with the ordered *Pmmm* structure giving additional tick marks for the difference reflection peaks, highlighted in the Figure. The arrows are discussed in the text.
The photograph shows clearly that the sample is made of two types of grains (large ones > 0.3 μm and smaller ones < 0.3 μm) as seen by the light and dark areas in Fig. 6.16(a). The results of the TEM analysis reveal that the large grains are pure Sb and the small grains are a mixture of In with oxygen. It can be seen from 6.16(b) and (c), showing an x-ray colour map at the O and In K-edges, that both elements are found in only the small grain regions in the light area of the image in Fig. 6.16(a), while the x-ray map at the Sb K-edge shows that the dark area in (a) indicates that the larger grains are composed of pure Sb. The TEM analysis has given experimental evidence that the sample contained pure Sb. The observation of a mixture of In and O could have been an indication than an indium oxide has been formed during the P-T treatment that may correspond to the unknown phase. However In oxidises only in the form of In₂O₃ that has the body-centered cubic structure Ia₃ with a = 10.118 Å (Wyckoff (1964)). This structure, clearly, does not correspond to the powder pattern observed.

However, the presence of oxygen, mixed with indium, can possibly be explained if any chemical reaction with the sample environment has occurred during sample heating (Pulham (2000)). As mentioned in Chapter 2, to ensure hydrostaticity, a mixture of methanol:ethanol (4:1 in volume) is used as a pressure-transmitting medium. All the samples studied to date, in this work, have been loaded with a small amount of this mixture. Piermarini et al. (1973) have shown that the 4:1 methanol:ethanol is the best mixture to produce hydrostatic conditions when pressure is applied to the sample. However their studies have only been carried out at room temperature. No information is reported above room temperature.

Therefore, a sample of InSb, loaded without the pressure-transmitting medium, has been pressurized to 5.5 GPa and heated off-line to ~560 K, in the Dynocell to investigate the matter. Because of the failure of the synchrotron, an x-ray diffraction pattern of the sample recovered back to ambient conditions had to be collected with the x-ray powder diffraction set-up in Edinburgh, using Mo radiation with wavelength 0.7106 Å. The Rietveld refinement fit ($\chi^2 = 7.447$) obtained is illustrated in Fig. 6.18. It is dominated by the zincblende phase, which is usually absent (or present in a small
Figure 6.16: (a) A TEM image of a small area of an InSb sample after P-T treatment, (b), (c) and (d) are respectively the x-ray colour map of the sample area at the oxygen, indium and antimony K-edges respectively
Figure 6.17: X-ray elemental spectra recorded at the (a) Sb and (b) In K-edges of a sample of InSb, recovered at ambient conditions, revealing (a) the presence of pure Sb and (b) In with oxygen. The Cu peaks are due to backscattered electrons from the Cu sample grid.
quantity) in the patterns collected with the medium. There is only a small amount of the previously dominant rhombohedral phase (see Fig. 6.13), but the simple cubic phase is quite strongly present. One low-angle peak could not be indexed. This perhaps suggests that considerably less of the sample has decomposed (more zincblende retained, and less of the rhombohedral phase present) but that a very significant amount of the cubic phase has still been produced. At least this cubic phase seems not to be a product of chemical reaction with the medium. However, the fact that none of the new phases has been observed in previous work cannot be explained. Therefore it is difficult to conclude whether or not the medium can be held responsible for a chemical reaction. For the present time, the question as to whether or not the sample decomposition is related to the intrinsic behaviour of InSb or is due to a chemical reaction on heating under pressure remains unclear.

If there is a chemical reaction in InSb, the fact that this process has not been observed in GaSb can be related to the fact that indium, being more reactive, has a strong tendency to oxidise if mixed with methanol:ethanol as temperature increases (Pulham (2000)), to produce a possible methoxide. This could explain why the "extra" phase appears at the same temperature. Consequently, the In atoms "involved" in this reaction may have left a sample containing more Sb than In. It is interesting to note, as mentioned earlier, that previous work performed on quenched samples (Degtyareva et al. (1983)) has found a simple cubic phase in a sample of In_{40}Sb_{60}. Starting from 7 GPa and 623 K, they obtained this structure with $a = 3.047 \text{ Å}$ with a $V_{st} = 28.3 \text{ Å}^3$, which is close to the value obtained in this work ($V_{st} = 27.95(1) \text{ Å}^3$). Also, in the previous work by Mezouar et al. (1996 and 1999b), they used boron nitride as a pressure-transmitting medium, which is, perhaps, a reason why these new phases have not been reported.

However, the presence of "extra" broad peaks, marked by an asterisk, as shown in Fig. 6.8, indicates that a possible reaction might have occurred in their sample (or perhaps a trace of a sample decomposition). As explained in Chapter 4, similar "extra" broad peaks have been observed in GaSb above $\sim 473$ K. Those peaks are not due to the pressure-transmitting medium but possible oxidation cannot be excluded (or again, perhaps, a sign of slight decomposition). A small amount of oxygen is always present since the samples are loaded in air and are held in a metallic gasket, which may contain a layer of oxygen due to the hole drilling process (Pulham (2000)).
Despite the uncertain origin of the new phases observed, the initial purpose of confirming and understanding the presence of the $\beta$-tin structure at high temperature as observed by Mezouar et al. (1999b), has been reached. The results of the work presented in Section 6.3.1 can be summarised by redrawing the phase diagram shown in Fig. 6.3.

### 6.3.4 P-T Phase Diagram

By reproducing the experiment performed by Mezouar et al. (1999b), it is shown that the field of stability of InSb-III at high temperature needs to be revised. The results of this work reveal that the transition from P4 to P3 occurs, as predicted by the existing phase diagram, but on further temperature increase P3 transforms to P2. It seems that the $\beta$-tin structure is stable at high temperature, as observed in GaSb. The present work confirms and extends further what has been observed by Mezouar et al. (1999b). A possible new phase diagram is proposed and illustrated in Fig. 6.19, where a dashed line would represent the boundary between InSb-III and the new InSb-II. P2 is the dominant phase at elevated temperatures above $\sim$5 GPa. A sequence of phase transitions below $\sim$5 GPa shows the present of the strongest P2 peaks in the region of
InSb-IV where P4 is still dominant. However, those patterns were dominated by the presence of the cubic and rhombohedral phases. Therefore it is difficult to tell what was the dominant phase (P4 or P2) in that pressure range, as shown by the question mark in Fig. 6.19. There is a possibility that P4 transforms directly to P2 at these lower pressures. The proposed phase diagram illustrates why Mezouar et al. (1999b) have observed P2, as indicated by the cross in Fig. 6.19.

### 6.4 Conclusions

The high-pressure high-temperature diffraction studies of InSb have revealed new information about the high-pressure high-temperature behaviour of InSb. The exploration of the phase diagram has shown that the well-established P4-to-P3 transition does occur from ~5.0 GPa up to ~7.0 GPa at the predicted transition boundary but P3 transforms to P2 at a higher temperature. Below ~5 GPa, a possible direct transition from P4 to P2 may take place. The observation of this order-disorder transformation (P4-to-P3-to-P2) suggests that InSb, like GaSb, behaves as a metallic alloy under pressure and temperature treatment.

The observation of the cubic and rhombohedral phases, previously found as interme-
diate phases in In-Sb alloys at different compositions, could be an indication that strengthens such a behaviour. These two phases have been observed at high temperature and found on recovering samples held above \( \sim 473 \) K up to \( \sim 5.0 \) GPa back to ambient conditions. Further analysis has shown that the rhombohedral phase corresponds to the structure of Sb-I. The presence of pure Sb was subsequently confirmed by high-resolution TEM analysis.

However, it is very surprising that previous \textit{in situ} hp/ht work has not reported the presence of these new phases. There is a possibility that sample decomposition may be caused by chemical reaction with the pressure-transmitting medium. This reaction would produce, perhaps, an indium methoxide that could explain the appearance of the "extra" peaks at \( \sim 473 \) K under pressure. If it is the case, it would be interesting to perform further experiments where samples would be loaded in a pure oxygen-free environment. Nevertheless, the present work has yielded a possible new version of the P-T phase, showing P2, the (most probably) site-disordered \( \beta \)-tin, as a dominant phase at high temperature. It has been thus demonstrated that the field of InSb-III at elevated temperature was incorrect and a boundary to a new InSb-II area should be included. This new proposed InSb-II is located at a rather different place than the one drawn by Banus and Lavine (1969).

From the determination of the first pressure-temperature phase diagram of InSb until the present work, more than thirty years of high-pressure diffraction work have been dedicated to the study of this binary compound. The high-pressure powder-diffraction technique developments described here have allowed the collection of better quality data that has led to a revision of the phase diagram. The diffraction studies presented in this thesis have brought further progress in the P-T work on InSb and invite future experimental and theoretical investigations towards a complete understanding of this fascinating system.
Chapter 7

Summary and Conclusions

The understanding of the structural systematics of the III-V and II-VI semiconductors has been considerably improved by the substantial developments in high-pressure powder diffraction techniques in the early 1990s. The high-sensitivity of a 2-D image-plate area detector combined with angle-dispersive techniques at a synchrotron radiation source has revealed that most of the long-established structures of the binary semiconductors were incorrect and therefore needed to be revised. Most of the previous work had been performed at room temperature and only a few systems such as GaAs, GaSb and InSb, ZnTe, CdTe and HgTe, have been investigated above room temperature. High-temperature studies under pressure open a vast area of new physics that allow, for example, the exploration of the full P-T phase diagram, the determination of the true equilibrium phases or the pressure-temperature dependence of the structural systematics. The work presented in this thesis has concentrated on structural hp/ht studies of GaSb and InSb.

A detailed review of the experimental methods and techniques developed to achieve simultaneous hp/ht conditions, from the pioneering work up to the present, has been given. It has served as an introduction to illustrate the difficulties and constraints imposed by these developments and has underlined the optimal criteria to perform hp/ht experiments with the purpose of being able to determine accurately crystal structures under these extreme conditions. The technical developments described in the present work have shown how the use of the Dynocell has allowed routine high-temperature
experiments under pressure at the powder-diffraction beamline at the Synchrotron Radiation Source, Daresbury. The installation of a new heater and thermal insulation has made it possible to reach temperatures of up to 673 K in a range of pressure up to \( \sim 15 \) GPa. These successful technical improvements have been described.

A high-pressure high-temperature diffraction study of GaSb was presented. Simple heating experiments have been carried out at \( \sim 473 \) K up to 22.5 GPa and have revealed the presence of a new orthorhombic phase, not observed at room temperature (without heating). A single \textit{in situ} hp/ht experiment has been performed using the Dynocell at \( \sim 15 \) GPa up to 673 K. This study has shown a transition from the \textit{Imma} to the \( \beta \)-tin phase and discussions as to which is the "true" structure have been made. The results of the diffraction studies have demonstrated that all the hp and hp/ht phases of GaSb, found so far, are long-range site-disordered, as indicated by the complete absence of the difference reflection peaks in the diffraction profile. This behaviour, unique among the III-V semiconductors, has been studied further for the purpose of determining the length scale of ordering in each of the three hp and hp/ht phases of GaSb. The structural investigation of site-ordering over nearest-neighbour distances (a few Ångströms) has required the use of a completely different experimental technique based on absorption spectroscopy.

An extended x-ray absorption fine structure (EXAFS) study was carried out at room temperature. This work has demonstrated that none of the three phases studied exhibit a complete short-range order over one unit cell. These results have revealed that a Ga atom is almost equally likely to be surrounded by another Ga atom or a Sb atom. The possible deviation from a complete disorder (50:50) has been attributed to the fact that data have been collected on phases recovered back to room temperature. A successful combination of diffraction and EXAFS studies has given the first experimental evidence of such a behaviour among the binary semiconductors and the interpretation of these results are related to the unusual, possible, phenomena observed in InSb.

A detailed high-pressure high-temperature diffraction study of InSb up to 7 GPa and 633 K was also presented. A review of the previous work on this complex compound has been given to illustrate the different steps that have led to a complete revision of the P-T phase diagram, almost thirty years after its first determination. The work
presented in this thesis has revised the most recently accepted version of the phase diagram, by investigating the transition from P4 to P3. The results have clarified some misinterpretations in previous work and has shown that the well-established P4-to-P3 transition is more complex than previously thought. It has been demonstrated that P4 transforms to P3 then P2. This has given evidence of an order-disorder transition, as observed in GaSb, as the (presumably) site-disordered P2, the $\beta$-tin phase, appeared to be stable at elevated temperatures. The stability of InSb-III has been revised and a possible new version of the P-T phase diagram, including a new InSb-II has been proposed.

In addition to the complexity found in the P4-to-P3-to-P2 transition, the patterns of InSb collected at high pressure and high temperature have revealed the unexpected presence of two new high-symmetry phases: a simple cubic and rhombohedral structures. These two new phases were observed with an additional unknown phase, possibly body-centered orthorhombic. The rhombohedral phase was attributed to the structure of pure Sb. This surprising sample behaviour indicates that InSb decomposes at simultaneous high-pressure high-temperature, a phenomenon that had not been reported in previous in situ hp/ht work. Both structures had been observed, in previous work, only in quenched samples as intermediate phases of non-stoichiometric composition.

A TEM study confirmed the presence of elemental Sb and revealed, surprisingly, the presence of a mixture of In and O. Since the x-ray powder pattern could not be fit with the structure of an indium oxide, the In-O, observed by TEM, could possibly be understood if a chemical reaction occured between the sample, maintained at high pressure and high temperature, and its environment. This was rather unexpected but could, perhaps, explain the sample dissociation. An obvious source of oxygen comes from the pressure-transmitting medium used in the sample preparation. It can be concluded that if a chemical reaction occurs, it would be more appropriate, in the future, to prepare samples in an oxygen-free environment. Sample decomposition can be, therefore, interpreted either as an instrinsic behaviour of InSb or as being a consequence of a chemical reaction, at high pressure and high temperature. Unfortunately, this question remains unsolved.

The results obtained in the high-pressure high-temperature studies of both GaSb and
InSb can be brought together as the manifestation of the same phenomenon. Both of these semiconductor compounds are the only binary systems, found so far, to exhibit the \(\beta\)-tin structure, as observed in Si and Ge. This observation has raised the question of the significance of the presence of a "monatomic" structure in binary systems. The work presented in this thesis has provided possible answers to that matter. In GaSb, the combination of the diffraction and EXAFS techniques has revealed that complete short-range order is absent in all of its hp and hp/ht phases. The low ionicity of GaSb, the similar atomic size of Ga and Sb atoms and the large entropy accompanying the \(\beta\)-tin phase at high temperature greatly favour an order-disorder transformation, as observed in metallic alloys. Pseudopotential calculations have shown that the ordered form of the \(\beta\)-tin structure should exist in the III-V semiconductors at very low temperature and as temperature increases, the site-ordered \(\beta\)-tin would transform to a "frustrated" ordered state, which then would go into a disordered structure on further temperature increase. It was calculated that the disordered \(\beta\)-tin phase in GaSb should appear at 92 K, well below room temperature, which explains why the site-ordered structure has never been observed in data collected at and above room temperature. Similarly, in InSb, the order-disorder transitions (P4-to-P3-to-P2) at elevated temperatures and the possible sample decomposition at simultaneous high-pressure high-temperature demonstrate a behaviour similar to those of metallic alloys. It seems that those two semiconductors, under P-T treatment, behave as if they were binary alloys. The presence of site-disordered structures observed in the \textit{Cmcn} phase of GaP and the body-centered cubic phase in HgTe suggests that similar behaviour may take place in other binary III-V and II-VI semiconductors and encourage further hp/ht studies of those systems.

Much effort has been made to make possible high temperature experiments under pressure with the use of the Dynocell at SRS, Daresbury. It is clear that these important technical developments represent the first steps towards even more efficient data collection, at SRS, at simultaneous high-pressure high-temperature where it will be possible, for example, to perform high-pressure melting experiments and to determine and control \textit{in situ} pressure variations with temperature. The development of laser-heating techniques already allow scientists to melt samples under pressure and reproduce in the laboratory conditions similar to those sustained at the Earth's core in the laboratory. It is, therefore, a great technical challenge for the future to make these techniques
available to non-specialised users. With the evolution towards ultra high-energy sources (such as fourth generation synchrotrons) and the fast growing technological developments, there is no doubt that the XXIst century will see a vast amount of new scientific discoveries under extreme conditions.

The high-pressure high-temperature work presented in this thesis has revealed a few rather complex phase transitions in two of the III-V binary semiconductors, observed already at temperatures not greater than 673 K. This strongly suggests that further structural investigations at even higher pressures and temperatures (e.g. after the melt) will lead, perhaps, to new phenomena that may illuminate numerous unanswered questions about the structural systematics of the binary semiconductors, right at the start of the new millenium.
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Published Work
High-Pressure High-Temperature Studies of Structural Ordering in GaSb

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Both angle-dispersive and EXAFS experiments have been carried out to investigate the structural ordering of the high-pressure (hp) and high-pressure high-temperature (hp/ht) phases of GaSb. The diffraction patterns of all the different phases of GaSb have shown an absence of long-range order, while the EXAFS studies have demonstrated the lack of complete short-range order. GaSb is the only semiconductor compound among the III–V and II–VI systems to present such behaviour in all of its different hp and hp/ht phases.

GaSb is the least ionic of the III–V semiconductors and its high-pressure behaviour is expected to be the closest to that of more covalent-like Si and Ge [1–5]. High-pressure structural studies of GaSb show that it is the only compound among the III–V and II–VI binary semiconductors [6] to have a lack of long-range order in all of its several high-pressure phases discovered so far. At room temperature and 7.0 GPa, it transforms from the cubic site-ordered zincblende structure to a site-disordered and thus quasimonatomic, orthorhombic structure with the Imma symmetry [7]. More recent high-pressure work on GaSb [8] has shown that the zincblende phase transforms to a site-disordered β-tin structure and the Imma phase may be stabilised only under non-hydrostatic conditions.

Further work performed at simultaneous high pressure and high temperature has revealed transitions from Imma to a site-disordered β-tin structure and from Imma (taken above 20 GPa) to a site-disordered orthorhombic structure with Ammm symmetry [9]. The lack of ordering of the β-tin phase is an example of an interesting feature of the general behaviour of the III–V and II–VI semiconductors: in none of these systems has a long-range site-ordered diatomic β-tin structure been observed [10]. It is of considerable interest to determine whether the disordering in the β-tin and other high-pressure phases is completely random or there is some ordering over very short length scales.

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Since X-ray diffraction cannot distinguish random site-disordering from site-ordering over a short length scale, an extended X-ray absorption fine structure (EXAFS) study, which allows the investigation of structural details on a local scale, has been undertaken on the hp and hp/ht phases of GaSb. A previous EXAFS study of just the β-tin phase of GaSb concludes that some structural disorder is required for a better data fit, but no determination of the site-ordering has been attempted [11].

GaSb samples were prepared as a fine powder from a starting material of 99.99% purity from Aldrich Company. Diffraction data were collected using an image-plate area detector on Station 9.1 at the SRS, Daresbury Laboratory [12]. The incident wavelength was set up at 0.4654(1) Å. Experimental details for combined hp/ht studies are explained elsewhere [9]. The data were refined by the Rietveld method [13] with the program GSAS [14]. The EXAFS data were recorded at room temperature at the Ga K-edge on Station 9.3 at the SRS, Daresbury Laboratory, with the HI-PREXX facility [15]. The data analysis was carried out using EXCURV98 [16]. This paper presents the results obtained by both X-ray diffraction and EXAFS techniques on the structural ordering of the β-tin phase.

The site-disordered β-tin structure is obtained by heating the Imma phase below ~20 GPa. The diffraction profile is characterised by the complete absence of the (110) and (310) peaks. These depend on the (rather large) difference in scattering between Ga and Sb and would be readily detected for a site-ordered structure. These peaks were still absent at 673 K, indicating that kinetic effects are not responsible for site-disordering, as illustrated in Fig. 1. The additional peaks marked by an open circle reveal the presence of a minor unknown high-temperature phase discussed in [9]. The length scale of ordering can be estimated from these diffraction data to be about two unit cells or less.

Fig. 1. Rietveld refinement fit of the β-tin structure to a profile of GaSb at 15.2 GPa and 673 K. The two insets show the complete absence of the (110) and (310) difference peaks in the data (+). The open circles are discussed in the text.
The EXAFS data were collected at 8.6 GPa. At that pressure, the lattice parameters were $a = 5.3119(1)$ Å and $c = 2.9549(1)$ Å. The nearest-neighbour distances from the central atom, located at (1/2, 1/2, 1/2) in the body-centered tetragonal unit cell, are then 2.7568(1) and 2.9547(1) Å. These two distances define the radii of the so-called first and second coordination shells, as shown in Fig. 2. The refinement was set up to estimate the fractional occupancy of each type of atom, Ga and Sb, on each coordination shell. The refined spectrum, illustrated in Fig. 3, gives $(75 \pm 10)$ % of Sb ($(25 \pm 10)$ % of Ga) in the first shell and $(41 \pm 12)$ % of Sb ($(59 \pm 12)$ % of Ga) in the second shell. The respective Debye-Waller factors were 0.016(3) and 0.001(4) Å$^2$. Simulated spectra of the randomly disordered and completely ordered structures are illustrated in Fig. 4. It can be seen that the EXAFS data are much closer to the randomly site-disor-

![Diagram of the body-centered tetragonal unit cell of GaSb](image_url)

**Fig. 2.** Body-centered tetragonal unit cell of the β-tin structure, where each lattice site represents a 50:50 occupancy of Ga and Sb atoms. The nearest-neighbour distances 2.7568(1) and 2.9547(1) Å from the central atom define the radii of the first and second coordination shells (the atoms marked by 1 belong the first coordination shell and the atoms marked by 2 belong to the second one.)

**Fig. 3.** Least-squares refinement of the EXAFS $k^2$-profile from the β-tin structure of GaSb at 8.6 GPa. $k$ is defined as $\sqrt{2m(e - E_0)/\hbar^2}$
Fig. 4. Simulated $k^2$-profiles of a site-disordered and site-ordered structure of GaSb.

disorder

order

-2
-1
0
1
2

$k(A)$

-2
-1
0
1
2

$k(A)$

ordered profile. The β-tin structure has also been investigated at 11.2 GPa. The results show a fractional occupancy of $(62 \pm 10)\%$ of Sb $(38 \pm 10)\%$ of Ga) in the first shell and $(55 \pm 12)\%$ of Sb $(45 \pm 12)\%$ of Ga) in the second shell.

Our data thus show that, within the uncertainties, the structure is nearly but not completely site-disordered. However, the EXAFS data have all been collected at room temperature and complete 50:50 disorder cannot be excluded at high temperature. Similar results have been obtained for the Imma and Ammm phases of GaSb [17]. It thus seems that GaSb behaves intrinsically as a quasi-monatomic system. It could also be that GaSb goes through an order–disorder transition as observed in metallic alloys. Some numerical simulation has shown that the disordered β-tin structure is stable at high temperature [18].

The presence of site-disordered phases has also been detected in diffraction studies of other semiconductor compounds, such as the β-tin and bcc phases of InSb [18]. This suggests quasi-monatomic or alloy-like behaviour is a more widely occurring phenomenon in these systems, and merits further experimental and computational investigation.

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