Complex Structures In Tetrahedrally Bonded Semiconductors

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Abstract

Complex tetrahedral structures form good models for amorphous Group IV and III-V semiconductors. With a view of working towards examining non-crystalline materials, the structural, electronic and vibrational properties of complex tetrahedrally bonded semiconductors are investigated by various molecular dynamics techniques. First principles quantum mechanical molecular dynamics calculations are performed on two such structures and the effects of pressure on their behaviour is reported. A full free energy calculation using this method remains infeasible and therefore an empirical bond charge model is used to calculate the full pressure-temperature phase diagram of the structures. Several surface reconstructions of a complex phase of silicon are then examined and the lowest energy surface of any silicon structure so far is found. Point defects in the diamond phase of silicon and carbon also give insight into various unusual bonding topologies that could be found in their amorphous phase. Structural and vibrational properties of several defects are considered. Finally, calculations on amorphous carbon and silicon at several densities are done and a comparison between the structural and electronic properties made. New bonding topologies are found in the structures including three centre bonding orbitals in the amorphous carbon models.
Much of the work presented in this thesis has now been accepted for publication in journals. The references are as follows:


Other work which has been performed, but not included in this thesis for reasons of continuity, was done jointly with Hadi Akbarzadeh of Isfahan University, Iran. The references are as follows:


Declaration

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

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Contents

Abstract i

1 Modelling complex structures 1
  1.1 Introduction .................................................. 1
  1.2 Pressure Effects in Semiconductors .......................... 2
  1.3 Molecular Dynamics ......................................... 5
    1.3.1 Modelling the Interactions ............................. 5
    1.3.2 The Molecular Dynamics Method ......................... 8
  1.4 Layout of Thesis ............................................ 12

2 First Principles Molecular Dynamics 13
  2.1 Introduction ................................................. 13
  2.2 Earlier Approximations ...................................... 14
  2.3 Density Functional Theory .................................. 16
  2.4 Exchange, Correlation and the Local Density Approximation .... 19
  2.5 Bloch’s Theorem and Plane Wave Basis Sets ................. 21
  2.6 k-point Sampling ............................................ 25
    2.6.1 Discretisation of k-space ............................... 25
    2.6.2 Special k-point Sets ................................... 27
    2.6.3 Charge Symmeterisation ................................ 29
  2.7 Ion-Electron Interactions .................................. 30

iv
Chapter 1

Modelling complex structures

1.1 Introduction

One of the most challenging problems in condensed matter physics today is the description of the properties of non-crystalline materials. The immediate difficulty arises from the need to describe the ‘structure’ of the amorphous phase. The amorphous forms of silicon and germanium have other important topological properties in addition to the absence of long range order. One of the more important of these is that amorphous silicon and germanium are tetrahedrally coordinated having bondlengths close to those of their crystalline counterparts. Similarly, this is true for the high density $sp^3$ bonded form of amorphous carbon.

Fortunately, it is these short range properties which, to a large extent, govern the electronic and vibrational properties of the amorphous phases of these elements. This is shown, for example, by the presence of an energy gap in the electronic density of states of amorphous semiconductors and in the similarity of the vibrational spectra between amorphous and crystalline materials. It might, at first, be expected that any successful model of an amorphous semiconductor would necessarily involve a very large number of atoms in order to sensibly describe a non-repeating structure, but the above considerations regarding the importance of short ranged correlations in the structure
suggest a more economical strategy. One would instead consider a sequence of more complex crystalline structures having increased short range disorder but still retain relatively small unit cells. This would allow reliable theoretical methods to be applied to such complex crystalline materials.

Such structures metastably exist in silicon and germanium, although as yet, none have been found in carbon. The trends in the electronic and vibrational properties of these complex semiconductors give unique insight into the nature of the amorphous phase. It is in this context that the dense polymorphs of semiconductors are of the greatest value.

In view of the considerable difficulties associated with performing a full theoretical study of non-crystalline solids, these complex phases and also the bonding topologies in defected crystals are useful in that an understanding of their properties provides insight into the essential physics of amorphous tetrahedral semiconductors.

1.2 Pressure Effects in Semiconductors

The study of the pressure and temperature phase diagram of semiconductors has continued for several decades now using powerful experimental techniques such as x-ray and neutron diffraction and light scattering. The high pressure polymorphism, as yet, is neither fully known nor completely understood. This is due to the extreme complexity and to large hysteresis observed on release of pressure. Silicon is known to display at least eleven different crystalline phases at pressures up to 248 GPa[1] some of which can be recovered as complex metastable phases at atmospheric pressure. In germanium transitions to the $\beta$-Sn structure, hexagonal close-packed (hcp) and distorted-hcp have been observed up to 125GPa[2]. In addition, metastable phases can be obtained either by pressure decrease from the metallic phases[3] or by chemical leaching of lithium from Li$_7$Ge$_{12}$[4]. Very recently, it has been found that small regions of metallic silicon can be obtained by nanoindentation[5].
For carbon it is impossible to perform experiments on phases with higher density than diamond because of the huge pressures involved. Indeed, in most pressure experiments, carbon diamond-anvil cells are used to produce the required pressure. In view of the existence of a covalently-bonded diamond phase, it seems reasonable to investigate whether the phase diagram may be similar to Si and Ge. Calculations of metallic phases in carbon do, however, suggest that these are not significantly denser than diamond.

Silicon has been an ideal material for combining experiment and total energy calculations. In their groundbreaking paper, Yin and Cohen\cite{7} predicted that the $\beta$-Sn phase would transform to hcp at 43GPa. In searching for this transition, experimental results revealed another phase, simple hexagonal, which Yin and Cohen had not examined. On repeating the calculation the stability of the simple hexagonal structure was confirmed. Similar calculations have been carried out in germanium and carbon, examining both stable and metastable phases\cite{6, 8, 9}.

Ab initio total energy calculations are sufficiently accurate to have a predictive capability, and certainly their success in reproducing many experimental features of condensed matter is impressive.

As illustrated by the above example, however, it is often important to know what to expect before beginning the calculation, so that all reasonable possibilities are examined. However, the calculation of intermediate stages of these first order phase transition is much more complicated. This is because the rate at which first order phase transitions occur varies enormously, so that the lifetimes of some metastable phases is essentially infinite because of the large kinetic barrier to transition. Since the transition path is seldom known, the lifetime of metastable phases cannot be readily calculated.

Metastable phases of the group IV elements have long been of great practical and theoretical interest. The hardness of diamond has been utilized since ancient times,
while more recently amorphous silicon has found numerous uses. With pressure treat-
ment it is also possible to create high-density phases of Si and Ge which are long-lived
under normal conditions. These complex structures have been shown to be useful
models in exploring the effect of increasing short range disorder on optical properties
and have provided a vital insight into the nature of the amorphous phase of these
materials[10, 11]. A thorough study of these metastable phases: BC8 and ST12, both
in silicon and germanium has been carried out, where they have been observed ex-
perimentally, and also in carbon. In addition to revealing the structural stability and
nature of the bonding, the results will be a useful guide in determining the degree to
which simple empirical models can account for the structural trends.

Silicon BC8 and germanium ST12 phases are reasonably easy to synthesize. Under
a pressure of about 12.5GPa diamond Si transforms to the $\beta$-Sn phase[12]. This is
a massively first order phase transition in which the structure transforms from four-
fold to sixfold coordination and the material itself transforms from semiconductor to
metal. There is no easy kinetic path for this transition, and on depressurization there
is considerable hysteresis. Eventually, at about 8GPa the $\beta$-Sn phase transforms back,
not to diamond, but to the BC8 phase[13]. The lifetime of BC8 silicon under ambient
conditions seems to be indefinite.

The nature and number of metastable phases formed on depressurization appears
to depend upon the temperature and rate of depressurization. Slow decompression
from crystalline ($\beta$-Sn phase) Si at ambient temperature gives a mixture of amorphous
silicon, diamond and BC8[14]. Upon rapid release of pressure from the metallic state,
two tetragonal phases have been obtained[15]. It appears that once converted to any
metallic form by application of pressure, silicon reverts to BC8 and the diamond form
cannot be recovered, even by heat treatment and recrystallization where the Lonsdaleite
structure (hexagonal diamond) is formed.

The polymorphism of germanium is similarly complex. Pressure increase from the
cubic diamond structure results in the $\beta$-Sn structure at 10.6GPa[16]. Slow pressure
decrease results in the formation of diamond and ST12\cite{17} germanium at 7.6GPa. A metastable form of germanium in the BC8 structure has also been observed on pressure decrease\cite{18, 19}.

In carbon no phases with higher density than diamond have been made.

The discovery of the BC8 phase, its identification as a semimetal (with resistivity about a thousand times lower than the semiconducting diamond form and a hundred times higher than the $\beta$-Sn form), and the crystallographic structural solution have been reported previously\cite{20, 21, 22, 23, 24, 25}. There have also been some total energy calculations on the BC8 phase in silicon\cite{6, 9, 10, 26}, and in carbon\cite{6, 9} where it has been predicted to be stable over a range of very high pressures. This has not been experimentally verified, and for obvious reasons is impossible with conventional diamond anvil pressure cells.

\section{1.3 Molecular Dynamics}

\subsection{1.3.1 Modelling the Interactions}

In order to carry out a theoretical study of complex materials, it is important to model the interactions between the ions in these structures as accurately as possible, but still keeping the calculations computationally feasible. The two methods used to model these interactions are described below.

With the onset of more powerful computers, the molecular dynamics technique has become an effective tool in the physics of condensed matter systems. In the molecular dynamics method, the forces acting on particles in a cell are found and the classical Newtonian equations of motion are solved numerically. The largest part of a molecular dynamics simulation is the evaluation of the forces which are required to be known in order to find the relaxed ionic positions. In general each particle can interact with all the other particles in the simulation, although one method of increasing the computational speed is to limit the range of the potential.
There are several methods by which the forces on particles can be evaluated. One of the simplest and most computationally efficient is by the use of an empirical potential, where the nature of the interactions between particles is fitted to various properties which are found experimentally such as lattice parameter and bulk modulus. In general, an empirical potential is constructed by summing contributions of pairwise interactions, 3-body interactions and so on. Such a potential can be expressed generally as

\[ V(R_i) = \sum_{j \neq i} \alpha_{ij} f(R_{ij}) + \sum_{j \neq i} \sum_{k \neq i} \beta_{ijk} g(R_{ij}, R_{ik}, R_{jk}) + \ldots \]  

(1.1)

where \( R_i \) is the position of particle \( i \) relative to a given origin, \( R_{ij} \) is the separation between particles \( i \) and \( j \), \( \alpha \) and \( \beta \) are constants which are fitted to data obtained, for example, by experiment, and \( f \) and \( g \) are chosen functional forms which best represent the interactions. It is then a simple matter to obtain the force on particle \( i \) by

\[ F_i = -\nabla_i V. \]  

(1.2)

Using such a potential can give great deal of insight into microscopic structure of solids and liquids.

Although empirical potentials are of great use, they are limited by the fact that they can only describe a system to the accuracy of the parameterisation of the potential. In general they are good at describing the interactions of the system to which their parameters were fitted but their transferability to other environments can be quite poor. There are many different interactions which are necessary to fit the potential to in order to describe even a small range of physical properties. For example, the Tersoff silicon potential accurately describes properties such as lattice parameter, elastic constants and phonon dispersion curves but requires the complexity of 14 different fitted parameters. But such a complex empirical potential still gets such basic quantities as the melting temperatures wrong because it was not designed to examine such properties. Thus
transferability is limited. It may then be asked, why use empirical potentials which only reproduce the experimental results to which they fitted? It is because they will describe details of structures which may not be amenable to experimentation. For example, in Chapter 4, the phonon density of states of complex tetrahedrally bonded structures are found which is a non-trivial experiment to perform. This potential is fitted to properties of covalently bonded diamond-like materials. From the calculations presented in Chapter 3, it is found that the nature of this diamond-like bonding is similar to that of the complex structures found in diamond and germanium. Therefore, although the potential is not fitted to these complex materials, the environment in which the ions are found is very similar to the diamond structures. That is, they are 4-fold coordinated and covalently bonded.

In order to perform molecular dynamics simulations using an empirical potential, one must know beforehand the type of structure (that is, the nature of the bonding in the material) in order to use the correct model in which to construct the potential. In many cases this is not possible. To model interactions in which no a priori bonding information is known, an approach at a more fundamental level is required. One must turn to the formidable task of solving the Schrödinger equation for the electrons (in fact it is the Kohn-Sham equations that are solved where the many electron interactions are approximated by a local potential). It is this method that is described fully in Chapter 2 and then used in later chapters where the bonding topologies of the structures under consideration are unknown. On analysis it is found that some structures are well described by a covalent bond charge model which lends itself to a simple empirical parameterisation. Thus, calculations can be performed which would be computationally prohibitive in a first principles quantum mechanical method.

There are obviously great advantages in using a molecular dynamics method where the only specification of the atomic numbers of the ions present (so called ab initio methods) are required. The drawback is the extremely large compute intensive nature of the calculations. Before an evaluation of the forces on the ions can be performed,
a massive minimisation calculation is required in the extremely large phase space of the basis set of the electronic wave functions - the size of this calculation can easily overwhelm any but the smallest simulations. For example, the calculations which are presented in Chapters 6 and 7 are approaching the reasonable limit for the size of \textit{ab initio} calculations with only 64 atoms, whereas an empirical calculation of a similar scale would be using $\sim 10^6$ particles. The empirical potentials allow this because forces are calculated by the evaluation of a simple function.

Although the empirical potential, modelling a system of complicated ‘springs’, is an invaluable tool in determining the microstructure of bulk systems as demonstrated in the calculations in Chapters 4 and 6, which are unfeasibly large for \textit{ab initio} calculations, they give very little information about the electronic structure of a system. (In fact, they are usually based on some supposition about the general form of the electronic structure\textsuperscript{1}). In \textit{ab initio} calculations the electronic charge density is evaluated directly, and is in fact the fundamental quantity used in the calculations. An example of such a charge density is illustrated in Figure 1.1

The covalent bonds are clearly shown. Examination of the charge densities from \textit{ab initio} calculations on the structures described in later chapters show where an empirical covalent bond charge model will be valid.

\section*{1.3.2 The Molecular Dynamics Method}

Whether the interatomic forces are calculated by an empirical potential or by \textit{ab initio} techniques, the methodology for moving the ions in a molecular dynamics simulation is the same. Each method produces the force $\mathbf{F}_i$ exerted on particle $i$ by the rest of the system. The ions are large enough that quantum mechanical techniques are unnecessary - only the Newtonian equations of motion need to be integrated.

Throughout this work, periodic boundary conditions are used on a cell containing

\textsuperscript{1}eg. metals, covalent bonding, etc.
Figure 1.1. The figure shows several surfaces of constant charge density of the valence electrons of silicon in a complex metastable configuration known as ST12. It can be seen that the high regions of charge density lie between pairs of atoms showing the covalently bonded nature of the material. Figures such as these lend support that a covalent bond charge model will be a good description for the ST12 structure in silicon.

$N$ ions. Some initial starting configuration $\mathbf{R}_i$ is assumed and $\mathbf{F}_i$ is calculated for each $i$ using one of the methods discussed above. The initial positions $\mathbf{R}$ and velocities, $\dot{\mathbf{R}}$, are given and the equations of motion

$$\mathbf{F}_i = m_i \ddot{\mathbf{R}}_i$$  \hspace{1cm} (1.3)

are then integrated numerically (for example using a Runge-Kutta algorithm) over a small timestep $\Delta t$. The size of $\Delta t$ for atomic systems is of the order of $10^{-15}$ sec=1fs. This allows the positions to be updated and the process repeated. One of the more intuitive methods of finding the a minimum energy structure is to extract kinetic energy (thus eventually finding a 0K configuration) by quenching the system. That is, removing kinetic energy by stopping the ions when the force exerted on them is in the opposite direction to their velocities, $\dot{\mathbf{R}}_i$. In practice, this can be slow and therefore
more efficient methods are employed, as discussed below.

This method will continue until the forces are sufficiently small, where the ions are in a local minimum of energy. However, if this is the result that is required there are more efficient methods to achieve this such as steepest descents or conjugate gradients which is able to find local minima of functions (such as the energy as a function of atomic coordinates) much faster than a molecular dynamics technique.

Introducing temperature into the system is also desirable. An intuitive method for stabilising the temperature is to scale the velocities of the particles at every timestep so that the total kinetic energy of the system is given by \(3/2k_BT\) per degree of freedom. Although this ensures that the temperature is constant at every timestep by adding or removing energy from the system, it is not physically correct. Temperature is a statistical quantity and therefore an average over many timesteps is required to define the temperature. A method which allows the instantaneous temperature, \(T\), to fluctuate but where \(<T>\) remains constant was suggested by Nosé[27]. This couples the temperature to an external heat reservoir, allowing the temperature to become a dynamical variable of the system. It is analogous to attaching a ‘spring’ to the temperature so that \(T\) can fluctuate around a mean value. This implies that once the system has reached a thermal equilibrium, the total energy remains constant although ionic, kinetic and potential energies vary.

To use the Nosé thermostat, the Newtonian equations of motion have to be integrated at each timestep requiring knowledge of the instantaneous force on each particle. As described above, calculation of the forces by \textit{ab initio} methods is extremely compute intensive, whereas the use of empirical potentials requires only the evaluation of simple functions. Therefore \textit{ab initio} molecular dynamics is very limited so that even for very small unit cells it is only practical to simulate a real time of 1-10ps. For this reason, empirical potentials are still very useful and are the most practical method for simulating longer timescales. A comparable simulation using an empirical potential would be able to run for the order of several tens of nanoseconds.
A Nosé thermostat is used in the finite temperature molecular dynamics simulations in later chapters and all zero temperature configurations have been found by using conjugate gradients to move the ions.

It is also possible to perform constant pressure molecular dynamics and therefore allow the size of the unit cell to change (and also fluctuate with temperature). There are fundamental difficulties in doing this by \textit{ab initio} methods, which are summarised below, and therefore this method has only been implemented in the empirical calculations in Chapters 4 and 6. Allowing for fluctuations in the size of the unit cell requires the particles coordinates $R_i$ to be expressed as fractional coordinates, $f_i$, and the parallelepiped defining the shape of the cell can be expressed in matrix form, $B$, (the volume then being $W = \det(B)$) giving the relation

$$R_i = B f_i.$$  \hfill (1.4) \smallskip

The dynamics of the boxmatrix can then be included in the Lagrangian of the total particle-boxmatrix system\cite{28}

$$L = \frac{1}{2} \sum_i m_i \dot{f}_i^T B^T B \dot{f}_i - V(B f_i) - P W + \frac{1}{2} M \text{tr}(B^T B)$$ \hfill (1.5) \smallskip

where the first two terms are the Lagrangian of the particles, the third is the term for constant pressure, $P$, and the final term defines the kinetic energy for the box and introduces the box mass, $M$, which is a fictitious mass that is required in order to integrate the equations of motion for the box over a given timestep.

This allows a full relaxation of the cell shape and lattice parameters to be performed simultaneously with the particle relaxation for a given $P$. Unfortunately this is not easily achieved with the \textit{ab initio} techniques. This is because the basis set in which the wavefunctions are expressed are plane waves whose energy depends on the size of the unit cell. Therefore changing the size of the cell will change the basis set of
the wavefunctions and therefore introduce the further complication of Pulay stresses. Due to the difficulties in calculating the Pulay stresses caused by the changing basis set, a full unit cell relaxation using ab initio methods is obtained by performing many simulations at different B matrices and plotting a hydrostatic curve through the phase space of B given by the lowest total energy found by varying B constrained to a given volume det(B). The effective pressure can then be found for a given W by the tangent to the energy volume curve.

1.4 Layout of Thesis

The thesis is arranged as follows. Chapter 2 describes the technique of ab initio molecular dynamics used to calculate the properties of two complex structures of carbon, silicon and germanium in Chapter 3. It is found that ab initio methods are too compute intensive for a full free energy calculation and therefore empirical methods are used to calculate the full pressure-temperature phase diagram of these complex structures. One of these structures, BC8, is found to have several natural (001) cleavage planes. Several possible reconstructions of these surfaces are considered for silicon in Chapter 5. Since it is short range correlations that govern the properties of amorphous materials, the local bonding topologies found in point defects within the diamond structure are also likely to be found in the amorphous structure. Several point defects are therefore investigated by both ab initio and empirical molecular dynamics in Chapter 6. Finally, in Chapter 7, relaxed structures of randomly packed silicon and carbon atoms are examined in order to make a comparison between the complex crystals and their amorphous counterparts.
Chapter 2

First Principles Molecular Dynamics

2.1 Introduction

In principle, all knowledge about a system can be obtained from the quantum mechanical wave function. This is obtained (non-relativistically) by solving the Schrödinger equation of the complete many electron system. However in practice solving such an N-body problem proves to be impossible. This chapter will give a brief description of earlier approximations made to solve this many-body problem and a description of the important physical features omitted from these theories. For these reasons it is necessary to use density functional theory developed by Kohn and Sham[29] based on the theory of Hohenberg and Kohn[30] which, in principle, is an exact ground state theory. As the name suggests, the fundamental variational parameter is the electron charge density rather than the electronic wavefunctions. In this formalism, the N-electron problem is expressed as N one-electron equations where each electron interacts with all other electrons via an effective exchange-correlation potential. These interactions are then calculated using the local density approximation to exchange and correlation. Plane wave basis sets and total energy pseudopotential techniques are then used to
solve the Kohn-Sham one electron equations. The Hellmann-Feynman theorem can then be used to calculate the forces required to integrate the ionic equations of motion within a molecular dynamics simulation.

There are now many articles on this subject which review the topics involved in total energy calculations in depth such as those in references [31, 32, 33, 34, 35, 36]. Therefore in this chapter only a brief description of the methods used for the total energy calculations used in later chapters will be discussed.

2.2 Earlier Approximations

A calculation to obtain the properties of electrons in a solid starts with the interacting N-body Schrödinger equation to obtain the N-electron wavefunction \( \Psi(r_1, r_2, ..., r_N) \) (for simplicity, spin is not explicitly mentioned):

\[
H \Psi = E \Psi \tag{2.1}
\]

where the Hamiltonian describing the interaction of electrons and nuclei is

\[
H = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - Z e^2 \sum_{R} \frac{1}{|r_i - R|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}. \tag{2.2}
\]

The first term is the many-body kinetic energy operator and the second describes the interaction of the electrons with the bare nuclei at fixed positions in the solid, \( R \). The final term represents the interactions of electrons with each other. The total energy of the system will also include the Coulomb repulsion between the ions. In general, it is not possible to solve this equation. In the Hartree approximation, it is found that \( \Psi \) can be written as a product of \( N \) one-electron wavefunctions thus:

\[
\Psi(r_1, r_2, ..., r_N) = \psi_1(r_1)\psi_1(r_2)\ldots\psi_1(r_N). \tag{2.3}
\]
This condition follows from the assumption that the electrons interact only via the Coulomb force (see equation (2.6) below).

The one-electron Schrödinger equations are now

\[-\frac{\hbar^2}{2m} \nabla^2 \psi_i(r) + V(r)\psi_i(r) = \epsilon_i \psi_i(r)\]  

(2.4)

where the first term is now the one-electron kinetic energy and \(V(r)\) is the potential in which the electron is moving. The choice of \(V(r)\) is then made such that equation (2.4) is solvable. Clearly it should include the potential that the electron would feel from the ions

\[V_{\text{ion}}(r) = -Ze^2 \sum R \frac{1}{|r - R|}\]  

(2.5)

However the electron also feels the field from all other electrons. To incorporate this into \(V(r)\), the remaining electrons are assumed to be a smooth distribution of negative charge density \(\rho(r')\). Therefore the potential energy of an electron in their field (often referred to as the direct term) would be

\[V_{\text{elec}}(r) = -e \int d\mathbf{r}' \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|}\]  

(2.6)

There are however several important features which cannot be represented in such a simple self-consistent field approximation. In particular the product of one electron wave functions is incompatible with the Pauli exclusion principle which requires the many-body wavefunction to be antisymmetric under the interchange of two electrons, that is

\[\Psi(\mathbf{r}_1, ..., \mathbf{r}_a, ..., \mathbf{r}_b, ..., \mathbf{r}_N) = -\Psi(\mathbf{r}_1, ..., \mathbf{r}_b, ..., \mathbf{r}_a, ..., \mathbf{r}_N).\]  

(2.7)

This cannot be satisfied by a non-zero wavefunction of the form given by Equation
(2.3). The form of the wavefunction can be generalised to incorporate asymmetry by replacing the Hartree wavefunction by a Slater determinant of one electron wavefunctions. This is a linear combination of all possible Hartree wavefunctions obtainable from permutations of \( \mathbf{r}_i \) added together with weights \( \pm 1 \) so as to give condition (2.7). The resultant ground state electron wavefunctions can be found variationally by using this trial wavefunction to obtain the Hartree-Fock equations of the orthogonal one electron wavefunctions \( \psi_i \). These are

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{r}) + V_{\text{ion}}(\mathbf{r}) \psi_i(\mathbf{r}) + V_{\text{elec}}(\mathbf{r}) \psi_i(\mathbf{r}) - \sum_j \int d\mathbf{r}' \left| \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \right| \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}') \psi_j(\mathbf{r}) \psi_i^*(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})
\]

These equations differ from the Hartree equations by the exchange term on the left hand side. Similar to the direct term it is non-linear in \( \psi_i \), but it has the structure if an integral operator. As a result the complexity added to the Hartree calculation by the incorporating electron exchange is considerable.

Although the Hartree-Fock approximation treats electron exchange exactly, this is only a first order approximation to the total energy due to many body interactions. Electron correlations are introduced at the next level of approximation. This is discussed further in Section 2.4 where both exchange and correlation are described by a simple functional of the charge density.

### 2.3 Density Functional Theory

Hohenberg and Kohn[30] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the
exact single particle ground state energy.

It was then shown by Kohn and Sham\cite{29} that it is possible to replace the many electron problem by an exactly equivalent set of self consistent one electron equations. The total energy functional can be written as a sum of several terms:

$$E[n(r)] = \int V_{\text{ion}}(r)n(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|}drdr' + G[n(r)] \quad (2.8)$$

for a fixed set of atomic nuclei at \{R_i\}. The first two terms are the classical Coulomb interaction between the electrons and ions and between electrons and other electrons respectively, both of which are simply functions of the electronic charge density n(r).

This equation is analogous to the Hartree method, but the term G[n(r)] contains the effects of exchange and correlation and also the single particle kinetic energy:

$$G[n(r)] = T[n(r)] + E_{\text{xc}}[n(r)] \quad (2.9)$$

where T[n(r)] is the kinetic energy of a system of non-interacting electrons with density n(r) and E_{\text{xc}}[n(r)] is the energy of exchange and correlation of an interacting system. There is no simple expression for the exchange and correlation - this will be considered in Section 2.4

According to the Hohenberg-Kohn theorem, the total energy function given by equation (2.8) is stationary with respect to variations in the ground state charge density, that is, it is subject to the condition

$$\int \delta n(r) \left\{ \frac{\delta T[n(r)]}{\delta n(r)} + V_{\text{ion}}(r) + \int \frac{n(r')}{|r-r'|}drdr' + \mu_{\text{xc}}(r) \right\} = 0 \quad (2.10)$$

where \mu_{\text{xc}}(r) is the functional derivative of the exchange-correlation energy with respect to the electronic charge density. There is also the requirement that a variation in the
charge density leaves the particle number

\[ N = \int n(r) \, dr \]  \hspace{1cm} (2.11)

unchanged. This can be ensured by the condition

\[ \int \delta n(r) \, dr = 0. \]  \hspace{1cm} (2.12)

Applying the condition of constant particle number, (2.12) to Equation (2.10) gives the result

\[ \frac{\delta E(r)}{\delta n(r)} = \frac{\delta T[n(r)]}{\delta n(r)} + V^{\text{ion}}(r) + \int \frac{n(r')}{|r-r'|} \, dr + \mu_{xc}(r) \]  \hspace{1cm} (2.13)

is a constant, \( \nu \), which is the Lagrange multiplier associated with the requirement of constant particle number. Comparing this to the corresponding equation for a system with an effective potential \( V(r) \) but without electron-electron interaction results in

\[ \frac{\delta E(r)}{\delta n(r)} = \frac{\delta T[n(r)]}{\delta n(r)} + V(r) \]  \hspace{1cm} (2.14)

\[ = \nu. \]

It can be seen that the mathematical representations are similar provided that

\[ V(r) = V^{\text{ion}}(r) + \int \frac{n(r')}{|r-r'|} \, dr + \mu_{xc}(r). \]  \hspace{1cm} (2.15)

The effect of this is to allow an indirect variation in \( n(r) \) through variation in the Kohn-Sham single particle orbitals, \( \psi_i \), where the kinetic energy operator can be expressed in terms of the single particle states as

\[ T = \sum_{i=1}^{N} \frac{\hbar^2}{2m} \int \psi_i^*(r)(-\nabla^2)\psi_i(r) \, dr. \]  \hspace{1cm} (2.16)
It then follows that the solution can be found by solving the Schrödinger equation for noninteracting particles moving under the influence of an effective potential $V(r)$

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right\} \psi_i(r) = \epsilon_i \psi_i(r) \quad (2.17)$$

which gives the charge density

$$n(r) = \sum_{i=1}^{N} \psi_i^*(r) \psi_i(r). \quad (2.18)$$

The solution of the system of equations (2.17) leads to the energy and electronic charge density of the ground state and all quantities which can be derived from them. The minimum of the Kohn-Sham energy functional, (2.8), leads to the ground state charge density of the electronic system which ions at the fixed positions $\{R_i\}$. It is only this minimum which has any physical meaning, therefore the path by which this minimum is found is unimportant. This point will be returned to later when minimisation techniques will be discussed.

### 2.4 Exchange, Correlation and the Local Density Approximation

In seeking the solutions to the system of equations (2.17), it is found that all quantities are represented as functionals of the electronic charge density. The important point that makes this system easier to solve (or more precisely, require less computation) than, for example the Hartree-Fock equations, is that the effective potential is local (although note Section 2.7 discussing the use of nonlocal pseudopotentials). Therefore there is no more complexity added in solving (2.17) than there is in the Hartree approximation. Of course, this is only true if the exchange-correlation energy can be described as a function of the local charge density. A method of doing so is known as the *local density approximation* \(^{[29]}\) (LDA). In LDA, the exchange-correlation energy of an electronic
system is constructed by assuming that the exchange-correlation energy per electron at a point \( r \) in the electron gas, \( \epsilon_{xc}(r) \) is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same electron density at the point \( r \). It follows that

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

so that

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

with

\[
\epsilon_{xc}(n(r)) = \epsilon_{xc}^{\text{hom}}(n(r))
\]

where Equation (2.21) is the assumption that the exchange-correlation energy is purely local. Several parameterisations for \( \epsilon_{xc}^{\text{hom}}(n(r)) \) exist, but the most commonly used is that of Perdew and Zunger\[37\]. This parameterisation is based on the quantum Monte Carlo calculations of Ceperley and Alder\[38\] on homogeneous electron gases at various densities. The parameterisation uses interpolation formulas to link these exact results for the exchange and correlation energy at many different densities.

In LDA, corrections to the exchange-correlation energy due to the inhomogeneities in the electronic charge density about \( r \) are ignored. Considering this inexact nature of the approximation, it may at first seem somewhat surprising that such calculations are so successful. This can be partially attributed to the fact that LDA gives the correct sum rule to the exchange-correlation hole. That is, there is a total electronic charge of one electron excluded from the neighbourhood of the electron at \( r \). Attempts to improve on LDA, such as gradient expansions to correct for inhomogeneities do not seem to show any improvement in results obtained by the simple LDA. One of the
reasons for this failure is that the sum rule is not obeyed by the exchange-correlation hole\(^1\).

A summary of the contributions of electron-electron interactions in N-electron systems is shown in Figure 2.1. It illustrates the conditional electron probability distributions \(n(r)\) of \(N-1\) electrons around an electron with given spin situated at \(r = 0\). In the Hartree approximation, Figure (a), all electrons are treated as independent, therefore \(n(r)\) is structureless. Figure (b) represents the Hartree-Fock approximation where the N-electron wavefunction reflects the Pauli exclusion principle. Around the electron at \(r = 0\) the exchange hole can be seen where the the density of spins equal to that of the central electron is reduced. Electrons with opposite spins are unaffected. In the LDA, where spin states are degenerate, each type of electron sees the same exchange-correlation hole (the sum rule being illustrated where the size of the hole is one electron). Figure (d) shows electron-electron interaction for non-degenerate spin systems (the local spin density approximation (LSD). It can be seen that the spin degenerate LDA is simply the average of the LSD).

### 2.5 Bloch’s Theorem and Plane Wave Basis Sets

As yet there has been no mention of how to handle the infinite number of interacting electrons moving in the static field of an infinite number of ions. Essentially, there are two difficulties to overcome: a wavefunction has to be calculated for each of the infinite number of electrons which will extend over the entire space of the solid and the basis set in which the wavefunction will be expressed will be infinite.

The ions in a perfect crystal are arranged in a regular periodic way (at 0K). Therefore the external potential felt by the electrons will also be periodic - the period being the same as the length of the unit cell, \(l\). That is, the external potential on an electron at \(r\) can be expressed as \(V(r) = V(r+l)\). This is the requirement needed for the use of

---

\(^1\)Although recent improvements have been made by Perdew et al\([37]\).
Figure 2.1. Summary of the electron-electron interactions (excluding coulomb effects) in (a) the Hartree approximation, (b) the Hartree-Fock approximation, (c) the local density approximation and (d) the local spin density approximation which allows for different interactions for like-unlike spins.
Bloch’s theorem. By the use of this theorem, it is possible to express the wavefunction of the infinite crystal in terms of wavefunctions at reciprocal space vectors of a Bravais lattice.

Bloch’s theorem uses the periodicity of a crystal to reduce the infinite number of one-electron wavefunctions to be calculated to simply the number of electrons in the unit cell of the crystal (or half that number if the electronic orbitals are assumed to be doubly occupied - that is, spin degenerate). The wavefunction is written as the product of a cell periodic part and a wavelike part:

$$\psi_i(r) = \exp(i k \cdot r) f_i(r). \quad (2.22)$$

The first term is the wavelike part which will be discussed below. The second term is the cell periodic part of the wavefunction. This can be expressed by expanding it into a finite number of plane waves whose wave vectors are reciprocal lattice vectors of the crystal

$$f_i(r) = \sum_G c_{i,G} \exp(i G \cdot r) \quad (2.23)$$

where $G$ are the reciprocal lattice vectors which are defined by $G \cdot l = 2\pi m$ for all $l$ where $l$ is a lattice vector of the crystal and $m$ is an integer. Therefore each electronic wavefunction is written as a sum of plane waves

$$\psi_i(r) = \sum_G c_{i,k+G} \exp\{i (k + G) \cdot r\} \quad (2.24)$$

By the use of Bloch’s theorem, the problem of the infinite number of electrons has now been mapped onto the problem of expressing the wavefunction in terms of an infinite number of reciprocal space vectors within the first Brillouin zone of the periodic cell, $k$. This problem is dealt with by sampling the Brillouin zone at special sets of $k$-points discussed in Section 2.6.
The electronic wavefunctions at each \( k \)-point are now expressed in terms of a discrete plane wave basis set. In principle this Fourier series is infinite. However, the coefficients for the plane waves, \( c_{i,k+G} \), each have a kinetic energy \((\hbar^2/2m)|k + G|^2\). The plane waves with a smaller kinetic energy typically have a more important role than those with a very high kinetic energy. The introduction of a plane wave energy cutoff reduces the basis set to a finite size.

This kinetic energy cut-off will lead to an error in the total energy of the system but in principle it is possible to make this error arbitrarily small by increasing the size of the basis set by allowing a larger energy cut-off. The cut-off that is used in practice depends on the system under investigation. For example, to describe the \( 2p \) valence electrons in carbon will require a large plane wave basis set to span the high energy states described by the wavefunction close to the carbon nucleus. However in silicon, the \( 3p \) valence electrons do not acquire such a high energy since they are repelled from the nucleus by orthogonalisation to the lower lying \( 2p \) core states. This will be discussed in more detail in later chapters.

Another advantage of expanding the electronic wavefunctions in terms of a basis set of plane waves is that the Kohn-Sham equations take a particularly simple form. Substitution of Equation (2.24) into the Kohn-Sham equations, (2.17), gives

\[
\sum_{G'} \left\{ \frac{\hbar^2}{2m} |k + G| \delta_{GG'} + V_{\text{ion}}(G - G') + V_{\text{elec}}(G - G') + V_{\text{xc}}(G - G') \right\} \times c_{i,k+G'} = \epsilon_i c_{i,k+G'}
\]  

(2.25)

It can be seen in this form that the reciprocal space representation of the kinetic energy is diagonal and the various potentials can be described in terms of their Fourier components. Usual methods of solving the plane wave expansion of the Kohn-Sham equations is by diagonalisation of the Hamiltonian matrix whose elements \( H_{k+G,k+G'} \) are given by the term in curly brackets. It follows that the size of the Hamiltonian
matrix is determined by the energy cut-off

$$\frac{\hbar^2}{2m} |k + G_c|^2.$$

(2.26)

It will be shown in a later section that it is not necessary to solve this by conventional matrix diagonalisation techniques, but a more computationally efficient method exists where the plane wave coefficients are treated as dynamical variables.

## 2.6 $k$-point Sampling

### 2.6.1 Discretisation of $k$-space

The first Brillouin zone can be mapped out by a continuous set of points, \( \{ k : k = (k_x, k_y, k_z) \} \), throughout that region of reciprocal space (\( k \)-space). The occupied states at each \( k \)-point contribute to the electronic potential of the bulk solid. Since the set \( \{ k \} \) is dense, there are an infinite number of \( k \)-points in the Brillouin zone at which the wavefunctions must be calculated. Therefore if a continuum of plane wave basis sets were required, the basis set for any calculation would still be infinite, no matter how small the plane wave energy cut-off was chosen.

For this reason electronic states are only calculated at a set of \( k \)-points determined by the shape of the Brillouin zone compared to that of its irreducible part. The reason that this can be done is that the electronic wavefunctions at \( k \)-points that are very close together will almost be identical. It is therefore possible to represent the electronic wavefunctions over a region of reciprocal space at a single \( k \)-point. This approximation allows the electronic potential to be calculated at a finite number of \( k \)-points and hence determine the total energy of the solid.

The error incurred by this approximation can be made arbitrarily small by choosing a sufficiently dense set of \( k \)-points. This is easily made clear by the use of an example. Each \( k \)-point has energy eigenvalues associated with it which is usually presented in
the form of a band structure - the band structure of GaAs in the zincblende structure along several lines through the Brillouin zone is given in Figure 2.2[39]. At each \( k \)-point the energy eigenvalues are averaged, which gives a measure of the energy associated with the electrons which occupy that region of \( k \)-space. These average energies are given in Figure 2.3. It can be seen that there is a large variation in energy over the Brillouin zone. In this case it is found that the average band energy is -4.8eV with a standard deviation of 1.7eV. This shows that there is a large dispersion in the band energies of GaAs in the zincblende structure. Therefore, in order to converge the total energies of the structure to within 0.01eV it seems that \( \sim 100 \) \( k \)-points randomly spread throughout the first Brillouin zone is necessary. Fortunately, there are more efficient methods of choosing the \( k \)-point set in which to sample the Brillouin zone.

Methods have been devised for obtaining very accurate approximations to the electronic potential from a filled electronic band by calculating the electronic wavefunctions at special sets of \( k \)-points. The two most common methods are those of Chadi and Cohen[40] and Monkhorst and Pack[41] which will be described below.

\textbf{Figure 2.2.} The band structure of GaAs (zincblende) along several lines of high symmetry.
2.6.2 Special $k$-point Sets

The $k$-point sampling approximation is used by evaluating Equation (2.18) with

$$n(r) = \frac{v}{(2\pi)^3} \int_{BZ} n_k(r) dk$$

(2.27)

where $v$ is the unit cell volume,

$$\int_{BZ} n_k(r) dk = \sum_k n_k(r),$$

(2.28)

where

$$n_k(r) = \sum_i \psi_{k,i}^*(r) \psi_{k,i}(r),$$

(2.29)

and $\psi_{k,i}(r)$ is the Fourier transform of $\psi_i(k)$, that is, the region of space which is occupied by electrons given by the contribution of $k$-point $k$. Here $k$ runs over the a set of $k$-points and $i$ labels the occupied states and the integral over the Brillouin zone.
is replaced by a sum over the discrete $k$-point set. This shows that a calculation to obtain the charge density is required at each $k$-point in the set. To optimize any total energy calculation it is necessary to compute the charge density at a carefully chosen set of $k$-points which characterises the shape of the reciprocal space of the cell. For example, the space group operations of a given cell will map some $k$-point onto others - these will have a related reciprocal space charge density\[42], therefore only a single computation is necessary.

This fact is used by Chadi and Cohen to generate a special set of $k$-points at which the reciprocal space should be sampled. The $k$-point set is generated as follows: picking two starting $k$-points $k_1$ and $k_2$ satisfying certain uniqueness conditions\[40] in the reciprocal space of the cell with point group operations $T = \{T_p\}$ then a new set of points can be generated by

$$\{k_i\} = k_1 + \{T_p\}k_2. \tag{2.30}$$

The new set of points generated in this way can then be used in a similar process to generate larger sets.

This procedure does not generate $k$-points that are necessarily unique in the irreducible part of the Brillouin zone. Through the symmetry operations, $T$, the new set of $k$-points can be ‘folded back’ into the irreducible part. A normalised weighting factor can then be associated with each point with their ratios indicating the number of times that each point in the irreducible zone has been generated. The generation procedure can be repeated until a sufficiently dense set of $k$-points is achieved to give as small an error required by the approximation given by Equation (2.27).

The Monkhorst-Pack scheme uses an alternate approach which gives an identical set of $k$-points to Chadi and Cohen. It is based on generating periodic functions based on the point group symmetries on a regular grid of points in the Brillouin zone.
2.6.3 Charge Symmeterisation

The use of special points in the Brillouin zone allows calculations to be carried out on a small number of \( k \)-point within the irreducible part of the Brillouin zone. The charge density obtained from these calculations can then be associated with other points throughout the zone by use of the point group operations, \( T \).

This can be done as follows: let the special set of Chadi-Cohen or Monkhorst-Pack \( k \)-points be \( \{ \mathbf{k}_j : j = 1, m \} \). Each \( k \)-point has a weighting of \( w_j \), as described above. If the wavefunction for each band, \( i \), at the special \( k \)-point \( \mathbf{k}_j \) is \( \psi_i(\mathbf{k}_j) \) then the reciprocal space charge density at that point in the irreducible part of the Brillouin zone is

\[
\begin{align*}
n(\mathbf{k}_j) &= \sum_i \psi_i^*(\mathbf{k}_j)\psi_i(\mathbf{k}_j) \\
\end{align*}
\]

The symmeterised charge density associated with the point \( \mathbf{k}_j \) with respect to the full point group \( T \) is then

\[
\begin{align*}
n(\mathbf{k}_j)_T &= \frac{1}{N_T} \sum_{T_p \in T} n(T_p \mathbf{k}_j) \\
\end{align*}
\]

where \( N_T \) is the number of operations, \( T_p \), in the point group \( T \). It is then simple to construct the full reciprocal space charge density by

\[
\begin{align*}
n(\mathbf{k}) &= \sum_j w_j n(\mathbf{k}_j)_T. \\
\end{align*}
\]

The fully symmeterised real space charge density \( n(\mathbf{r}) \) for a crystal with point group operations, \( T \), is obtained by Fourier transforming \( n(\mathbf{k}) \).
2.7 Ion-Electron Interactions

2.7.1 The Pseudopotential Approximation

It has been shown by the use of Bloch’s theorem, that a plane wave energy cut-off in the Fourier expansion of the wavefunction and careful $k$-point sampling (see Section 2.5 and 2.6 respectively) that the solution to the Kohn-Sham equations for infinite crystalline systems is now tractable. Unfortunately a plane wave basis set is usually very poorly suited to expanding the electronic wavefunctions because a very large number are required to accurately describe the rapidly oscillating wavefunctions of electrons in the core region.

It is well known that most physical properties of solids are dependent on the valence electrons to a much greater degree than that of the tightly bound core electrons. It is for this reason that the pseudopotential approximation is introduced. This approximation uses this fact to remove the core electrons and the strong nuclear potential and replace them with a weaker pseudopotential which acts on a set of pseudo wavefunctions rather than the true valence wavefunctions. In fact, the pseudopotential can be optimised so that, in practice, it is even weaker than the frozen core potential[43].

The schematic diagram in Figure 2.4 shows these quantities. The valence wavefunctions oscillate rapidly in the region occupied by the core electrons because of the strong ionic potential. These oscillations maintain the orthogonality between the core and valence electrons. The pseudopotential is constructed in such a way that there are no radial nodes in the pseudo wavefunction in the core region and that the pseudo wavefunctions and pseudopotential are identical to the all electron wavefunction and potential outside a radius cut-off $r_c$. This condition has to be carefully checked for as it is possible for the pseudopotential to introduce new non-physical states (so called ghost states) into the calculation.

The pseudopotential is also constructed such that the scattering properties of the pseudo wavefunctions are identical to the scattering properties of the ion and core
Figure 2.4. An illustration of the full all-electronic (AE) wavefunction and electronic potential (solid lines) plotted against distance, $r$, from the atomic nucleus. The corresponding pseudo wavefunction and potential is plotted (dashed lines). Outside a given radius, $r_c$, the all electron and pseudo electron values are identical.
electrons. In general, this will be different for each angular momentum component of the valence wavefunction, therefore the pseudopotential will be angular momentum dependent. Pseudopotentials with an angular momentum dependence are called non-local pseudopotentials.

The usual methods of pseudopotential generation firstly determine the all electron eigenvalues of an atom using the Schrödinger equation

\[
\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V \right\} \Psi_{AE_l} = \epsilon_l \Psi_{AE_l} \quad (2.34)
\]

where \( \Psi_{AE_l} \) is the wavefunction for the all electron (AE) atomic system with angular momentum component \( l \). The resulting valence eigenvalues are substituted back into the Schrödinger equation but with a parameterised pseudo wavefunction function of the form[43]

\[
\Psi_{ps_l} = \sum_{i=1}^{n} \alpha_i j_{l_i} \quad (2.35)
\]

Here, \( j_{l_i} \) are spherical Bessel functions. The coefficients, \( \alpha_i \), are the parameters fitted to the conditions listed below. In general the pseudo wavefunction is expanded in three or four spherical Bessel functions.

The pseudopotential is then constructed by directly inverting the Kohn-Sham equation with the pseudo wavefunction, \( \Psi_{ps_l} \).

A pseudopotential is not unique, therefore several methods of generation also exist. However they must obey several criteria. These are:

1. The core charge produced by the pseudo wavefunctions must be the same as that produced by the atomic wavefunctions. This ensures that the pseudo atom produces the same scattering properties as the ionic core. This will be discussed further in Section 2.7.2.

2. Pseudo-electron eigenvalues must be the same as the valence eigenvalues obtained
CHAPTER 2. FIRST PRINCIPLES MOLECULAR DYNAMICS

from the atomic wavefunctions.

3. Pseudo wavefunctions must be continuous at the core radius as well as its first and second derivative and also be non-oscillatory.

4. On inversion of the all electron Schrödinger equation for the atom, excited states may also be included in the calculation (if appropriate for a given condensed matter problem), for example, generating a \( d \) component for a non-local pseudopotential when the ground state of an atom does not contain these angular momentum components.

There are several ways in which these conditions can be satisfied leading to the non-uniqueness of a pseudopotential. This can be traced back to the expansion of the wavefunction in terms of a plane wave basis set. The set of plane waves, \( \{ \exp((k + G).r) \} \), forms a complete basis set (assuming a high enough cutoff) and the additional core states to which they are orthogonal results in a linearly dependent spanning set, that is, an over complete basis set. This linear dependance leads to non-unique pseudopotentials.

2.7.2 Norm Conserving Pseudopotentials

To obtain the exchange-correlation energy accurately it is necessary that outside the core region the real and pseudo wavefunctions be identical so that both wavefunctions generate identical charge densities (see conditions listed above). Generation of a pseudopotential that satisfies

\[
\int_0^{r_c} \psi_{AE}^*(r) \psi_{AE}(r) \, dr = \int_0^{r_c} \psi_{ps}^*(r) \psi_{ps}(r) \, dr, \tag{2.36}
\]

where \( \psi_{AE}^*(r) \) is the all electron wavefunction and \( \psi_{ps}^*(r) \) is the pseudo wavefunction, guarantees the equality of the all electron and pseudo wavefunctions outside the core region[31]. In practice this is achieved using a non-local pseudopotential which uses
a different potential for each angular momentum component of the pseudopotential. This also best describes the scattering properties from the ion core.

Pseudopotentials of this type are known as non-local norm-conserving pseudopotentials and are the most transferable since they are capable of describing the scattering properties of an ion in a variety of atomic environments.

### 2.7.3 Kleinman-Bylander Pseudopotentials

The most general form of a non-local pseudopotential is

\[
V_{\text{ion}} = \sum_{lm} |Y_{lm} > V_l < Y_{lm}|
\]  

(2.37)

where \(Y_{lm}\) are spherical harmonics and \(V_l\) is the \(l^{th}\) angular momentum component of the pseudopotential acting on the wavefunction. If there are \(N_{pw}\) plane waves in the expansion of the wavefunction at each \(k\)-point and there are \(N_k\) \(k\)-points then the evaluation of \(V_{\text{ion}}\) will require \(N_{pw}N_k(N_{pw} + 1)/2\) projectors of the above form to be calculated for each angular momentum component \(l\).

This can be seen as follows[44]: the crystal potential \(V_{cr}(r)\) is obtained by placing a pseudopotential for each species at each site in the lattice. The structure factor incorporates the crystal symmetry, hence

\[
V_{cr}(G - G') = \sum_s s_s(G - G')V_{ps}(G - G')
\]  

(2.38)

where the summation index is over ionic species and the structure factor for each species is \(s_s(G - G') = \sum_i \exp(i(G - G').R_i)\). The total ion-electron energy is then

\[
E_{\text{elec-ion,lm}} = \sum_{GG'} <\psi|Y_{lm} > V_{cr}(G - G') < Y_{lm}|\psi >.
\]  

(2.39)

It can be seen that this gives an inseparable double sum over \(G\) and \(G'\). Evaluation of the ion-electron contribution to the total energy therefore scales as the square of the
number of plane waves used in the expansion. This is computationally inefficient and will severely limit the size of any calculation.

A more efficient way of evaluating this contribution is due to Kleinman and Bylander [45]. By expressing the pseudopotential in a different form they were able to split the double sum into a product of two single sums. The Kleinman-Bylander pseudopotential has the form

\[ V_{\text{ion}} = V_{\text{LOC}} + \sum_{lm} \left| \psi_{lm} \right| \delta V_l \langle \delta V_l | \psi_{lm} \rangle \langle \psi_{lm} | \delta V_l \rangle \]  

(2.40)

where \( V_{\text{LOC}} \) is an arbitrary local potential, \( \psi_{lm} \) are the pseudoatom wavefunctions and \( \delta V_l \) is defined by

\[ \delta V_l = V_{l,NL} - V_{\text{LOC}} \]  

(2.41)

where \( V_{l,NL} \) is the \( l \) angular momentum component of a non-local pseudopotential.

To evaluate the electron-ion interaction using this form of the pseudopotential it is found that if the pseudo wavefunction is expanded in plane waves the double sum over \( G \) and \( G' \) becomes separable. This allows the expression to be evaluated in only \( N_{pw}N_k \) calculations. As a result the pseudopotential part of the calculation now scales linearly with the size of basis set.

2.8 The Car-Parrinello Method

2.8.1 Car-Parrinello Lagrangian

Until recently first principles electronic calculations where based on techniques which required the computationally expensive matrix diagonalisation methods. Car and Parrinello[46] formulated a new more efficient method which can be expressed in the language of molecular dynamics. The essential step was to treat the expansion coefficients of the wavefunction as dynamical variables.
In a conventional molecular dynamics simulation a Lagrangian can be written in terms of the dynamical variables which normally are atomic positions \( \{ \mathbf{R}_i \} \) and the unit cell dimensions \( \{ \mathbf{B} \} \). The Car-Parrinello Lagrangian can similarly be written, but also includes a term for the electronic wavefunction. Ignoring any constraints for the moment, it is

\[
\mathcal{L}' = \sum_i \left( \mu < \dot{\psi}_i | \dot{\psi}_i > - E[\{\psi_i\}, \{\mathbf{R}_i\}, \{\mathbf{B}\}] \right)
\]

(2.42)

where \( \mu \) is a fictitious mass which is associated with the expansion coefficients of the Kohn-Sham electronic wavefunctions \( \psi_i \). \( E \) is the Kohn-Sham energy functional. This is analogous to the usual form of the Lagrangian where the kinetic energy term is replaced with the fictitious dynamics of the wavefunctions and the Kohn-Sham energy functional replaces the potential energy.

The Kohn-Sham electronic orbitals \( \psi_i \) are subject to the orthonormal constraints

\[
\int \psi_i^* (\mathbf{r}) \psi_j (\mathbf{r}) d\mathbf{r} = \delta_{ij}.
\]

(2.43)

These constraints can be simply incorporated into the Car-Parrinello Lagrangian as follows:

\[
\mathcal{L} = \mathcal{L}' + \sum_{i,j} \Delta_{ij} \left( \int \psi_i^* (\mathbf{r}) \psi_j (\mathbf{r}) d\mathbf{r} - \delta_{ij} \right)
\]

(2.44)

where \( \Delta_{i,j} \) are the Lagrange multipliers ensuring the wavefunctions remain orthonormal. In terms of molecular dynamics, these can be thought of as additional forces on the wavefunctions which maintain orthonormality throughout the calculation.

From \( \mathcal{L} \), it follows that the Lagrange equations of motion

\[
\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{\psi}_i^*} \right) = \frac{\partial \mathcal{L}}{\partial \psi_i^*}
\]

(2.45)
give

$$\mu \ddot{\psi}_i = -H \psi_i + \sum_j \Delta_{ij} \psi_j$$  \hspace{1cm} (2.46)

where $H$ is the Kohn-Sham Hamiltonian and the force $-H \psi_i$ is the gradient of the Kohn-Sham energy functional at the point in Hilbert space that corresponds to the wavefunction $\psi_i$.

### 2.8.2 Orthonormality

The orthonormal constraints in the equations of motion are vital to give the correct electronic states in the molecular dynamics method. If the equations are solved in the absence of the orthonormal constraints the time evolution of the one electron wavefunctions are found to be either oscillatory or convergent to a single degenerate ground state\cite{31}, depending on initial conditions. The initial wavefunctions will only converge to different eigenstates if orthogonality is imposed.

Equation (2.46) ensures that the $\psi_i$ remain orthogonal at all instants in time. However, to ensure this, the Lagrange multipliers must vary continuously with time and so the implementation of these equations require the evaluation of $\Delta_{ij}$ at infinitely small time separations. To make the calculation possible, in practice, $\Delta_{ij}$ are held constant throughout each timestep of integration. This leads to non-orthogonality of the wavefunctions at the end of each timestep which then requires a separate orthogonalisation step. This is done by Gram-Schmit orthogonalisation

$$\psi'_i = \psi_i - \sum_{j<i} < \psi_{i}^{orth} | \psi_i > \psi_{j}^{orth} \hspace{1cm} (2.47)$$

and normalisation

$$\psi_{i}^{orth} = \frac{\psi'_i}{< \psi'_i | \psi'_i >} \hspace{1cm} (2.48)$$
where the orthonormalised set \( \{ \psi_{orth}^i \} \) is generated from the linearly independent set \( \{ \psi_i \} \) obtained from integration of the equations of motion.

As a result of this, the constraints of orthogonality are imposed each time the electronic equations of motion are integrated. \( \Delta_{ij} \) can then be approximated by the expectation values of the eigenstates, \( \gamma_i = < \psi_i | H | \psi_i > \) giving the equation of motion of the form

\[
\mu \ddot{\psi}_i = -(H - \gamma_i) \psi_i.
\]  

(2.49)

The wavefunctions are then an exact eigenstate when their accelerations \( \ddot{\psi}_i \) are zero which are found self-consistently.

### 2.8.3 More Efficient Methods: Conjugate Gradients and Preconditioning

After the original idea of Car and Parrinello in treating the plane wave coefficients as dynamical variables there have been several methods suggested to find the ground state. For example, numerical integration of the equations of motion such as the Verlet algorithm is several times slower than evaluation after analytic integration. Williams and Soler[47] made a change to first order equations of motion of the electronic degrees of freedom, which, although no more efficient than the analytic method per timestep, requires only half the memory and input/output operations therefore increasing the speed.

Each of these methods involve an indirect search for the self-consistent Kohn-Sham Hamiltonian. These methods have further complications such as smaller timesteps are required for larger systems - too large a timestep leading to unstable evolution of the wavefunctions. Such instabilities are not encountered if the Kohn-Sham energy functional is minimized directly. This is because the energy functional usually has only one well defined minimum for a fixed set of ions, therefore a direct search for this
minimum does not lead to instabilities.

In the absence of any information about a function, the optimum direction to move from a point in order to find the minimum is the steepest descent direction. The function is evaluated at steps along that direction until the minimum along that line is found. The steepest descent direction at that minimum is found at the procedure repeated until convergence to the desired accuracy is achieved. The rate of convergence of the steepest descents method is limited by the fact, that after minimisation is performed along a given direction it does not use the information found in that calculation in subsequent iterations. A more optimum method combines the information of previous iterations so that the subsequent search direction is in an independent direction to all of the previous ones. That is, the set of search directions form a linearly independent set. This method is known as the conjugate gradients method and it is a variation (as described below) of this method which is used in all subsequent total energy calculations. By using the information about previous search directions, this method is guaranteed to find the minimum of an \( n \)-dimensional function in \( n \) iterations (assuming a perfect line search at each iteration).

Unfortunately, \( n \) is usually in the order of \( 10^5 \) to \( 10^6 \). Each function evaluation is computationally very expensive also, and therefore each iteration could take a long time. What is required is a method that will get close to the minimum of a function very quickly. This is achieved by preconditioning the function. This is best described by assuming that the problem can be given by an \( n \)-dimensional quadratic, for example

\[
f(x) = x_0 + g^T x + \frac{1}{2} x^T G x
\]  

(2.50)

where \( G \) is known as the Hessian. In application to energy minimisation problem described here, \( x \) would be the coefficients of the wavefunction. The Hessian is equivalent to the Kohn-Sham Hamiltonian.
If the function, \( f \), is well conditioned \((G \sim I)\) then the conjugate gradients algorithm will converge very quickly. (In fact if \( G = I \) it will take only one conjugate gradient iteration to minimise \( f \)). In solving for the Kohn-Sham Hamiltonian, the problem is ill-conditioned because \( G \) has a wide range of eigenvalues. This is mainly due to the kinetic energy term which causes the diagonal terms in \( G \) to become large as the energy of the plane wave increases (given by Equation 2.26). A change of variables \( \tilde{x} = Cx \) is required such that \( \tilde{x} \) minimises \( \tilde{f}(\tilde{x}) = f(x) \) and \( \tilde{f} \) is well conditioned.

Substituting this change of variable gives the Hessian

\[
\tilde{G}(\tilde{x}) = C^{-T}G(x)C^{-1}.
\] (2.51)

So a \( C \) is required such that \( C^{-T}G(x)C^{-1} \sim I \). At first sight, this looks as if a full matrix inversion is required in order to obtain \( C \). But, in solving the Kohn-Sham Hamiltonian, the diagonal terms \( G_{ii} \) get increasingly large as explained above. They will eventually dominate the row in which they are on so that \( G_{ii} \) approximate the large eigenvalues of \( G \).

Now consider preconditioning with the matrix \( M = C^TC \) where

\[
C = \text{diag}(c_1, ..., c_n)
\] (2.52)

and \( c_i = \sqrt{G_{ii}} \). If \( \lambda_i \) is an eigenvalue of the Kohn-Sham Hamiltonian, \( G \), then \( \lambda_i c_i^{-2} = \lambda_i / G_{ii} \) is approximately an eigenvalue of \( C^{-T}G(x)C^{-1} \). The matrix \( C^{-T}GC^{-1} \) has a much narrower spectrum of eigenvalues than \( G \) and therefore the energy minimisation problem will converge much quicker using conjugate gradients that the unpre-conditioned case.

In practice the energy convergence achieved by (preconditioned) conjugate gradients is excellent and in general it takes only a few tens of iterations to converge total energies adequately even though the electronic wavefunctions are expanded up to \( \sim 10^5 \) to \( 10^6 \).
2.9 Molecular Dynamics

So far, total energy calculations have been described for only fixed set of atomic coordinates. A natural consequence of the Car-Parrinello formalism is that electronic and ionic relaxation can take place simultaneously. For this to be performed, the total forces on the ions must be found in order to update the ionic positions.

The force on an ion, $I$, at position $R_I$ can be obtained from the full derivative of the total energy, $E$, by

$$F_I = -\frac{dE}{dR_I}.$$  (2.53)

As the electronic wavefunctions change, the force on the ions will be altered, therefore the full derivative has to be expressed in terms of changes in the wavefunction:

$$F_I = -\frac{\partial E}{\partial R_I} - \sum_i \frac{\partial E}{\partial \psi_i} \frac{\partial \psi_i}{\partial R_I} - \sum_i \frac{\partial E}{\partial \psi_i^*} \frac{\partial \psi_i^*}{\partial R_I}.$$  (2.54)

Now, since

$$E = \langle \psi | H | \psi \rangle$$  (2.55)

it follows that $\frac{\partial E}{\partial \psi_i}$ is just $H \psi_i$. But $\psi_i$ are electronic eigenstates with eigenvalues $\epsilon_i$. Therefore after some algebraic manipulation the final two terms can be written

$$\sum_i \epsilon_i \frac{\partial}{\partial R_I} \langle \psi_i | \psi_i \rangle.$$  (2.56)

which is zero since $\langle \psi_i | \psi_i \rangle$ is the normalisation constant. This shows that when each electronic orbital is an eigenstate of the Hamiltonian, then the partial derivative of the total energy with respect to the ionic positions is the force felt by the ions. This is the
Hellmann-Feynman theorem\[49, 50\] and can be generalised to any order of derivative of the total energy.

In practice, the wavefunctions are only calculated to a given tolerance therefore they are never exact eigenstates of the Kohn-Sham Hamiltonian. As a result the forces calculated using the Hellmann-Feynman theorem incur error. This can be seen when the expression for the force is written formally as

$$ F_I = -\frac{\partial E_{\text{ext}}}{\partial R_I} - \int n(r) \frac{\partial V_{\text{ion}}}{\partial R_I} dr - \int \frac{\partial E}{\partial n(r)} \frac{\partial n(r)}{\partial R_I} dr $$  \hspace{1cm} (2.57)

where $E_{\text{ext}}$ are all external energies such as the Ewald energy. The final term, called the variational force, vanishes when the wavefunctions are completely converged so that the conditions of the Hellmann-Feynman theorem are satisfied. It is in this term that the errors occurring from unconverted wavefunctions or incomplete basis sets are incurred. The error on the force is first order with respect to error in the wavefunction (as compared to errors in the total energy which are second order). It follows that the Hellmann-Feynman theorem can only be implemented when the wave functions are very close to self consistency. Only then can the ionic equations of motion be integrated and the ionic positions updated.

This leads to the use of the Born-Oppenheimer approximation. This is based on the fact that typical electronic velocities are much greater than that of the ions. It can therefore be assumed that the ions move so slowly relative to the electrons that at any point in time, the electrons will be in their ground state for that instantaneous ionic configuration. A schematic view of such an ionic trajectory is given in Figure 2.5. The need for the system be be kept close to the Born-Oppenheimer surface governs the method in which Car-Parrinello molecular dynamics is used in practice. The ground state wavefunction is first calculated self-consistently for a fixed set of ionic coordinates. In this method an initial wavefunction has to be assumed - this is given by initializing the expansion coefficients of the wavefunction by random numbers. Although this
initial state is far from the Kohn-Sham eigenstates it does not assume any initial symmetries which, if incorrect, could lead to prohibitively long calculation to find the correct wavefunctions. The total energy is reduced by the conjugate gradients method (ensuring the wavefunctions are orthogonalised at the end of each iteration) until the wavefunctions are sufficiently converged to give correct forces. New ionic positions are then calculated under the influence of these forces either by integration of the equations of motion or by direct minimisation techniques. After each change in the position of the ions, the wavefunctions will no longer be eigenstates of the new ionic positions. In order to find the wavefunctions for this better set of ionic positions it is not necessary to randomise the wavefunctions. The motion of the ions will be sufficiently small that the old wavefunctions will be a good place to initialise the iterative procedure again.

This process of calculating the electronic wavefunctions, using the Hellmann-Feynman theorem to calculate the forces on the ions, moving the ions under the influence of these forces and updating the wavefunction will be a will keep the trajectory of the molecular dynamics simulation on the Born-Oppenheimer surface if a sufficiently small
A summary of the computational procedure is shown in Figure 2.6.

This process forms the method which is used in later chapters to find a 0K local minimum of the ionic positions and the ground state electronic structure of materials. But this method also lends itself to finite temperature *ab initio* molecular dynamics simulations. Instead of moving the ions in order to reduce the forces acting (and therefore reduce the total energy of the system) the ions are initially given a random velocity, with a total kinetic energy given by $\frac{3}{2}k_B T$ per degree of freedom. Temperature is a time averaged quantity as energy interchanges between potential and kinetic forms, therefore it is not physically correct to scale the velocities every timestep to remain at a fixed temperature. The time averaged temperature is maintained by means of a Nosé thermostat. Integration of the ionic equations of motion continue at that temperature/kinetic energy governed by the thermostat allowing the ions to move under the influence of the Hellmann-Feynman forces. The system is returned as close as possible to the Born-Oppenheimer surface before the ions are moved at each timestep.

### 2.10 Metals

So far, it has been assumed that each Kohn-Sham eigenstate has been fully occupied. That is, each state $\psi_i(k)$ has associated with it an electronic charge $\psi_i^*(k)\psi_i(k)$ for each point $k$ in the Brillouin zone sampling which contributes to the total energy of the system. This is not true for metals. In metals there are partially filled bands because the Fermi surface cuts through some bands.

In order to find the Fermi surface it is necessary to sample part of the unoccupied band structure because of the partial occupancy of some bands. This is done by weighting each state near the (estimated) Fermi surface by the occupied portion of the reciprocal space volume it represents. An effective technique of doing this is Gaussian smearing[51] which is a method that has been also used to treat electrons at non-zero...
CHAPTER 2. FIRST PRINCIPLES MOLECULAR DYNAMICS

Figure 2.6. This flow chart illustrates the procedure used in *ab initio* molecular dynamics simulations.
temperatures\cite{52}. In this scheme, the energy of each calculated band is broadened by a gaussian. That is to say, the weight (or occupation number) is chosen by the portion of the gaussian distribution which lies under the Fermi level. The Gaussian is given by

\[ f_{i,k}(E_F) = \frac{1}{\sqrt{2\pi}\Delta} \exp \left( -\frac{(E_F - E_{i,k})^2}{2\Delta^2} \right) \]  

(2.58)

where \( E_{i,k} \) is the energy of band \( i \) and \( k \)-point \( k \), \( E_F \) is the Fermi energy and \( \Delta \) is the width of the Gaussian which is chosen appropriate to the spacing between the energy bands. It is initially chosen large and gradually reduced as the convergence to the Fermi surface improves.

As stated above, the occupation number \( o_{i,k} \) is chosen by the area under the Gaussian that lies below the Fermi surface:

\[ o_{i,k} = \int_{-\infty}^{E_F} f_{i,k}(E)dE \]  

(2.59)

\[ = \frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{E_F - E_{i,k}}{\sqrt{2}\Delta} \right) \]

where \( \text{erf}(x) \) is the standard error function and normalisation gives

\[ 2 \sum_{i,k} o_{i,k} = N_e \]  

(2.60)

where \( N_e \) is the total number of electrons in the unit cell.

In this method using a generalisation of density functional theory to non-zero temperatures, it is more useful to work in a free energy formalism\cite{53} which depends on both the wavefunctions and the single particle occupation numbers

\[ F(\psi_i, o_{ik}) = E(\psi_i, o_{ik}) - TS(o_{ik}) \]  

(2.61)
which introduces an entropy correction

$$S = -2k_B \sum_{ik} \left[ o_{ik} \ln o_{ik} + (1 - o_{ik}) \ln (1 - o_{ik}) \right]$$  \hspace{1cm} (2.62)

to the total energy of the system\cite{53}. Clearly as $T \to 0$, the entropy goes to zero and the usual zero temperature scheme is recovered. This addition of the entropy term to the standard energy functional makes it possible to treat a system with fractional occupancies within a global minimisation procedure with respect to the wavefunction coefficients and the occupation numbers\cite{54}.

It is important that a large number of $k$-point is used to sample the Brillouin zone so that the Fermi surface is accurately mapped out. A failure to do so will result in a large error in the Fermi energy leading to incorrect part of the band structure to be occupied or empty.

This method is used in Chapter 3, where the the metallic phase, $\beta$-Sn, of silicon is considered.

### 2.11 Summary of MD Codes

All of the \textit{ab initio} molecular dynamics calculations reported in Chapters 3 and 5 have performed using the CASTEP$^2$ and CETEP$^3$ codes. The large scale calculations in Chapters 6 and 7 have been done using code which we have implemented on the massively parallel Connection Machine CM200 at the Edinburgh Parallel Computing Centre.

CASTEP and CETEP use a plane wave basis set to expand the electronic wavefunction on which a band-by-band minimisation is achieved by the preconditioned conjugate gradients method in the space of the expansion coefficients, but constrained to maintain orthogonality of the single particle states. The Brillouin zone is sampled

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$^2$CAmbridge Serial Total Energy Package\cite{31}$^3$Cambridge Edinburgh Total Energy Package\cite{31}
using the special \( k \)-points scheme of Monkhurst and Pack. On calculations on metallic systems the Gaussian smearing method of Fu and Ho is used with the entropy correction scheme of Devita.

Massively parallel computation provides an excellent technique for working with larger systems. Unlike the use made of CASTEP and CETEP in the calculations given in Chapters 3 and 5, the emphasis in Chapters 6 and 7 is on solving a single large problem rather than many smaller ones.

The CM200 code is implemented for semiconducting and insulating systems only. Expanding the wavefunction in plane waves gives a natural variable in which to parallelise over when using a very large number of processors (>16000). The plane wave coefficients \( c_{i,k+G} \) are operated on in parallel along the \( G \) axis of the array in which they are stored. Axes \( i \) (bands) and \( k \) (special \( k \)-points) are relatively small in comparison to the Fourier expansion in \( G \) and are therefore operated on in series. This is the most efficient method since, generally, the number of \( G \) components at each band and \( k \)-point is larger than the number of processors on the CM200. With this data distribution, the only necessary interprocessor communication (which slows the algorithm) is in summing over \( G \)’s when orthogonalising the wavefunctions, performing the FFT's on the charge density and packing/unpacking the wavefunction in order to construct the 3d charge density from the 1d wavefunction \( G \)-axis.
Chapter 3

Complex Phases: Ab Initio Treatment

3.1 Introduction

After many years of study, the polymorphism of group IV elements still remains unresolved. This is due to the existence of metastable phases. On depressurisation of the group IV elements silicon and germanium from their first high pressure metallic phase, they do not return to the initial diamond phase, but form complex 4-fold coordinated high density structures.

This chapter presents complete \textit{ab initio} total energy calculations on the behaviour of diamond and dense metastable 4-fold coordinated phases (known as BC8 and ST12) carbon, silicon and germanium. The effects of pressure on structure and bonding is also discussed. The calculations incorporate direct relaxation of the atomic positions under the Hellmann-Feynman forces and a search through unit cell parameters for the BC8 structure and, in the case of ST12, a full relaxation of the $c/a$ ratio of the tetragonal unit cell is performed at each volume in order to obtain the complete pressure dependence of the unit cell.

Experiment suggests that similar structures in III-V semiconductors do not exist.
For this reason _ab initio_ calculations have been performed to try to explain why these phases are not found.

This chapter is organised as follows. A summary of the total energy calculations discussed in Chapter 2 including the conditions for convergence are given in the next section. A discussion of the BC8 and ST12 structures will be given next followed by the full pressure dependance of these structures. It is possible to extract phonon frequencies from an _ab initio_ molecular dynamics simulation at finite temperature from the ensemble average of the velocity autocorrelation function. This method will be given in Section 3.6 and the method is applied to silicon in the diamond, BC8 and ST12 structures. This can be compared to the phonon calculations in Chapter 4 found using an empirical potential and the harmonic approximation. The electronic structure of carbon, silicon and germanium in these three structures will be discussed in the form of band structures in Section 3.7. It is found that there is a fundamental difference in the nature of the bonding between carbon and silicon or germanium which is presented in Section 3.8. Finally, an investigation into why these metastable structures are not found in III-V semiconductors will be presented in Section 3.10 in terms of a total energy calculations, molecular dynamics and a fully _ab initio_ calculation of ionicities.

### 3.2 Total Energy Calculations

This work was carried out using the CASTEP code using first principles molecular dynamics as discussed in Chapter 2 and in reference [31]. The electronic wavefunctions are expanded in a plane wave basis set with periodic boundary conditions, the basis set being expanded to a cut-off of 250 eV for silicon and germanium and 408 eV for carbon. This higher value is required to ensure energy difference convergence for carbon because of the greater depth of the pseudopotential. This in turn arises because of the $2p$ character of the valence orbitals are not kept away from the nucleus by orthogonalisation to other $p$ orbitals as in silicon or germanium.
CHAPTER 3. COMPLEX PHASES: AB INITIO TREATMENT

The electronic degrees of freedom are relaxed using the conjugate gradients routine and orthogonalisation of the wavefunctions is restored at the end of each iteration. This electronic relaxation is continued until the Hellmann-Feynman forces have converged to better than three significant figures, and then the ions are moved also using a conjugate gradients routine. The ions are allowed to relax until the forces are below 0.001eV/Å. The unit cell for each calculation is not allowed to relax during the run due to the difficulty in dealing with enlarging or reducing the basis set. As the plane wave basis set is not localised there are no Pulay forces arising from changes in the basis set while the ions are relaxing. This was discussed briefly in Chapter 1.

For silicon and carbon in the diamond, ST12 and BC8 structures 4 special k-points at which the band structure is sampled were used. The same special k-point sets were found to be insufficient to converge the very small ST12-diamond energy difference in germanium. Several sets of k-points were tested and a set of 10 was found to be sufficient. This will be discussed further in Section 3.7. It is also possible that the frozen core approximation for the germanium 3d electrons may not be entirely justified, but a full potential treatment would be required in order to explore this. The combination of cut-off and k-point sampling gives total energies which are converged to approximately 0.1eV, however the physically significant quantities are total energy differences between total energy-volume curves which are converged to better that 0.01eV, of which a significant amount can be attributed to curve fitting schemes (Murnaghan vs. polynomial). In germanium the better k-point sampling gives still better convergence.

3.3 Internal Structure of BC8 and ST12

Diffraction evidence suggests that the postrecovered form of silicon has body-centered cubic symmetry with sixteen atoms in the cubic unit cell and a lattice parameter of 6.64Å. The space group of the structure is Ia\textsuperscript{3}-T\textsuperscript{7}\text{h}. The structure is then fully specified by a single lattice parameter, \( a \), and a single positional parameter \( x \) which has been
Figure 3.1. Projection of the structure of BC8 on (001). Elevations (in a/10) are given by the numbers inside the circles. A and B label the two distinct bonds.

Experimentally reported as being 0.1003 $\pm$ 0.0008\[56\] in silicon. A projection of the BC8 structure is shown in Figure 3.1. The structure is based on tetrahedrally coordinated atoms, but with a rather more efficient packing than in diamond. This efficiency leads to a higher density structure (hence favoured at high pressures) at the expense of small distortions from the diamond bondlength but with an appreciable change in the tetrahedral angle relative to the diamond structure. The distortions can be described by the existence of two bondlengths ($R_A$ and $R_B$) and two bond angles ($\Theta_{AB}$ and $\Theta_{BB}$). It is possible to choose special values of $x$ to satisfy either $R_A=R_B$ or $\Theta_{AB}=\Theta_{BB}$ but in practice the observed values ($R_A=2.30\text{Å}, R_B=2.39\text{Å}, \Theta_{AB}=117.9$ and $\Theta_{BB}=99.2[56]$) seem to be a compromise between the two. All atoms are equivalent, and the structure contains only evenfold rings, the smallest being sixfold, as with diamond. Although BC8 exhibits a density some 10% higher than diamond, the B bondlengths are slightly larger. The relations connecting bondlengths and the
internal parameter $x$ are as follows:

\begin{align*}
R_A/a_0 &= 2\sqrt{3}x \\
R_B/a_0 &= \sqrt{8x^2 - 2x + 0.25} \\
R_5/a_0 &= \sqrt{3}(0.5 - 2x)
\end{align*} \tag{3.1, 3.2, 3.3}

Where $R_A$ and $R_B$ are the bondlengths of the A and B bonds, while $R_5$ is the length of the nearest non-bonded neighbour and $a_0$ is the lattice parameter (see Figure 3.1).

The two bond angles also depend on $x$ via the following relations:

\begin{align*}
\theta_{AB} &= \cos^{-1}\left(\frac{8x - 1}{\sqrt{96x^2 - 24x + 3}}\right) \tag{3.4} \\
\theta_{BB} &= \cos^{-1}\left(\frac{4x^2 - x}{8x^2 - 2x + 0.25}\right) \tag{3.5}
\end{align*}

This allows a perfect tetrahedral angle at $x = \frac{5 - \sqrt{5}}{40}$. This is never realised in atomic systems because it would require the A bond to be only 62% as long as the B bond. These expressions are useful because they show that the bond angles become less ideal with increasing $x$. Other values of $x$ having interesting structural consequences are $x = \frac{1}{8}$ where the structure becomes a threefold coordinated layer structure with graphitic layers of type B bonds, and $x \to \frac{1}{2} - x$ which is a transformation which leaves the structure unchanged. Thus increasing $x$ can be regarded as a ‘magic internal strain’[57] similar to the so-called magic strains used to generate the BCT5 structure proposed as a high pressure phase of silicon[58].

The postrecovered form of germanium, ST12, is more complex. A projection of the ST12 structure is shown in Figure 3.2. Like BC8 it is based on tetrahedrally coordinated atoms packed in such a way as to increase the density to 10% above diamond. Crystallographic solution[22] of this phase cites it as having a simple tetragonal unit cell with 12 atoms. The structure would appear to have unusual optical properties since it has left- and right-handed forms, although there has not yet been any experiment done
to examine this, presumably because of the difficulty in obtaining suitable single crystals. The space group is $P4_{3}2_{1}2(D_{4}^{8})$ or its enantiomorph. The fully relaxed structure can be defined by two lattice parameters and four atomic positional parameters.

In ST12 there are two distinct atomic environments, which leads to some rather complicated topological substructures. Four of the twelve atoms are in environment $a$, and the remaining eight in $b$. The $b$ type can be viewed as forming spiral chains along the unique axis, while the $a$ atoms bridge different spirals. All the spirals rotate the same way, giving the structure a well-defined helicity as noted above. Although the atoms are still fourfold co-ordinated, there are now five and seven membered rings, and the variation in bond-angles (ranging from $87^\circ$ to $130^\circ$) is greater than in BC8 but the bond lengths are clustered more closely around the value found in diamond. In Chapter 4 it is shown that the stability of ST12 against BC8 rests in the compromise between equalizing bond lengths at the expense of increasing bond angle distortions.

**Figure 3.2.** Projection of the structure of ST12 on (001). Elevations (in fractional co-ordinates) are given by the numbers inside the circles. $A$, $B$ and $C$ label the three distinct bonds.
Figure 3.3. Graph of energy against volume for fully relaxed diamond, BC8 and ST12 structures in silicon.

ST12 occurs when the bond angles are relatively easier to distort.

3.4 Results on Structure

3.4.1 Silicon and Germanium

Graphs of Murnaghan equation fits to energy against volume for silicon and germanium in the ST12, BC8 and diamond phases are shown in Figures 3.3 and 3.4. The initial unit cell dimensions and internal structural parameters for ST12 were obtained from the empirical calculations described in Chapter 4. These graphs show that in each case the relaxed structures are unstable with respect to diamond at low pressures.

To obtain the curve for ST12 under hydrostatic pressure it was necessary to perform several series of calculations at several different $c/a$ ratios, and to construct Figure 3.5 which is a contour plot of the energy against volume and $c/a$. The hydrostatic curve is then the lowest value of the projection of this surface onto the volume axis. Figure
Figure 3.4. Graph of energy against volume for fully relaxed diamond, BC8 and ST12 structures in germanium.

3.6 shows the variation of $c/a$ with volume under hydrostatic pressure.

In silicon there is no intercept between the diamond-$\beta$-Sn common tangent (Figure 3.3) and BC8 or ST12 curves, from which it is deduced that these phases are, at best, metastable. The common tangent construction can also be used to predict the $\beta$-Sn $\rightarrow$ BC8 transition pressure using the metal calculation described in Section 2.10. From these graphs it is predicted that, for silicon, a pressure of only 11GPa will transform the diamond structure to BC8. This is lower than the observed pressure for the diamond $\rightarrow$ $\beta$-Sn transition at 12.5GPa[12]. This experimental value is above the theoretical value because of hysteresis effects resulting from the absence of an easy transition mechanism. The theoretical diamond $\rightarrow$ BC8 transition pressure is greater than the calculated diamond $\rightarrow$ $\beta$-Sn pressure (9GPa) found here. The calculated pressure between $\beta$-Sn and BC8 is 8GPa in good agreement with depressurisation experiments and suggestive of a relatively easy transition path. This will be discussed further when the III-V semiconductors are discussed which show no metastable high density phases.
Figure 3.5. Contour plot of energy against $c/a$ ratio and atomic volume for ST12 silicon.

Figure 3.6. Graph showing the variation of $c/a$ ratio in ST12 silicon as a function of volume.
on depressurisation from their high pressure metallic phases.

In germanium the broad picture is similar but with ST12 being stable at intermediate pressure. The contour plot of energy against \(c/a\) and volume and the variation of \(c/a\) with volume for germanium ST12 are similar to that of silicon shown on Figs. 3.5 and 3.6. Unlike silicon, the common tangent between \(\beta\)-Sn and diamond cuts the ST12 curve (not shown), implying that for a range of pressures ST12 is the stable structure. This result appears to contradict the observation of the first transition being to \(\beta\)-Sn. However, given the long experimental lifetime of the ST12 phase at ambient pressure[18, 22], it is clear that no easy diamond \(\rightarrow\) ST12 transformation path exists and is therefore likely that before the kinetic barrier can be overcome, the experimental pressure has been raised to that at which \(\beta\)-Sn is stable. Thus the only way to make ST12 germanium is via the \(\beta\)-Sn phase. It may even be that the retransformation from \(\beta\)-Sn to BC8 is easier than to ST12 because both structure have evenfold rings. The BC8 structure will also be favoured at low temperatures (this will be discussed in Chapter 4) although at room temperature, BC8 germanium has been observed to exist for several hours[18] when the sample was rapidly depressurised from the high pressure metallic phase.

For all phases, the calculated results for the equilibrium structural parameters are in good agreement with those reported in previous studies. The lattice parameters and bulk moduli as determined by fits to a Murnaghan equation of states,

\[
E = \frac{BV}{B'} \left( \frac{1}{B' - 1} \left( \frac{V_0}{V} \right)^{B'} + 1 \right) + E_0,
\]

(3.6)

where \(B = -\frac{\partial^2 E}{\partial V^2}\) is the bulk modulus and \(B'\) is its pressure derivative. These are given in Table 3.1. As is usual in LDA calculations, the lattice parameters are underestimated by about 2\% (except for diamond germanium where the underestimate is only 0.5\%). This means it is expected that the bulk moduli will be overestimated; where experimental data exist this is indeed the case, \(B_0\) is overestimated by up to 8\%. 

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**CHAPTER 3. COMPLEX PHASES: AB INITIO TREATMENT**

58
Table 3.1. Calculated structural properties of carbon, silicon and germanium in the diamond, BC8 and ST12 structures. The units are in eV and Å. The values are taken from fits to the Murnaghan equation of states.

Determination of the equilibrium axial ratio in both ST12-Si and ST12-Ge is crucial for accurate determination of energy differences in these phases. This is because it is found that the ST12 total energy for both materials varies by several tens of meVs over a c/a ratio range of 1.1 to 1.3. For the case of germanium the equilibrium axial ratio occurs at 1.24 which represents a 6% overestimate of the experimental value[18, 22]. The calculated values for the relaxed atomic positional parameters, which are also sensitive to the c/a ratio, are discussed in more detail in the following section.

The Murnaghan equation of state assumes a linear pressure dependence of the bulk modulus. The pressure derivative of the bulk modulus, \( B' = dB_0/dP \), is a dimensionless quantity describing the third volume differential of the energy in units normalised to the volume and bulk modulus. In all cases it is found that this is in the region 4-6, typical of experimental values. The fitting errors for this quantity are of order 25%, being especially unstable with respect to data points taken at high compression.

It is also observed that there is some debate as to whether a Murnaghan fit is
Figure 3.7. Valence charge density of germanium in the BC8 structure showing both $A$ and $B$ bonds. The charge density for BC8 Si on the same plane is similar.

appropriate in these structures\cite{59}. Some of the calculated points are at unphysical compressions of up to 30\%. Since compression is taken up by a combination of internal distortion and bond compression, the approximation that $dB/dP$ is a constant throughout this huge pressure range is extremely doubtful.

The calculated valence charge densities for germanium in the BC8 structure is shown in figure 3.7 and ST12 structure is shown in Figure 3.8. The figures for the BC8 structure show the valence charge density in a plane containing both $A$ and $B$ bonds. Figure 3.9 shows a schematic representation of the atomic positions and bonding configurations for both structures.

\textbf{3.4.2 Carbon}

The energy vs. volume graph for carbon is shown in Figure 3.10. It is immediately clear that the atomic volumes of all phases are rather similar, and therefore that BC8 is unlikely to be even a metastable phase. The energy difference is also very much greater
Figure 3.8. Valence charge density of germanium in the ST12 structure. The charge density for ST12 Si on the same plane is similar.

Figure 3.9. Schematic diagram illustrating the atomic positions and bonding configurations for planes through the BC8 and ST12 structures.
than for silicon. These results for BC8 are in agreement with previous calculations\cite{9}, where the rather surprising conclusion that BC8 may exist was drawn (from extrapolation of the murnaghan curves to 12Mbar. In Figure 3.11 the value of the BC8 internal parameter $x$ is shown. It is clearly very different from Si and Ge, and consideration of the bondlengths shows that the short A bond is much shorter than the B bonds.

All these results suggest that carbon is behaving very differently to the other materials, and the difference in bonding can be clearly seen in Figures 3.12, 3.13 and 3.14. Far from being fourfold coordinated, the valence electrons are concentrated in one bond only, with the three B bonds much reduced.

To examine this more closely, the amount of charge in each bond was estimated by integration of the valence charge density. There is no unique way of doing this: the method used here consists of defining the bonds by the line joining the two atoms, and then associating with that bond the region of space closer to the bond’s line than to any other bond’s line. This construction produces space-filling polyhedra and ensures that

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{energy_volume_graph.png}
\caption{Graph of energy against volume for fully relaxed diamond, BC8 and ST12 structures in carbon.}
\end{figure}
Figure 3.11. Graph showing the variation of the BC8 internal parameter, $x$, as a function of normalised atomic volume in carbon, silicon and germanium.

Figure 3.12. Valence charge density of carbon in the BC8 structure showing both $A$ and $B$ bonds.
Figure 3.13. Valence charge density of carbon in the ST12 structure.

Figure 3.14. Three dimensional representation of a valence charge density isosurface of carbon in the BC8 structure.
the total integrated density is equal to the number of electrons. It has the drawback that purely spherical charge densities give the same number of electrons per bond as purely covalent ones, but in the current case covalency is assumed, and studying whether the bonds are of similar order is all that is required. In Figure 3.15, the charge densities in slices of these polyhedra perpendicular to the bond direction along C-C bonds in the BC8 structure are compared to the corresponding bonds in silicon. The electron density in the Si bonds is localized between the atoms with a total charge of 2.0 electrons in each type of bond. This situation corresponds to completely covalent bonding in BC8 silicon. In carbon however, it is evident that the B bonds are different in nature from those in BC8 silicon. The charge density has a minimum between the two B-bonded atoms, suggesting a much weaker bond. Integration over the charge density gives a total charge of only 1.8 electrons in the carbon B bonds. For the BC8 carbon A bond, the integrated charge is approximately 2.6 electrons. This suggests that BC8 carbon A bonds are stronger than single bonded C-C. This is attributed to the formation of an unstable molecular crystal phase of carbon, with the fourfold coordinated BC8 phase being still less stable.

The apparent metastable BC8 state in carbon arises from constraining the simulation to have certain symmetries. The Hellmann-Feynman forces must have the same symmetries as the ions and the current method of minimisation does not break these symmetries. Consequently, although the BC8 phase is extremely unfavourable in carbon, the minimisation routine finds the best compromise structure subject to those assumed symmetries, which turns out to be the molecular crystal.

There have been a number of previous calculations of BC8 carbon, limited by computing resources to much smaller cutoff energies. The results of these are rather similar to Figure 3.10 but have been interpreted as generating a phase transition between diamond and BC8 at extremely high pressures (Biswas et al quote the massive pressure of 1200GPa). This crossover is not observed here, and moreover the evidence of the charge density plot leads one to suspect that BC8 may not even be metastable.
Figure 3.15. Valence charge density contour plot for BC8 Si (top left) and C (bottom right). The electron charge density along the $A$ and $B$ bonds are shown suggesting that significantly different bonding occurs in C in the BC8 structure. Integration of the charge densities along bond directions reveal that there are 2 electrons in both the $A$ and $B$ bonds in BC8 Si. For C there are approximately 2.6 electrons per $A$ bond suggesting a stronger than single C-C bond exists. Only 1.8 electrons per $B$ bond are found for C in the BC8 structure.
Table 3.2. Differences in energies, $\delta E$, between the diamond and BC8 and ST12 structures in carbon, silicon and germanium. The units are in eV/atom. Note that the difference in energy between the diamond and ST12 structures changes by nearly two orders of magnitude for the group IV elements considered here.

<table>
<thead>
<tr>
<th>$\delta E$</th>
<th>Carbon</th>
<th>Silicon</th>
<th>Germanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{BC8}$</td>
<td>0.5876</td>
<td>0.1100</td>
<td>0.0325</td>
</tr>
<tr>
<td>$\delta_{ST12}$</td>
<td>0.7634</td>
<td>0.1181</td>
<td>0.0147</td>
</tr>
</tbody>
</table>

To test this latter hypothesis, a calculation was performed in which all the atoms were given a small random displacement from their equilibrium sites. From there, free relaxation under the Hellmann-Feynman forces restored the atoms to their BC8 symmetric positions. Thus the BC8 phase is at least metastable against any small atomic displacements.

For the ST12 structure of carbon, the equilibrium $c/a$ ratio is 1.30 and the equilibrium atomic volume is slightly larger than that calculated for diamond. This suggests that, for carbon, unlike the other group IV elements considered, the ST12 structure does not constitute a dense phase.

The calculated difference between diamond and BC8 silicon was found to be 0.11 eV per atom. This is in good agreement with the value reported by Biswas et al. We find the difference in energy of the diamond and BC8 structure in carbon to be 0.7 eV/atom which is also in good agreement with Biswas et al. In germanium the differences are very small, about 0.01 eV/atom to ST12-Ge and 0.03 eV/atom to BC8-Ge. This distinct trend down the group can be understood as an increasing ease of distortion of $sp^3$ hybrids with principle quantum number$^1$. Our results for the differences in energy between diamond and the BC8 and ST12 structures are summarised in Table 3.2.

$^1$see Chapter 4
3.5 The Structural Response to Compression

In both dense phases, as the volume is reduced the distortions of the tetrahedra increase. In the BC8 structure these distortions are uniquely described by the variation in the $x$ parameter as described in Section 3.3. For the BC8 structures of Si, Ge and C the structural response to applied pressure is shown is represented in Figure 3.11 where the calculated variation in the free structural parameter, $x$, is shown. It is clear that both BC8-Si and BC8-Ge behave similarly under pressure as the equilibrium value of $x$ and its slope are nearly equal in the two materials. For Si, the value of $x$ which fully relaxes the structure is found to be $x = 0.1001$ at the equilibrium lattice constant of 6.54 Å. The experimental value is reported to be $x = 0.1003 \pm 0.0008$. For fully relaxed BC8-Ge, $x = 0.1013$. In BC8-carbon, the equilibrium value of $x = 0.0935$ is approximately 6% smaller than it is for Si or Ge.

Although plots of $x$ give a complete representation of the data from the calculations, which are done at constant volume, it is more informative to examine the variation of bondlengths with pressure, and this is plotted in Fig. 3.16. Notice that under pressure $x$ increases, which tends to compensate for decreasing $a_0$ in $R_A$, but enhances the reduction in $R_5$. The effect on $R_B$ is small ($\frac{dR_B}{dx} = (8x - 1)a_0/R_B$) but gives rise to a small additional decrease in $R_B$ with pressure, in addition to the reduction in $a_0$.

The effect of this compensation against decreasing $R_A$ is that whilst at ambient pressure the A bonds are shorter, as the pressure increases the B bond contracts until at $x = (\sqrt{2} - 1)/4$ all bonds are the same length. There is no special symmetry associated with this coincidence, and the B bond length continues to contract. A qualitative explanation of this comes from the empirical model in Chapter 4.

Consideration of the differentials of expressions (3.1) to (3.5) makes it clear that $\theta_{AB}$ decreases with increasing $x$ (pressure) while $\theta_{BB}$ increases. Thus pressure serves to increase the distortion of the tetrahedra: the price which must be paid for maintaining bondlengths. It is thus clear that the observation of increasing $x$ with pressure means
Figure 3.16. Variations in bondlengths and near neighbour distances with volume change for BC8 silicon. The graph for germanium is similar. Note that $R_5$ is most sensitive to isotropic compression. The $A$ bond changes by less than 0.1Å over the range shown. This insensitivity results in a bondlength crossover at a lattice parameter of 6.25Å.

that the bond-stretching forces have a greater bearing on the structure than the bond-bending ones.

In ST12 the structure is only fully defined by four internal parameters. For this reason it is essential to relax the structure under the Hellmann-Feynman forces, and thus study of ST12 is ideal for the plane-wave basis set method. The relationships between these internal parameters and the bondlengths and bond angles are complex, and for clarity only the latter quantities are considered. The evolution of the internal structure under pressure is described by Figure 3.17 which depict the change of the three different bondlengths under pressure.

Following the notation of Kasper and Richards[22] for ST12-Ge, the four atomic positional parameters are shown for axial ratios of 1.2, 1.25 and 1.3 in Figure 3.18. It is evident from the figure that the $z$-parameter for the 8($b$) site has the strongest dependence on isotropic compression of the unit cell and that the positional parameters
Figure 3.17. Variation of the three different bondlengths on ST12 germanium with volume. The graph for silicon is similar.

are not greatly affected by changes in axial ratio over the range considered here. The ST12-Ge positional parameters near the equilibrium volume and $c/a$ ratio may be found from Table 3.1. The calculated value of $x$ for the 4(a) sites is 0.0882 compared to 0.0912 found experimentally. The calculated $x$, $y$ and $z$ values for the 8(b) sites are $x=0.1693$, $y=0.3771$ and $z=0.2454$. The corresponding experimental values at ambient pressure are $x=0.1730$, $y=0.3784$ and $z=0.2486$. The agreement is encouraging and suggests that future experiments using recent advances in angle-dispersive powder diffraction[60] to determine the pressure dependence of this structure would be of value.

As in BC8, the ST12 internal parameters vary with pressure to maintain the bondlengths at the expense of further distorting the bond angles. For a constant $c/a$ ratio the bondlengths are reduced more slowly as a function of volume than the unit cell parameters. In practice the $c/a$ ratio also changes under pressure in such a way as to reduce the changes in bondlengths. The fully relaxed unit cell dimensions and atomic positions in for silicon, germanium and carbon in the BC8 and ST12 structures are summarised in Tables 3.3 and 3.4.
Figure 3.18. The relaxed ST12 structural parameters for germanium against volume. The circles, squares and triangles represent axial ratios of 1.25, 1.30 and 1.35 respectively.

| Table 3.3. The full set of positions are given for the BC8 structure in terms of the one free structural parameter $x$. Also shown is the relaxed lattice parameter $a$ in Å and the corresponding $x$ for carbon, silicon and germanium. |  |
|---|---|---|---|
| Carbon | 0.0935 | 4.44 |
| Silicon | 0.1001 | 6.54 |
| Germanium | 0.1013 | 6.81 |
Table 3.4. The full set of positions are given for the ST12 structure in terms of the 4 free positional parameters $x$, $y$, $z$ and $x$ which correspond to the (8b)-x, (8b)-y, (8b)-z and (4a)-x sites respectively. Also shown is the relaxed lattice parameters $a$ and $c$ in Å and the corresponding positional parameters for carbon, silicon and germanium.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$x$</th>
<th>$a$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.1641</td>
<td>0.3803</td>
<td>0.2143</td>
<td>0.0743</td>
<td>3.71</td>
<td>4.82</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.1752</td>
<td>0.3792</td>
<td>0.2742</td>
<td>0.0849</td>
<td>5.51</td>
<td>6.94</td>
</tr>
<tr>
<td>Germanium</td>
<td>0.1693</td>
<td>0.3771</td>
<td>0.2454</td>
<td>0.0882</td>
<td>5.75</td>
<td>7.13</td>
</tr>
</tbody>
</table>
3.6 Constant Volume MD

In this section, the zone centre phonon frequencies of diamond, BC8 and ST12 structure in silicon are calculated from \textit{ab initio} molecular dynamics simulations at non-zero temperature. In principle, any phonon mode may be calculated in an MD simulation but very large supercells are required to give a normal mode of any general \(k\)-vector, but the molecular dynamics method has the advantage that it includes anharmonicity in the calculation. It should be noted however that there are several other methods in which to calculate phonon modes for arbitrary wavevectors such as the frozen phonon approximation\cite{61, 62, 63} or linear response schemes\cite{64}.

The unit cells used in these calculations are the cubic 8 atom diamond cell which will give the phonon spectral density at the \(\Gamma\) and \(X\) points of the primitive cell, the 16 atom cubic representation of BC8 also giving phonons at the \(\Gamma\) and \(X\) points and 12 atom tetragonal cell for ST12 giving only the \(\Gamma\) point modes.

A molecular dynamics timestep consists of relaxing the electrons to the ground state for a fixed ionic position and then allowing the ions to move under the influence of the Hellmann-Feynman forces, integrating the ionic equations of motion with a timestep of 0.5fs. To ensure accuracy of the forces the energy was converged to better than \(10^{-4}\)eV per ionic degree of freedom, ensuring that the system is kept close to the Born-Oppenheimer surface at all times.

The initial configuration was that of the fully relaxed structures. Each atom is given a random velocity with the ensemble average corresponding to a temperature of 500K. The average temperature was maintained close to this by using a Nosé thermostat, that is, the instantaneous temperature is allowed to vary but the time averaged value is maintained near to 500K. This thermostat introduces a coupling of the system to an external heat reservoir which has the effect of keeping the average temperature of the ions close to a fixed value. This also corrects for the errors in integrating the ionic equations of motion using a finite timestep. The unit cell dimensions are kept constant.
at the equilibrium lattice parameters therefore thermal expansion and fluctuations are not incorporated into the simulation.

The phonon modes can be extracted from the velocity autocorrelation function

$$A(t) = \frac{\langle v(0) \cdot v(t) \rangle}{\langle v(0) \cdot v(0) \rangle}$$  \hspace{1cm} (3.7)

where $v(t)$ is the ionic velocity at time $t$ and the triangular brackets denote the ensemble average. The denominator is simply a normalising factor. $A(t)$ for silicon in each of the three structures is shown in Figures 3.19, 3.20 and 3.21. It can be seen that $A(t)$ oscillates about zero indicating that each structure is mechanically stable. The spectral density can then be obtained simply by Fourier transforming the velocity autocorrelation function. This is shown in Figures 3.22, 3.23 and 3.23. In each case the first 0.3ps of the simulation were not included in the Fourier transform to allow for equilibration of the system.

These figures should be compared to the phonon calculations in Chapter 4, although
Figure 3.20. Velocity autocorrelation function for silicon in the BC8 structure.

Figure 3.21. Velocity autocorrelation function for silicon in the ST12 structure.
Figure 3.22. Phonon density of states obtained by molecular dynamics for silicon in the diamond structure. The phonon modes are those at the Γ and X points.

Figure 3.23. Phonon density of states obtained by molecular dynamics for silicon in the BC8 structure. The phonon modes are those at the Γ and X points.
they show the density of states allowed in the limit of high temperature. A direct comparison can be made only if the density of states found from the lattice dynamics are weighted by the Boltzmann factor, $\exp(-\hbar\omega/k_B T)$. Similar to the empirical calculations it would be possible to calculate the vibrational free energy and entropy from the density of states. A similar calculation at various pressures would then lead to a prediction of the full pressure-temperature phase diagram of these structures. Unfortunately, this is not a good approximation to the vibrational properties given by the full vibrational density of states since the vibrational wavevectors in the calculations are extremely limited. In particular, the zone centre modes are probably the worst sampling point to represent the entire vibrational spectrum.

The calculation to obtain the vibrational free energy and entropy from the vibrational density of states will be fully described in Chapter 4, but for completeness, these properties are calculated here for the each of the MD calculations performed here at ambient pressure. These results are given in Figure 3.25. Unlike in the empirical calculations of Chapter 4 where the full phonon density of states is evaluated, the results
Figure 3.25. Thermodynamic properties calculated from the MD simulations. The solid line refers to the BC8 structure of silicon and the dashed line to ST12. The zero of each quantity is that of diamond and the quantities are given per atom in each case.
from this limited spectral density predict that the BC8 structure has a lower free energy. At ambient pressure BC8 is also energetically more stable than ST12 silicon. This indicates that ST12 will never be stable at any temperature. When all phonons are taken into account, the opposite situation is found where ST12 silicon is found to have a greater free energy than the BC8 structure. This difference is also found to increase with temperature. This indicates, that with suitable heat treatment, ST12 will become the stable structure.

This difference in results show that one has to be careful when sampling the Brillouin zone, in that too few \( k \)-points or a badly chosen set can introduce large errors and give contradictory results.

### 3.7 Band Structures

The electronic structure of BC8 and ST12 materials will now be considered. The method of energy minimisation at sets of special \( k \)-points as described in Chapter 2 is at first sight unsuitable for general band structure calculations since

1. unoccupied states do not contribute to the total energy in the minimisation calculation since they do not contribute to the ground state electronic charge density.

2. the minimisation calculation has to be done at a set of special \( k \)-points rather than, for example, on lines of high symmetry where conventional band structures are shown.

Both of these problems are easily overcome. The self consistent charge density obtained by the minimisation procedure contains all the ground state information (assuming the calculation has been done at \( k \)-point convergence). Thus for any \( k \)-point a minimisation of the Rayleigh-Ritz ratio

\[
\frac{\langle \psi_i | H | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} = \frac{\langle \psi_i | H | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle}
\]  

(3.8)
constructing $H$ each time from the previously found charge density will give the correct energy eigenvalues. Note that the eigenvalues have to be found by diagonalisation since methods such as conjugate gradients only find linear combinations of eigenvalues and eigenvectors.

The above method can also be used to obtain energies of the unoccupied bands. However there are problems which prove difficult to overcome using density functional theory. Density functional theory gives a variational method of finding the ground state charge density only. Therefore the above method of evaluating the energy eigenvalues gives the energy of an empty excited state when there are $N$ electrons still in the ground state (for an $N$ electron system). The actual excited state should be evaluated from $N - 1$ electrons in their ground state with one electron in the excited state under consideration. The charge density for this state cannot be found using density functional theory. As a consequence, a band gap found by this method is usually underestimated by up to 50%.

The band structures of silicon in the diamond, BC8 and ST12 structures are shown in Figures 3.26, 3.27 and 3.28. It is found that silicon in the diamond structure is semiconducting with an indirect band gap of 0.589eV along the $\Delta$ line ($\Gamma \rightarrow X$). This is in agreement with other ab initio calculations\[65\] although, as expected, the band gap is underestimated with experimental measurements giving a gap of 1.1eV\[.\]

In contrast, BC8 silicon is found to be semimetallic. This occurs at the $H$ point in agreement with empirical pseudopotential calculations\[66\] where band energies are fitted to experimental measurements. The lowest energy conduction band is found to drop below the highest point of the valence band (the $H$ point) along the $\Delta$ ($\Gamma \rightarrow H$) line by 0.046eV and along the $G$ line ($H \rightarrow N$) by 0.071eV. Silicon ST12 is found also to be semiconducting with an indirect gap of 0.7eV between the $\Gamma$ and $Z$ points.

\[2\]Also note that the highest energy valence bands are triply degenerate at the $\Gamma$ point. It will be seen in Chapter 6 that the introduction of point defects in to the structure causes this degeneracy to be lost.
Figure 3.26. Electronic band structure of silicon in the diamond structure along several high symmetry lines in the FCC Brillouin zone. The calculations predict a semiconducting structure with a band gap of 0.59eV.

Figure 3.27. Electronic band structure of silicon in the BC8 structure along several high symmetry lines in the BCC Brillouin zone. The calculations predict a semimetallic structure.
Figure 3.28. Electronic band structure of silicon in the ST12 structure along several high symmetry lines in the tetragonal Brillouin zone. The calculations predict a semiconducting structure with a band gap of 0.7eV.

3.8 Nature of Bonding

BC8 Si has a small Fermi surface and thus electronically can be regarded as a semimetal as suggested by its band structure. Its fourfold coordination and brittleness suggest that it is predominantly held together by directional covalent bonds. To resolve this apparent contradiction, the valence charge density has been examined within BC8 and ST12. Figure 3.29 shows an electron density isosurface in ST12 silicon. It bears an uncanny resemblance to a ball and stick model of the structure, showing clearly that the electron density is concentrated into four ‘bonds’ emanating from each atom - the covalent picture.

This covalency is illustrated even more clearly in Figures 3.7, 3.8 and 3.15 which shows the valence charge density in the 110 plane of BC8. Along the 111 direction are atoms separated by $2\sqrt{3}xa_0$ and $\sqrt{3}(\frac{1}{2} - 2x)a_0$ alternately. Although these distances are similar, it can very clearly be seen that the slightly closer pairs are bonded, while the more distant pairs are not. This effect cannot be seen in diamond because there
are no 'second neighbours' as close. An interesting aspect of this structure is that if the
topology of the crystal is defined by bonds, it requires six steps to get from an atom to
its 'second neighbour', and there is only one such second neighbour per atom. Under
pressure the increase in $x$ has the effect of pushing these second neighbours together,
but there is still no increase in the charge density between the atoms.

It is therefore deduced that while the electronic properties of BC8 are dominated
by its small Fermi surface, and hence it is regarded as a semimetal, the cohesion is
dominated by covalent bonding of each atom to four neighbours. This observation has
been used in constructing a simple empirical model potential for silicon, which will
then apply to structural features of the semimetallic BC8 phase. Calculations using
the empirical model are presented in Chapter 4.

ST12 is a semiconducting phase, and again the charge density plots suggest that a
covalent picture for the bonding is appropriate.
3.9 Trends

It is now possible to make some comment about the trends in behaviour down group IV. In Si, Ge and Sn the stable phase at low pressure and temperature is diamond whilst in C this phase is metastable with respect to graphite. Under pressure the transformation to the metallic $\beta$-Sn structure occurs at progressively lower pressures in Si - Ge - Sn (in tin itself, this transition occurs at ambient pressure due to temperature alone). Likewise, metastable phases exist which have intermediate density and maintain fourfold coordination. These are easier to form as one goes down group IV, apparently because bond-bending is easier for $sp^3$ hybrids with larger $n$ (and therefore smaller overlap under distortions). These concepts are used in the development of empirical potentials, and are developed further in Chapter 4. Carbon is different. Not only does it exhibit the graphite phase under ambient pressure but it cannot form a metastable phase with BC8 or ST12 symmetry without a significant departure from fourfold coordination.

3.10 III-IV Semiconductor Calculations

3.10.1 Introduction

Upon increase in pressure, both the group IV elements and III-V semiconductors display a broadly similar behaviour. The diamond and zincblende structures transform to a sixfold coordinated metallic structure similar to that of either $\beta$-Sn or NaCl. Experimental results\cite{21, 22} and the above calculations establish that depressurisation of silicon and germanium result in dense metastable crystalline phases (although not true of carbon where distortion of the tetrahedral bonding is extremely unfavourable). As yet, there has been no experimental evidence showing the existence of such dense phases in III-V semiconductors. For this reason ab initio calculations are now performed on GaAs, InAs and AlSb to investigate the nature of these materials in the BC8 structure. The ST12 structure is not examined as a possible high density structure in the III-V’s
since it contains rings of odd numbers of atoms requiring like species bonding which is unfavourable[67].

Firstly the diatomic equivalent of the BC8 structure, SC16, is described and then the energetics of it is considered at various volumes (pressures) to investigate as to whether the structure is even metastable. Also to be truly metastable the structure must be able to support small displacements of the atoms from their equilibrium sites. Therefore a non-zero temperature molecular dynamics simulation is performed to examine the optic $\Gamma$ point phonon modes. The bonding is then considered by looking at the band structure and the (fully *ab initio*) ionicity of SC16 GaAs.

### 3.10.2 The SC16 Structure

Since the BC8 structure is characterised by even membered rings, is is possible to construct a diatomic analogue in which only unlike species are bonded. However the 8 atom body centered cell is not appropriate for this. If the BC8 structure is considered to be simple cubic with 16 atoms in the unit cell then 2 species can be arranged with only unlike species bonding. It follows that this structure has lower symmetry - primitive cubic, with point group symmetry $P2_13$ and unlike BC8 it does not have a centre of inversion. The effect of this is that the structure can be fully described by two internal parameters, $x_s$, where $s = 1, 2$ labels the species. Curiously, the lengths of the bonds depend only on one parameter, $x_1 + x_2$. The distance to the nearest non-bonded neighbour, $R_5$, is species dependent. These lengths can be expressed in terms of the lattice parameter and $x_s$ by

\[
\begin{align*}
R_A / a_0 &= \sqrt{3} (x_1 + x_2) \\
R_B / a_0 &= \sqrt{2(x_1 + x_2)^2 - (x_1 + x_2) + 1/4} \\
R_5^1 / a_0 &= \sqrt{3} (1/2 - 2x_1) \\
R_5^2 / a_0 &= \sqrt{3} (1/2 - 2x_2).
\end{align*}
\]
Table 3.5. Results of total energy calculations on compound semiconductors in the SC16 structure. Values of the transition pressure from zincblende to the high pressure metallic phase, P(zb-metal), are taken from experiment and represent upstroke measurements. The units are in GPa, eV and Å. $x_\text{s}$ is in fractional coordinates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta E$</th>
<th>$V_0$</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>P(zb-SC16)</th>
<th>P(zb-metal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>0.0275</td>
<td>20.727</td>
<td>0.0947</td>
<td>0.1034</td>
<td>2.0</td>
<td>12.0</td>
</tr>
<tr>
<td>InAs</td>
<td>0.0293</td>
<td>22.501</td>
<td>0.0988</td>
<td>0.1037</td>
<td>1.7</td>
<td>7.0</td>
</tr>
<tr>
<td>AlSb</td>
<td>0.0228</td>
<td>25.439</td>
<td>0.1002</td>
<td>0.1059</td>
<td>1.4</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Like the BC8 structure in Group IV elements, the SC16 structure with its distorted tetrahedral units is a tractable complex crystal model of amorphous III-V semiconductors having short range disorder and zero like species bonding. Studies of the structural, optical and electronic properties of GaAs in the SC16 structure have been made using an empirical pseudopotential method in an attempt to investigate the amorphous phase [66].

### 3.10.3 Total Energy Calculations

Total energy calculations were performed on GaAs, InAs and AlSb using a plane wave energy cutoff of 250eV where total energy differences are found to be converged. The ions are allowed to move under the influence of the Hellmann-Feynman forces until all forces are below 0.04eV/Å. The initial configuration of each compound at each of the volumes considered was the one given by $x_1 = x_2 = 0.1$. This does not introduce any additional symmetry into the structure. Identical sets of four equally weighted special $k$-points were chosen for each structure. To check the validity of this approximation it was found that increasing the number of $k$-points to the $6 \times 6 \times 6$ Monkhorst-Pack set gave no appreciable difference in energy or forces of any of the three semiconductors considered here.

The results of the total energy calculations for GaAs, InAs and AlSb are shown in Figure 3.30. The main results are summarised in Table 3.5. The energy differences
Figure 3.30. The total energy of GaAs, InAs and AlSb in the zincblende (points marked by a square) and SC16 structures (points marked by a circle).
between the zincblende and SC16 structures are much less than the 0.11eV/atom difference for that of silicon (BC8-diamond structures). This reduction in energy may be partially due to the ionic character of the III-V compounds which favours the denser SC16 structure while the 4-fold coordination can simultaneously accommodate covalency.

For the three compounds considered here, the calculated pressure at which the zincblende phase undergoes a structural transition to the SC16 structure is significantly lower than the corresponding transition pressure associated with the semiconducting zincblende to the sixfold coordinated metallic phase. For example, these calculations predict that GaAs transforms from zincblende to SC16 at only 2.0 GPa, whereas the earliest experimental indications of a structural transition are not observed until 16.4 GPa to the metallic structure[68]. The transition on the downstroke is not complete until 5.5 GPa. It must be emphasized that the total energy calculations presented above only yield energy differences at zero temperature and do not take kinetic factors of phase transitions into account - this point will be returned to later.

3.10.4 Molecular dynamics

To ensure that the SC16 structures are mechanically stable a finite temperature molecular dynamics simulation was performed. For a structure to be mechanically stable, positive restoring forces must oppose any small displacement of an atom about its equilibrium position. An equivalent statement is that the square of all phonon frequencies must be greater than zero (except for the Γ point acoustic modes).

Ideally, all possible vibrational modes should be investigated in order to fully explore mechanical stability, but due the extremely long run time required to run a molecular dynamics simulation on a large unit cell only the zone centre modes are investigated here.

A similar calculation to that described in Section 3.6 is performed on a single GaAs SC16 unit cell. The initial configuration is that of the fully relaxed structure described above. The average temperature was maintained at 300K by use of a Nosé
thermostat. The simulation was run for a time of 2.0ps in steps of 0.5fs. The velocity autocorrelation function was found and Fourier transformed to obtain the zone centre spectral density given in Figure 3.31. Again, the first 0.3ps of the simulation was not included in the phonon calculation to allow for equilibration of the system. The position autocorrelation function (and hence the velocity autocorrelation function) was found to oscillate about zero indicating that the Γ point modes are stable. Note that Figure 3.31 shows the phonon spectral density at a temperature of 300K. To make a comparison to a full density of states calculation, i.e. in the high temperature limit, the density must first be corrected by multiplication by the Boltzmann factor, which, in this case, increased the height of the density of the high frequency phonons.

The effect of disorder on the vibrational spectrum is expected to be similar to its effect on the electronic spectrum. That is, disorder introduces a broadening relative to the crystalline density of states. In the calculation of the Γ point density of states it is found that the positions of the prominent features at 2THz and 8THz correspond to the positions of the TA and TO phonon branches of the zincblende phase. These
features are also seen in the amorphous form of GaAs at similar frequencies.

The vibrational density of states obtained for SC16 GaAs in this way appears similar to that of BC8 silicon. Thus, the non-existence of SC16 cannot be attributed to entropic effects.

3.10.5 Ionicity

The valence charge density in a plane containing both A and B bonds is shown in Figure 3.32. It can be seen that there is a significant charge transfer from the Ga to the As atom. If the ionicity of the Ga-As bond were significantly higher in the SC16 structure than in the zincblende structure it could be argued that wrong bond defects which are likely to be present in the high pressure recovered phase[67] would be more unfavourable in the SC16 structure than in either zincblende or β-Sn phases.

To explore this possibility the ionic character of the Ga-As bond in the zincblende and SC16 structures are investigated. An *ab initio* method of doing this was recently suggested by Garcia and Cohen[69]. The method allows an ionicity scale to be defined.
using only the overall asymmetry of the charge density as a fundamental quantity. The charge density is decomposed into symmetric and antisymmetric part as follows:

\[ n(r)_{\text{symm}} = \frac{n(r) + n(-r)}{2} \]  

(3.10)

and

\[ n(r)_{\text{anti}} = \frac{n(r) - n(-r)}{2}. \]  

(3.11)

The origin of the coordinates is defined so that atoms of different species are interchanged upon inversion through the origin. The origin is therefore half way along the A bond.

Fourier decomposition of the symmetric and antisymmetric parts of the charge density give

\[ n(G)_{\text{symm}} = \frac{n(G) + n^*(G)}{2} \]  

(3.12)

and

\[ n(G)_{\text{anti}} = \frac{n(G) - n^*(G)}{2}. \]  

(3.13)

from which a measure of the amount of asymmetry, S, over the entire unit cell can be defined:

\[ S_{\text{symm}} = \sum_G |n(G)_{\text{symm}}|^2 \]  

(3.14)

\[ S_{\text{anti}} = \sum_G |n(G)_{\text{anti}}|^2. \]
The overall degree of charge asymmetry, \( g \), is then given by

\[
g = \sqrt{\frac{S_{\text{anti}}}{S_{\text{symm}}}}.
\]

(3.15)

This method applied to GaAs gives \( g = 0.3014 \) in the zincblende structure which agrees well with the value of 0.316 reported by Garcia and Cohen. For SC16 GaAs it is found that \( g = 0.3090 \). This near equality of the calculated ionicities suggests that wrong bond energies in each structure will be similar, although the effect of atomic size should be noted - this will be greater in the denser SC16 structure.

### 3.10.6 Electronic Band Structure

The electronic band structure of GaAs in the SC16 structure along several lines of high symmetry is shown in Figure 3.33. The electronic structure of SC16 GaAs has been published previously[66] but these were calculations based on empirical pseudopotentials where the experimental band gap of the zincblende structure is one of the fitted parameters. It clearly revealed an energy gap in the electronic states of SC16 GaAs of the same magnitude as that found in the zincblende and wurtzite structures. Furthermore, it was suggested that like-species bonds must be present in amorphous heteropolar semiconductors in order to account for the observed reduction in energy gap. The density of occupied states calculated here exhibits a close resemblance to that previously reported. However, as is evident from inspection of the band structure, the valence and conduction bands touch at the \( \Gamma \) point of the Brillouin zone. In view of the well known inadequacies of density functional theory in determining the electronic excitation energies in solids this issue cannot be investigated further using these techniques although partial reduction of the energy gap may be due to the fact that both the bondlengths in the fully relaxed structure of SC16 GaAs are smaller than the ideal value found in the zincblende structure. This situation could have the effect of broadening the \( p \)-like region (approximately -5eV to 0eV) of the density of states[66].
**Figure 3.33.** The band structure of GaAs in the SC16 structure shown along several lines of high symmetry in the simple cubic Brillouin zone.
CHAPTER 3. COMPLEX PHASES: AB INITIO TREATMENT

3.11 Conclusions

Total energy pseudopotential calculations have been performed on high density phases of the Group IV elements C, Si and Ge and also on a high density phase of several III-V compound semiconductors. Using a density function molecular dynamics method similar to that proposed by Car and Parrinello[46], the fully relaxed BC8 and ST12 structures of these elements and the compound form, SC16, have been found. This was determined by relaxation under the influence of the Hellmann-Feynman forces. There is excellent agreement with experimental data where it exists. The structural response to compression has also been investigated. Using these results, other properties could also have been calculated such as the response to optical properties by pressure (although other methods exist such as the GW approximation[70] which produces a much better band gap than LDA can, giving better results on optical properties).

Using this molecular dynamics method, properties such as lattice parameters, bulk moduli and behaviour of the internal structure under pressure has been determined. These are all found to be in good agreement with experiment where available data exists, although, as usual within the LDA the structures tend to be overbound slightly. This overbinding means that the lattice parameters are inevitably too small (although in structures which have a lattice parameter which actually increases with pressure, for example Se-I, this lattice parameter can be overestimated[59, 71]). It is found that the lattice parameters are approximately 2% too small with a binding energy 15% too large. It is well established, however, that the energy differences between various structures as used here are well reproduced by LDA.

The calculations presented here predict that BC8 silicon is the low temperature metastable phase. Ab initio calculations of entropy at high temperatures are currently impractical over the full pressure-temperature phase space and so those calculations are carried out using an empirical potential and are presented in Chapter 4.

In germanium the energies of all phases are similar, reflecting the ease with which
the germanium bonds can be distorted, and that cohesive energy is dominated by the
requirement of fourfold coordination. It was found that the internal parameters in
both BC8 and ST12 germanium adjust to maintain all bondlengths to be similar. The
energy difference between the ST12 and diamond structures were much smaller than
that of carbon or silicon. Convergence of this difference required the use of a denser
$k$-point set for band structure sampling.

Although the germanium energy differences are close to the accuracy of the code
used here, it is predicted that within a range of pressures ST12 will actually be the
stable phase of germanium. It would be interesting to attempt to verify this experiment-
ally, although the large kinetic barrier makes the direct transition between diamond
and ST12 impossible. It seems that ST12 may be made via the $\beta$-Sn phase. BC8 is
found to be close but slightly higher in energy which has now been confirmed experi-
mentally, where at room temperature BC8 Ge is found for short periods of time before
transforming to the more stable Lonsdalite$^3$ structure[18].

In carbon it was found that diamond will be completely stable with respect to BC8
or ST12 at all pressures considered, and that those phases, while not mechanically
unstable, have fundamentally different bonding to Si and Ge.

In the case of III-V semiconductors, the SC16 or ST12 phases have not been found
experimentally (although recently SC16 CuCl has been found[72, 73]). The calculated
transition pressures from zincblende to SC16 structures are about 1.5GPa which are
an order of magnitude smaller than that for zincblende to $\beta$-Sn. This suggests that
the SC16 structure is thermodynamically stable over a large range of pressures for
the III-V semiconductors considered here. This is in contrast to silicon where these
calculations show it to be only metastable. The case of the III-V’s is somewhat similar
to germanium where the intermediate phase is ST12.

All calculations presented here indicate that the SC16 structure should be found.

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$^3$Hexagonal diamond.
This difference between experimental results and theoretical can be resolved by considering the kinetics of the phase transition which was not considered in the calculation presented here. It has recently been shown that there is a simple transition route in silicon between the high pressure metallic phase, $\beta$-Sn and BC8[39]. On consideration of the difference in pressures in which the III-V semiconductors transform to the $\beta$-Sn on the upstroke and back to zincblende on the downstroke, it was concluded that this transformation is not easy. Considering the same reaction kinetics as that proposed for $\beta$-Sn→BC8 Si it was found that like bonds would be formed in the III-V SC16 structure which is extremely unfavourable[67]. As a result the difficult retransformation to the zincblende structure is favoured in the compound semiconductors.

The results presented here and in reference[39] show that SC16 should be a stable phase with respect to higher pressure metallic phases. Therefore possible methods of forming it can be suggested, such as cooling the melt of the high pressure metallic phase slowly while allowing the pressure to reduce. If formed, the large kinetic barrier would ensure that SC16 III-V’s would be long lived at ambient pressure.

*Added Note*: Very recent high pressure studies on phases in silicon formed from depressurisation from the $\beta$-Sn structure show that a new rhombohedral phase exists under pressure with 16 atoms per unit cell (R. O. Piltz, J. McLean, S. J. Clark, P. D. Hatton, J. Crain, G. J. Ackland and G. S. Pawley, *Phys. Rev. B*, To be published, 1994). X-ray diffraction results on the structure show it to have a lattice parameter of $a=6.43\text{Å}$ with a rhombohedral angle of $\alpha=91.296^\circ$ at 8.2GPa. Our preliminary calculations find that is topologically different from BC8-Si, containing 5-fold rings - the first crystalline structure of silicon to do so. This has been confirmed from the experimental data. It seems likely that this is the intermediate phase in the $\beta$-Sn→BC8 transition. The rhombohedral→BC8 transition route is rather simple - the A bonds are broken along the (111) direction and rebonded to the $R_5$ neighbour. Relaxation of the atoms and unit cell gives a rhombohedral distortion and forms 4 different bondlengths, all of which are of the order 2.5Å. If this is the case, then the 5-fold ring structure
will inhibit the formation of SC16 III-V compounds due to the presence of like-species bonding.
Chapter 4

Complex Structures: Empirical Treatment

4.1 Introduction

This chapter continues the study of high density metastable phases found in the tetravalent group IV semiconductors. Presented here is a treatment based on empirical potentials which allows intuitive insights into the stability and pressure response of these materials, along with estimates of free energy to describe finite temperature behaviour.

*Ab initio* calculations were presented in Chapter 3 which are based on density functional theory in the local density approximation. These calculations reproduced accurately the properties known experimentally, and furthermore gave some predictions for the exact behaviour of the internal structure of BC8 and ST12 as a function of pressure. Despite the success that density functional total energy calculations have had in describing the relative phase stability in crystals there remain limitations which render the treatment of several important physical properties beyond that which can be achieved by these methods. This is particularly true in the case of free energy calculation at finite temperature and relaxation of unit cell dimensions under hydrostatic
pressure. The explicit treatment of finite temperature effects by first principles methods is extremely difficult to incorporate in practice, although a rigorous extension of density functional theory to finite temperature does exist[52]. This is because of the long simulations required to obtain good thermodynamic averages and the difficulties associated with changing the box volume with thermal expansion and fluctuations. Current computational power limited the non-zero temperature calculations presented in Chapter 3 to single unit cells and did not allow for changes in the size of the unit cell as described below.

Regarding structural relaxation, the plane wave pseudopotential total energy method has been shown to substantially alleviate complications which arise in atomic force calculations. These difficulties include basis set corrections (Pulay forces) which must be considered when localised basis sets are used and corrections which arise from non-self-consistency in the solution of the Kohn-Sham equations which are particularly problematic in full potential treatments. The advantages of the pseudopotential plane wave methods, however, do not apply in the case of unit cell relaxation which remains a formidable task to implement for first principles calculations. Schemes which have been proposed to accomplish this show extremely unfavourable scaling with system size.

These two complications associated with density functional methods coupled with the urge to explore the P-T diagram of dense metastable phases of Group-IV semiconductors have provided the motivation for the present work. Chapter 3 reported \textit{ab initio} pseudopotential density functional calculations which accurately reproduced known structural properties and allowed for predictions as to the internal relaxation of the BC8 and ST12 structures of Group-IV elements under pressure. To make the thermodynamic problem more tractable, the \textit{ab initio} force calculation is now replaced with an empirical potential which agrees well with the structural results.

With a view towards a full theoretical investigation of the P-T diagram of these
phases, including hydrostatic effects, the structural analysis in Chapter 3 was first repeated using a previously published empirical model for covalent bonding[74, 75]. This potential was parameterised to model quite different situations such as the diamond structure and small clusters. It has, however, been shown to be successful in other regimes very different from that for which it was parameterised. It has previously been shown to provide an accurate description of defects, vibrational properties, rebonding effects in surface reconstructions and in the formation of clusters. It is now also parameterised to give a good description of the optic phonon frequencies similar to that of silicon. It has not been applied previously in the present context of dense phases of covalent semiconductors, so comparisons with the ab initio structural results are essential.

The compute-intensive nature of density functional calculations means that finite temperature studies at many points in the phase diagram are currently impractical, especially in view of the pressure and temperature dependence of the $c/a$ ratio although finite temperature calculations at the relaxed unit cell size are now able to be done and are performed in Chapter 3. To investigate the stability of the phases it is, however, necessary to evaluate free energies throughout the pressure-temperature phase space. To achieve this, in the next section we outline the method of lattice dynamics, which is included here for completeness but essentially taken from the famous “Dynamical Theory of Crystal Lattices” by Born and Huang. From that, the empirical potential enables calculations to be carried out for a model covalent material, whose properties are fitted as closely as possible to those of silicon in the diamond structure.

4.2 Lattice Dynamics

The thermal properties of the diamond, BC8 and ST12 structures are extracted from phonon calculations. In this section the method of calculating phonon dispersion relations from an empirical potential will be presented. It is, in general, very complicated
to include anharmonic terms in such calculations. All phonon calculations presented in this chapter will be found using the harmonic approximation. The validity of this approximation is examined more fully in Chapter 6 when self-interstitial configurations in the diamond structure are examined. In that case it is found that anharmonic effects are negligible and therefore it is assumed here that they can also be neglected.

Phonon dispersion relations are calculated by looking for wavelike solutions to the classical equations of motion of atoms under a small displacement from their equilibrium sites. Firstly, a crystal is composed of an infinite number of primitive unit cells in three dimensions labelled \( l = (l_1, l_2, l_3) \) where \( l_i, i = 1, 2, 3 \) are integers. Each primitive unit cell is defined by three linearly independent vectors \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \) forming a parallelepiped. The origin of the \( l^{th} \) unit cell can then be defined as

\[
\mathbf{r}_l = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3
\]

(4.1)

relative to the origin \( l = (0,0,0) \) This unit cell defines the periodic structure of the crystal by repeating its primitive unit cell throughout space.

Each unit cell contains \( n \) atoms which are labelled by \( k = 1, ..., n \) each of which are at positions \( \mathbf{r}_k \) relative to the origin of each cell \( \mathbf{r}_l \), therefore the position of any atom \( lk \) is given by \( \mathbf{r}_{lk} = \mathbf{r}_l + \mathbf{r}_k \).

Vibrations occur when the atoms are displaced from their equilibrium positions. If the atoms are allowed to move from their equilibrium positions by an amount \( \mathbf{u}_{lk} = (u_{lkx}, u_{lky}, u_{lkz}) \) then the actual position of any atom under the influence of a vibration (thermal fluctuation) is \( \mathbf{R}_{lk} = \mathbf{R}_{lk} + \mathbf{u}_{lk} \).

The potential energy, \( \phi \), of the crystal is obtained from a potential which itself is a function of the instantaneous coordinates, \( \mathbf{R}_{lk} \), of the atoms.

If the displacements are assumed to be small compared to interatomic distances (which is generally true for stable crystals at a temperature well below its melting
point), then the potential function can be expanded about the equilibrium positions:

\[ \phi = \phi_0 + \sum_{lk\mu} \phi_{lk\mu} u_{lk\mu} + \frac{1}{2} \sum_{lk\mu,l'k'\nu} \phi_{lk\mu,l'k'\nu} u_{lk\mu} u_{l'k'\nu} + \ldots \]  \hspace{1cm} (4.2)

where \( \mu \) and \( \nu \) vary over all \( x, y \) and \( z \) coordinates and the coefficients \( \phi_{lk\mu} \) and \( \phi_{lk\mu,l'k'\nu} \) are

\[ \phi_{lk\mu} = \left( \frac{\partial \phi}{\partial u_{lk\mu}} \right)_0 \]  \hspace{1cm} (4.3)

and

\[ \phi_{lk\mu,l'k'\nu} = \left( \frac{\partial^2 \phi}{\partial u_{lk\mu} \partial u_{l'k'\nu}} \right)_0, (lk) \neq (l'k'). \]  \hspace{1cm} (4.4)

The subscript 0 means that the coefficients are evaluated at the equilibrium positions, \( r_{lk} \).

The first term in the series is constant, that is, it is independent of the displacements of the atoms from their equilibrium sites and so can be taken as the zero of the potential energy. The force on the atom is given by

\[ F_{lk\mu} = -\frac{\partial \phi}{\partial u_{lk\mu}} \]  \hspace{1cm} (4.5)

which is the coefficient of the second term in the series. Provided the derivative is evaluated at the equilibrium position, this term will be zero since at equilibrium the total force on any atom is zero. In the harmonic approximation all terms in cubic or higher order are assumed negligible, therefore the potential can be expressed simply as the third term in the expansion.

That term is not defined for self interactions, that is, it allows only the \( (lk) \neq (l'k') \) terms. To define the self interaction term consider a rigid translation of the entire crystal. This can be defined by replacing all the displacements \( u_{lk\mu} \) by a constant value.
The equations of motion of the atoms is then

\[ m_k \dddot{u}_{lk\mu} = \sum_\nu \sum_{l'k'} \phi_{lk\mu,l'k'\nu} v_{lk\nu} \sum_{l'k'} \phi_{lk\mu,l'k'\nu} \]  

(4.6)

which must be equal to zero because such a translation clearly cause the forces, \( F_{\mu} \), to vanish. But the \( v_{lk\nu} \) are arbitrary hence the sum over the coefficients \( \phi_{lk\mu,l'k'\nu} \) must be zero. Therefore in addition to the definition of \( \phi_{lk\mu,l'k'\nu} \) given above, the diagonal terms must be given by

\[ \phi_{lk\mu,lk\nu} = -\sum_{(l'k') \neq (lk)} \phi_{lk\mu,l'k'\nu}. \]  

(4.7)

Now that all the elastic constants \( \phi_{lk\mu,l'k'\nu} \) are well defined it is possible to solve the equations of motion

\[ m_k \dddot{u}_{lk\mu} = \sum_{l'k',\nu} \phi_{lk\mu,l'k'\nu} u_{l'k'\nu} \]  

(4.8)

by looking for the wavelike solutions

\[ u_{lk\mu} = \frac{1}{2\sqrt{m_k}} \left[ A(q)e_{k\mu}(q) \exp\{i(q \cdot r_{lk} - \omega(q)t)\} + c.c \right] \]  

(4.9)

where c.c. stands for the complex conjugate of the first term and \( A(q) \) and \( e_{k\mu} \) are amplitudes of the wave. Note here that \( q \) is used for the wavevector here so as not to confuse it with \( k \) which is the index of the atoms within the primitive unit cell.

On this substitution into the equations of motion the following dispersion relation is found:

\[ \omega^2(q)e_{k\mu} = \sum_{k',\nu} D_{\mu\nu} \left( \frac{q}{kk'} \right) e_{k\mu} \]  

(4.10)
where $D$ is known as the dynamical matrix. The elements of $D$ are given by

$$D_{\mu\nu}^{(q, k,k')} = \frac{1}{\sqrt{m_\mu m_\nu}} \sum_{l,l'} \phi_{lk_\mu,l'k'_\nu} \exp[iq.(r_{l'k'} - r_{lk})]. \quad (4.11)$$

The dimension of the dynamical matrix in $3n$. Therefore using the symmetry of the crystal by expressing it in terms of repeating primitive unit cells replaced an infinite set of equations of motion of an infinite number of atoms by a set of $3n$ linear homogeneous equations. The condition that the homogeneous system of equations have a non-trivial solution is that the determinant of the coefficients in Equation (4.10) vanish, that is to say

$$\left| D_{\mu\nu}^{(q, k,k')} - \delta_{\mu\nu}\delta_{kk'}\omega^2(q) \right| = 0 \quad (4.12)$$

therefore the eigenvalues of the dynamical matrix give the allowed (squares of) phonon frequencies for a given $q$. The dynamical matrix is Hermitian therefore the eigenvalues, $\omega(q,k)$ are real.

This lattice dynamics method has been coded for the massively parallel CM200 Connection Machine and is described elsewhere[76]. Although, in the present case, using such a large computer is unnecessary, it becomes so when very large dynamical matrices are required as in Chapter 6 where eigenvectors of matrices up to dimension $3000 \times 3000$ are needed. The parallelisation strategy is straightforward, with the elements of the dynamical matrix spread across the $2^{14}$ processors. This data-driven parallelisation is an inevitable consequence of the ‘single instruction multiple data’ architecture of this machine. The matrix diagonalisations are done using the Jacobi rotation method.
4.3 The Empirical Potential

Much effort has been invested in deriving simple potential models for covalent materials such as silicon. The intuitive picture of a covalent bond suggests that pairwise interactions should dominate the structural properties, and yet no standard short-ranged pair-potential stabilises the diamond structure. Various methods have been introduced to circumvent this: several authors have introduced potentials with a strong angular dependence\[77, 78, 79\]. Pettifor\[80\] arrived at a similar solution from approximate tight-binding ideas. Models based on the notion of a bond charge\[81\], or on a function of the local coordination (see for example \[82\]) have also been tried. Most of these models were successful in the regime for which they were parameterised, but showed a lack of transferability. The fourth version of the model of Tersoff perhaps comes closest to being transferable, but at the price of considerable functional complexity and 13 fitted parameters. A recent survey of six such potentials\[83\] concluded that each has strengths and limitations, none appearing clearly superior to the others, and none being fully transferable.

For the present study we require a potential which gives a reasonable treatment of high-pressure phases and phonons, and can give an insight into the different behaviours of silicon and germanium. Recently, it has been shown that a very simple model, based on analytic pair potentials representing one bond per electron, gives good results in studies of phonons, high-pressure phases, surface reconstruction, defects and cluster formation. An unusual aspect of this potential is its simplicity (three free parameters, two more to define length and energy scales) and its transferability.

In its parameterised form, this potential is written as follows:

$$E = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} A(r_{ij}) - \frac{1}{2} \sum_{i=1}^{N} \sum_{k=1}^{4} B(r_{ik}) + \sum_{i=1}^{N} \sum_{n=1}^{3} \sum_{m=n+1}^{4} C(r_{in,m})$$

The function \(A\) term represents the short-ranged repulsion due to core overlap. \(B\) represents the covalent bonds themselves, the sum is interpreted as being over \textit{electrons}.
but can be written as a sum over atom pairs (limited here to four neighbours per atom, though double bonds $i_m = i_n$ could be incorporated in to the model). $C$ represents the repulsion between adjacent bonds as the angle between them is reduced, due mainly to distortions in the orbitals to preserve orthogonality. Again, although the final term is interpreted as a sum over pairs of bonding electrons sharing a common atom, it can be written as a sum of pairwise interactions between pairs of neighbours of a given atom. Thus, the rather complicated notation in which $i_m$ means the label of the $m$th bonded neighbour of atom $i$.

The chosen functional forms of each term of the potential are

\begin{align*}
A(x) &= Ae^{-\alpha x} \\
B(x) &= Bxe^{-\beta x} \\
C(x) &= C(\cos wx + \frac{1}{3})^2.
\end{align*}

The parameters used in the following calculations are as follows: $A = 330816.2$, $B = 36.39820$, $\alpha = 5.693400$, $\beta = 1.450982$ and $C = 1.0$.

In general there is no unique way to select the four ‘bonded’ neighbours (choosing the four nearest neighbours may not satisfy the requirement that if $i$ is bonded to $j$ then $j$ must be bonded to $i$). In the present case, however, the structures which will be considered (diamond, BC8 and ST12) are fourfold co-ordinated crystal structures so this difficulty does not arise. The extension to non-fourfold structures is probably invalid.

The electronic structure calculations also provide strong evidence that this model will not be suitable for modeling BC8 carbon, because that appears to be more like a molecular crystal. This is similar to the situation found in clusters\cite{75}, where small silicon and germanium clusters form distorted structures maximizing their number of bonds (up to four). By contrast, rather than distort bond angles, small carbon clusters form rings and chains containing double bonds. This preference for double bonding
rather than massively distorted bond angles is a qualitative difference between silicon and carbon. It is difficult for a single potential formalism to describe both behaviours.

Within the current model, the physical picture which explains the difference is that the bond-bending arises primarily from orthogonalization within the atom core (which is why it runs over pairs of bonds from the same atom). In silicon the $3s3p^3$ valence electrons are kept away from the centre by orthogonality to the $2s2p^3$ (this effect is even more pronounced in germanium), consequently their overlap and attendant orthogonality contribution to bond angle distortions are smaller. The consequence of this is that in Si and Ge, distorted tetrahedra are favoured over double bonding.

This argument can be developed further to explain the differences between Ge and Si found in the previous chapter. ST12 has bondlengths clustered more closely around the ‘ideal’ (diamond) value than does BC8, but at the expense of a much wider spread of bond angles. Consequently, in germanium where smaller overlap allows for easier bond angle distortion, the ST12 structure is favoured. In silicon the bond-bending is more costly, so the BC8 structure is found. Finally in carbon, with no core $p$ electrons, the orthogonalization cost of bond angle distortion is too great for either ST12 or BC8 to form with true fourfold coordination.

Thus the model of equation 4.13 appears to meet the criteria for the current study.

4.4 Effect of Pressure on Structure

Figure 4.1 shows the relative stability of the diamond, BC8 and ST12 phases for the potential with the length scale parameters fitted to silicon. From these curves the lattice parameter and cohesive energy for these phases can be deduced and are shown in Table 4.1. The graphs representing ST12 are under hydrostatic pressure, obtained by minimising enthalpy with respect to all internal parameters and the $c/a$ ratio. Including these degrees of freedom makes a significant difference to the curve, softening the bulk modulus considerably.
Figure 4.1. Graphs of energy against volume for the diamond, BC8 and ST12 phases. The range shown for each curve represents the structure under pressures from -3 GPa to 10 GPa.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice Parameter(s)</th>
<th>Cohesive Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>5.429</td>
<td>-4.6302</td>
</tr>
<tr>
<td>BC8</td>
<td>6.572</td>
<td>-4.6274</td>
</tr>
<tr>
<td>ST12</td>
<td>5.762, 6.254</td>
<td>-4.6258</td>
</tr>
</tbody>
</table>

Table 4.1. Lattice parameters in Å and cohesive energies in eV given by the empirical potential.
The potential can sometimes give rise to ambiguities in choosing the neighbours, especially if considerable relaxation is required after the choice has been made. BC8 has a single internal parameter to relax. It has four nearest neighbours and so there is no difficulty in determining the bonding arrangement $r_{ik}$. Although the fifth neighbour is relatively close the charge density plots in the previous chapter confirm the assumption implicit in the form of the empirical potential that there is no bond to it. If the fifth neighbour is included as one of the four bonds at the expense of the B bond, it gives a higher energy structure. Including it at the expense of the A bond leads to massive increase in $x$, achieved by simulated annealing, back to a BC8 structure: the broken A bond now becomes the new fifth neighbour (see added note in Chapter 3).

ST12 has four internal degrees of freedom and, because of its tetragonal symmetry, two independent lattice parameters. In germanium ST12 the bondlengths are on average about 1% longer than in the diamond structure, which leads to a density about 10% greater. All the atoms are fourfold coordinated, and there are two distinct atomic environments $a$ and $b$. The eight type $b$ atoms per unit cell form spiral chains with a unique helicity, bridged by the four type $a$ atoms. A combination of seven and fivefold rings means that the bond angles are much more diverse than in BC8, but also enables the bondlengths to be much closer to one another than in BC8.

In the ST12 structure the enthalpy is minimised with respect all the internal degrees of freedom and also the lattice parameters. Once again, it is a fourfold coordinated phase and so there is no difficulty in selecting the correct bonding arrangement. As with BC8, the charge density plots in Chapter 3 give a clear indication that four covalent bonds is the correct description of the bonding.

The diamond structure can only respond to pressure by contraction of its bonds, but pressure increase in BC8 and ST12 can be taken up by increased internal distortion and change in bondlengths. The ST12 structure can also relax by changing the $c/a$ ratio. In practice all of these happen simultaneously.

This simultaneous relaxation is non-trivial to implement by ab initio methods. Due
to problems with changing basis sets, many *ab initio* calculations are unable to calculate forces and then relax the relative atomic positions. They are therefore restricted to rescaling all bondlengths. With a plane wave basis set this problem is somewhat alleviated, and for a given unit cell the atomic position can be determined. This still does not fully allow for relaxation of $c/a$ ratio with pressure. Implementation of the unit cell relaxation is now a relatively straightforward procedure. By minimizing the enthalpy using a conjugate gradients procedure with the Parrinello-Rahman Lagrangian[28] it is possible to allow both internal and unit cell parameters to relax simultaneously, as they would in a real material.

Figure 4.2 shows the importance of including all degrees of freedom in the case of ST12. The graph shows the change in length of the three distinct bonds with volume under full relaxation and under conditions of constant $c/a$. For reference, the variation of a typical bondlength when no relaxation is allowed is also shown (it simply remains proportional to the cube root of the atomic volume). It is clear that the change in $c/a$ with pressure is such as to reduce the necessary change in bondlengths. In both ST12 and BC8 the material is able to reduce its volume without commensurate reduction in bondlengths by adjusting its internal degrees of freedom. This has a very significant effect on the bulk modulus, which is lower in the denser phases than in diamond, in spite of a much greater number of bonds per unit volume. It can be seen from the energy-volume curves how the effect of increasingly large numbers of free structural parameters rapidly decrease the bulk modulus. The curvature of each graph quickly decreases as the number of free parameters change from $1 \rightarrow 2 \rightarrow 6$ in the diamond$\rightarrow$BC8$\rightarrow$ST12 structures. Note that in polycrystalline ST12, large changes in the $c/a$ ratio may be inhibited.

Figure 4.3 shows the variation of the BC8 internal parameter, $x$, with change in volume as determined by empirical methods. The empirical model predicts that $x$ is slightly larger found from the *ab initio* calculations, but the trend of increasing $x$ with pressure is still found.
Figure 4.2. Comparison of empirical bond lengths in ST12 with full relaxation (full lines), fixed $c/a$ ratio (dashed lines) and no relaxation (dotted lines).

Figure 4.3. Variation in the BC8 internal parameter $x$ with pressure in the empirical model.
The cross-over in BC8 bond-lengths occurs with both empirical and \textit{ab initio} methods, although at different pressures. The empirical model gives an intuitive explanation for this. The compression of the type $A$ bond is restricted by repulsion arising from the orthonormality requirement with the type $B$ bonds. Since the angle $\Theta_{AB}$ is smaller than $\Theta_{BB}$, the $AB$ overlap is greater than the $BB$ overlap, and so this term dominates the differential short-ranged repulsion. There are three times as many $AB$ angles to the $A$ bond as to the $B$ bond, so we expect its compression to be three times more difficult. Indeed, this result is found.

4.5 Phonon Dispersion

The empirical potential has been used to calculate the phonon spectra for diamond, BC8 and ST12 phases at various pressures up to 10GPa. Atomistic relaxations, as described in Chapter 1, have been performed under constant pressure allowing the atoms and box size to relax into their equilibrium state. These atomic positions and cell parameters are used in conjunction with the potential to calculate the vibrational frequencies allowed in the crystals by the methods described in Section 4.2. The phonon dispersion curves are calculated along several lines of high symmetry, but to calculate thermodynamic properties, only the phonon frequency density of states are required rather the dispersion curves. For this reason it is necessary to calculate the allowed phonon frequencies at points throughout the Brillouin zone rather than along lines of high symmetry. A good description of the vibrational density of state is required as illustrated in Chapter 3 where the vibrational spectrum of only the $\Gamma$ point modes of the ST12 structure and $\Gamma$ and $X$ modes of the diamond and BC8 structures could be calculated due to the large compute time of \textit{ab initio} calculations. It was found that the BC8 structure had lower vibrational free energy than ST12 at all temperatures and therefore would always be more stable that the ST12 structure. A similar result is obtained with the empirical potential on calculation of the $\Gamma$ point modes only. In order
Figure 4.4. Phonon dispersion curves for the diamond structure along several lines through the first Brillouin zone of the primitive unit cell.

to obtain a good density of states the Brillouin zone is sampled in a regular grid of $100^3$ $k$-points for the diamond structure and $70^3$ in the BC8 and ST12 structures. It will be shown in Section 4.6 that this full description of the vibrational spectra means that the ST12 structure always has a lower vibrational free energy than the BC8 structure and hence the possibility of ST12 becoming the more stable structure is found.

The phonon dispersion curves along several lines of high symmetry for the diamond, BC8 and ST12 structures at zero pressure are shown in Figures 4.4-4.9. The phonon density of states used in the free energy calculations are also given in these figures.

There is no experimental data on phonon frequencies for the ST12 structure and very little on BC8 due to the difficulty in making reasonable samples. The phonon density of states for the diamond structure is in excellent agreement to that of experiment[84]. The peaks from 3 to 5 THz correspond to the low frequency acoustic modes associated with bond bending and can easily be fitted to experiment by adjustment of the $C$ parameter in the potential. The high frequency TO(Γ) modes can also be fitted by setting the second derivative of the $A$ and $B$ functions in the potential to give a
Figure 4.5. Phonon density of states for the diamond structure calculated on a regular grid of $100^3$ $k$-points.

Figure 4.6. Phonon dispersion curves for the BC8 structure along several lines through the first Brillouin zone of the the primitive unit cell.
Figure 4.7. Phonon density of states for the BC8 structure calculated on a regular grid of $70^3$ $k$-points.

Figure 4.8. Phonon dispersion curves for the ST12 structure along several lines through the first Brillouin zone of the the primitive unit cell.
frequency of 15.5THz. Fitting only these two values produces a dispersion curve for modes that are not fitted which is also in reasonable agreement with experiment[84]. This gives confidence that the results for the BC8 and ST12 structures will also be reliable since the potential is made to describe the tetrahedral nature of such structures.

A recent light scattering experiment[85] obtained frequencies of Raman active modes at ambient pressure in the range of 10.5THz to 13THz although the authors do not identify which modes they are. The BC8 structure phonon dispersion curve (Figure 4.6) and density of states (Figure 4.7) show a high density of modes at 12.8THz at the Γ point (and could therefore be Raman active) and also along the Γ → N and Γ → P lines at approximately 12.5THz to 13.0THz respectively and at the H point at 10.3THz (although these modes cannot be seen by Raman experiments). This good agreement of the Γ-modes to a Raman experiment also indicates that the potential is transferable to these complex phases to which the parameters are not fitted.

The general trend in the density of states as the structure becomes more complex (diamond → BC8 → ST12) with increasing numbers of different bond lengths and
bond angles shows a reduction in the height of the peaks of the high frequency (TO) modes in favour of the lower frequency bond bending modes. This behaviour is also observed as the pressure is increased. It is also interesting to note that there is a range of forbidden frequencies in the higher range of the spectrum for the ST12 structure. As pressure increases, the gap increases from 0.8THz at ambient pressure to almost 1.6THz at 10GPa.

In all cases the effect of pressure on the structures is to increase the frequencies of all the modes although this increase varies - in general the high frequency (mostly bond stretching) modes shows a large change in frequency with pressure while the acoustic modes remain relatively unchanged. The frequencies of the zone centre phonons have been picked out for comparison with Raman spectroscopy. The variation in frequency with pressure of zone centre phonons in BC8 is remarkably similar to that measured experimentally[86, 85] in silicon BC8. The low frequency modes are almost unchanged with pressure, consistent with the TA phonons in most tetrahedral semiconductors. These may even be anomalous in that their frequency is slightly reduced with pressure. This implies that the effective force constants for these modes are unchanged or even slightly weakened by pressure. The lack of anomalous modes in the simulation can be associated to the lack of explicit bondlength dependence in the term which describes the low frequency modes. The effect of such a change in pressure on the phonon modes can be characterised by the Grüneisen parameter defined by the ratio of the logarithmic change in frequency to volume, thus:

$$\gamma_i = -\frac{\Delta \ln \omega}{\Delta \ln V}.$$  \hspace{1cm} (4.17)

Therefore a softening of a mode with pressure results in a negative Grüneisen parameter. The Grüneisen parameters have been calculated for the zone centre modes and are shown in Table 4.2. The variation in frequency of the zone centre modes for the BC8 structure with increasing pressure is shown in Figure 4.10. Comparison to experimental
Figure 4.10. Change in zone-centre phonon frequencies with increase in pressure for the ST12 (left hand plot) and BC8 (right hand plot) structures.
results on BC8 silicon[85] show remarkably good agreement. The equivalent plot for the ST12 structure is also shown although there exists no experimental data for comparison.

The predicted Grüneisen parameter for the TA(X) phonon is small, 0.28, an order of magnitude smaller than the bond stretching modes, but non-negative. This mode is dominated by the bond bending term[77, 80, 82], and the Grüneisen parameter is always positive for models with this type of bond bending term, because the third derivative of \((\cos \theta + 1/3)^3\) is \(\sin \theta (8 \cos \theta + 2/3)\) which is negative for all angles occurring in the BC8, ST12 and diamond structures. Since the entropy calculations performed below requires a sum of (logarithms of) frequencies and not the product, the absolute error in this quantity, regardless of sign, is the important feature. This is small.

4.6 Free Energies

From the phonon calculation, the temperature dependent vibrational free energy and total vibrational energy associated with all three structures can be calculated. Since the phonon density of states has been evaluated, the partition function of the vibrations can be simply obtained using Bose-Einstein statistics from which the thermal properties of
the structures in the harmonic approximation can be found. Graphs of this temperature dependence are shown in Fig. 4.11 at ambient pressure. The graphs show the total vibrational free energy, entropy and total vibrational energy per atom. On this scale, the quantities are almost indistinguishable between the three structures, but it is this difference in the free energy between the BC8 and ST12 structures that will govern the temperature at which each structure will be the most stable structure. Also shown in Figure 4.11 is the differences in the thermal properties. The zero of each scale is the value that the diamond structure takes at each temperature. Notice that on the plot of differences in vibrational free energy it can be seen that vibrational free energy for ST12 is significantly lower than that for BC8 which contrasts with the structural cohesive energy which is lower in BC8. Also note that the difference in vibrational free energy for the BC8 and ST12 structures increases with temperature, therefore whenever this difference is larger than the difference in structural energy, the ST12 structure will be favoured.

Another interesting point to note from the plots of differences in thermal properties is that at low temperatures (up to approximately 200K) the diamond structure has lower vibrational free energy and entropy than the BC8 structure. This can be attributed to the fact that there is a greater density of low frequency modes in the diamond structure than in BC8. At low temperatures these low frequencies will be favoured over the more energetic bond stretching modes, thus lowering the free energy.

By scaling the phonon density of states plots by \( \exp(-\hbar \omega/k_B T) \) it can be seen that low temperatures favour higher occupation of the lower frequency modes.

The lattice dynamics techniques described in Section 4.2 have been applied to these relaxed structures which has enabled the calculations to span the entire pressure-temperature regime in the evaluation of free energy. The total Gibbs free energy in the harmonic approximation can now be calculated by

\[
G = U_{\text{struct}} + U_{\text{vib}} - TS + PV
\]  

(4.18)
Figure 4.11. The three plots on the left show the vibrational properties of the diamond, BC8 and ST12 structures as a function of temperature at ambient pressure. The plots on the right show the differences in these quantities with the zero of each taken to be that of the diamond structure. The solid line is the difference BC8-diamond and the dashed line ST12-diamond.
at all points in the pressure-temperature phase space for the ST12 and BC8 structures. For a given temperature and pressure, the structure which has the lowest total free energy, $G$, will be favoured. The structural (cohesive) energy $U_{\text{struct}}$ and $PV$ can be obtained from either the \textit{ab initio} or empirical molecular dynamics and the energy associated with the vibrations, $U_{\text{vib}}$ and entropy, $S$, are calculated from the statistics of the lattice vibrations. Note that the temperature dependence on volume is not included here since the harmonic approximation is used in the lattice dynamics and therefore does not incorporate thermal expansion. The error in this assumption is relatively small since the volume of a tetrahedral semiconductor has a much greater response to pressure than to temperature.

Anharmonic contributions to the total free energy have been estimated from molecular dynamics simulations at a range of temperatures using the empirical potential. These results were obtained from runs with the molecular dynamics code, MOLDY\cite{87}, using 768 and 1024 atoms in a supercell for the ST12 and BC8 structures respectively, running for 25000 timesteps of 1.0fs. This is approximately 100 times longer than the period of the lower frequency modes therefore producing good statistics on the vibrations. Similar runs for diamond yield similar results. The absolute contribution to the energy arising from anharmonic effects was found to be negligibly small, while calculating them is extremely computationally demanding. Consequently, the harmonic approximation for the vibrational properties are used throughout.

It is possible to derive the specific heat capacity from these calculations, and in each case this was found to be $25 \pm 1.5$ Jmol$^{-1}$, indistinguishable from the harmonic case. There is, of course, no electronic contribution to the heat capacity in this model. One useful anharmonic quantity which can be derived from the molecular dynamics is the thermal expansivity of the two structures. The behaviour of the third derivative is not included in the fit, so it is not expected that the expansivity will be very well reproduced by the potential. However, it is expected that the trend observed from the diamond phase through BC8 to ST12 to be correct. The values are found to be $12 \pm 4 \times 10^{-6} K^{-1}$.
Figure 4.12. Relative stability fields of the ST12 and BC8 structures as determined from the empirical potential using the vibrational free energies as a function of temperature and the structures found under pressure from the molecular dynamics simulations.

and $11 \pm 2 \times 10^{-6} K^{-1}$ for BC8 and ST12 respectively. These are somewhat smaller than the value for diamond of $14.5 \times 10^{-6} K^{-1}$ (about 20% higher than experiment). As yet there has not been any experimental measurement of expansivity in the metastable phases.

The empirical model predicts that the difference in structural energy, $U_{\text{struct}}$, to be smaller than that of the ab initio calculations for silicon. This will affect the position of the stability field boundary in the phase diagram. For internal consistency the empirical potential was used throughout to calculate a full pressure-volume phase diagram for ST12 and BC8 silicon which is shown in Fig. 4.12. Note that this is a metastable phase diagram since the diamond structure is stable throughout the P-T region shown.

The main contribution to the vibrational free energy comes from the low vibrational frequencies. These are mostly the bond bending modes which are determined by the $C$ parameter in the final term of the potential. Reduction in the $C$ parameter softens these modes and therefore increases the vibrational free energy. Hence for lower $C$, the
minimum temperature at which the ST12 structure is favourable is lowered. The first
two terms in the potential essentially determine the depth, curvature and position of the
minimum of the structural energy of a tetrahedrally bonded crystal, therefore a simple
rescaling could be used to give a germanium-like potential which in effect would weaken
the bond stretching and lower the corresponding phonon frequencies. As noted above,
this would retain the general shape of the phase diagram, but lower the temperature
required to favour the ST12 structure. However, the bond bending term in germanium
will be even more significantly reduced and therefore reduce the low bond bending
modes even further, an effect which can be traced back to the smaller overlap of 4s4p^3
orbitals on distortion. This also lowers the temperature and the pressure at which the
ST12 structure will become stable over the BC8 structure. It makes ST12 germanium
the metastable depressurised structure at room temperature. It therefore seems likely
to be the case that BC8 germanium will be favoured only at low temperatures and
low pressures, perhaps forming on rapid depressurisation. Recently this was found
to be the case[18] where BC8 germanium was recovered from rapid depressurisation
from the metallic phase. The effects of temperature were not reported but at room
temperature BC8 germanium was found to be short lived, although increasing the
pressure significantly increased its lifetime.

4.7 Conclusions

Structural and vibrational calculations have been performed on the diamond, BC8 and
ST12 structures using an empirical potential designed specifically for 4-fold covalently
bonded structures. The length scales have been fitted to that of diamond-Si. The agree-
ment between experimental, \textit{ab initio} and empirical results for the structural properties
of high-density phases of Si and Ge gives us confidence to proceed with empirical cal-
culations to a scale beyond that which can be achieved by \textit{ab initio} techniques. As a
result of the above calculations it is found that a model whose parameters are fitted to
describe the diamond structure, the BC8 structure becomes unstable with respect to ST12 at high temperature and pressure. Note that both phases are metastable with respect to diamond, each having very different topologies. It therefore seems unlikely that BC8 silicon will transform to the ST12 structure simply by heating. In fact it is found that on heating, BC8 silicon transforms into the Lonsdaleite structure[15], the monoatomic equivalent of wurtzite. However, in view of the kinetic difficulty in transforming from $\beta$-Sn to diamond, it may be possible to depressurise silicon from the $\beta$-Sn phase at high temperature to a pressure above 8GPa to form ST12 silicon.

Although the empirical model has not been explicitly parameterised for germanium, it is possible to make some general comments. The parameter $C$ governs the shear moduli and the vibrational frequency of the low-frequency phonons. In germanium the shear moduli are considerably smaller than in silicon, so a smaller value of $C$ would be appropriate. This would lead in turn to a downscaling of the phonon frequencies, and therefore of the entropies and entropy difference. In germanium, therefore, it would be expected that the transition temperature should be much lower than in silicon - perhaps below room temperature. Thus it might be possible that BC8 germanium will be produced and remain stable over the ST12 structure by depressurisation below room temperature.

The structural properties of BC8 and ST12 silicon and germanium are well described by a model designed for covalently bonded materials. This suggests that although the electrical properties of BC8 may be dominated by a small Fermi surface, the primary contribution to structural bonding comes from covalent bonds. The same model is then used to determine phonon spectra based on the covalent concepts of bond bending and bond stretching.

Although all structures are based on covalent bonding, the bulk moduli are lower in the denser phases than in diamond. This is because they are able to contract both by bond shortening and bond bending, whereas diamond can contract only by bond shortening.
As noted previously[75], both silicon and germanium can be described with this model, the main difference being that the bond-bending forces are lower in germanium relative to the bond stretch.

The ST12 structure has a wider spread of bond angles but more closely matched bond lengths. Its many degrees of freedom allow it to take up external pressure with internal relaxations, giving it a large compressibility. These internal modes also give rise to many low frequency phonon modes, making ST12 a high entropy structure and therefore favoured at high temperature and in germanium where the large bond-bending distortions are less unfavourable.

Experimentally, both ST12 and BC8 germanium have been reported, but the conditions in which they were made are not clearly documented and seem to lack reproducibility. ST12 silicon has not yet been found. The calculations presented here suggest that by conducting high pressure experiments at different temperatures, the preferred phase can be altered. In particular, it may be possible to synthesize ST12 silicon by depressurisation from the metallic $\beta$-tin structure at high temperature.
Chapter 5

The Lowest Energy Silicon Surface?

5.1 Introduction

In this chapter, *ab initio* molecular dynamics is applied to several possible reconstructions of the (001) surface of BC8 silicon. On creating a surface on bulk crystal, bonds are cut at a surface layer. Dangling bonds or localised atomic orbitals remain at the surface which can be unfavourable due to the large increase in energy that is involved.

At the surface of a solid the three dimensional periodicity of a crystal no longer exists so that the surface atoms relax from what would have been their positions in the bulk. This forms the simplest form of surface construction. Due to the nature of the highly directional covalent bonding in semiconductors this relaxation can be quite substantial. Surface atoms with dangling bonds can move closer together to form covalent bonds thus lowering their number per unit area and reducing the total energy of the system.

In an attempt to reduce the energy of the surface further, we place additional atoms on the surface in order to saturate some of the dangling bonds. One of the more common types of surface reconstructions in tetrahedrally bound semiconductors is the
addition of atom pairs (dimers) to the surface. An atom in the dimer is bonded to two
atoms on the surface and to the other atom of the dimer. The net effect of this is to
half the number of dangling bonds per unit area of the surface and therefore reduce
the surface energy. This is the method by which the (001) surface of BC8 silicon is
reconstructed here.

Addition of dimers to a surface can have the effect of lowering the symmetry of
the surface and increasing the size of the surface unit cell. This will also be investi-
gated on the BC8 silicon surface, where the symmetric (1×1) dimer formation and the
antisymmetric (2×1) dimers are found to give rather different surface energies.

As discussed earlier, complex crystalline forms of silicon form good models for
amorphous silicon due to the short ranged disorder contained in such structures. It
may be possible that surfaces of the BC8 structure also forms a reasonable model in
which to study the surfaces of amorphous silicon.

5.2 Surfaces of the Diamond Structure

It is now well established that the clean surface of diamond structure silicon under-
goes reconstructions characterised by dimer formation in the top surface layer. Also
found on many diamond surfaces are stacking faults, rings and chains of atoms and
adatoms. These structures have the effect of reducing the number of dangling bonds
and increasing the surface repeat distance as described above.

A great deal of attention has been paid to reconstructions of the diamond silicon
surface in particular. In vacuum and at ambient temperature, this surface forms a 2×1
unit cell with a surface energy of 0.098eV/Å²[88]. Upon heat treatment, an intermedi-
ate 5×5 surface develops which then converts to a 7×7 reconstruction [89, 90, 91] with
an energy of 0.092eV/Å². Both the 5×5 and 7×7 surfaces involve complex combina-
tions of adatoms, dimers and stacking faults. Other surfaces have been investigated by
\textit{ab initio} techniques, such as reconstructions of the Si-I (311) and (001) surfaces[92, 93]
where even higher surface energies $0.138\text{eV}/\text{Å}^2$ and $0.126\text{eV}/\text{Å}^2$ are reported. Concurrent advances in both experimental and computational methods have allowed for even these high-order reconstructions to be studied in great detail. The family of $(2n+1) \times (2n+1)$ reconstructions of Si-I(111) has now been studied up to $n=3$ by first principles methods [91, 94].

The germanium (100) surface also reconstructs by the formation of dimers[8]. It is found that high order reconstructions characterises this surface with the most stable states being $2 \times 2$ and $4 \times 1$ unit cells forming symmetric buckled dimer formations.

5.3 *Ab Initio* Modeling of Surfaces

In this chapter, the Car-Parrinello method is applied in an investigation of the energetics of surfaces. As described in Chapter 2, in order to make the calculation tractable, periodic boundary conditions are used. This is necessary in order to apply Bloch’s theorem. This implies that Bloch’s theorem cannot be applied in the direction perpendicular to the surface. Therefore an infinite cell or a non-plane wave basis set would be required in order to describe the wavefunction in that direction. This problem is easily avoided by the use of a periodic *supercell* that reintroduces the periodicity which is required to carry out the calculation with a plane wave basis set and Bloch’s Theorem.

A surface still has periodicity in the plane of the surface, but it loses this periodicity perpendicular to the plane of the surface. In order to reintroduce the required periodicity into the calculation, the supercell contains a crystal slab and a region of vacuum. This is illustrated schematically in Figure 5.1. To ensure that the results of such an *ab initio* calculation accurately describe an isolated surface, the vacuum regions must be wide enough so that the faces of the adjacent surfaces do not interact across the vacuum region. But the surfaces could also interact through the bulk of the crystal, therefore this region must also be thick enough so that this interaction is also eliminated.
By use of this supercell method it is now possible to employ the \textit{ab initio} calculations using a plane wave basis set. Throughout the following calculations, the wavefunctions were expanded in a basis set with an energy cut of 200eV. The ionic positions are relaxed under the influence of Hellmann-Feynman forces until the calculated forces are below 0.1eV/Å. The supercells are found to be large enough that sampling of the Brillouin Zone is required only at the Γ point. Total energy convergence with respect to \( k \)-point sampling is checked by repeating the calculation with a set of 4 special \( k \)-points. The difference is surface energies is found to be negligible. The basic unit cell parameter is taken as being 6.54Å as found from the previous pseudopotential calculations in Chapter 3. All surfaces in this work are treated using supercells containing a slab of BC8 Si (and region of vacuum) to which periodic boundary conditions are applied. A sufficiently large supercell must be constructed so as to isolate the two surfaces from each other. In all cases considered, the dimension of the supercell perpendicular to the surface is 3 cubic unit cell lengths, 19.62Å, and the thickness of the vacuum region is
1 unit cell. In all cases, it is found that the atoms in the two furthest layers from the surface remain in their initial positions and their bondlengths also remain unchanged, implying that sufficient bulk material has been included.

### 5.4 Construction of Si-BC8 Surface

Despite the complexity of the surface reconstructions now known, certain simple assumptions remain. The most obvious of these is that the reconstruction is always treated as taking place on the stable diamond structure bulk material. However, as described previously, Si is known to also exist at ambient pressure in the metastable low-symmetry crystal structure BC8.

The departures from ideal tetrahedral bonding in BC8 silicon also make it an important prototype crystal for understanding the effects of short range disorder on the properties of amorphous Si[66]. It is therefore important to study the surface of such a structure since features common to amorphous silicon may exist.

Band structure calculations suggest that BC8 Si is semimetallic, as calculated in Chapter 3, however, integration of the BC8 Si bond charge yields exactly 2.0 electrons (see the discussion on bond charge integration in Chapter 3) per bond with a maximum of charge density between the two atoms indicating that its cohesion is dominated by covalent bonding despite its semimetallic transport properties. This suggests that a covalently bonded model of the surface is an appropriate description. The reconstructive pressure-induced transitions which lead to BC8 Si formation occur with large volume discontinuities and do not preserve single crystals. This has so far precluded examination of the BC8 Si surface by conventional experimental methods and makes computer simulations essential.

In what follows, the notation used (for example, (001) surface, $2 \times 1$ reconstruction, etc.) refers to the 16 atom simple cubic representation of the BC8 structure as opposed to the 8 atom body centred description of the unit cell.
**Figure 5.2.** The $1 \times 1$ reconstruction of the Si-BC8 (001) surface showing dimerization of the adatoms. The numbers in the circles gives the height of the atoms in units of $a/10$ ($a = 6.54\, \text{Å}$ is the BC8 unit cell parameter). The figure illustrates systems-I (without the adatoms), III and IV. The letters $a$ to $p$ are used to label the atoms. Adatoms $v$ and $w$ show the position of the dimer reconstruction of the surface and the dashed lines indicate the bonds formed by the adatoms.

The BC8 unit cell has two double layers perpendicular to the (001) direction. This gives two distinct possible terminations of the crystal normal to this direction. As pointed out by Biswas *et al* [9], (001) possesses a natural cleavage plane which breaks the least number of bonds (all B-bonds), 17.5% more broken bonds per unit area than the Si-I (111) cleavage plane, but half as many as the alternate BC8 (001) truncation discussed below. Structurally, the resulting surface (which is hereafter referred to as system-I) consists of B bonds lying in the plane linking dimers of threefold coordinated atoms. This surface is shown in Figure 5.2 and does not include atoms labeled $v$ and $w$. Each atom in the dimer has an A and B bond extending into the bulk and a dangling B-bond. This is similar in nature to the dimers formed on $2 \times 1$ reconstruction of the Si-I (111) surface[88]. The supercell representing system-I involves 32 silicon atoms.

The other possible (001) termination of the BC8 crystal is a cut leaving each of the
CHAPTER 5. THE LOWEST ENERGY SILICON SURFACE?

Figure 5.3. This figure illustrates the reconstruction undergone by system-II. The notation is similar to that of the previous figure and the dashed lines illustrate the bonds formed by the four 5-fold coordinated atoms on the layer below the surface.

Four resulting surface atoms having two dangling bonds. This surface (referred to as system-II) is shown in Figure 5.3 and it contains two surface dimer bonds $O - D$ and $I - F$. Each atom in a dimer has only one B-bond directed into the bulk. A simple counting of broken bonds suggests that this surface will be considerably less favorable than that of system-I. This supercell also contains 32 atoms.

Both systems-I and II are allowed to relax from their initial starting configurations which is that of the terminated bulk crystal by allowing the atoms to move using a conjugate gradients algorithm. This represents the two simplest forms of surface reconstructions possible on the (001) plane of BC8 silicon.

After relaxation of system I, the surface dimers $b - g$ and $i - p$ (see Figure 5.2 which describes the notation) reduce in length from the unrelaxed bulk value of 2.36Å to 2.28Å. The charge density within the bond is integrated by the method given in Chapter 3. The charge associated with a surface dimer increases to 2.2 electrons with the remaining 1.8 electrons localised in non-bonding orbitals directed into the vacuum.
The A and B bonds from each surface atom extending into the bulk contain a charge of 2.0 electrons. The length of each bond increases, although most notably the A bonds $o - b$ and $p - a$ become the longest at 2.60\,\text{Å}. These changes in bond lengths are associated with a tilt of the dimer from initially lying parallel to the surface. Atoms $b$ and $p$ are displaced upwards by 0.13\,\text{Å} such that the dimers tilt at 3.3° to the plane of the surface. The total surface energy of system-I (after ionic relaxation) is found to be 0.1057\,\text{eV/Å}^2.

For system-II it is found that substantial structural relaxation occurs in the top surface layer and that the resulting surface energy is only 0.0047\,\text{eV/Å}^2 higher than that of system-I. With two dangling bonds per surface atom, system II relaxes in a somewhat different manner as shown in Figure 5.3. The surface atoms $D, F, I$ and $O$ relax in such a way as to reduce the second nearest neighbour distance to atoms on the lower plane. Atoms $A, G, L$ and $N$ become five fold coordinated, where the dangling bonds are partially saturated in order to create the fifth bond, that is, charge goes out of the dangling bond to create a new covalent bond. These extra bonds fall into two distinct categories. Bonds $A - F$ and $G - D$ are slightly shorter at 2.61\,\text{Å} than bonds $L - O$ and $N - I$ at 2.64\,\text{Å}. In both cases the atoms of each bond have moved together from the unrelaxed second nearest neighbour distance of 3.39\,\text{Å}. Although the two fifth neighbour bondlengths only differ by approximately 1% the charge differs by 15% with 2.0 electrons in the short bond and 1.7 electrons in the long bond. The two surface dimers in the unit cell $I - F$ and $D - O$ reduce in length from the bulk B bond length to 2.25\,\text{Å}. Although the dimer remains in the plane of the surface, the dipole formed by the movement of charge from the dangling bond causes the dimers to rotate by an angle of 22.9° from the bulk position about the center of the bond in a direction such that the fifth nearest neighbour (the new donated bond) distance is shortened.
CHAPTER 5. THE LOWEST ENERGY SILICON SURFACE?

5.5 Adatom Reconstructed Surfaces

This section will concentrate on the further stabilization of system-I by means of the addition of adatoms and will investigate the effect of symmetric and antisymmetric dimer bond tilting on surface energy. The next thing considered is a $1 \times 1$ adatom reconstruction of the Si-BC8(001) surface. Atoms $v$ and $w$ are placed close to the surface (see Figure 5.2) such that a dimer is formed bonding to each of the dangling bonds on atoms $g$, $i$, $b$ and $p$ thus reducing the number of dangling bonds to 2 per unit cell. The initial configuration is set such that the five bonds created by the adatoms are approximately equal in length and the adatoms are placed at the same height above the cleavage plane. On relaxation of this (from now on known as system-III), the dimer tilts from being parallel to the surface to an angle of $6.5^\circ$. A three dimensional representation of the charge density of the $2 \times 1$ symmetric dimer is shown in Figure 5.5 where four symmetrically tilted dimers are illustrated. The bond length of the dimer relaxes to a length of 2.31 Å. This bond length is shorter than either of the bulk bondlengths. This is probably due to $\pi$-bonding between the atoms of the dimer. The bonds formed from the dimer to atoms $i$, $b$, $g$ and $p$ relax to approximately equal lengths (2.45 Å, 2.39 Å, 2.34 Å and 2.46 Å, respectively). The valence charge in the dimer is found to be 2.3 electrons while the dimer-to-bulk bonds contain approximately 2.1 electrons. A contour plot of the electronic charge density in a slice through the surface dimer is shown in Figure 5.4. The charge in the dimer being larger than that of a single covalent bond also suggests $\pi$-bonding in the dimer. The surface energy of system-III is found to be $0.0796\text{eV} \cdot \text{Å}^{-2}$ which is lower in energy than that of any other previously reported silicon surface. To check that no further relaxation takes place between dimers in neighbouring cells, a $2 \times 1$ symmetric dimer configuration was examined. The surface energy and dimer tilt angle of the corresponding $2 \times 1$ configuration was found to be identical to the $1 \times 1$ case which indicates that the symmetric dimer configuration is completely described in system-III.
The $2\times1$ dimer configuration was set up in a symmetric formation. It is possible that this is only a local minimum energy configuration, being metastable with respect to an antisymmetric dimer configuration. To investigate this point further, the $2\times1$ antisymmetric-tilt reconstruction of BC8 Si is also considered. This configuration is referred to as system-IV. In this case the calculation is begun by tilting alternate dimer bonds in opposite directions and then allowing the configuration to relax. It is found that this corresponds to a metastable situation in which the antisymmetric configuration is preserved. However, the angle that each dimer forms to the surface differs greatly. One dimer forms an an angle to the surface of only $3^\circ$ where atom $v$ is $0.11\text{Å}$ below the level of atom $w$. Using the same notation to label the atoms in the cell containing the other dimer, atom $v$ is $0.44\text{Å}$ above the level of atom $w$ therefore tilting in the opposite direction at an angle of $11^\circ$ to the plane of the surface. Similar to that of the symmetric case the dimer bondlengths both reduce in length, in this
Figure 5.5. Three dimensional valence charge density of the (001) surface with the symmetric dimer configuration of silicon in the BC8 structure. The figure shows an isosurface of the charge density where the symmetrically tilted dimers can clearly be seen. This figure gives evidence that, although BC8 Si is semimetallic, the bonds are covalent in nature. Note the slightly larger bonds on the dimers illustrating they contain more electronic charge than that of the single covalent bonds found in the bulk.
CHAPTER 5. THE LOWEST ENERGY SILICON SURFACE?

<table>
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</tr>
</thead>
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</tr>
<tr>
<td>(II) Bulk Terminated</td>
<td>0.1104</td>
</tr>
<tr>
<td>(III) Symmetric Dimer</td>
<td>0.0796</td>
</tr>
<tr>
<td>(IV) Antisymmetric Dimer</td>
<td>0.1460</td>
</tr>
</tbody>
</table>

Table 5.1. Surface energies of the relaxed (001) surfaces of BC8 silicon.

case to 2.26Å each containing a charge, slightly greater than that of a single bond, of 2.3 electrons. Quite surprisingly, this antisymmetric dimer configuration is found to be the least favorable of any of the surfaces considered here, having a surface energy of 0.1460eV/Å².

5.6 Discussion and Conclusions

It is found that the symmetric dimer reconstruction of the BC8 silicon (001) surface to be stable with respect to both of the possible unreconstructed terminations of the bulk. A summary of the energies found for the (001) surfaces of silicon in the BC8 structure considered here is given in Table 5.1. Unlike various silicon and germanium surfaces, the antisymmetric dimer is not favoured. In all cases the surface dimers reduce in length below that of the bulk bond length. In doing so the bonds become slightly stronger than that of a Si-Si single bond, with the electronic charge within the bond increasing to more than 2.0 electrons. Where two unbonded electrons per surface atom remain, a bond to an atom in the bulk is formed. This reconstruction forms five fold coordinated atoms with all electrons involved in bonding and is quite close to being stable. The possibility of under coordinated atoms forming donated bonds with neighbouring atoms at little energy cost suggests new topological possibilities for amorphous silicon. The low energy of this surface may also provide new insight into the nature of the bonding on amorphous silicon surfaces, and into silicon clusters which are stabilised because of their high surface/volume ratio.
In spite of the 17.5% additional broken bonds per unit area over the diamond Si (111) cleavage plane the calculated surface energy (0.0796 eV/Å$^2$) is lower than that of any previously reported silicon surface. Although *ab initio* studies cannot consider all possible atomic configurations and reconstructions, the central result that BC8 Si has surfaces of lower energy than diamond Si remains. There is a strong implication that amorphous silicon will behave likewise.

The stability of this surface with respect to other diamond Si surfaces suggests that the metastability of BC8 will be enhanced because of impeded nucleation and growth of the diamond structure at the BC8 silicon surface. This result is of particular relevance in view of the recent report of pressure-induced phase transitions in Si by nano-indentation[5]. A semimetallic region formed by such a process might be expected to have a very long lifetime, determined by the stability of the semiconductor-metal boundary.

A qualitative explanation of the lower BC8 surface energy can be ventured by considering the strain energy required to distort $sp^3$ bonding away from the prefect tetrahedral angle. Any reconstruction of a Si-I surface will cause such distortions, but since the bonds in BC8 silicon are already distorted away from the tetrahedral configuration, in some cases the surface reconstruction actually reduces this distortion. This argument also applies to amorphous silicon and suggests that amorphous silicon surfaces may be lower in energy than those in crystalline diamond Si.
Chapter 6

Point Defects In Silicon

6.1 Introduction

It is short range properties that govern the nature of disordered silicon and germanium. These depend on the local bonding configurations of atoms in these systems. It is therefore important to look at the changes that small volumes of local disorder effect an otherwise perfect crystal. Such an environment occurs in point defects in a crystal which effects the bonding topologies and therefore the electronic structure by introducing new energy levels to the electronic density of states.

The two types of defects considered here are silicon self interstitials and vacancies. Self-interstitials are among the basic intrinsic defects that are important in many solid state processes such as diffusion. A silicon interstitial is an atom within the structure which is located at a non-crystallographic position. This causes the structure to relax around this additional atom and also changes the local bonding configuration. An interstitial atom can assume one of many different bonding topologies in tetrahedral semiconductors. The more common sites considered in previous calculations are those where the interstitial atom has a position with hexagonal or tetrahedral symmetry[95, 96, 97], (and references therein) although these are not necessarily the most stable interstitial configuration. The bonding of these atoms within the crystalline structure
depends on whether the defect carries a charge which also changes the defect states found in the band gap[95]. Only neutral defects will be considered here.

A lattice site where no atom is found is known as a vacancy. Again, there is substantial relaxation of the crystal around the defect site. For a neutral vacancy the bonding topology is simpler than for that of the interstitial. This has been examined previously by several methods such as empirical potentials and Green’s functions methods[95, 98, 99, 100]. The surrounding atoms relax into the site of the vacancy and the dangling bond on each atom surrounding the defect pair up to form two new covalent bonds.

It is possible to apply the empirical and \textit{ab initio} molecular dynamics methods used previously to systems which are non-periodic by the use of supercells. This is similar to the technique used for the surface calculation presented in Chapter 5. In that case, the system was periodic in two directions, requiring the supercell geometry only in the direction perpendicular to the plane of the surface. In this chapter point defects of silicon, where the structure is non-periodic in all three dimensions, are examined by this method, using both empirical and \textit{ab initio} techniques.

Interstitial configurations and the vacancy defects will be examined by both \textit{ab initio} and empirical molecular dynamics techniques. Firstly, total energy pseudopotential calculations will be used to determine the bonding topologies of the defects which are useful input for the empirical potential described in Chapter 4. There have been previous first principles calculations on such defects, but due to the high computer time necessary only very small supercells have been used. The use of small supercells is investigated by the empirical method and it is shown that large supercells are required in order to eliminate finite size effects that are evident in the smaller calculations. The calculations performed here are at zero temperature so that the interstitial configuration found in each case is the ‘nearest’ metastable state to the initial atomic positions. It is still impractical to carry out finite temperature \textit{ab initio} molecular dynamics in order to perform annealing to find lower energy defect configurations. In order to investigate
CHAPTER 6. POINT DEFECTS IN SILICON

point defects further, an empirical potential is then used. The phonon spectra of
the large supercells containing the defects are calculated directly by diagonalisation
of the $3N \times 3N$ dynamical matrix. Since this contains all the vibrational information,
localised vibrational modes around the defect are found. Also, a similar statistical
analysis of the vibrational spectra as that in Chapter 4 gives the free energy of the
defects. Knowledge of the vibrational free energy for two interstitial configurations
then allows the transition temperature from one defect site to another to be found.
This analysis of free energies of the defects from the phonon states is important for the
study of defect migration through a crystal.

The dynamical matrix of a system contains all the information about elasticity of
the crystal. Therefore, in principle, it is possible to calculate the elastic constants of the
crystal just from the dynamical matrix. This is done at several defect concentrations
and characteristic defect stiffening is observed.

6.2 \textit{Ab Initio} Calculations

6.2.1 Vacancy

The lattice vacancy in diamond structure silicon has probably been the most studied
defect in a semiconductor, therefore only a brief account of the work presented here
will be given for completeness. Interest in vacancies derives from its importance for
understanding the mechanisms responsible for diffusion in silicon. There have been
many reports on the formation energy, the result varying tremendously depending on
the method used and the charge of the defect. Also, most \textit{ab initio} methods have not
allowed for full relaxation of the surrounding crystal structure of an isolated vacancy.
Other errors have included incomplete basis sets used because of the large number of
calculations necessary. For example, Car \textit{et al}[101] reports a vacancy formation energy
of 5.0eV but with an improved basis set the formation energy reduces to 3.8eV[102].
Using a Green’s function method and a different basis set the same authors report a
value of 4.4eV[95] although allowing only nearest neighbour relaxation gives a formation energy of 3.8eV. A first principles calculation carried out by the supercell method (which will be applied to the vacancy in this section) quoted a neutral vacancy formation energy of 3.6eV[103]. In that case the size of the unit cell was very small and therefore could only include nearest neighbour relaxation. In each case there appears to be inaccuracies in the results either due to incomplete basis sets or inadequate system size which will not allow a full relaxation of the system. It will be seen in the following calculation that there is substantial relaxation occurring around the vacancy.

In Section 6.3 the change in the properties of the defect with supercell size is investigated. Due to computational limitations the system size used here is a $2 \times 2 \times 2$ cubic unit cell consisting of 63 atoms (64 for the perfect crystal with one removed for the vacancy). It is shown later that a 63 atom cell the calculation is not quite converged, but the errors incurred are small.

The initial configuration for the simulation consists of 63 atoms displaced a small amount in a random direction from their perfect diamond lattice sites. It would be possible to relax these positions using the empirical potential and use that final result to start the \textit{ab initio} calculation, but this would require that bonding topology surrounding the vacancy to be used as input. Anyway, it is preferable that no initial assumptions are used in the calculation, therefore the full relaxation of the system is purely from the \textit{ab initio} Hellmann-Feynman forces.

It is found that there is substantial relaxation towards the vacant site by each of the surrounding four atoms. This is illustrated in Figure 6.1 summarising the change in atomic distances from the vacant site. Each atom moves inwards from the initial first neighbour distance from the vacancy of 2.351Å to $\sim$2.22Å. In turn, two new covalent bonds are formed between pairs of atoms of length 2.41Å and 2.38Å while

---

1. This small random displacement is necessary to ensure that the risk of spurious symmetries are eliminated from the relaxation procedure.
2. The forces are converged to better than 0.02eV/Å therefore the error in the bond lengths are expected to be small. This symmetry break in the new bond lengths is therefore expected to be real.
Figure 6.1. Schematic diagram showing the relaxation of the near neighbours around the vacancy defect site calculated by the \textit{ab initio} method. The distances (in Å) on the outer shell of atoms show the distance from the vacant site. The lengths of the two new bonds are also indicated.
the non-bonded pairs are slightly closer together than the bulk second nearest neighbour distance at 3.74Å. This new bonding configuration forms two five fold rings and two seven fold. Unlike in several previous calculations[103, 95], the unit cell is large enough to examine the relaxation undergone by the second shell of atoms around the defect. Of the twelve atoms in the second shell of neighbours, which started at the diamond silicon second neighbour distance of 3.839Å, eight remain almost unmoved, relaxing outwards slightly to 3.85Å. The remaining four atoms in the second shell move inwards to a distance of 3.67Å from the vacant site. The third shell remains almost unchanged. This configuration is found to have a defect formation energy of 3.38eV. This is 0.5eV lower than that of previously published values which do not allow for relaxation on such a long range as presented here.

There is also a significant change in the electronic structure of the crystal on the introduction of the vacancy. The electronic density of states for silicon in the perfect diamond structure calculated by the ab initio methods described in Chapter 2, is given in Figure 6.2. A schematic diagram of the region about the Fermi level is shown in Figure 6.3 as found after full relaxation of the structure containing the vacancy. The tail of both the conduction and valence bands are broadened into the gap reducing the semiconducting gap. The triply degenerate Γ point state found in the top band is found to split, having energies of $E_F$, $E_F - 0.019eV$ and $E_F - 0.025eV$, where $E_F$ is the highest energy valence band. There is also a non-degenerate state in the gap close to the conduction band at $E_F + 0.495eV$. On reconstruction of the valence electronic charge density using this state only, it is found that it is localised orbital at the site of the vacancy.

### 6.2.2 Self Interstitials

The problems incurred with first principles calculations on self-interstitials are similar to that of the vacancy. There have been many reports on the interstitial site and bonding configurations (see, for example references [96, 98, 99, 101, 102, 103]). The results
vary depending on the method used (supercell vs. Green’s function techniques), and with which basis set is used. The Green’s function methods allow for only local atomic relaxation around the defect (up to approximately 3-4 Å) with the further out regions treated as a macroscopically averaged region. In the supercell method, relatively small cells have also been used and are therefore not able to take longer range relaxation into account, for example Bar-Yam et al.[103] describe various self interstitial configurations with a supercell of only 8 and 16 atoms. Results were later obtained by Chadi[96] for defects in GaAs and Si using supercells of 32 atoms.

Most calculations have been on interstitials which are located at points of high symmetry, although their are many more possible interstitial sites within the diamond structure. This is explicitly shown in the following calculations. An interstitial was introduced into an otherwise perfect crystal of diamond silicon. A supercell of 65 atoms

\footnote{These calculations have been performed using the code parallelised for the CM200 Connection Machine.}
Figure 6.3. Schematic diagram of the region about the Fermi level of Si-diamond containing a defect as found from the 63 atom supercell calculation. The dotted lines show both the conduction bands and valence bands broadening into the gap. The localised band gap state is also indicated.
was used (a $2 \times 2 \times 2$ unit cell plus one interstitial atom). The additional atom was placed at the hexagonal symmetry point as shown in Figure 6.4 and the structure allowed to relax under the forces calculated by the Hellmann-Feynman theorem. This configuration will be referred to as $I_H$. Since the initial configuration of the defect was highly symmetric, the molecular dynamics method did not break this symmetry and the final configuration was that of the hexagonal interstitial. An similar simulation was also done where the starting point of the interstitial atom was offset slightly from the hexagonal symmetry point in order to investigate whether a breaking of this symmetry would result in the interstitial moving to give a different defect configuration (referred to as system $I_A$).

It is found that on relaxation, the two similar starting configurations result in quite different bonding topologies, but have similar defect formation energies of 2.25eV for $I_H$ and 2.12eV for $I_A$. As expected, $I_H$ remained in the highly symmetric hexagonal site but was found to have a lower formation energy than previously reported calculations\cite{96, 95}. This is due to the converged plane wave basis set, which had an
energy cutoff of 250eV\(^4\), and the larger supercell size used here, whereas other calculations have not allowed for longer range atomic relaxation. A schematic representation of the final bonding configuration of the \(I_H\) defect is given in Figure 6.4. The first shell of atoms surrounding the interstitial atom relax outwards leaving all atoms four fold coordinated. This creates two four-fold and two seven-fold bonded rings of atoms around the additional atom in the structure. This severely buckles the hexagon in which interstitial is located in order to sustain the four-fold coordination of all atoms. The bond lengths to the four atoms surrounding the interstitial are 2.33Å, 2.35Å, 2.57Å and 2.60Å. The next shell of atoms consist of the two atoms of the hexagon that the interstitial did not bond to. It is found that they relax outwards slightly to \(\sim 2.8\)Å. This is slightly larger than previously reported results which did not include relaxation of more distant atoms. Here, the next shell of atoms are found at a distance of 3.3Å to 4.0Å from the defect (compared to the perfect second neighbour distance in diamond silicon of 3.84Å).

On consideration of the electronic structure (see Figure 6.5), similar to that of the vacancy, the tails of the valence and conduction bands extend slightly into the band gap closing it by \(\sim 0.05\)eV. There are two electronic states found in the gap - one is very close to the top valence band at an energy of only \(E_F + 0.007\)eV, the other slightly further in to the gap at \(E_F + 0.03\)eV.

The interstitial configuration \(I_A\) is found to have a relaxed structure quite different from that of \(I_H\). A three dimensional ‘ball and stick’ representation of the \(I_A\) configuration is given in figure 6.6 The most significant feature of this defect is that it unusually forms a three-fold ring of silicon atoms. There are no four or five-fold rings formed although all atoms remain fully four-fold coordinated. In order to investigate the bonding topology of this feature, the valence electron charge density in the plane of the ring is plotted in Figure 6.7. This is the \((2, 1, T)\) plane of the supercell. The

\(^4\)16384 plane waves per band per \(k\)-point where used in the calculation - a total of 3276800 using 128 occupied and 72 unoccupied bands.
Figure 6.5. Schematic diagram of the electronic states near the Fermi level for Si-diamond containing a hexagonal interstitial.

Figure 6.6. The final relaxed atomic configuration of the self interstitial $I_A$. In this figure the bonds are created by choosing the four nearest neighbours of each atom. It is found that this does not make any unreciprocated neighbouring atoms.
Figure 6.7. The electronic charge density of the plane of the three-fold ring of silicon atoms of the $I_A$ interstitial configuration.

The figure shows that, rather than the configuration being a three-fold ring of covalent bonds, which is generally accepted to be unstable in silicon structures, a three centre bonding orbital is formed. On consideration of the defect formation energy in comparison to other calculations\cite{95, 96, 104, 105, 106, 107} on neutral self interstitials, this three centre orbital is found to be more stable that the highly symmetric hexagonal or tetrahedral interstitials where the $I_A$ configuration is found to have a defect formation energy of 2.12eV. This is a similar result to the empirical calculations of Maroudas and Brown\cite{105} where they also find that a low symmetry configuration, the extended self interstitial, is also a low energy defect.

The low formation energy of the $I_A$ interstitial is also reflected in the band structure. As with the other point defects considered here, the band gap becomes smaller as the conduction and valence bands tail off in to the gap. In this case it is found decrease by half to 0.21eV as illustrated in Figure 6.8. The highest $\Gamma$ point state loses the 3-fold degeneracy to form three states of energy $E_F$, $E_F-0.046$eV and $E_F-0.061$eV.
These states are higher in energy than the 3-fold degenerate state found in the perfect structure, hence the band gap is reduced. This is because the defect introduces a lower energy doubly degenerate state at $E_F-0.603\text{eV}$, repelling the higher energy states into the gap. Note that the $I_A$ defect adds new states to the electronic structure which are of a lower energy than the perfect triply degenerate $\Gamma$ point state. This low energy state is in contrast to the vacancy and $I_H$ configurations which are found to have defect states within the band gap.

The low energy of defects such as this also imply that they could be typical of local configurations found in more complex forms of Group IV elements such as amorphous silicon. This will be discussed in more detail in Chapter 7 where the supercell method is used to model the amorphous structure of Si and C.
6.3 Empirical Calculations

6.3.1 Structural and Vibrational Calculations

In this section, the results of several calculation will be presented. Firstly, the 0K configurations of the hexagonal and tetrahedral interstitials and the vacancy are determined by the use of the empirical potential given in Chapter 4. The Parrinello-Rahman Lagrangian is used to allow the size of the unit cell to change so that no external stresses act upon the supercell. This was not done in the \textit{ab initio} calculation due to the difficulties in dealing with a changing basis set for the wavefunctions. The relaxed positions of the atoms and the force constants calculated directly from the potential are then used to construct a dynamical matrix for the entire supercell. Subsequent diagonalisation gives the vibrational frequencies and their corresponding eigenvectors which will enable a search for localised modes caused by the defects.

The covalent bond model discussed in Chapter 4 required the bonding configuration of the defects to be known. The bonding configuration for the tetrahedral interstitial is well known (for example, see [103]) and it is this one which is used. The bonding topologies found from the \textit{ab initio} calculations presented above are used for the hexagonal interstitial and vacancy. It is not possible to use the empirical potential to calculate the vibrational properties of the \textit{I}_A interstitial formation found in the \textit{ab initio} calculations presented above. This is because the potential models simple four-fold covalent bonds, whereas the \textit{I}_A defect was found to contain a three-fold bonding orbital which will not be described correctly with a simple covalent bond model.

For a given bonding arrangement, the energy minimum is located using a conjugate gradients routine starting from a configuration in which all atoms are given a small random displacement to break all symmetries. The supercells used for the perfect crystal contain 64 and 216 atoms, with plus and minus one atom for the interstitials and vacancy respectively. It is found that the defect formation energies and formation volumes differ slightly between the two sizes of simulation, therefore a larger cell based
Table 6.1. The defect formation energies in eV and formation volumes in Å³ is shown as the system size changes. Systems I, II, and III are for supercells based on 64, 216 and 512 atoms respectively. The first three columns show the formation energies, the next three show formation volumes.

These defect formation energies and volumes are shown in Table 6.1. It was found that the formation energies and volumes for the two larger simulations are identical showing that the defects are isolated for the simulations based in the 216 atom supercell. For this reason, the vibrational simulations are carried out on the 216 atom supercells only. The results of the defect formation energies are in agreement with other empirical results[108] in that the tetrahedral interstitial is energetically more favourable than the hexagonal interstitial. It is also in agreement with the above \textit{ab initio} calculations although the formation energies are slightly lower than that of other results[95]. This is believed to be due to finite size effects, and in this context, note that there is a strong dependence on system size exhibited in Table 6.1. Also note that the normal correlation between low formation volume and low formation energy is observed in all cases.

The relaxed atomic positions and supercell sizes can now be used to calculate the vibrational modes of the entire system. The theory of lattice vibrations is presented in detail in Chapter 4. Continuing from that point, the method which is used here is presented.

Defects in the crystal remove the periodicity from the structure. Therefore the entire supercell can be described by \( l = (0, 0, 0) \) only, and \( k = 1, ..., N \) for \( N \) atoms

<table>
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<td>2.25</td>
<td>16.08</td>
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</tr>
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</table>
in the simulation. To make a comparison, the perfect diamond crystal will be treated
in the same way. The perfect lattice is treated as one large unit cell which therefore
has a very small Brillouin zone. This allows sampling at \( q = 0 \) to suffice resulting in
\( D_{\mu\nu}^{(q=0)} \) being a real symmetric matrix. This ranges over the same reciprocal space
points allowed by that of a fully symmeterised calculation with \( n \times n \times n \) unit cells.
Thus, in effect, the phonon frequencies of higher valued wavevectors relative to the
standard diamond cell are being calculated but without the need for diagonalisation
of complex matrices. The phonon density of states and the displacements associated
with each normal mode can be found. In the case of lattices containing defects, the
periodicity of supercells is unwanted hence sampling of wave vectors other than \( q = 0 \)
is unnecessary.

The \( l \) subscripts in the dynamical matrix can be dropped, and setting \( q = 0 \), the
dynamical matrix of the supercell is now given by

\[
D_{\mu\nu}^{(0)} = \frac{1}{m} \Phi_{k\mu k'\nu}
\]  

where the matrix of force constants is now

\[
\Phi_{k\mu k'\nu} = \left[ \frac{\partial^2 \Phi}{\partial u_k \partial u_{k'}} \right]_0, k \neq k' \tag{6.2}
\]

and

\[
\Phi_{k\mu k'\nu} = -\sum_{k' \neq k} \Phi_{k\mu k'\nu}. \tag{6.3}
\]

By removing the sum over unit cells and carrying out the calculation as if there were
no symmetry within the supercell (which is true in the case of crystals containing
defects), the phonon frequencies which have higher order wave vectors in the standard
FCC-diamond Brillouin zone will be mapped onto the zero wave vector relative to the
supercell.
The calculations were carried out on a silicon crystal containing 216 atoms in the perfect lattice. Similar calculations were also done on crystals containing interstitial atoms in the hexagonal and tetrahedral sites and on a crystal containing a vacancy. Point defects are well described by the covalent bond charge potential used here, and the validity of using it to calculate phonon spectra is established here and in Chapter 4.

Similar phonon density of states curves were found for the 64 and 216 atom simulations which gives confidence that the unit cells are large enough for such calculations. Figure 6.9 show plots of the density of states of phonon frequency for the larger simulations. The shapes of the curves are similar to that found in Chapter 4 and to experiment[109] although the density of the low frequency bond bending modes has been enhanced relative to the high frequency. It can be seen that the defects cause all the peaks to broaden, which is most notable at the higher frequencies where several localised modes are located. There are additional modes of higher frequency added to the spectrum which are associated with the defects in the structure. These have frequencies above the cut off frequency for the perfect diamond structure and, as shall be demonstrated below, are localised near the defects.

The eigenvector corresponding to a particular mode gives the directions and relative amplitudes that each of the atoms in the supercell move under excitation of that mode[110]. Localised modes are found by searching through the normalised eigenvectors for large displacements of any individual atom. In the cases of the interstitials, the localised mode with the largest element from the matrix of normalised eigenvectors corresponds to the interstitial atom itself. Figures 6.10(b) and 6.10(c) show the atoms around the interstitial and the directions and relative amplitudes in which they move under excitation of this mode. It can be seen from Figure 6.9 that modes of higher frequency than the maximum found in the perfect crystal occur. In the vacancy the density of states no longer has a sharp cut-off, but instead tails off with the highest frequency mode found at 15.98THz. The tetrahedral interstitial causes four localised
Figure 6.9. Density of states plots of vibrational frequencies for the perfect and defected crystals. The density is in arbitrary units. (a) is for the vacancy, (b) the tetrahedral interstitial, (c) the hexagonal interstitial, and (d) is the perfect crystal. Note here that sampling at Γ is equivalent to 256 $k$-points in the primitive diamond cell and is therefore much less than the brillouin zone sampling carried out in Chapter 4. This illustrates the difficulty in performing calculations where the symmetries of a crystal are lost.
Figure 6.10. Line drawings of the silicon crystals showing the localised modes. The bold lines at each atomic site show the direction and relative magnitudes of the vibrational mode under consideration. Figure (a) shows the vacancy where the positions of the atoms surrounding the defect can be seen to relax to reduce the vacancy formation volume. There are four atoms vibrating with large amplitude for this localised mode surrounding the vacant site at the top of the diagram. (b) shows the tetrahedral interstitial and (c) the hexagonal interstitial where the single localised vibration of the interstitial atoms are clearly seen, with very little motion of the surrounding atoms.
mode higher than the cut-off for the perfect diamond structure. These are at 18.25THz, 17.49THz, 16.92THz and 16.16THz. Similarly, the hexagonal interstitial causes high frequency modes at 17.71THz (doubly degenerate), 16.94THz (double), 16.36THz (single), 16.17THz (double) and 15.98THz (single). The maximum frequency mode that can be supported by the perfect structure is 15.80THz. The perfect crystal is found to have no such localised modes. For the vacancy, Figure 6.10(a), the atoms close to the defect are found to have large vibrational amplitudes in the high frequency modes while the other atoms in the supercell are almost stationary. The localised modes shown in the figure correspond to the eigenvectors with the largest single element. It is found that this is also the eigenvector associated with the highest frequency (18.25THz for the tetrahedral interstitial and 17.71THz for the hexagonal interstitial). Each eigenvector is normalised to unity (that is, the sum of the coefficients of each vector is one). The vibrational energy of the localised mode is concentrated in a single atom. For the hexagonal interstitial the fraction of the vibrational energy localised in this atom is 0.502, while for the tetrahedral interstitial it is 0.505. This is an order of magnitude greater than that of the largest normalised element of any eigenvector for the perfect crystal. The vacancy shows similar characteristics, with the localised modes having the highest frequencies, although the majority of the vibrational energy is associated with the four atoms adjacent to the vacant site.

6.3.2 Free Energy and Entropy

Temperature dependence of thermodynamic quantities can be calculated from simulations performed with temperature[111, 112]. For example, the free energy of a solid can be determined from the local atomic configuration, hence a minimisation of the free energy with respect to atomic coordinates give both the equilibrium structure and free energy of the solid which could contain defects. This requires thermal statistics to be gathered in either a molecular dynamics or Monte Carlo simulation to calculate the canonical average of the thermal property.
It is not necessary to do this here since the phonon modes for a given defect concentration have been calculated directly for a given defect concentration (which is inversely proportional to the size of the supercell containing the defect). Thermodynamic properties using the vibrational spectra for the crystal can be found simply from the partition function calculated from Bose-Einstein statistics as demonstrated in Chapter 4 where a P-T phase diagram was found. The partition function allows the vibrational free energy and vibrational entropy to be calculated.

By taking the differences between the perfect crystal and the crystals containing defects (scaled to the same number of atoms) the effects that the defects have on the thermal properties can be seen. The plots of these excess free energies, total vibrational energy and vibrational entropies varying with temperature are shown in Figure 6.11. These can be compared to Figure 6.12 which shows the total vibrational energy, free energy and entropy for the perfect crystal. These quantities for the defected crystals are not shown in Figure 6.12 since they are indistinguishable on that scale. It is found that the tetrahedral interstitial has a free energy higher than that of the hexagonal interstitial at any temperature. Note that this excess free energy is $\sim 1000$ times smaller than that of the defect formation energy and hence the tetrahedral interstitial is stable with respect to the hexagonal site. This leads to the conclusion that the defect formation energies for interstitials and vacancies within a crystal in the harmonic approximation are almost independent of temperature. The free energy of a silicon crystal at ambient pressure was found from the Stillinger-Weber potential\cite{77} by summing the logarithms of the frequencies obtained from the dynamical matrix method used here. Broughton and Li\cite{113} find the sum of the logarithms to be 4.7533$^5$ per particle, although a full free energy analysis with temperature was not given. A similar calculation using the dynamical matrix for the perfect crystal, described above, gives the value of 4.6442. Calculations on the hexagonal and tetrahedral interstitials and the vacancy give (in

\footnote{In the reduced units given in reference \cite{77}.}
Figure 6.11. Differences in (a) vibrational free energy, (b) vibrational entropy and (c) total vibrational energy are shown as temperature varies. The zero of each scale is taken to be the value of that quantity of the perfect diamond structure at each temperature. (Full line - hexagonal interstitial, dashed line - tetrahedral interstitial, dotted line - vacancy).
Figure 6.12. Plots of total vibrational energy, vibrational free energy and vibrational entropy per atom against temperature. Only the plots for the perfect crystal are shown since the differences in the curves for the defects are too small to be seen on this scale (see previous figure).
Defect          | Small Supercell | Large Supercell |
----------------|-----------------|-----------------|
Hexagonal Interstitial | 5.377           | 4.635           |
Tetrahedral Interstitial | 6.572           | 5.831           |
Vacancy                  | 6.312           | 5.575           |

Table 6.2. Configurational entropies for the large $4 \times 4 \times 4$ supercell and the smaller $3 \times 3 \times 3$ supercell. The units are in $10^{-4}$eV/K per defect.

the same reduced units) 4.6449, 4.6452 and 4.6444 respectively. It can be seen that the introduction of defects to the crystal only changes the free energy slightly. It is the small difference in this free energy in addition to the difference in defect formation energies that determines properties such as diffusion in defects through the crystal.

The free energies of the defects can also be found, including the anharmonic effects, by running the molecular dynamics simulations at finite temperature over an extended period of time to collect thermal averages. These simulations comprised of the crystal with defect running for 12000 molecular dynamics time steps of 1.0fs which is longer than 10 periods of the lowest frequency vibrations. This allowed the evaluation of the anharmonic terms to a reasonable tolerance. It was found that the defect formation energy is unchanged within a temperature range of 0-1000K. This confirms the validity of obtaining the above results using the harmonic approximation.

Finally, the configurational entropy of the defects can be calculated to give a comparison to the vibrational entropy. The Boltzmann definition of entropy, $S = k_B \ln \Omega$, where $\Omega$ is the number of configurations, can be used to calculate the configurational entropy per atom, after simplification by Stirling’s formula, by

$$S = c k_B \ln \left( \frac{m}{c} \right), \quad (6.4)$$

where $m$ is the number of possible different defect sites and $c$ is the defect concentration. The configurational entropies for the three defects considered are shown in Table 6.2. It is found that under the harmonic approximation, the contributions to the entropy
of a crystal are given by the configurational entropy and the vibrational entropy in roughly equal proportions at non-zero temperatures.

In the converged calculations the differences in the interstitial formation energy is 0.51eV (Table 6.1). From Figure 6.11, it can be seen that the vibrational free energy is not enough to transform a tetrahedral interstitial to the hexagonal site within the temperature range shown. The relative stability of the anharmonic case is tested by running a molecular dynamics simulation at increasing temperature, allowing the bonding to change throughout the simulation\(^6\). A transition from one defect site to another is not found until 1360K. Higher temperatures were required to allow the interstitial atom to move freely throughout the crystal. This also indicates that the harmonic approximation taken here is quite accurate up to relatively high temperatures. Recent work using the Stillinger-Weber potential on self interstitial diffusivity in silicon\(^{113, 105}\) has found a simple migration path for several self interstitials over a temperature range of 733-1473K. In the work by Maroudas and Brown\(^{105}\) the relaxation was done in a somewhat different manner from the molecular dynamics simulations here. Energy minimisation was carried out by quenching the system by a steepest descents algorithm after relaxing the system by a lengthy Monte Carlo method at 500K with system size of the host crystal ranging from 60 atoms to 512. The work of Maroudas and Brown and the calculations given here suggest that the tetrahedral interstitial configuration is the most stable (by 1.74eV and 0.51eV, respectively) with respect to the hexagonal interstitial, but the Stillinger Weber formation energies are both significantly larger by about 2eV. However, they find that a self-interstitial (which they name an extended interstitial), which has lower symmetry than either of the hexagonal or tetrahedral sites, is an even more stable configuration. This is similar to the \textit{ab initio} calculations, above, where a low symmetry configuration was also found to be stable. Their calculations suggest a migration mechanism of the extended interstitial where the extra atom moves

\(^{6}\)The bonding was allowed to change when an unbonded neighbour of an atom became closer than a bonded one.
from this low energy state to an identical one by passing through the state of a tetra-
hedral interstitial, thus requiring less energy than the tetrahedral-hexagonal transition
that was calculated above. The migration paths have not been examined here, but they
agree that diffusion of the tetrahedral interstitial via a path though the hexagonal state
does not occur until a much higher temperature than the Maroudas-Brown diffusion
mechanism[105].

6.3.3 Effect on Elasticity

There are several ways of calculating the elastic properties of a material from the knowl-
edge of the interaction potential. They can be found either from gathering statistics
from long molecular dynamics calculations using the fluctuation formula method[107],
or directly from inverting the matrix of spring constants which can easily be calculated
from the interaction potential. The advantage of using the molecular dynamics method
is that the elastic constants can be calculated at temperature and the other thermody-
namic averages can be calculated simultaneously. Obviously, inverting a $3N \times 3N$ ma-
trix at every timestep in the simulation of temperature is computationally prohibitive,
but the calculations presented here are carried out at 0K, therefore making the latter
method more effective since the dynamical matrix has already been calculated.

A full derivation of the calculation of elastic coefficients can be found in reference
[114]. The final method for a crystal containing many atoms in a single primitive unit
cell will be given here. The elastic coefficients can be calculated directly from $\Phi_{kk'}$ as
follows. Allow $\alpha, \beta, \gamma, \lambda, \mu$ and $\nu$ to run over the co-ordinate axes $x, y$ and $z$. Then
define

$$C^{0}_{\alpha\beta}(kk') = \Phi_{k_\alpha k'_\beta}, \quad (6.5)$$
$$C^{1}_{\alpha\beta,\gamma}(kk') = -2\pi \Phi_{k_\alpha k'_\beta} \Delta \gamma_{kk'}, \quad (6.6)$$
$$C^{2}_{\alpha\beta,\gamma,\lambda}(kk') = -4\pi^2 \Phi_{k_\alpha k'_\beta} \Delta \gamma_{kk'} \Delta \lambda_{kk'}. \quad (6.7)$$
There will be three modes that have zero frequency due to the three translational degrees of freedom of the entire crystal. Therefore \( C^{0}_{\alpha\beta}(kk') \) will be singular since it will have linearly dependant rows and columns. Now we introduce the \((3N-3) \times (3N-3)\) matrix \( \Gamma^{3N-3} \) which is defined to be the inverse of \( C^{0}_{\alpha\beta}(kk') \), where we allow \( k, k' = 2, 3, \ldots, N \), and for convenience of calculation define

\[
\Gamma_{\alpha\beta}(kk') = \Gamma^{3N-3}(kk'), \quad k, k' \neq 1 
\]

(6.8)

\[
= 0, \quad \text{otherwise.}
\]

For convenience, the \( k = 1 \) rows and columns are removed from the dynamical matrix for the inversion. The choice of \( k \) is arbitrary and therefore can be taken to be \( k = 1 \) without loss of generality.

Now define the following brackets where \( v_a \) is the volume of the supercell:

\[
[\alpha\beta, \gamma\lambda] = \frac{1}{8\pi^2 v_a} \sum_{kk'} C^2_{\alpha\beta, \gamma\lambda}(kk'), 
\]

(6.9)

and

\[
(\alpha\gamma, \beta\lambda) = -\frac{1}{4\pi^2 v_a} \sum_{kk'} \sum_{\mu\nu} \Gamma_{\mu\nu} \left\{ \sum_{k''} C^1_{\mu\alpha, \gamma}(kk'') \right\} \times \left\{ \sum_{k'''} C^1_{\nu\beta, \lambda}(k'k''') \right\}. 
\]

(6.10)

The elastic coefficients are then

\[
c_{\alpha\gamma\beta\lambda} = [\alpha\beta, \gamma\lambda] + [\beta\gamma, \alpha\lambda] - [\beta\lambda, \alpha\gamma] + (\alpha\gamma, \beta\lambda) 
\]

(6.11)

provided the strain energy of the crystal is invariant against rigid body rotations, the force on each atom is zero and the stresses on the crystal vanish. The atomistic relaxation simulation which relaxed the atoms into the lowest local energy configuration and
CHAPTER 6. POINT DEFECTS IN SILICON

Table 6.3. Elastic coefficients in eV/Å³ for both sizes of supercells. The numbers in the brackets are the number of atoms in the simulation.

<table>
<thead>
<tr>
<th></th>
<th>Perf(216/64)</th>
<th>Hex(217)</th>
<th>Hex(65)</th>
<th>Tetra(217)</th>
<th>Tetra(65)</th>
<th>Vac(215)</th>
<th>Vac(63)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₁</td>
<td>0.9291</td>
<td>0.9314</td>
<td>0.9427</td>
<td>0.9328</td>
<td>0.9436</td>
<td>0.9348</td>
<td>0.9410</td>
</tr>
<tr>
<td>C₁₂</td>
<td>0.7156</td>
<td>0.7190</td>
<td>0.7241</td>
<td>0.7213</td>
<td>0.7293</td>
<td>0.7212</td>
<td>0.7301</td>
</tr>
<tr>
<td>C₄₄</td>
<td>0.1692</td>
<td>0.1681</td>
<td>0.1670</td>
<td>0.1679</td>
<td>0.1678</td>
<td>0.1668</td>
<td>0.1680</td>
</tr>
<tr>
<td>B</td>
<td>0.7868</td>
<td>0.7898</td>
<td>0.7970</td>
<td>0.7917</td>
<td>0.8007</td>
<td>0.7924</td>
<td>0.8005</td>
</tr>
</tbody>
</table>

the periodic boundary conditions on the supercells in conjunction with the Parrinello-Rahman Lagrangian ensures that these conditions are satisfied.

The elastic coefficients can then be expressed in their more familiar form by pairing the indices by the equivalences \( xx \rightarrow 1, \ yy \rightarrow 2, \ zz \rightarrow 3, \ yz, \ zy \rightarrow 4, \ xz, \ zx \rightarrow 5 \) and \( xy, \ yx \rightarrow 6 \).

The bulk modulus, \( B \) (for a cubic crystal) is then

\[
B = \frac{C_{11} + 2C_{12}}{3} \tag{6.12}
\]

Table 6.3 shows the independent elastic coefficients for the various supercells in the two simulations. The entire \( 6 \times 6 \) elastic matrix is calculated in all cases. It is found that \( C_{11} = C_{22} = C_{33}, \ C_{44} = C_{55} = C_{66} \) and \( C_{12} = C_{21} = C_{23} = C_{32} = C_{13} = C_{31} \). All other coefficients are almost zero\(^7\). The bulk modulus is higher than that of experiment (\( B=0.61 \) eV/Å³) because the parameters of the potential were fitted for \( C=0 \)\(^8\), although the elastic coefficients are sensitive to the value of \( C \). It can be seen, however, that the change in bulk modulus seems to be almost independent of the type of defect under consideration. The elastic coefficients are also calculated for the smaller supercells, which allows the change in elastic coefficients with respect to concentration to be calculated. The coefficients are seen to rise with concentration, (Figure 6.13), apart

---

\(^7\)They would be identically zero for a cubic system, but the unit cell relaxation allows this symmetry to be broken.

\(^8\)Recall from Chapter 4 that the \( C \) term in the empirical potential describes the ‘bond bending’ interactions, which is characterised by a repulsive force between neighbouring unbonded atoms. Increasing \( C \) will increase the bulk modulus.
CHAPTER 6. POINT DEFECTS IN SILICON

Figure 6.13. Change in elastic coefficients with respect to concentration are shown for the hexagonal interstitial. It is found that the change in elastic coefficients with respect to concentration, $d\varepsilon_{ij}/dC$, is fairly constant over the range considered. Note the change in scale for $C_{44}$ from $C_{44}$ which decreases very slightly. This shows the characteristic defect stiffening in silicon[74, 75].

6.4 Conclusions

The supercell method has been applied to several point defects of the diamond structure. The lower defect formation energies found in the ab initio calculations relative to previously published results imply that large cells are necessary for this technique. This is also shown by the large relaxation undergone by the second shell of atoms surrounding the defect. Surprisingly, a three centre bonding orbital is found in a low symmetry interstitial configuration which is also associated with a rather low formation energy. Direct calculation of the energy eigenstates of the electrons finds that this bonding configuration introduces a state below the top valence band causing the band gap to become smaller. This is in contrast to the vacancy and the hexagonal interstitial where
The defects were found to introduce new states in the band gap. The \textit{ab initio} calculations on a supercell of that size are compute intensive and therefore only allowed a simple atomic relaxation under the Hellmann-Feynman forces. In order to investigate the effects of temperature on point defects it was necessary to use the empirical potential described in Chapter 4. This allowed a complete analysis of the harmonic behaviour of the defects, although the unusual three-centre bonding orbital could not be examined in this manner due to the nature of the potential.

The supercell method has allowed the calculation of phonon densities of states and elastic constants for various point defect concentrations and compare the results by applying the same method to the perfect crystal. Knowledge of the complete densities of states also allowed for the determination of the change in thermodynamic properties of the crystal caused by the defects and for the comparison to the configurational properties. The supercell method has also allowed us to calculate the small change in defect formation energies with respect to temperature. This result could not be obtained with comparable computational effort by running a molecular dynamics simulation and collecting thermal averages due to the short timestep required in the simulation compared to the lowest frequency vibrations. The molecular dynamics results were only accurate enough to show that the formation energies were not significantly changed.

It was found that the covalent bond charge potential gives a reasonable description of many properties of point defects in silicon, being able to predict the relative stability of the defects and their configuration, although it is unable to correctly describe three-centre bonding orbitals or the Maroudas-Brown configuration. It inaccurately describes the values of some elastic coefficients because of the parameterisation, but does find that defect stiffening occurs in this tetrahedrally bonded model.

Analysis of the normal modes shows that some high frequency modes are highly localized at the defect, whereas the perfect crystal has no modes closely associated with any particular atom.

The free energy of defects is dominated by the internal energy contribution, and to
a first approximation the entropic and vibrational effects can be ignored. Moreover the entropy is dominated by the harmonic contribution, and again to first order anharmonic effects can be ignored. Thus is was not possible to measure any anharmonic entropy effect in the free energy of formation of point defects.

Defects such as these are expected to be good models for possible local bonding configurations in amorphous silicon and therefore should be included in any such model. The surprising result that silicon forms a three centre orbital has not been included in any model so far. This type of defect would go unnoticed in experimental measurements of the radial distribution function of amorphous silicon since the atomic separations in this bond is similar to that of the normal Si-Si covalent distance.

This work has been made possible by applying standard lattice dynamics techniques on a large supercell using a massively parallel CM200 computer as described in Chapter 4. The diagonalizations take approximately 12 minutes and the matrix inversions 7 minutes on $2^{14}$ processors. Only memory requirements prohibit larger systems to be considered here since the size of the dynamical matrices are of order $(3N)^2$. A possible method of increasing the size of system and hence the complexity of the defects that could be considered is to use a large cluster of atoms without periodic boundary conditions, so that the dynamical matrices become band matrices although this would add the extra complication of surface modes, it would reduce the memory requirements of the problem, scaling as $N$ with a large prefactor, and allow use of an algorithm for diagonalising sparse matrices which is an order of $N$ faster than the Jacobi method we used to diagonalize dense matrices. This method could also be of use by using a short-ranged potential where interactions larger than a given distance were assumed to be zero.
Chapter 7

Amorphous Carbon and Silicon

7.1 Introduction

Amorphous materials are of interest because of their complexity and unique structural and electronic properties. While crystalline and amorphous silicon are widely used in the manufacture of semiconductor devices, the carbon analogues at first seem of limited value in that context. This is due to the lack of electronic levels in the band gap of diamond on the introduction of n or p doping. However this is not true of the dense form of diamond-like amorphous carbon as opposed to the lower density graphitic form of amorphous carbon. To investigate the properties of such structures a model is first required of pure amorphous carbon. It is this problem which will be discussed in this chapter.

Of fundamental interest is the microscopic origins of such properties ranging from mechanical and elastic characteristics to the electronic and optical properties. As seen in Chapter 3, and in many recent publications (for example [115, 116, 117, 118]), carbon can display many different bonding configurations with varying coordination number due to the ability to form both $sp^2$ bonding such as in graphitic structures and $sp^3$ bonding as in diamond, although it seems energetically unfavourable to distort the bonding angles. Silicon also forms an amorphous phase which has generally been modelled using
4-fold coordinated continuous random networks of $sp^3$ bonded atoms\[115, 119\]. These have used empirical and tight-binding force models which agree well with experiment. It is possible that this type of model may not be complete in view of the unusual interstitial configuration found in the previous chapter which was associated with a low defect formation energy. This implies that such a bonding topology could easily be formed in amorphous silicon\[120\].

In chapters 3 and 4, calculations were performed on complex forms of silicon and carbon which are characterised by short range order but still retain long range crystalline order. In view of the difficulties associated with performing full theoretical calculations on amorphous structures they proved to be a useful insight into the physics of short range disorder. It therefore seems a natural conclusion to attempt a molecular dynamics calculation on the amorphous structures of silicon and carbon and examine their differences.

Previous experimental and theoretical studies of the microscopic structure of amorphous carbon\[121, 122, 123, 124\] show that it is dependent on the macroscopic density which in turn depends on the method in which the sample was made. The trend in structures is from graphitic-like structures embedded in a matrix of both two-fold and four-fold coordinated atoms at a low density of 2.20 to 2.69 g/cm$^{-3}$ (found from tight binding molecular dynamics\[124\]), to diamond-like amorphous carbon containing ‘defected’ three fold sites at a high density of 3.35 g/cm$^{-3}$\[121, 125\]. This change in density also changes the bonding properties considerably\[126\], where the ratio of $sp^2/sp^3$ is found be inversely proportional to the density of the amorphous carbon.

Studies of amorphous silicon seem to show a somewhat simpler behaviour\[116, 119\] where the microscopic structure consists of distorted tetrahedral units. Numerous hand built and computer models have been constructed\[127, 128, 129\]. In the relaxed continuous random network models various potentials and bond charge models have been used (for example, the Keating and Stillinger-Weber potentials) in order to minimise
total energies. Other models have included ‘defect’ atoms that are three fold coordi-
nated which have been obtained from various molecular dynamics techniques by cooling
from the melt[130].

One of the main methods used recently for obtaining better models of both amor-
phous carbon and silicon[131] is that of reverse Monte Carlo simulations[132]. This
method involves fitting the structure factors for trial atomic configurations to exper-
imental results (measured, for example, by neutron diffraction) by moving the atoms
at random and accepting the move by a probability given by the difference in the
new structure factor and the experimental measurements. Configurations are accepted
under certain constraints, such as bond length, coordination number, etc. Some con-
figurations are not accepted such as those containing three membered rings. This may
be incorrect given the results presented in Chapter 6 and the results for carbon given
below. Also calculations on very small cells of silicon atoms arranged randomly have
been found to contain 3-fold rings which was found to be relatively stable under small
atomic displacements[133].

7.2 Modelling Amorphous Materials

A major difficulty which is not easily overcome by the \textit{ab initio} and empirical methods
used previously is the non-periodicity displayed in amorphous materials. For this reason
it is necessary to use the supercell method again. Also, in order to get a reasonable
range of bonding configurations a large number of atoms per supercell are required.
Due to the compute intensive nature of \textit{ab initio} methods coupled with the high energy
plane wave cut off required for the carbon pseudopotential, a 64 atom supercell was
the largest that could be reasonably dealt with.

The initial starting configuration of atoms in the supercell was that of randomly
packed particles constrained by a minimum separation. This is equivalent to a random
packing of hard spheres. Both the carbon and silicon simulations were started with
the identical random configuration. In order to make a comparison to the complex structures studied in chapters 3 and 4, the density of the amorphous carbon was set to $3.4 \text{g/cm}^{-3}$ which, experimentally, is found to form a distorted diamond-like structure. The density chosen for amorphous silicon was $2.6 \text{g/cm}^{-3}$ and also the slightly lower density of $2.3 \text{g/cm}^{-3}$ which is about the same density as the amorphous silicon made from evaporated silicon samples which, again, is thought to predominantly formed from distorted tetrahedral units. In the ab initio calculations in Chapter 3, it was found that LDA tended to underestimate the lattice parameter of structures by about 2%. The density of the structures are therefore overestimated. For this reason the density chosen above are higher than experiment by this amount.

Earlier calculations performed by modelling the atomic interactions by the empirical Tersoff potential[118, 134] or a tight-binding approach[121, 122] were computationally fast enough to allow quenching from the melt to be performed in order to construct the model amorphous materials. A similar approach has been tried with a full ab initio calculation[117] with a smaller supercell of 54 atoms (at the graphitic-like density of $2 \text{g/cm}^{-3}$), but this required the rather unrealistic cooling rate of the bulk material of $10^{15} \text{K/s}$.

In the calculations given here, the atoms are simply allowed to relax by a conjugate gradients algorithm under the influence of the Hellmann-Feynman forces - there is no finite temperature molecular dynamics performed for annealing due to the long simulation times required. This will only create a single structure in the large phase space of possible configurations at the respective densities, but it will give a reasonable range of bonding topologies and will highlight the differences in the nature of amorphous silicon and diamond-like amorphous carbon. Since the calculations are fully ab initio there are no a priori bonding characteristics required unlike other large empirical calculations that have been performed (where normally either $sp^2$ or $sp^3$ bonding is assumed depending only on the coordination number of the respective atom, and therefore ignores the more unusual bonding topologies such as two-fold $sp$ bonds or three-centre
Figure 7.1. Radial distribution function of amorphous silicon calculated at a density of 2.6g/cm$^{-3}$.

orbitals). This will allow any unusual types of bonding to be found such as the two or five fold coordination[125].

A $64 \times 64 \times 64$ FFT grid was required for the silicon using a plane wave cutoff of 250eV. The calculation for carbon required a $60 \times 60 \times 60$ using a cutoff of 408eV.

7.3 Structural Details

7.3.1 Silicon

Two samples of amorphous silicon have been generated at slightly different densities using the same initial random configuration. The higher density sample will be referred to as system-I, the other being system-II. After relaxation, the final configurations are found to be rather different. Given in Figures 7.1 and 7.2 are the radial distribution functions, $g(r)$, of each sample. The radial distribution function of system-I is in excellent agreement to that of experiment[131, 135]. For comparison, an experimental
radial distribution function\footnote{As found from the Fourier transform of the experimental structure factor given in reference [131].} for an amorphous silicon sample which has a density of 2.45g/cm$^{-3}$ is given in Figure 7.3. System-II differs slightly in that the second neighbour peak at 3.5-4Å is too low and slightly wider than experiment. Integration under this part of the curve (taken from 2.9Å to 4.3Å) however indicates that the average number of nearest neighbours per atom is similar in each case. The lower density of system-II allows for a wider spread in second neighbour distances than system-I.

In both cases the height and width of the first peak of the radial distribution functions are in agreement with experiment. This implies that the average coordination number is correct in both cases. To find the coordination number, the maximum length of a silicon bond must be known. Unfortunately, the first minimum in the radial distribution function does not go to zero showing that there is a continuous range of neighbour distances. For this reason a maximum bond length is chosen arbitrarily to be 2.55Å. This then defines all the bonds within the structure. Some structural details of systems I and II are summarised in Table 7.1.


Figure 7.3. Experimental radial distribution function of amorphous silicon as found from neutron diffraction measurements.

<table>
<thead>
<tr>
<th></th>
<th>System-I</th>
<th>System-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>10.45</td>
<td>10.83</td>
</tr>
<tr>
<td>$\rho$</td>
<td>2.606</td>
<td>2.343</td>
</tr>
<tr>
<td>$R_3$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$R_4$</td>
<td>8</td>
<td>14</td>
</tr>
<tr>
<td>$R_5$</td>
<td>39</td>
<td>33</td>
</tr>
<tr>
<td>$C_2$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$C_3$</td>
<td>7</td>
<td>7</td>
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<tr>
<td>$C_4$</td>
<td>45</td>
<td>52</td>
</tr>
<tr>
<td>$C_5$</td>
<td>11</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 7.1. Structural data for both amorphous silicon simulations. $a_0$ is the lattice constant (Å) of the 64 atom cubic supercell, $\rho$ is the density (g/cm$^{-3}$), $R_i$ give the number of $i$-fold rings and $C_i$ is the number of atoms with coordination number $i$. Note that, somewhat unexpectedly, the denser simulation has fewer 4-fold rings.
The coordination number of each atom can now be calculated. It is found that most atoms are four-fold coordinated (70.3\% for system-I and 81.3\% for system-II) while only a few atoms are either 3 or 5 fold coordinated. In system-I a single two-fold coordinated site is found. Such a feature has not been included in reverse Monte Carlo studies of amorphous silicon. In figure 7.4 is a schematic diagram of some 2, 3, and 4 fold coordinated atoms found in system-I. The 4-fold coordinated site is typical of the atomic structure of most of the atoms in the sample. It consists of a distorted tetrahedral bonding arrangement with a more distant, but unbonded, 5th neighbour, somewhat similar to that found in the BC8 structure. In the case shown in Figure 7.4, the bond angles for each site are given in Table 7.2.

The average bond angle for each coordination number is also shown in Table 7.2. As expected, the mean angle for the 4-fold coordinated sites are approximately that of
CHAPTER 7. AMORPHOUS CARBON AND SILICON

Table 7.2. Bond angles of specific 2, 3 and 4 fold coordinated sites found in amorphous silicon in system-I. Also shown is the average bond angle for the 3, 4 and five fold coordinated sites for both systems. The angles are in degrees.

<table>
<thead>
<tr>
<th></th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2$</td>
<td>103.3</td>
</tr>
<tr>
<td>$C_3$</td>
<td>124.5 103.0 106.3</td>
</tr>
<tr>
<td>$C_4$</td>
<td>77.4 114.3 81.2 111.4 126.1 122.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Average Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3$</td>
<td>(I) 105.2 (II) 96.6</td>
</tr>
<tr>
<td>$C_4$</td>
<td>(I) 107.1 (II) 106.8</td>
</tr>
<tr>
<td>$C_5$</td>
<td>(I) 104.3 (II) 103.9</td>
</tr>
</tbody>
</table>

the perfect tetrahedral angle. It may have been expected that the mean bond angle at a 3-fold site to be 120° similar to that of an $sp^2$ graphitic-like region, but instead it is found that it is less than 109°. This leads to the implication that 3-fold sites are tending to have $p$-like character (at an angle of 90°). The bonding topology of the 3-fold site resembles a triangular pyramid with a well defined bond to the three neighbours of a central atom. A non-bonding orbital is formed at the top of the pyramid indicating that the ‘defect’ site still retains $sp^3$ bonding characteristics.

A typical five fold site is shown in Figure 7.5. On examination of the valence electron charge density it is found that there are no bonds formed between atoms more that 2.6Å distant (hence the choice of $r_{max}$ when calculating the coordination number). There exist several sites with 5 atoms much closer than this (there are no 6-fold sites found) and hence covalent bonding is expected to occur. On examination of the valence electron charge density around these sites, we find that the $C_5$ sites tend to be fully 3 or 4 fold coordinated where the remaining atoms are relatively close and form slightly weaker bonds. When a fifth atom is found in an otherwise tetrahedral configuration it tends to weaken the longer bonds further. Such a configuration is shown in Figure 7.5 where the two more distant atoms form much weaker bonds that the three closer ones. Also, it is found that usually one of the neighbours of a five-fold coordinated atom has
Figure 7.5. A five-fold coordinated silicon atom. The solid lines show the five covalent bonds from the central atom. The bond lengths are given in Å.

only three neighbours. This suggests that the electrons for the fifth bond is ‘donated’ from the undercoordinated atom. Note that this is similar to the five-fold configuration found in the Si-BC8 surface in Chapter 5.

The average coordination number for system-I is 4.03 while the slightly lower density structure of system-II is found to have a coordination number of 3.97. Most models of amorphous silicon, such as random networks, assume from experimental measurements that the structure is fully four-fold coordinated. The fact that both simulations have found a structure which is very close to those found in other calculations from an initial random packing indicates that a full annealing treatment may not be necessary. There have been previous ab initio calculations on amorphous silicon and germanium (for example, see [135, 130]) which have rapidly cooled the melt in order to form models of their amorphous structure which reduces the percentage of ‘wrongly’ coordinated sites, but giving an average coordination number similar to that found here. This suggests that cooling from the melt followed by annealing may not be the most efficient method
of obtaining a reasonable model of amorphous silicon since there results do not differ significantly from those given here.

The ring statistics are also given in Table 7.1 for both systems. This can be compared to the BC8 and ST12 structures which contain a range of small ring sizes from 5 to 7 fold rings. There are no three fold rings (and therefore no three-centre bonding orbitals) found in either sample which is somewhat unexpected considering the low formation energy of the interstitial configuration found in Chapter 6.

Since the bond lengths found in amorphous silicon (and also in the BC8 and ST12 structures) are similar to that found in the diamond structure it is generally assumed that the energy associated with straining the bond angle away from the perfect tetrahedral value gives the main proportion of excess energy of the amorphous structure relative to that of diamond Si[130]. This distortion of angles away from 109.47° is illustrated in Figures 7.6 and 7.7 which show the bond angle distribution functions for systems I and II respectively.
Figure 7.7. Bond angle distribution function of amorphous silicon system-II.

As can be seen, a relatively small change in the size of the unit cell of the 64 atom simulation (a change of 3.5%) makes a rather large change to both the radial and bond angle distribution functions despite the same random starting configurations. The main features however seem to remain similar in both cases. There is a very large spread in bond angles centred about the maximum of 100° – 110°. This spread is much more pronounced in system-II. This can also be seen in the radial distribution function for system-II where the second neighbour peak is lower and wider than the corresponding peak in system-I. A smaller peak exists in both cases at about 120° indicating the possibility of a small number of planar $sp^2$-like bonding configurations. In fact, a search through all bonding topologies containing an angle of about 120° shows that they belong to distorted tetrahedrally bonded structures. No such planar threefold atomic configurations were found.

Also, as found above, there is also a tendency for the bond angles to be smaller than $\sim 109°$ which show $p$-like character. This is shown by a shoulder/peak at about
90° in both cases.

Finally, a comparison to the BC8 and ST12 structures in silicon is given in Figure 7.8. The average first five neighbour distances for the two amorphous silicon simulations are shown along side a similar plot silicon in the BC8 and ST12 structures. Also shown is a plot of these distances for a third simulation of amorphous silicon as a much reduced volume to emphasize this trend. The neighbour distances for BC8 and ST12 are shown over a wide range of pressures. Firstly, it should be noticed that the distance to the first four bonded neighbours remains relatively unchanged with respect to the (generally unbonded) fifth neighbour distance. It can be seen that this is increasingly true in the trend of BC8 → ST12 → amorphous as the structure becomes more disordered. In the similar plot for a highly compressed amorphous silicon simulation the trend in neighbour distances becomes linear. It should be noted, however, that this third simulation is done only to show this reduction in the trend of reducing the $C_5$ distance in the extreme case\(^2\) where experimental verification of this linear trend in neighbour distances may be infeasible.

### 7.3.2 Carbon

The amorphous carbon structure is generated by the same method used above for silicon where the same initial random configuration is used. This allows a direct comparison between the amorphous silicon and carbon structures. Figures 7.9 and 7.10 show the radial and angle distribution functions of the final atomic configuration of the sample.

It should be noticed that, unlike both silicon simulations, the radial distribution function drops to zero after the first neighbour peak. This leads to an unambiguous method of locating bonded pairs of atoms: $r_{\text{max}} < 1.85\,\text{Å}$. Examination of the electronic charge density indicates that this definition of a bond is correct. Using this $r_{\text{max}}$ the coordination numbers and ring statistics can be found. These are summarised in Table

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\(^2\)In fact, at this compression, the system has become metallic.
Figure 7.8. A comparison between the first five neighbour distances in BC8, ST12 and amorphous silicon. The points on the BC8 and ST12 graphs show the neighbour distances at several different compressions.
CHAPTER 7. AMORPHOUS CARBON AND SILICON

Figure 7.9. Radial distribution function of amorphous carbon calculated at a density of 3.4g/cm$^{-3}$.

Figure 7.10. Bond angle distribution function of amorphous carbon.
7.2˚
279 3.4g/cm$^{-3}$
R$_3$ 2
R$_4$ 4
R$_5$ 37
C$_2$ 0
C$_3$ 6
C$_4$ 58
C$_5$ 0

Table 7.3. Structural data for the amorphous carbon simulation.

7.3. As can be seen from the coordination numbers there exists no atom to which a fifth nearest neighbour is bonded. On consideration of the case of BC8 carbon this is expected. It was found that carbon is unable to form highly distorted tetrahedral bonding, favouring instead multiple bonding to a single atom. In order for silicon to form a 5-fold coordinated atom it is necessary to form a wide range of bond angles (from about 70° to 145° was found in the two silicon samples for C$_5$). Although the chemistry of carbon allows it to form many bonding configurations, this one is unstable with respect to multiply covalent bonds.

Although the radial distribution function is a very useful quantity in determining averages for shells of neighbouring atoms it is not unambiguously related to the spatial distribution of the carbon atoms. The bond angle distribution function is also necessary to determine the types of bonding. The bond angle distribution function contains several interesting features. Other experimental and theoretical results indicate that amorphous carbon contains mainly four-fold coordinated $sp^3$ bonded atoms. This is also evident here in the large peak at about 109°. Averaging the bond angles subtended by all four-fold coordinated atoms gives an angle of 108.7°. Also of note is the shoulder at 120° indicating planar graphitic-like $sp^2$ bonding is also present, although in a smaller amount. Averaging the bond angles of three-fold coordinated atoms gives 115.3° which is slightly less than the expected 120° for perfect $sp^2$-like bonding although the statistics
are rather limited since only six $C_3$ sites are found. There is also an indication that the amorphous carbon may be forming some $p$-like bonding due to the peak in the distribution function at 90$^\circ$. A small peak also appears at 60$^\circ$. Such a small bond angle indicates the possibility of 3-fold rings exist in the sample. A ring counting calculation in fact confirms that there are two such 3-fold rings (Table 7.3).

There have been several studies on the structure of amorphous silicon and carbon using the method of reverse Monte Carlo simulations which fits trial atomic configurations to the experimental radial distribution function. This may not fully describe all the atomic bonding environments in view of the large number of possible bonding topologies evident in the bond angle distribution function. Unfortunately obtaining this three-body function experimentally proves to be extremely difficult.

The amorphous structure is found to contain only three and four-fold coordinated atoms. Example of their bonding topologies are illustrated in Figure 7.11. There is a large number of 4-fold coordinated sites (90.6%) formed from slightly distorted $sp^3$
Figure 7.12. A 3-fold ring of carbon atoms found in the amorphous structure. On examination of the charge density it was found that the electronic structure within the ring is best described as a 3-centre orbital, rather than three simple covalent bonds. Also shown is a four fold ring of carbon atoms is formed from a ring of covalent bonds unlike the 3-fold ring.

bonding. All of the remaining sites are found to be 3-fold coordinated, but are not all necessary sp² bonded. Of particular interest is the 3-fold rings that are found in the structure (see Figure 7.12). Like the silicon interstitial configuration found in Chapter 6 which formed a three fold ring, the charge density for this configuration in amorphous carbon formed a three-centre bonding orbital. Such a feature will not be found on examination of a radial distribution function alone since the inter-atomic distances are close to the C-C bond length. To find the electronic band(s) which are associated with the three-centre orbital, the electronic charge density was constructed from each individual band. This unusual feature is found to be very stable with its eigenvalue lying 24eV below the highest occupied band. However, another localised bonding orbital was found be be associated with it whose eigenvalue showed that it occupied the most energetic band.
7.4 Electronic properties

This section will discuss the electronic structure of amorphous silicon and carbon found in the above simulations. There have been many calculations on the electronic density of states of amorphous group IV materials in recent years, each result varying from the others depending on the model used to obtain the atomic coordinates\cite{115, 116}. Amorphous carbon is atypical of the group IV semiconductors because of the large number of different bonding types that it can form. The electronic structure is governed by the relative importance of three and four fold sites. A purely four fold coordinated model of amorphous carbon\cite{136} predicts only \( sp^3 \) bonding to occur which gives a large gap in the electronic density of states. The electronic structure predicted by this model is similar to a broadened diamond-carbon density of states. It is now clear that this is not the correct model for diamond-like amorphous carbon and later tight-binding calculations\cite{122, 125, 137} have found states which close the gap and have been associated to 3-fold coordinated atoms exhibiting \( sp^2(\pi) \) bonding. The total number of states in the ‘\( sp^3 \) gap’ increase when \( sp^2 \) orbitals are introduced into the simulation. However, some models\cite{137} produced from the Tersoff potential have a significant density of states near the Fermi level. This is in contradiction to experimental and other \textit{ab initio} calculations\cite{117, 125} which show only a small density of states at the Fermi level.

The electronic structure of the amorphous carbon simulation performed here is shown in Figure 7.13. The method detailed in Chapter 3 for calculating band structures is used here, where diagonalisation of the Hamiltonian matrix consisting of 128 occupied bands and a further 64 unoccupied bands is performed. The part of the density of states corresponding to \( sp^3(\sigma) \) bonding is very similar to a broadened diamond-like electronic structure. Most of the states around the Fermi level are found to be \( \pi \)-like in nature leaving no band gap. Therefore the optical properties of amorphous carbon will be dominated by the \( sp^2(\pi) \) bonded sites. There are however, relatively few of these (less
than 10% of the atoms in the sample are 3-fold coordinated). They are not found to be clustered together as some earlier models of amorphous carbon predicted[116]. Instead they are found either bonded to three 4-fold coordinated atoms leaving a single electron in a localised $p$-like orbital, or rather often to two 4-fold atoms and another 3-fold site. This structure is similar to a recent *ab initio* calculation on diamond-like amorphous carbon where 3-fold sites are found to group in pairs[138]. Due to the lack of clustering of $sp^2$ sites, it follows that it is the *intermediate* range correlations of the $sp^2$ sites which will have profound effects on the optical spectrum.

It is also rather interesting to note that the density of states of diamond-like amorphous carbon calculated here is remarkably similar to *ab initio* calculations on the less dense graphitic form of amorphous carbon[117, 121, 122].

Contrary to that of carbon, the electronic structure of amorphous silicon is found to be predominantly composed of $sp^3$-bonding orbitals. It is now well established that the effects of structural disorder on $sp^3$-bonded tetrahedral systems are governed almost
Figure 7.14. Electronic density of states for system-I of amorphous silicon.

entirely by short ranged correlations. It is this fact that makes the ‘complex crystal
model’ of amorphous silicon a good approximation, but fails to do so in carbon where
the medium range $sp^2$ correlations play an important role.

The electronic density of states for systems-I and II of amorphous silicon are given
in Figures 7.14 and 7.15 respectively.

On comparison of the two density of states diagrams, they are found to be very
similar. Thus, a relatively large change in density and structure does little to change
the electronic nature of the samples. Both exhibit a zero density at the Fermi level
which agrees well with models based on random tetrahedral networks, although they
are not in agreement with other $ab$ initio calculations of amorphous silicon[130] which
show a non-zero density at the Fermi level. This indicates that there are probably a
large number of structural defects in their sample. However, experiment[139] shows
a gap does exist in the density of states, in agreement with our calculations. On
reconstruction of the charge density from the occupied bands around the Fermi level,
these states are found to be localised mainly on the 3-fold coordinated atoms and can be classified as dangling bonds. Other localised states are found at atoms which are five-coordinated. These eigenstates are distributed throughout the five highly strained bonds at each 5-fold site. All of these localised states are found between the Fermi level and the large peak in the density of states at -2.5eV.

7.5 Discussion

Two \textit{ab initio} calculations on amorphous silicon and one on amorphous carbon close the experimentally measured density have been presented in this chapter\(^3\). The initial starting configurations were identical in all cases. Since it is believed that the binding is more reliably described in these calculations than by empirical rules, the atoms were distributed at random within the supercell subject only to the constraint the

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\(^3\) A further silicon simulation was carried out in order to examine the fifth neighbour distances at high densities.
atomic pseudopotential cores should not overlap. Considering that the initial atomic configurations were the same in all cases, the difference in relaxed structures between silicon and carbon are found to be remarkably different.

In both silicon simulations, the bonding is found to be predominantly $sp^3$ in nature although the spread in bond angle in rather large (cf. the BC8 and ST12 structures) but centred on the perfect tetrahedral angle. The comparison between neighbouring bond lengths is also interesting. It is found that the first four neighbour distances are all in the region of 2.4 Å which seems to be independent of the unit cell size in systems-I and II, that is, independent pressure and manufacturing conditions. This is not the case for the fifth neighbour distance. As the density of the sample is increased, the fifth neighbouring atom becomes closer. Both BC8 and ST12 silicon exhibit this behaviour under pressure. This trend is seen to increase with increasing disorder in the system from BC8 through ST12 to amorphous structures. In the extreme case, the fifth neighbour becomes bonded to the central atom creating locally a fully five coordinated structure.

The electronic structure of amorphous silicon is dominated by the short ranged interactions of the $\sigma$ bonds. Unlike in carbon, undercoordinated silicon atoms do not seem to form $\pi$-bonded structure, but instead favour the retention of the $\sigma$-bonded system with dangling bonds. These states are found to be close to the Fermi level but still localised on specific sites.

Carbon, on the other hand, does not form over coordinated sites. Similar to that of both silicon simulations, the carbon structure is dominated by diamond-like tetrahedral bonding, but no 5-fold ‘defects’ are found. It appears that amorphous carbon forms only 3 and 4 fold coordinations. Carbon 3-fold graphitic-like sites form a very stable configuration and are found throughout the sample. Although they appear in low concentrations, it is the $sp^2$ electrons which govern the optical properties of amorphous carbon. It therefore seems that the complex tetrahedral structures BC8 and ST12 will not form a good model for the electronic properties of amorphous carbon due to the
importance of low concentrations of $\pi$-bonding that appears in the system.

Another interesting structure that was found in the amorphous carbon simulation which did not appear in silicon was that of the three fold rings. Such a structure has not been included in any model of amorphous carbon so far, and is in fact conventionally (and incorrectly) excluded from the model. Examination of the bonding orbitals of the 3-fold ring indicate that a low energy 3-centre orbital is evident in the configuration. Associated with this though, is a higher energy state localised around the three atoms in the structure. This unusual feature cannot be found simply from the radial distribution function because the atomic separations are very similar to other 2-centre covalent bonds. Instead, three-body information is required such as the bond angle distribution function.

In conclusion, the amorphous structures of silicon and carbon contain a rich mixture of possible bonding topologies. It has been possible to model such a wide range of electronic structures because of the use of the plane wave basis set in the \textit{ab initio} calculations. It would not be possible to find some of the configurations obtained here, such as five fold coordination and 3-centre orbitals, by use of an empirical potential unless it is specifically fitted to such structures. It is also very unlikely that a single potential could describe this large range of bonds. It is found that the properties of amorphous silicon are dominated by the short ranged nature of the material. This indicates that the complex tetrahedrally bonded systems discussed in earlier chapters do form good crystalline models of amorphous silicon. Conversely, the structural and optical properties of amorphous carbon are found to be mainly governed by the intermediate ranged interactions of the $\pi$ states in the structure. Thus, the BC8 and ST12 structures do not form such a good model for amorphous carbon.
Bibliography


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