Structural Studies Of Amorphous Metal-Metalloid Thin Films

Thesis submitted for the degree of
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at the University of Leicester

by

Ben Williams
Department of Physics and Astronomy
University of Leicester

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In amorphous materials we are faced with two difficulties; the lack of a rigorous theory and great uncertainty about their structure. May I make a plea, then, for more experimental work on this subject to make it possible to formulate a theory.

- Sir Neville Mott
I know why there are so many people who love chopping wood. In this activity one immediately sees the results.

- Albert Einstein
Amorphous materials offer not only novel technological applications, but a valuable insight into the condensed state. Interest in this relatively new field has created a demand for new theories to describe the subtle electronic, optical and physical properties associated with disorder necessary if new devices are to be exploited. Metal-metalloid alloys in particular have found use in the electronics industry because of their wide-ranging electronic properties, from metallic to semiconducting, via the so-called metal-insulator transition. The underlying mechanism of this process is still widely disputed and a comprehensive theory remains to be found. Most researchers agree that to fully understand these materials a knowledge of the atomic structure must be obtained. Furthermore, recent work has shown that this information should be considered alongside a picture of the general homogeneity of any material being investigated.

We present in this work the results of a structural study of four metal-metalloid systems; a-Ge$_{1-x}$Ti$_x$, a-Si$_{1-x}$Ti$_x$, a-Si$_{1-x}$Ni$_x$, and a-Ge$_{1-x}$Ni$_x$, prepared in thin-film form across a wide composition range by RF Sputtering, encompassing the metal-insulator transition. These samples have been subjected to an optical study to determine the extent of the band gap and hence the composition of the MIT. An EXAFS study has been performed to determine the atomic structure, such as interatomic distances and the number and type of near-neighbours. A relatively new atomic simulation code, RMC, has been applied to the analysis of EXAFS data with the hope that information such as partial radial distribution functions may be directly obtained. SAXS measurements have been made to probe any medium-range structure and to assess the homogeneity of the samples.

Optical results show that the MIT occurs at compositions in the 0-20 at.% metal range. We find no obvious structural changes to accompany this event, but observe the high coordination of metal atoms at all compositions, in three of the four systems (a-Si$_{1-x}$Ti$_x$, a-Si$_{1-x}$Ni$_x$, a-Ge$_{1-x}$Ni$_x$). This is characteristic of a close-packed, conducting structure. Metalloid atoms, meanwhile, appear to exist within a tetrahedral random network at low metal content, rising to close-packed at metal rich compositions. SAXS results clarify these findings by revealing the presence of phase separation, suggesting that the homogeneity of samples should not automatically be assumed. We conclude that our samples contain regions of a conducting phase embedded in a semiconducting host network and suggest that the MIT proceeds not through the traditional Anderson mechanism but by the percolation of these regions at some threshold composition.
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Chapter 1

Introduction

The science of amorphous materials has enjoyed the frustration and excitement of being a new discipline and bears all the hallmarks of such: general theories, contradictory results and unexpected behaviour in new materials are all too common. The parallels with the fledgling science of crystalline semiconductors of 60 years ago are obvious and perhaps reassuring. The once mysterious properties of crystalline silicon have been responsible for the largest cultural revolution in 300 years. Who can say what new implications the properties of chalcogenide glasses or amorphous III-V films hold?

In attempting to answer such questions, new phenomena have been uncovered stimulating fundamental new ideas about the solid state and offering new device applications, fulfilling the eleventh commandment of Wealth Creation. Great progress has been made but many contentious issues still remain. It is clear to all those involved that continuous rigorous investigation is the only way a full understanding of this growing branch of materials science will be achieved. This thesis is offered as a small step towards achieving this aim.

The complexity of the problem in hand is illustrated by the reductionist manner in which the majority of research has approached the disordered system; properties of materials are classified and then addressed individually, hence the large number of titles in the literature such as 'Optical Absorption Effects', 'Conductivity of ...', 'Structural Studies of ...', 'The Magnetic Properties of ...'. This appears to be an intelligent first step in gaining an holistic understanding of a real amorphous semiconductor, but lip service must be paid to the fable of the four blind men trying to describe an Elephant,
each in turn giving precise information on leg, trunk, tail and ear, insisting the others are wrong.

This ongoing search for answers will involve a researcher in ever deeper and more complex questions until ultimately one may be addressing a highly specific area of science. There is a real danger then, of losing sight of the original purpose, so it is of considerable importance to place the proceeding observations and ideas thoroughly in context. In order to understand why the structural and optical properties of four series of amorphous thin film samples of metal-metalloid alloys should be studied, the importance of the metal-insulator transition must be discussed, and this itself within the context of amorphous materials. These branches owe their existence to the study of semiconductors, whose origins lie in the middle of the last century. This then, is perhaps a good place to begin.

1.1 A History of Semiconductor Research

In 1833, Michael Faraday observed that the resistance of silver sulphide decreased when heated\(^\text{1}\), quite the reverse of a metal. This negative temperature coefficient of resistance was the first distinguishing characteristic of semiconductors to be observed. There was little interest in these 'poor conductors' for nearly half a century until in 1873 W. Smith\(^\text{2}\) noted photo-sensitive behaviour in selenium; daylight produced a voltage across the material, an effect later put to use in solar panels. However, efforts to control and reproduce this phenomenon failed. This was characteristic of the early work on semiconductors because the purity of the materials then available fell far below the very high standards we now know to be necessary if unambiguous results are to be obtained. It was perhaps unfortunate that Smith happened across selenium as even today the element is notoriously hard to purify.
In 1874, F. Braun discovered that the conductivity of lead sulphide and iron pyrites depended on the direction of current flow, the phenomenon of rectification. A rectifier was built in 1886 by C.E. Fritts and was the first practical semiconducting device.

The discovery of the Hall effect in 1879 allowed an essential distinction to be made between a metal and a semiconductor; the number of charge carriers in a semiconductor increases significantly as the temperature is raised whereas the number in a metal remains approximately constant. This observation explained the negative temperature coefficient of resistance and was to form the basis of semiconductor theory.

The rectifying properties of semiconductors found application in the early days of broadcasting as copper oxide and selenium devices were widely used to detect the high frequency currents induced in electrical circuits by radio waves. Interest subsided in the 1930's as thermionic valves became more popular but, with the development of radar during the Second World War, came the demand for materials which could cope with the higher frequencies involved. A great deal of interest was shown in silicon because of its fast response time. To assist in the necessary research germanium was employed, as it is similar to silicon in many respects but is easier to purify because of its lower melting point. This was fortunate as the work on germanium lead to the discovery of transistor action by Bardeen and Brattain in 1949 and to the development of the first transistor in the Bell Laboratories. This device has, of course, revolutionised the electronics industry and has subsequently been the cause of a massive research effort. The result has been a deep understanding of the electronic processes involved, an understanding that can predict phenomena and create new electronic and opto-electronic devices. The history of semiconductor research is a perfect example of the symbiotic relationship between fundamental and applied science.

Crystalline semiconductors have formed the basis of this research, primarily because they form the most stable phases and are easiest to produce. Besides, periodicity allows elegant simplifications in the theory which predicts the semiconducting behaviour. This begged the question as to whether destroying long
range order would remove these properties. Demands were also being made to increase the area and decrease the cost of devices; both demands are restricted by the processes needed to make a good crystal. So the discovery by Ovshinsky\textsuperscript{1,4} that certain chalcogenide glasses display novel memory and current switching effects meant that serious research into the behaviour of non-crystalline materials was called for.

1.2 The Amorphous State

Disordered materials have been used by Man since the beginning of the Neolithic age when he first knapped flint. Around 3000 BC the first decorative glass started to appear in Egypt, spreading throughout the western Mediterranean countries and then, after the introduction of glass blowing in 50 BC, across the globe. It was not until the end of the eighteenth century with the production of the first optical lenses that the mechanical properties of glass were exploited and a great many new types of glass were developed. This enhanced the scientific study of these materials and by 1933 they were recognised as a separate physical state with novel mechanical, optical and electronic properties. For instance, metallic glasses offer the mechanical strength associated with a metal but with an immunity to the fatigue caused by crystal defects. Amorphous carbon can be grown as a film with a diamond-like structure\textsuperscript{1,9} and is finding applications as a hard coating, prolonging the life of machine tools and protecting spectacle lenses. Photocopiers owe their very existence to the photosensitive behaviour of amorphous selenium\textsuperscript{1,10}. But what exactly is an amorphous material and how do they differ from the crystalline phase?

The word 'glass' has a specific meaning within the context of amorphous materials. It is used to describe solids that have been produced from a melt, where the material has passed through the glass transition point sufficiently quickly to prevent crystallisation from taking place. In this way, a liquid-like structure can be 'frozen in' to the solid structure. For many materials such as silicon, where the melt is metallic and has a different structure to the solid amorphous phase, quenching cannot be carried out fast enough, so polycrystallinity is the result.
A material is either crystalline or non-crystalline. The atoms in a perfect crystal are arranged periodically in three dimensions in a repeating pattern and to an infinite extent. Any material which does not meet this criterion is non-crystalline, or amorphous. Classification of a material as disordered has, however, always been difficult. The negative definition causes problems as a crystal with a few point defects should, strictly speaking, be called amorphous. The term imperfect crystal is more appropriate in this case, as the accepted view of a non-crystalline solid is one which displays far more drastic forms of disorder, i.e. a complete lack of long range order. However, an amorphous solid is not completely random. For example, amorphous silicon is very similar to crystalline silicon on the short-range scale. Nearest neighbour bond lengths and coordinations are virtually identical to those found in the crystalline material. However, the bond angles in the amorphous case are distributed about the crystalline value of 109.5° with an average deviation of ±10°. It is this bond angle deviation that is responsible for the observed disorder in the amorphous material.

A physical sample can be defined as being amorphous if the X-ray diffraction pattern consists of diffuse rings rather than sharply defined Bragg rings or spots.

The disorder described above is structural, or topological in nature where periodicity has broken down to a certain degree. A further manifestation of disorder can occur when more than one atomic species is present. Known as chemical disorder, it involves one atom type substituting for another in the network. Again, this is not necessarily a random process as strength of atomic interaction will play a part in the atomic arrangement.

In many respects, defining the properties that characterise the amorphous state is the central aim of research. Only by observing the differences and similarities with crystalline materials and drawing on experiences gained from ordered materials can theories of the disordered state evolve. A good illustration of this is the way in which crystalline and amorphous materials respond to doping. The electrical properties of crystalline silicon and germanium are very sensitive to the addition of small quantities of certain impurities, whereas amorphous silicon and germanium require large amounts, typically 10^20 cm^-3, to affect conductivity. This was thought to be due to defect sites taking up the donated electrons until W. Spear demonstrated that it was possible to fabricate p- and n-type amorphous silicon with much reduced amounts of
dopant (a few parts per million) through glow-discharge deposition$^{1,12}$. Besides having serious ramifications in the realm of devices, the notion that deposition techniques affect physical behaviour suggested that the true intrinsic properties of amorphous silicon had not yet been isolated and a review of the theory was in order.

The similarities in optical properties of the amorphous and crystalline semiconductors have offered further scope for new ideas. The electronic theory of crystals, based on Bloch's theorem$^{1,13}$, uses long-range order to invoke the existence of energy bands and gaps. This formalism is particularly neat, providing a quantitative description of the macroscopic behaviour of crystals and it is easy to assume that these energy bands are a consequence of long-range order. However, amorphous materials have no long-range order but display a band gap close in energy to their crystalline counterparts. The most striking example is soda glass, or common window glass; this is a non-crystalline solid, yet the photon energy of visible light cannot excite electrons. The transparency of soda glass implies a region of energy forbidden to electrons. This observation gave rise to the first theory of the amorphous semiconducting state, the law of Ioffe and Regel$^{14}$ which states that 'an amorphous semiconductor will retain its semiconducting properties if the short range order of the crystal is preserved'.

1.3 The Role Of Metal-Metalloids

How then to quantify an apparent band gap if the essence of Bloch's theorem is no longer valid? Reconciliation of this question has caused much debate and generated many hypotheses, the most favoured of which is that of Mott$^{15}$ whose 'mobility gap' allows the idea of a band structure to be retained, although of a different nature. The theory of the amorphous state is by no means complete and the general opinion is that a useful insight can be gained through investigation of conductive behaviour. An important tool for these investigations are metal-metalloid alloys, a class of material whose conductivity can be varied a great deal by small variations in composition. Pure metalloids, such as silicon or germanium, have a low conductivity ($\sim 10^3 \, \Omega \cdot \text{cm}^{-1}$) and display a band gap whereas pure metals, such as nickel or titanium, have a high
conductivity ($\approx 10^4 \text{ } \Omega^{-1} \text{ } \text{cm}^{-1}$) and no band gap. One would assume that a mixture would produce a conductivity somewhere between the two, but the alloy is either semiconducting or metallic. Only over a small composition range does the material change electronic state, undergoing a metal-insulator transition (MIT). For most amorphous metal-metalloid alloys, this occurs at 10-20 atomic % metal.

Metal-metalloid alloys are also useful from a technological point of view. As the size of devices decreased, it became apparent that the resistance of pure silicon would become too large. By adding a quantity of metal, resistance can be tailored. A review of the technological applications of transition metal silicides is given by Reader et al.\textsuperscript{1,23}

There appear to be two schools of thought as to how the MIT should be modelled. One involves the concept of a density of states while the other involves nanometre scale phase separation. A density of states is applicable to crystalline and amorphous materials alike; the former display an abrupt termination at the top of the valence band and the bottom of the conduction band, producing a well defined forbidden energy gap, while electron states in the band are extended. Mott argues that the gap is preserved for the amorphous case and renames the bands as mobility edges. The spatial fluctuations in the potential caused by structural disorder will lead to the formation of localised states which form a tail above and below the normal bands. Opinion varies as to the extent of this tailing, from a slight intrusion into a large gap\textsuperscript{1,6} to no distinct gap at all\textsuperscript{1,7}, merely a minimum in the density of states. The main speculation is that at some point the Fermi energy passes through a mobility edge and the electron wavefunction changes from a localised to an extended state, the so-called Anderson transition\textsuperscript{1,8}, with an associated increase in conductivity as the insulator becomes metallic, i.e. a metal insulator transition.

The above approach relies on a random distribution of metal atoms in an amorphous network. Recently, however, investigations have shown that thin film samples are not homogeneous but contain defects such as voids and regions of phase separation\textsuperscript{1,9}. This observation has led to a new approach in defining the MIT; the presence of a metallic phase may lead to a discontinuous rise in conductivity when these regions interconnect at some percolation threshold. When a simple model is adopted, the threshold is found to occur when 15% of the sample is a metallic phase.
1.4 Structural Determination

Most modern theories admit that the key to understanding amorphous materials lies with understanding their structure. Many authors link the electronic properties of amorphous semiconductors to short range structure, for instance the bonding chemistry\(^1\) or the chemically active sites of donor atoms\(^2\) or simply the atomic radius, as used by Mott to predict the critical metal concentration of the MIT\(^3\). Without long-range order, determination of this structure is a difficult task for which special techniques have been developed. In this study, the short range structure of our samples has been obtained using the Extended X-ray Absorption Fine Structure (EXAFS) technique, which allows the local structure around each atom type to be determined, even if these atoms are very dilute. In principle, the coordination number, interatomic spacing and mean square deviation in this distance, as well as the atomic species, is obtainable.

Other techniques for identifying short-range structure were rejected on the basis of sample limitations; neutron scattering requires bulk samples (~1cm\(^2\)) whereas scanning electron microscopy requires very thin samples (~100Å).

The great difficulty in producing homogeneous samples is widely recognised. Different preparatory techniques produce different heterogeneities so it is perhaps not surprising that two samples of the same composition can exhibit different behaviour (see, for example Regan et. al.\(^4\)). There is therefore growing support for investigations into the relationship between medium range structure (10-100Å) and electronic behaviour, in an effort to isolate the intrinsic properties of a material. We have employed Small Angle X-ray Scattering (SAXS) to probe this mid-range length scale.

This is the context in which this thesis is offered, i.e. as a step towards a more complete and fundamental understanding of the MIT and hence amorphous semiconductors in general. The lure of new and exciting devices plus unexplored theoretical avenues tend to make this subject rather inviting.
1.5 Thesis Structure

Chapter 2 describes the two main experimental tools used in this thesis: EXAFS and SAXS. Each technique is treated in depth, with discussions on theory, experimental technique and data analysis.

A limited amount of structural information is available from conventional EXAFS and SAXS analysis because only distinct features of the data are analysed and the rest of the spectrum is wasted. We have tried to correct this by employing a relatively new *ab initio* atomic simulation code, the Reverse Monte Carlo (RMC) method, in tandem with other methods. This produces a three-dimensional structural model which should agree quantitatively with the complete EXAFS spectrum. Chapter 3 describes the method in its entirety and compares it with the other analytical tool used in this work, the EXAFS data analysis package, EXCURV92.

Outlined at the beginning of Chapter 4 are the many ways of producing amorphous materials, with particular attention paid to the technique used to fabricate the samples under study in this thesis, RF sputtering. This is followed by a description of the various characterisation techniques employed, the most important of which is the optical study, used to determine the extent of the band gap and hence the composition of the MIT.

Chapter 5 presents results on the a-Ge$_{1-x}$Ti$_x$ system of samples. Quantities such as bond-length, nearest-neighbour coordination and Debye-Waller factors, extracted from EXAFS data, are shown and the degree of structural and chemical disorder is inferred. The results of the SAXS experiments are interpreted and all results discussed in terms of composition.

Chapters 6, 7 and 8 discuss results from a-Ge$_{1-x}$Ni$_x$, a-Si$_{1-x}$Ti$_x$ and a-Si$_{1-x}$Ni$_x$ respectively, in much the same way as Chapter 5; attempting to unite the disparate elements of EXAFS and SAXS results with the MIT by highlighting compositional variations in the structure.

Each of the four data chapters is kept distinct and self contained until Chapter 9 when a comprehensive conclusion is drawn. Some ideas as to how the methods could be improved and directions for future research complete the work.
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Chapter 2

Experimental Techniques And Theory
(EXAFS and SAXS)

2.1 Introduction

Two techniques have been employed in this work to characterise the short and medium range structure of the samples described in Chapter 4. The first half of this chapter describes a technique which is particularly suited to characterising the structure of amorphous materials. The technique is called Extended X-Ray Absorption Fine Structure, or EXAFS, and makes use of the small oscillations in absorption coefficient seen above absorption edges in solid and liquid materials. These ripples are caused by interfering electron wavefunctions created as X-rays excite a specific electronic transition. Since interference effects obey certain conditions which in turn depend on the structural parameters mentioned above, atomic structures can be extracted. It is most sensitive to the local atomic environment and therefore ideal for materials with a lack of long range order. The technique will yield coordination numbers, certainly first shell information and possibly second in which case bond angle distributions are available. Information about interatomic distances and the amount of variation therein is also obtainable.

EXAFS is highly dependant on atomic species, giving rise to some valuable advantages over other techniques; a specific absorption edge is chosen hence the local environment of a specific atom is probed. This holds true even for dilute samples: the application to doped semiconductors is obvious.
This chapter will explore EXAFS in some detail as it is the richest source of information available for the structurally disordered samples used in this thesis.

Presented alongside EXAFS is another X-ray based technique, Small Angle X-Ray Scattering (SAXS) which is complementary to EXAFS and exploits the relationship between scattering angle and particle size. This phenomenon is responsible for the 'halo' around a light source when observed through a misty window. In general it is sensitive to larger length scales than EXAFS (nanometers as opposed to Ångströms) and is classed as a probe of medium range order particularly suited to the detection of voids or phase separation within samples.

The second half of this chapter will investigate how this technique can be applied to amorphous materials. The experimental method and data analysis techniques are described.

2.2 EXAFS

Oscillations in the X-ray absorption spectra are small and were easily overlooked when X-ray tubes were the only source of these high energy photons. It was Kronig\(^\text{2,1}\) in 1931 who first spotted this structure but because of a poor signal to noise ratio and lack of an appropriate theory the phenomenon was largely ignored.

In the early 1970's however the combined effect of a new generation of high intensity X-ray sources and a promising theory indicating the potential of the technique in structural studies caused a renewed interest. In 1971, Sayers, Stern and Lytle\(^\text{2,2}\) pointed out that a short range order theory could describe the observed oscillations a few tens of eV beyond the absorption edge (hence the 'Extended' part in the EXAFS acronym). If this structure is treated in terms of the interference between the wavefunction of an outgoing photoelectron and the small part of itself that is scattered back from neighbouring atoms (see Figure 2.1), EXAFS can be thought of as a kind of electron diffraction where the atoms themselves are the electron source.
The theory and experimental techniques have evolved over the last twenty years into a complex and powerful set of ideas which demands a deeper study than is permissible in this work to be conclusive. However, the basic concepts will be outlined in the next section.

In Kronig's day data for a single absorption spectrum would be collected over a few weeks to achieve a significant number of counts to work with: a timescale suited more to curiosity than to practical research.

This was essentially the case until a new way of generating photons was realised in the form of the electron synchrotron, developed initially for particle physicists. Such sources radiate a continuous spectrum of high intensity, highly collimated light of wavelengths from IR through to hard X-rays as relativistic electrons are guided around a ring by means of 'bending' magnets (a more detailed description of their operation can be found elsewhere\textsuperscript{2,3}). No other source can rival the quality of synchrotron radiation and a complete EXAFS spectrum can be collected in a matter of minutes.

At first the X-ray users of these synchrotrons were termed parasitic as particle physicists took priority but as the advances and applications of this new source became apparent demand for a dedicated synchrotron radiation source increased until in 1966 a 240 MeV storage ring called Tantalus was opened at the University of Wisconsin. The advantages of a dedicated source became evident and this stimulated the allocation of
resources to build a second generation of rings throughout the world. This new X-ray source meant Kronig structure could be seriously studied.

2.2.1 The Elements of EXAFS Theory

As mentioned earlier, the fine structure above an absorption edge has been ascribed to the short range effect of interfering photoelectron wavefunctions\(^{3,4}\). This was the beginning of a chain of thought that refined the idea into a comprehensive theory to accurately characterise the short range structure in amorphous materials from measured spectra. For the purposes of this work, the first approximate form of the theory given by Stern\(^{3,5}\) in 1974 will serve to illustrate the various components of the EXAFS function, responsible for the oscillations in the absorption coefficient. His theory is known as the Plane Wave Approximation (PWA), so called because at high energies the curvature of the spherical wave can be approximated by a plane wave. As will be seen later the restriction to high energies is a major limitation.

Photoelectric absorption involves the excitation of an electron into a higher energy state. For EXAFS the energy is always very large (1-40 keV) so the electron is released into a continuum state. We may then use the dipole approximation which states the probability of X-ray absorption is

\[
P = \frac{2\pi^2e^2}{mc^2\omega} |\langle f|e\cdot r|i\rangle|^2 \rho(E_f) \]

(2.1)

where \(\langle f\rangle\) is the complex conjugate of the final state wavefunction and \(|i\rangle\) is the initial state wavefunction (written in the Dirac notation). The initial and final state wavefunctions interfere in the region close to the nucleus of the central atom where the initial state wavefunction is large. \(e\) is the electric field polarisation vector of the X-ray beam and \(\rho(E_f)\) the density of allowed states at the final state energy. The constants \(e\), \(m\) and \(\omega\) are the electron charge, electron mass and X-ray frequency.

The photoelectron, of wavevector \(k\), has an energy well above the highest bound state, therefore \(\rho(E_f)\) will be a function of \((\text{energy})^{3/2}\), since \(E=\hbar^2k^2/2m\). The
initial state wavefunction is fixed which leaves $f$ as the only cause of the oscillations. Isolated atoms do not exhibit any fine structure, as the photoelectron is lost to the vacuum, but if this emitting atom is surrounded by other atoms, part of the wavefunction will be reflected. The absorption coefficient, $\mu(k)$, must be composed of the atomic absorption from an isolated atom, $\mu_o(k)$ and the interfering component, called the EXAFS function, $\chi(k)$.

The X-ray absorption coefficient for a condensed sample can be written

$$\mu(k) = \mu_o(k) \{1 + \chi(k)\}$$  \hspace{1cm} (2.2)

Stern postulated the dominant aspect of $\chi(k)$ is its dependence on $R$, the distance to the nearest atoms and would have an oscillatory dependence on energy. It may be written as

$$\sin(2kR)$$  \hspace{1cm} (2.3)

The 2R arises because the wave travels out and back. However, the potential of the emitting atom will modify the phase of this wave as the charged electron moves through this field and can be represented by the addition of a phase shift, $2\delta$. Similarly the potential of the reflecting atoms will exert their influence giving another term in equation 2.3, denoted as $\phi$.

Not only will the potential of the reflecting atoms alter the phase of the EXAFS function it will affect the amplitude as well, hence an energy dependent backscattering amplitude is defined, $|f(k,\pi)|$, which, in theory, has a unique profile for every element. It is this term that allows the EXAFS technique to characterise the chemical environment. However, similar atoms will scatter X-rays in a similar way, making it difficult, in a real experiment, to distinguish atoms if they have similar atomic numbers.

The short mean free path length, $\lambda$, of the photoelectron also attenuates the amplitude with an exponential of the form

$$e^{-\frac{2R}{\lambda}}$$  \hspace{1cm} (2.4)
Structural disorder and thermal vibrations decrease the EXAFS amplitude as the wavefunction bounces off a 'rough' shell. This variation is measured in terms of a Debye Waller factor, \( \sigma^2 \), defined as the mean square deviation from the ideal distance, \( R \). It is expressed again in exponential form

\[
e^{-2\sigma^2 k^2}
\]

The EXAFS signal is also proportional to the number of atoms, \( N \) surrounding the emitting atom and inversely proportional to \( R^2 \), the decay of a spherically propagating wave.

Stern now had all the factors necessary to describe the EXAFS oscillations from a single shell of atoms at a distance \( R \) from a central atom. Including other shells was a simple matter of summing their contribution. (Because of the short mean free path of the photoelectron and the disorder present in our samples we only expect to detect one or two shells.)

The EXAFS function for \( j \) coordination shells is then given by

\[
\chi(k) = -\sum_j N_j \frac{1}{kR_j^2} f_j(k, \pi) \sin(2kR_j + 2\delta_j + \phi_j) e^{-2\sigma^2 k^2} e^{-2\pi i k R_j}
\]

The negative sign of the equation is used when describing the K edge.

This is essentially the theory that has been used since 1974 although modifications have been made to improve the allowed energy range and thus gain information on distant atoms. Lee and Pendry\(^{2,6}\) developed an exact theory in 1975 known as the Curved Wave Theory where the wavefunction is treated as spherical allowing low energies to be included in calculations which meant light atoms with low absorption edge energies could be treated but it did have the major drawback of being an extremely complex analysis and therefore CPU intensive.

This was overcome in 1984 by Gurman et. al.\(^{3,1}\) who reassessed the theory of Lee and Pendry as applied to amorphous materials and simplified the algebra by assuming that there is no preferred orientation. Hence the first interactive EXAFS analysis could be done. This theory is known as the Fast Curved Wave Theory.
A different approach was to assume that the atom is small so the wave may be treated as plane over this length. This is known as the Small Atom Approximation\(^{3,6,2,8}\); the smaller the atom the more accurate the calculation. The simplified mathematics associated with the SAA allows quick calculations still plus use of all information at most energies.

These two new theories have revolutionised EXAFS analysis giving highly accurate results very quickly and can be found at the heart of most data analysis packages, for instance EXCURV92, used in this work which is available on-line at EPSRC Daresbury Laboratory, Warrington, UK.

The proceeding sections look at how the theory is applied in practice to obtain structural parameters.

### 2.2.2 Extracting a Pure EXAFS Signal

The absorption profile of a material immersed in a beam of X-rays will look something like that shown in Figure 2.2(a). The dotted line represents the contribution from lower edge energies and was removed using the program EXBACK, which uses a least squares fit to a set of low order polynomials.

This will leave \( \mu(E) \) as shown in Figure 2.2(b) which comprises the smooth free atom contribution, \( \mu_0(E) \) plus the EXAFS function \( \chi(E) \). \( \mu_0(E) \) was fitted using a polynomial and this was subtracted using EXBACK again. This uses a sensitive fitting routine because \( \chi(E) \) is very small at large \( E \).

Finally \( \chi(E) \) vs. \( E \) is converted to \( \chi(k) \) vs. \( k \) using

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

\( E_0 \) is the threshold energy and marks the beginning of the continuum transition region for which \( k=0 \) for the final state electron. It is treated as an adjustable parameter during the fitting procedure and should be of the order of 10 eV. The result of this final step will give a plot similar to Figure 2.2(c) with \( \chi(k) \) oscillating about zero.
Figure 2.2  Extraction of structural information from a-SiNi EXAFS data taken about the Nickel K-edge energy of 8.33 keV. The total absorption spectrum is shown in (a) with the absorption from lower energy edges represented by the dashed line. This is subtracted to give only the K-edge contribution, shown in (b) which contains the atomic absorption factor, $\mu(E)$ (dashed line) and the pure EXAFS signal. Subtraction of $\mu(E)$ and conversion from eV to Å$^{-1}$ yields plot (c). (d) shows the result of a Fourier transform of $\chi(k)$ with respect to $2\pi r$, ignoring the phase factors. The apparent shift of the first shell of atoms from 2.4 Å (obtained from EXCURV92 analysis) to 2.0 Å is a result of this omission.
2.2.3 Retrieval of Structural Information

In recent years a variety of computer programs have been developed to extract structural parameters from EXAFS data. Of these, two have been employed in this work each with widely differing approaches, providing a useful check of results.

EXCURV92\(^{2,8}\) is an established program based on the fitting of an experimental spectrum to the theory outlined above. Starting parameters in equation 2.6 are chosen and a least squares fit is applied with N, R and \(\sigma\) as variables until a ‘Fit Index’ is minimised. In this way a picture of the atomic structure can be built up, coordination shell by coordination shell.

Alternatively a Reverse Monte Carlo method can be used where the opposite starting point is adopted. A simulated atomic structure is manipulated to fit the data. When the model gives the same EXAFS signal as the sample we can say the structure of the model is a valid description for our sample which can then be studied.

These two methods are very important to this work, RMC especially as it is a relatively new approach and deserves special attention. Chapter 3 has been devoted to it. EXCURV92 also merits more detail and is discussed below.

2.2.3.1 EXCURV92

As mentioned above, structural information can be gained by simply Fourier transforming the k-space EXAFS spectrum into r-space which will give an immediate representation of the positions of each coordination shell, as shown in Figure 2.2(d). This method was used for earlier work on EXAFS data but is limited by several problems.

1. The finite data range (usually 3-15\(\text{Å}^{-1}\)) will produce truncation effects in the form of spurious peaks in the transform which could be interpreted as real structural features. This can be overcome by using a window function but this introduces peak broadening and a loss of data at the extreme ends of the spectrum.
2. Fourier transforming data will smooth out experimental noise.
3. Peaks will be shifted from the true interatomic positions because of the $2\delta + \phi$ phase term. This will always be a negative shift of the order 0.2 - 0.5 Å. It can be corrected for by using tabulated phase factors.

Real space analysis does have the advantage that it is a quick way of visualising the information content of the data so has been included as a routine in EXCURV92. To gain quantitative results however, EXCURV92 uses a k-space fitting routine where the parameters of equation 2.6 are fitted for each shell (under the assumption that the peaks are Gaussian in shape and separate enough to be deemed independent), which can yield a large amount of structural information.

The theory of EXAFS involves a backscattering factor, $|f(k,\pi)|$ which is dependent on energy and atomic species. An atomic number dependence is also introduced with the phase factors because of their correlation with atomic potential $V(r)$ (the form of which is the subject of much debate$^{9,10,11}$). When this potential has been chosen, phase shifts can be calculated and hence the identity of the scattering atom can be deduced. These scattering phases apply to elastic scattering only. Inelastic processes will decrease the amplitude of the EXAFS signal as they are energetic but cannot contribute to interference. There are two inelastic processes worthy of mention; intrinsic events which occur around the excited central atom and extrinsic phenomena which take place as the photoelectron travels away from and back to the central atom. Intrinsic processes occur when other electrons around the central atom rearrange themselves or are ejected, resulting in a certain proportion of photoelectrons having an energy less than that given by equation 2.7. The effect is represented by an additional amplitude reduction factor, $A(k)$, in equation 2.6.

Another intrinsic factor is the core hole lifetime. A photoelectron returning to the central atom after the core hole has been filled will see a different potential to that which it left so cannot contribute to EXAFS. This is a time dependent effect and by the Uncertainty Principle will manifest itself as an energy uncertainty, $\Gamma_c$ and smear the EXAFS spectrum.

If the photoelectron undergoes inelastic scattering, electrons scattered elastically will have a finite mean free path and hence a finite lifetime which again introduces an energy uncertainty, $\Gamma_e$, the subscript denoting an extrinsic process. The combination of energy uncertainties will be in the range 2-6 eV.
With the above processes taken into account, Equation 2.6 becomes, for an accurate EXCURV92 fit

\[ \chi_{\text{scr}}(k) = A(k)e^{-2\pi\delta/R}\alpha e^{-2\pi\alpha/k} \chi(k) \]  

(2.8)

\( A(k) \) is called AFAC within EXCURV92 and is usually taken to be constant, in the range 0.6 - 0.8 depending on the type of the central atom. This parameter is transferable so that a standard sample with a known structure can be used to fix its value before fitting. AFAC must be known before analysis as it is inseparable from \( N \). The parameters in equation 2.8 are chosen from the results of the fit to the standard sample and \( N, R \) and \( \sigma \) can then be iterated until a best fit (i.e. a minimum in the Fit Index) is found.

The method is slightly more time consuming than \( r \)-space analysis as it involves iterative least squares fitting but the results are more detailed and their reliability can be tested. It is usual to achieve an accuracy for \( R_j \) of 0.01 - 0.04 Å. \( N_j \) can only be found to a 10% accuracy because it is strongly correlated with \( \sigma_j \). Atomic species are identified by the shape of the \( \chi(k) \) envelope (the energy dependent scattering amplitude, \( f(k,\pi) \)) which is unique to each element. In practice however, atomic numbers must differ by 5 or more to distinguish atoms, which is fine except for systems with components from the same group of the Periodic Table. Generally in this work there was no difficulty in distinguishing elements but problems were encountered with GeNi.

2.2.4 Instrumentation

All EXAFS experiments were undertaken at the Synchrotron Radiation Source at Daresbury Laboratory, Warrington, UK. Electrons are held at an energy of 2.0 Gev in a storage ring of radius 15.3m at a current of 200 mA, with a beam lifetime of about 30 hours. As the electrons curve around the ring the light fan passes one of sixteen high vacuum tubes known as beam lines, at the end of which are situated the various experiments and beam controls (referred to as Stations), each of which has a different
specification. Station 7.1 was used for the Ti, Ni and Ge K absorption edges (4.9, 8.3 and 11.1 keV respectively) and Station 3.4 for the Si K absorption edge (1.8 keV).

2.2.4.1 Station 7.1, X-Radiation (4 keV - 11 keV)

The source is centre tangent point on dipole 7 of the storage ring and is 15m from a Si(111) monochromator. The maximum useable beam width entering this monochromator is 15mm because of heat limitations on the crystals and is defined by a set of moveable input slits. The output beam can also be shaped by a set of slits which select the monochromatic beam and reduce scatter. The beam then passes through a Beryllium window to the sample. Immediately before and after the sample are placed ion chamber detectors. The front detector gives the reference signal, \( I_0 \) and the rear measures the transmitted intensity, \( I_T \). The absorption of an X-ray photon of energy, \( E \) by a sample of thickness, \( d \) is given by

\[
I_T(E) = I_0(E)e^{-\mu(E)d}
\]  

where \( \mu(E) \) is the total absorption of the sample.

The entire set-up is illustrated in Figure 2.3.

Figure 2.3 Schematic illustration showing the experimental lay-out of Station 7.1 at Daresbury SRS. The reference and transmission ion chambers are fed by an HT supply. The output current is amplified with a gain of up to \( 10^{11} \).
The first monochromator crystal is pivoted at one end while the second is fixed. The first crystal may be tilted with respect to the second either to maximise the output or to obtain the desired amount of harmonic rejection. In addition to the chosen wavelength, the output from a monochromator will contain higher order harmonics as these also satisfy the conditions for Bragg refraction. These higher energies are not absorbed by the sample in the same way and can distort the EXAFS amplitudes. Harmonic content can be reduced to an acceptable level by employing a double crystal monochromator. The output from such a monochromator is a maximum when both crystals are parallel to each other and falls off rapidly as they are offset. This angular dependence of the output is referred to as the 'rocking curve'. As angular acceptance decreases with wavelength, by deliberately introducing a small offset between the two crystals, ('detuning'), most of the harmonic content can be removed whilst retaining 50% or more of the fundamental.

In order to maintain constant harmonic rejection over the course of the scan a servo system is used. The maximum intensities at the beginning and end of the scan are found and the station computer calculates a servo reference value for each point in the scan, corresponding to the chosen degree of harmonic rejection. The servo then continuously adjusts the crystal offset to match the actual intensity to the reference value.

2.2.4.2 Station 3.4, Vacuum Ultra-Violet Radiation (0.8 keV - 4 keV)

The source is dipole 3 situated 20m from an InSb(111) monochromator. Situated in front of the monochromator is a chromium coated quartz pre-mirror which provides a high energy cut off (for \( \lambda < 4\AA \)). Because harmonics cannot exist, the monochromator crystal can be aligned to give the maximum signal. Between the pre-mirror and the monochromator is a toroidal focusing mirror.

This station differs from 7.1 in that it operates at a much lower energy so absorption by air is significant. The sample is therefore mounted in a vacuum chamber and pumped to a pressure of \(< 10^4\) Torr before opening it to the beam. Correspondingly, the operation becomes more complex as safety valves and shutters are in use to prevent the whole ring being let up to air.
The station uses the total electron yield method\textsuperscript{2,12} to measure the X-ray absorption and, therefore, the sample must be grown on a conductive substrate. Problems arise if the sample itself is a poor conductor. A more complete description of both stations may be found elsewhere\textsuperscript{2,13}.

### 2.2.5 Executing an EXAFS Experiment

Before any data was collected, the beam was aligned with the sample as it can move between refills. This is not such a problem on samples with a large target area such as ours but nevertheless the maximum beam intensity should be sought to obtain the best signal to noise ratio.

Samples on a Mylar substrate were then mounted in the path of the beam, simply using sticky tape on Station 7.1. Samples were grown on Cu foil for use on line 3.4 and mounted on special Aluminium blocks using a conductive adhesive. On line 7.1 the ion chambers were filled with noble gas to a specific pressure depending on which absorption edge was being studied to obtain the maximum ion current. For example, when looking at the Germanium K-edge which occurs at 11.1keV, the I\textsubscript{0} ion chamber was filled to 88 Torr with Argon and I\textsubscript{1} to 635 Torr, also with Argon.

A control file was set up containing the scan range (typically 500 eV), the number of data points within this range (~1200) and the dwell time at each point (~2 seconds). A single scan can therefore be completed in 30 minutes.

The data acquisition system records \( \ln \left( \frac{I_0}{I_f} \right) \), hence a plot of \( \mu(E) \) vs. \( E \) is output. Typically 5 scans per sample were taken and averaged using the program EXCALIB\textsuperscript{2,9}.
2.3 Small Angle X-Ray Scattering

In addition to the technique of EXAFS described in section 2.2 which probes structures on the 1-10 Å scale, larger compositional or density fluctuations can be detected by looking at the way samples scatter light into the small angle region.

All waves diffract when they meet an obstacle, significantly so when their wavelength is of the same order as the size of the object, X-rays being most strongly scattered by atomic scale features; conventional wide angle X-ray scattering is of fundamental importance in the study of the atomic arrangement of crystals. As photons scattered from periodic planes of atoms interfere, a reciprocal space image is observed as bright spots. Amorphous solids scatter X-rays to form bright rings centred around the through beam as there are no interlocking planes now and order is present only in the short range.

Diffraction patterns consist of intensity distributions of scattered radiation as a function of scattering angle, yielding average correlations such as shape, size and number. The relationship between correlation length, d and scattering angle, θ is given by the Bragg law

\[ n\lambda = 2d \sin \theta \]  

(2.10)

An increase in d or a decrease in wavelength, λ will cause radiation to be scattered into smaller angles.

If θ is to be a finite value then \( \lambda/d = 1 \). Hard X-rays of \( \lambda = 1-10 \) Å are used to probe atomic structures so why not simply use soft X-ray and UV wavelengths to observe larger features? Absorption is a significant problem at wavelengths of 10-1000 Å range which severely limits sample thickness. Structure of nanometre scale dimensions in bulk samples must be studied using X-rays scattered at small angles (<< 1°) if wavelengths of the order ~1 Å are to be used.

Many amorphous solids exhibit order on the macroscopic scale such as voids or phase separation, the scatter from which is characterised by a diffuse ring, the position of which in k-space represents the scale of the inhomogeneity and furthermore the
functional form of the intensity can be related to the size and periodicity of the scattering structure.

### 2.3.1 The Diffuse Scattering Ring

Because X-rays are scattered by electrons in the solid, fluctuations in electron density will produce interference fringes, seen as diffuse rings about the central beam. If these fluctuations are widely separated, only a single ring will be observed. These fluctuations can be represented by an electron density deficit, $\Delta p$ between two media in the sample, either void and matrix or between two phases. Since the scattered intensity tends to zero as $k$ tends to zero for homogeneous materials we can say the SAXS intensity is entirely due to the interference between waves scattered from these 'particles'. By summing the amplitude of the scattered waves from each electron in each particle we arrive at a quantification of the intensity.

$$I(k) = (\Delta p)^2 \left| \int \rho(r)e^{ikr}d^3r \right|^2$$

where $e^{ikr}$ represents a single wave scattered with a vector $k$ of magnitude $k = (4\pi\lambda)\sin \theta/2$. $\rho(r)$ is defined so that

$$\rho(r) = \begin{cases} 1 & r < a \\ 0 & r > a \end{cases}$$

where $a$ is the dimension of the particle.

Assuming the material is isotropic, the wavefronts can be averaged over all angles, so that Debye's theory can be applied, where

$$\left< e^{-ikr} \right> = \frac{\sin kr}{kr}$$
hence \( I(k) = (\Delta \rho)^2 V(a) N(a) \int_0^\infty 4\pi r^2 \gamma(r) \frac{\sin kr}{kr} dr \) \hspace{1cm} (2.13)

where \( N(a) \) is the concentration of particles in the volume \( V(a) \) and \( \gamma(r) \) is the correlation function, defined as

\[
\gamma(r) = \int \rho(r) \rho(r+R) d^3 r
\]

(2.14)

This is the probability that for a point, \( R \), within a particle of radius \( a \), a vector of length \( r \) also lies within the particle, so that \( \gamma(r=0)=1 \) and \( \gamma(r>a)=0 \). This correlation function effectively holds all the information about size and distribution of the inhomogeneities within a material.

2.3.1.1 Dilute Samples

When particles are widely separated, or dilute, interference between scatterers can be ignored. The Guinier approximation can be applied to the low \( k \) region, where the SAXS intensity is written

\[
I(k) = (\Delta \rho)^2 V(a) N(a) \exp \left( -\frac{R_g^2 k^2}{3} \right)
\]

(2.15)

\( R_g \) is the Radius of Gyration, measured from the centre of mass of the particle. For a homogeneous spherical particle, \( R_g \) is a fraction \((3/5)^{1/2}\) of the particle radius. Thus a plot of \( \ln I(k) \) vs. \( k^2 \), known as a Guinier plot (see Figure 2.4), will give a straight line of slope \( -R_g^2/3 \), subject to the condition that the particles are separate and \( k R_g < 1 \).

However, it is often the case that the scattering particles vary in size and shape, causing a deviation from linearity in the Guinier plot which can be corrected for (see Section 2.3.5.2).
Guinier analysis was employed in this work when voids were known to be causing the observed scatter.

![Graph](image)

Figure 2.4 SAXS data for a-GeNi containing 52% Ni. The characteristic Guinier rise can be seen in (a). The cut off at 0.03Å⁻¹ is due to the beam stop which limits the k range of SAXS. Arrows highlight the Guinier region which is plotted as ln(I(k)) vs k² in (b) where a straight line with a gradient corresponding to an Rg of 27Å can be seen.

2.3.1.2 Non-dilute System

When the distance between scattering centres is comparable to the scale of the particles a second maximum occurs, as seen for samples containing Nickel in this work. This was attributed to scattering from different phases in the sample, for reasons given in Section 2.3.5.1, and hence an appropriate theory applied for the analysis of data. (Strictly speaking, this is the first maximum because the peak in the Guinier region is caused by the beam stop and is not an intrinsic property of the sample. The term second maximum is used in this work to avoid confusion with the Guinier peak as the latter is not subtracted when the results are presented.)

The correlation function, γ(r) can be found through a thermodynamic investigation of phase separation on an atomic scale i.e. 10 - 1000 Å where the energy associated with surface tension between the two phases is significant. Here, the interface region occupies a large volume of the sample as the distance between particles is comparable to their size.
The change in the Gibbs free energy, $\Delta G$ associated with variations in phase has been represented as a power series expansion by Cahn:\(^2\)

$$\frac{\Delta G}{V} = a \int I(k) d^3k + b \int k^4 I(k) d^3k + c \int k^4 I(k) d^3k + d \int \left[ \int I(k) d^3k \right]^2 + e \int \left[ \int k^4 I(k) d^3k \right]^2$$

(2.16)

where $I(k)$ is the observed scattering intensity, $V$ the volume of the sample and $a, b, c, d$ and $e$ are coefficients of the expansion.

For unstable phase separation where $\Delta G > 0$, the thermodynamic probability can be related to the Boltzmann expression

$$P = e^{-\Delta G/kT}$$

so that the most probable system is that which has a minimum entropy, $S$.

For a system at constant temperature and pressure the equilibrium state is that of minimum $G$

$$P = e^{-\Delta G/kT}$$

(2.18)

By putting 2.16 into 2.18 and keeping only the $a, b$ and $c$ terms for simplicity, the probability of a system existing with a composition variation wavelength is given by

$$P(k) = e^{-\Delta G/kT} e^{\frac{V}{4\pi^2} \left[ \sum_{l=0}^{\infty} \frac{\delta_l}{l+1} \right]^2}$$

(2.19)

By integrating and normalising this probability over $k$, the expectation value of the observed intensity can be calculated as

$$I(k) = \frac{1}{a + bk^2 + ck^4}$$

(2.20)
This result was obtained by Teubner and Strey\textsuperscript{2,18} to describe microemulsions. It has the form illustrated in Figure 2.5. It can be seen that at large $k$, the intensity falls off as $k^{-4}$. This is known as the Porod region\textsuperscript{2,17} and indicates a sharp interface between regions of differing electron density. A second maxima is observed when $a, c > 0$ and $b < 0$.

To extract particle dimensions, Teubner and Strey demonstrated that equations 2.20 and 2.13 can be combined to give an expression for the correlation function

$$\gamma(r) = \frac{d}{2\pi r} e^{-r^2} \sin \frac{2\pi r}{d}$$ \hspace{1cm} (2.21)

where

$$d = 2\pi \left[ \frac{1}{2} \left( \frac{a}{c} \right)^{1/2} - \frac{1}{4} \left( \frac{b}{c} \right)^{1/2} \right]$$ \hspace{1cm} (2.22)

$$\xi = \left[ \frac{1}{2} \left( \frac{a}{c} \right)^{1/2} + \frac{1}{4} \left( \frac{b}{c} \right)^{1/2} \right]$$ \hspace{1cm} (2.23)

There are clearly two length scales involved; $d$ represents the size of the particles and $\xi$ the correlation length.

The constants are related to the physical data thus

$$\frac{a}{c} = \frac{k_{\text{max}}^4}{1 - I_b/I_{\text{max}}} \hspace{1cm} \frac{b}{c} = -2k_{\text{max}}^2$$ \hspace{1cm} (2.24)

where $k_{\text{max}}$ is the position of the maximum, $I_{\text{max}}$ the amplitude and $I_0$ the base level of the peak. It is clear that the data need not be absolute as the ratio of $I_b/I_{\text{max}}$ is used.

This general approach has been used successfully to model the scattering from a-Si:C:H\textsuperscript{2,19}. 

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Figure 2.5 Chart showing the intensity distributions of two models of phase separation, thought to be responsible for the second maxima in many SAXS spectra; stable phases where $\Delta G < 0$ (solid line) and unstable separation where $\Delta G > 0$ (broken line). Note the sharp cut-off expected for stable phase separation in contrast to the $k^4$ dependence of the $\Delta G > 0$ distribution.

Teubner and Strey have described the case for stable phase separation, when $\Delta G < 0$. This demands a different approach as $G_0$ is not in the equilibrium state so the thermodynamic probability cannot be used. We therefore minimise $\Delta G$ by taking the derivative

$$\frac{\partial \Delta G}{\partial I(k)} = 0 \quad (2.25)$$

then

$$a + bk^2 + ck^4 + 2d \int I(k) d'k + 2f \int k^2 I(k) d'k = 0 \quad (2.26)$$

from which we can say

$$I(k) \propto a + bk^2 + ck^4 \quad (2.27)$$

where $a$, $b$, and $c$ are constants of the expansion and will have different values to those used in the $\Delta G > 0$ scenario. The form of $I(k)$ is illustrated in Figure 2.5.
Again equating 2.27 with 2.13, an expression for $\gamma(r)$ can be found. In this case it is more complex than equation 2.21 so has not been recorded here. Suffice to say it has only one length scale and the constants are found to be

$$a = I_0 \quad b = \frac{2(I_{\max} - I_0)}{k_{\max}^2} \quad c = \frac{I_0 - I_{\max}}{k_{\max}^4}$$

(2.28)

The length scale can then be read directly from a plot of $\gamma(r)$ vs. $r$.

Unfortunately, neither theory could provide an adequate description of the data so that much information remains uninterpreted. The correlation length however, may be calculated by simply using

$$L_c = \frac{2\pi}{k_{\max}}$$

where $k_{\max}$ is the position of the second maximum.

### 2.3.2 SAXS Hardware

![Schematic illustration showing the experimental set-up of Station 8.2 at Daresbury Laboritories, including a watercooled aperture, a quartz mirror for vertical focussing and a position sensitive detector. Most of the beam path lies under vacuum to reduce air absorption.](image)

An important feature of the design of a SAXS experiment is the high degree of collimation, serving to reduce the background radiation and hence increase the signal to noise ratio. This is critical as the SAXS signal is $10^6$ times the strength of the direct beam.
All data in this thesis was collected on Station 8.2 at Daresbury Synchrotron Radiation Source, a dedicated SAXS experiment with a set up illustrated in Figure 2.6.

White synchrotron radiation travels 20m under ultra-high vacuum to a water-cooled aperture. The aperture serves to reduce the beamload on the Ge(111) monochromator and also reduces unused radiation which would otherwise contribute to the background.

The monochromator is aligned to allow radiation with a wavelength of 1.5 Å through. Further slits are positioned in front of a focusing mirror to prevent the beam hitting the edges of the mirror which would produce serious scatter. The uncoated silica mirror is located at 22.4m from the source and consists of a piece of quartz 70cm long, 9cm wide and 4cm thick, operating at a glancing angle of 4mrad and acts to cut out high energy photons and hence the unwanted harmonics. Two more slits are present after the mirror, placed 3m apart which serves to define the final output beam.

A mica window separates the UHV from the sample stage. Mica is used as it is a crystalline material and scatters in well defined directions at high angles.

To reach low angles the distance from sample to detector must be large (1-2m) so an evacuated pipe is used to minimise the effects of air absorption. The pipe has a diameter of 20cm and Kapton of 0.1 - 0.2mm thickness is used as a window material. Within this pipe, close to the exit, a beamstop is located to prevent the primary beam from hitting the detector and to reduce scatter from the exit window. This has the unfortunate effect of cutting off the signal at very low k (≤ 0.03 Å⁻¹).

Finally, the detector is mounted on a moveable platform that can be positioned between 0.5m and 3m from the sample to allow a suitable k-range to be selected. The detector is a 512 channel single wire anode proportional counter, known as a quadrant detector. The curved anode wire is enclosed in a gas filled chamber, a reactive rare gas mixture of Ar and CH₄ under pressure which induces an ionisation avalanche when struck by a photon. The instrument counts at a rate of up to 10⁵ events per second.

2.3.3 Collection of SAXS Data

The nature of the quadrant detector is such that its response is not spatially uniform and varies slowly with atmospheric conditions so that it must be checked
regularly for calibration purposes. This is achieved using a ‘flat’ radiation source, a small sample of $^{55}\text{Fe}$ mounted 50cm from the detector face. Data was collected for about half an hour after each beam refill.

The detector was then manoeuvred into position at the end of the camera to a distance of 1.5m from the sample. This allows a $k$-range of 0.02-0.50 Å or structures from 10-300Å across to be measured.

The detector is split into 512 channels which must be converted to $k$. To facilitate this a sample of rat tail collagen was exposed which exhibits strong peaks at known $k$ values. In this way channel number is equated to $k$ number. During the same run, the detector was aligned so that the direct beam fell onto the $0^\circ$ channel.

The collagen was removed and replaced with a sample, folded to optimum thickness i.e. maximum scattering with minimum absorption. For this work all samples used in SAXS measurements were deposited on thin Al foil which was found to give no appreciable peaks at this camera length. The countrate was checked before data collection to ensure it was below 8000 cs$^{-1}\text{m}^2$ to protect the detector. If exceeded, an attenuating Cu sheet was used.

The scattering profile of each sample plus the scattering from substrate alone were collected for ~2 minutes. Data files also contain information from the ion chamber, allowing the spectrum to be normalised during data analysis.

2.3.4 Extracting a Pure SAXS Signal

All data reduction (with the exception of the last step) was carried out using the specialised program XOTOKO at Daresbury Laboratories, compatible with the file format used by Station 8.2. The process can be divided into four stages.

2.3.4.1 Normalisation

This was performed by dividing the collected pattern by the read out value of the ion chamber to give an absolute intensity.
2.3.4.2 Subtraction of Background

The background consists of the scattering from windows, some air scatter and a contribution from the substrate. Often this pattern needs to be weighted because of nonlinearities in the ion chamber so that the patterns are of approximately equal height. Obviously this will affect the error margins. The background was normalised before subtraction.

2.3.4.3 Division by Detector Response

The normalised background subtracted pattern is divided by the detector response to give the recognised SAXS pattern.

The detector response is not absolute data, i.e. there is no normalisation factor because there is no ion chamber present to measure the flux of radiation. This means that the intensity at the origin, I_0 cannot be used in a quantitative way. If however the irradiation time is noted, patterns can be compared in a qualitative sense.

2.3.4.4 Adding an X-Axis

The k scale was established using the collagen data where each peak occurs at a known k value. In this way channel number was converted to Å⁻¹ and added to the data file using a program developed by the group at Leicester University.

2.3.5 Data Analysis

A good SAXS spectrum will contain much information about the scattering objects. The size of these has been extracted for all samples. Under special circumstances the shape of the scattering particles can be determined and the composition of these particles may also be deduced.

All data analysis was undertaken using EXCEL running under Windows on an ordinary PC.
by simply looking at a SAXS spectrum one cannot tell what is causing the scattered pattern without knowing any background information about the sample. (The technique of Anomalous SAXS whereby the X-ray wavelength is scanned through an absorption edge yields a lot of information on sample content.) However, certain features of the sample can be deduced by studying the way in which the spectrum changes with composition. It has been noted for FeGe and MoGe\(^{2,20}\) that for increasing metal content a second maximum appears, increasing in amplitude with the addition of metal to a maximum and then vanishing at a certain metal concentration. The phenomenon itself indicates the formation of a compound of different electron density within the pure metalloid, i.e., phase separation. As the composition passes through the point where the two media exist in equal quantities the scattering peak will reach a maximum and then disappear when the sample is composed only of the new phase. This is referred to as the end-point composition and can tell us what the sample has separated into (under the assumption that only two phases are present). (Taking SiNi for example, end-points at 0 at.\% and 33 at.\% Ni would indicate two phases present, pure Si and Ni\(_{33}\).) This type of analysis has been carried out by plotting the amplitude against composition. It should be noted however, that this is a relatively crude method; a better measure of the ratio of phases could be obtained from the 'invariant', given as

\[
S(k) = \int_{k_0}^{k_{\infty}} I(k)k^2dk \tag{2.29}
\]

Variations in the positions of the peaks are irrelevant, because the whole spectrum is treated.

Variation in peak height which is not related to composition indicates the presence of inhomogeneities introduced during fabrication. For RF sputtered samples, these are probably voids filled with Ar sputtering gas.

If the form of the second maximum can be fitted then the shape and the interfacial thickness of the inhomogeneities can be determined. As this was not possible with our samples the details shall be spared.
2.3.5.2 Length Scales

When extracting distances from SAXS data, the first theory to apply is the Guinier approximation. The peak in intensity about the central beam is fitted with equation 2.15b where \( R_g \) and \( I_0 \) are used as fitting parameters, or by plotting the small part of the k-range containing the exponentially varying data as \( \ln I(k) \) vs. \( k^2 \) and measuring the gradient, as described in section 2.3.1.1. However this result is only valid if \( kR_g < 1 \). If the Guinier plot deviates from linearity then more than one size of particle is present. This can be modelled by inserting a Gaussian distribution into equation 2.13 to give

\[
I(k) = (\Delta p)^2 V(a)N(a) \int_0^\infty 4\pi r^2 \gamma(r) \frac{\sin kr e^{-\left(\frac{r-r_0}{\sigma}\right)^2}}{kr \sqrt{2\pi} \sigma} dr \quad (2.30)
\]

![Graph](image)

Figure 2.7 SAXS intensity for a-GeNi containing 33% Nickel. A second maximum can be clearly seen at 0.17 Å\(^{-1}\) as well as the Guinier peak at 0.03 Å\(^{-1}\). The intensity at large k appears to drop abruptly to zero indicating stable phase separation.

If a second maximum is observed in the spectrum, the theory described in section 2.3.1.2 may be applied. The constants \( a, b \) and \( c \) are found using equation 2.24 or 2.28 and used to plot \( \gamma(r) \) against \( r \). The particle size is then measured as the point
where \( y(r) \) first crosses the x-axis i.e. where the material changes and becomes another phase. A second peak in \( y(r) \) will give the periodicity.

There are instances where neither theory, stable or unstable, fit the observed scatter in which case the data can be Fourier transformed (equivalent to transforming equation 2.13) to obtain a plot of \( y(r) \) vs. \( r \) and distances read from this. Figure 2.8 shows the correlation function obtained from each of these three methods.

A correlation length, \( L_c \), may be obtained by using \( L_c = 2\pi/k_{\text{max}} \) where \( k_{\text{max}} \) is the position of the second maximum. This is analogous to taking a Fourier transform of the data and was the method used to gain structural information from the data, in the absence of a suitable theory.

![Figure 2.8 Correlation functions for a-SiNi containing 12\% Nickel obtained using three theories of SAXS. The solid line represents \( y(r) \) for a material separated into stable phases, the dashed line unstable phases and the dotted line the Fourier transform of \( I(k) \) representing scales of 40\( \AA \), 44\( \AA \) and 38\( \AA \) respectively. A correlation function derived from a Fourier transform will be the most reliable but cannot reveal anything about the shape of the scattering structure. \( L_c \) for this sample was calculated as 37\( \AA \).](image-url)
2.4 References

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Chapter 3

The Reverse Monte Carlo Method

3.1 Introduction to Computer Simulation

In recent years an increase in the amount of computing power available has made the atomic modelling of materials on an atomic scale a realistic analytical tool. Three-dimensional structures containing the many particles necessary to approximate a real solid can be set up and manipulated under the constraint of experimental data. The result will be a three-dimensional representation of the material under investigation. The advantages of such an approach are clear; to be in possession of a map, statistically speaking, of the position of every atom in a sample is an invaluable resource.

Crystalline materials can be structurally characterised on an atomic level with a deal of accuracy using a variety of techniques. Non-crystalline materials however suffer from a lack of tools with which to characterise their inherent short range order. Until recently the only accepted procedure was to isolate certain features in the data such as peak positions and coordinations and fit them using an assumed theory but this approach is qualitative and ignores significant areas of data. Computer simulation overcomes both of these problems.

There are two basic techniques used for computer modelling, Monte Carlo (MC) and Molecular Dynamics (MD) both of which use a pair potential to manipulate atoms to the lowest possible energy state for the system.
MC seeks to produce a statistical ensemble of atoms (called a configuration) with a Boltzmann distribution of energy by randomly moving atoms subject to the criterion that a configuration occurs with a probability proportional to the Boltzmann factor \( \exp(-U_j/k_B T) \) where \( U_j \) is the total energy of the system and \( k_B \) the Boltzmann constant. Exactly how this is achieved will be discussed later.

MD is a fluid simulation so can be used to study time related effects. It uses the derivative of the potential, i.e. the force on each atom due to its neighbours, to arrange a configuration. The trajectories and velocities of each atom are calculated and new positions and velocities after a time step, \( \Delta t \), are determined. The process is repeated until the remnants of the starting configuration have died out, and a Maxwellian distribution of particle velocities exists.

The disadvantage of the above methods can be seen; the form of the potential used to guide the simulation must be essentially guessed and has to be adjusted after each run if the correct form is not found initially. An iterative method may be used but places unrealistic demands on computing time and is rarely applied.

These problems have been overcome by a technique known as the Reverse Monte Carlo (RMC) method where a three-dimensional model of a disordered structure is produced from all of the available structural data without assuming potentials or distribution functions. The model is fitted to the data itself so that if there are no significant systematic errors there must be quantitative agreement between the two. This is where the 'Reverse' term comes from. MC produces a model which is compared with the experiment after simulation whereas RMC fits directly to the data.

There are certain limitations on the usefulness of computer simulations in general which should be made clear, the most fundamental being the size of the configuration. Finite computing power restricts the number of particles to between \( 10^3 \) - \( 10^4 \) which will give rise to statistical errors. These can be minimised by averaging over many configurations. Another consequence of finite size is a maximum real space range of \( 10 - 20 \) atomic diameters. This means long range effects cannot be studied. There are also problems with surface effects from the perimeter of the configuration but these can be minimised by surrounding the structure with replicas of itself so that a particle which is moved beyond the boundary reappears on the other side of the
configuration. This is a simple periodic boundary condition but greatly reduces the complexity of the simulation. As long as any structural order has died out well before the edge of the model this remains a valid imposition.

3.2 RMC - The Basic Method

Reverse Monte-Carlo is based on the Metropolis Monte-Carlo algorithm\textsuperscript{1,4} so it is worth briefly outlining the principles involved in the standard Monte-Carlo technique.

The user sets up a three-dimensional configuration, usually a cube made up of $N$ atoms. The length of the cube, $L$ is varied to achieve the density of the material being modelled.

The probability of a configuration is given by

$$P_1 \propto \exp\left(-\frac{U_1}{K_B T}\right)$$

(3.1)

where $U_1$ is the total potential energy of the system calculated from a specified interatomic potential. $T$ is the temperature of the model and $K_B$ is the Boltzmann constant.

One atom is moved at random and the probability of the new configuration is calculated

$$P_2 \propto \exp\left(-\frac{U_2}{K_B T}\right)$$

(3.2)

If the second configuration is more probable than the first then it becomes the new configuration. If not then it is given the chance to be accepted as the new configuration, the probability of this being $P_2 / P_1$. If it is not accepted then it is rejected and we return to the previous configuration. This will give the simulation an opportunity to avoid local minima in total energy.

Sampling and weighting with a probability in this manner is known as a Markov chain\textsuperscript{1,5} which has the property that the probability distribution of the $(n+1)\textsuperscript{th}$
configuration is only dependant on the distribution of the $n^{th}$ element, with no ‘memory’ of the $(n-1)^{th}$, $(n-2)^{th}$ etc.

The process is repeated until $U_n$ reaches an equilibrium value, about which it will oscillate. Any configuration after convergence is a valid representation of the structure. These configurations are collected at intervals of no less than $N$ accepted moves and averaged to ensure statistical independence.

Instead of a potential, the RMC method samples a structure factor taken from experiment, $S^e(q)$ and a structure factor calculated from the configuration, $S^c(q)$. By minimising the difference between the two the model structure will be forced to agree with experiment to within experimental error. $S^e(q)$ is usually determined from neutron diffraction or X-ray diffraction measurements or a combination of these techniques. EXAFS data can also be modelled, whereby the EXAFS function (denoted as $E^F(q)$ during this chapter to avoid confusion with the Fit Index, $\chi^2$) is sampled. $S(q)$ and $E(q)$ are entirely analogous, only $E(q)$ is more complex because of the various phase and scattering corrections involved (see Section 2.2.1 for a detailed account of the EXAFS theory). This thesis is concerned with the application of RMC to the analysis of EXAFS data alone, therefore the following is presented in terms of the EXAFS structure factor.

The probability of the difference between the calculated and experimental EXAFS functions, $E^c(q)$ and $E^e(q)$ is given by

$$p(q) = \frac{1}{\sqrt{2\pi}\sigma(q)} \exp\left(-\frac{\varepsilon(q)^2}{2\sigma(q)^2}\right)$$

(3.3)

where $\varepsilon(q) = E^c(q) - E^e(q)$, the difference in structure factors and $\sigma(q)$ is the standard deviation of this assumed Gaussian distribution. The total probability of $\varepsilon$ is then

$$P = \prod_4 p(q) = \left(\frac{1}{\sqrt{2\pi}\sigma}\right)^n \exp\left(-\sum_4 \frac{\varepsilon(q)^2}{2\sigma(q)^2}\right)$$

(3.4)
where $m$ is the number of $q$ points and 

$$\bar{\sigma} = \left( \prod_q \sigma(q) \right)^{1/m}$$

By writing

$$\chi^2 = \sum_q \frac{(E^c(q) - E^s(q))^2}{\sigma(q)^2}$$

Equation 3.4 can be written as

$$P \propto e^{-\chi^2}$$

By minimising $\chi^2$ then, a configuration can be created with a statistical ensemble of atoms that represents a possible fit to the available data. This is achieved, for a single species material, using the following algorithm.

1. A configuration of $N$ atoms is set up so that the density $\rho$ is equal to that found experimentally or otherwise (see section 3.6), by using $\rho = N/L^3$ where $L$ is the length of one side of the containing box. Periodic boundary conditions are then applied.

   The position of each atom can be chosen randomly, set to that of a known crystal or those of a configuration of a previous run. Because a proper Markov chain is used the final configuration will be independent of the starting configuration. Thus RMC can be thought of as an Ab Initio method.

2. The radial distribution function (RDF) is calculated for this initial configuration;

$$g^c(r) = \frac{n^c(r)}{4\pi r^2 \Delta r \rho}$$

where $n^c(r)$ is the number of atoms between $r$ and $r + \Delta r$ from a central atom averaged over all atoms as centres. The size of the configuration should be chosen so that $g(r > L/2) = 1$, i.e. any structural features have disappeared well before the edge of the box. This is done for two reasons: $g^c(r)$ is calculated only out to $r = L/2$ so that,
at most, only one image of an atom is counted; also if this condition is not applied interference effects due to the periodic boundary could make the results unpredictable. The nearest image convention$^{10}$ is used to determine the atomic separation.

3. The RDF is transformed to the EXAFS function

$$E^c_i(q) = 4 \pi \rho \int_0^\infty r^2 (g^c_i(r) - 1) \tilde{f}(q, r) dr$$

(3.8)

where $f(q,r)$ is the contribution to the EXAFS signal of a single atom at a distance $r$, for a given energy. This value is calculated by one of the standard EXAFS data analysis packages, such as EXCURV92, and is used in the form of a look-up table. This data file can rapidly become large when more than one atomic species is present or if a high real-space resolution is required.

It is usual to weight the calculated and experimental spectra with $q^4$ in order to keep the amplitude approximately constant at all $q$.

4. The difference between the experimental EXAFS function, $E^e_i(q)$ and that determined from the configuration is calculated;

$$\chi^2 = \sum_q \frac{(E^c_i(q) - E^e_i(q))^2}{\sigma(q)^2}$$

(3.9)

The range of momentum transfer, $q$ is dictated by experiment.

$\sigma(q)$ is the move rejection probability function and is related to the experimental error. Since the distribution of systematic errors is normally unknown it is safest to assume a constant $\sigma$, taken as 1% of the amplitude of the data (or the amplitude of the noise).

The sampling procedure can be approached by transforming $E^e(q)$ to $g^e_i(r)$ and sampling $\chi^2$ in this way. This however upsets the distribution of errors which are likely to become highly non-uniform.
5. One atom is moved at random and new RDF's and structure factors calculated:

\[ \chi^2 = \sum_{q} \frac{(E^e_q - E^s_q)^2}{\sigma(q)^2} \]  

(3.10)

6. \( \chi^2 \) is then compared with \( \chi^2 \). If \( \chi^2 < \chi^2 \) the new configuration is accepted to become the new starting point. If \( \chi^2 > \chi^2 \) it is accepted with a probability \( e^{-(\chi^2 - \chi^2)/2} \). (This is analogous to choosing a random number between 0-1 and if \( \chi^2/\chi^2 \) is more than this value the move is accepted.) If the move is not accepted the initial configuration is used again.

7. The process is repeated from step 5.

\( \chi^2 \) will decrease until an equilibrium value is reached about which it will oscillate. The equilibrium configuration will be a possible representation of an actual three-dimensional structure consistent with the data to within experimental error. Configurations may be collected at this point and averaged to reduce the statistical errors associated with the finite size of the simulation. The configurations must be collected at suitable intervals so that they are independent of each other; in MMC configurations are usually deemed independent when separated by N accepted moves but 5N moves are used in practice for the RMC.

The above algorithm can be applied directly to a one component system. It is a simple modification though to extend the scope of RMC to minimise \( \chi^2 \) for multi-component systems.

3.2.1 Multiple Data Sets

Where binary systems are concerned, EXAFS can be performed on the absorption edges of each component in the same sample to double the amount of
structural information available. Whereas other analysis techniques treat each set independently, RMC can fit both edges simultaneously by summing the individual $\chi^2$ and minimising the total. For a system with $n$ relevant data sets;

$$\chi^2 = \sum_n \chi_n^2 = \sum_n \sum_q \frac{(E_n^c(q) - E_n^s(q))^2}{\sigma_n^2}$$

(3.11)

Using $\sigma_n$ now to weight the sets.

Any number of data sets can be combined irrespective of the origin of the data simply by adding the relevant $\chi^2$ term.

For EXAFS data from a sample containing two atom types, $\alpha$ and $\beta$;

$$E_n^c(q) = \sum_p 4\pi p \int_0^{r_2} \left( g_{\alpha\beta}(r) - 1 \right) f_p(q,r) dr$$

(3.12)

Where $\alpha$ represents the absorbing species, surrounded by atoms of type $\beta$. $f_p(q,r)$ represents the contribution to the EXAFS spectrum of a single $\beta$ atom at a distance $r$ from $\alpha$.

3.2.2 Constraints

The simulation may be allowed to run with the data alone shaping the configuration of atoms. This however can lead to spurious results as the errors inherent in the data may allow atoms to move to within unphysical distances of each other and still be consistent with observations. An ‘excluded volume’ is therefore defined around each atom, the equivalent of a hard sphere potential. This is a simple yet powerful constraint as it will greatly reduce the number of physically possible configurations, thus speeding up convergence to an equilibrium $\chi^2$. An appropriate volume, measured in terms of a ‘cut-off’ distance, $r_{cut}^2$ (assuming from now on a
binary alloy with components $\alpha$ and $\beta$ is usually taken as between 10-20% of the interatomic separation, depending on the quality of the data; for good data $r_c^{\alpha\beta}$ may be approximate but more care should be taken choosing the cut-off points for data with known large errors. A badly chosen cut-off will manifest itself after simulation in the form of sharp spikes at low $r$ in the partial RDF if $r_c^{\alpha\beta}$ is chosen too low or truncation of $g_{\alpha\beta}(r)$ will occur if $r_c^{\alpha\beta}$ is too high.

Other aspects of the model can be constrained too, such as coordination numbers and bond angles. In fact any measurable property of the structure can be defined by adding a suitable term to $\chi^2$:

$$\chi^2 = \frac{(N_{\text{req}}^{\beta} - N_{\text{present}}^{\beta})^2}{\sigma^2}$$  \hspace{1cm} (3.13)

Where $N_{\text{req}}^{\beta}$ is the required number of type $\beta$ atoms in the $j^{th}$ coordination shell around atoms of type $\alpha$ and $N_{\text{present}}^{\beta}$ is the number actually present.

If care is taken over the choice and implementation of constraints they form an indispensable aspect of computer simulation, enabling investigation of a wide range of structures consistent with the data while reducing convergence time. It should be noted however that constraining data is basically making an assumption about the structure, which detracts from the real value of RMC.

### 3.2.3 The Validity of Structural Models

RMC uses a one-dimensional quantity, $E^p(q)$ to generate a three-dimensional structure. It has been proven theoretically that for a purely pairwise additive potential this is justified and reliable\(^3\) because $g(r)$ determines the structure $g(r,\theta,\phi)$. For a (hypothetically) accurately defined $g(r)$, RMC will reproduce the correct three-dimensional structure\(^3\). Despite pairwise additive potentials being a purely theoretical simplification and the fact that real data contains errors, these results indicate that there
is a great deal of three dimensional information in $E^F (q)$ that can be extracted using a method such as RMC but there will be no unique solutions, i.e. each configuration after convergence is a valid model of the structure but none is definitive. After averaging several configurations the resulting structure will still not be the correct one, simply one that is consistent with the data.

It is important to bear in mind that RMC produces the most disordered structure consistent with the data, a result of the procedure used to select acceptable moves.

### 3.3 Simulation Details

We are now in a position to involve ourselves with the practicalities of RMC along with methods for accessing the information contained within a model.

The RMC code\(^5\) and characterisation software\(^9\)\(^10\) were provided by R.L. McGreevy of the Studsvik Neutron Research Laboratory, Sweden. The program CONFIG_MANIP was graciously provided by Y.L. Badyal of Delft University, Netherlands.

#### 3.3.1 Size of Configuration

Within most simulations the configuration size is limited purely by available computational power as calculating $g^C (r)$ involves a summation of the order $N^2$. Over the past two decades the size of model structures has grown from tens to thousands of atoms\(^9\)\(^11\) reflecting the phenomenal increase in processing power.

Large configuration sizes are available to RMC because only the $g^C (r)$ for the initial configuration is calculated, then for each subsequent move the change in $g^C (r)$ is calculated which is a sum of the order $N$. Obviously the larger the simulation the more accurate it can be but realistically beyond about 30,000 atoms the algorithm becomes too slow.
When selecting N, the stipulation \( g^k(r > L/2) = 1 \) must be observed to avoid truncation ripples when transforming \( g^k(r) \) to \( \mathcal{E}(q) \). In this thesis all data collected shows only short range order out to about 10Å where \( g^k(r) = 1 \). Therefore a box length, \( L \) of around 20Å was chosen corresponding to eight atomic diameters. Thus a configuration size of 512 atoms was deemed appropriate. The increased statistical error associated with a small configuration could be offset later by averaging configurations after convergence.

The atoms were set up, using the program CONFIG_MANIP, in a box whose size was determined by the density required;

\[
L = \sqrt[3]{8N / \rho}
\]

The program creates a random configuration of the appropriate number of each atom type conforming to the required cut-off distances.

### 3.3.2 Maximum Move

The speed of convergence will depend on the ratio between the number of accepted moves to moves rejected. If an atom is moved only slightly then the move will most likely be accepted but won’t significantly change the structure. If an atom moves a long way it will significantly alter the structure but the move will probably be rejected. A maximum move, \( \delta \) is therefore defined to strike a balance between these two extremes to minimise convergence time. It is usually set to \( 0.1 > \delta > 1.0 \) Å; in all simulations in this thesis to 0.5 Å. It has been noted during this work however, that certain converged configurations, where chemical order is expected, are predominantly randomly ordered: The chosen maximum move size may not be large enough to allow atoms to move past each other, so that the final structure contains a ‘memory’ of the initial random configuration.

If convergence around a local minimum rather than the required global minimum is suspected, \( \delta \) can be set to a large value. In a close packed structure such as our binary metallic glasses the atoms may shuffle around a local arrangement,
trapped by the closest approach distances, in which case setting \( \delta > r_c \) should release them.

### 3.3.3 r-spacing

The value which defines the resolution of \( g^C_{\text{sep}}(r) \), \( r_{\text{sep}} \) must be decided upon by weighing up certain considerations;

1. Physically, real-space resolution is defined as \( 2\pi/Q_{\text{max}} \), where \( Q_{\text{max}} \) is the extent of the experimental data. Five points in this range is appropriate so \( r_{\text{sep}} = 2\pi/5Q_{\text{max}} \).
2. A small \( r_{\text{sep}} \) means peak position can be determined more accurately.
3. A smaller \( r_{\text{sep}} \) will increase the statistical error in \( g^C_{\text{sep}}(r) \) so a corresponding increase in model size may be necessary.
4. A smaller \( r_{\text{sep}} \) will mean more \( r \)-points and hence an increase in transform time and memory space. As regards the coefficient file used for inserting \( S_p^C(q) \) when using EXAFS data, for every \( q \)-point there are \( L/2r_{\text{sep}} \) associated \( r \)-points so these files can become very large.

The value of \( r_{\text{sep}} \) chosen for all simulations in this thesis was 0.05 Å. This involved a 0.5Mb coefficient file per absorption edge per sample.

### 3.3.4 Experimental Error

If a fit is not possible using the RMC method it is usually due to systematic errors in the data as only statistical errors are assumed in the algorithm. This means that the model is consistent with experimental data to within experimental error, but the error is not well defined.

If large errors are known to be present within a region of data, \( \sigma \) can be set very high within this region to effectively ignore this data. Usually though there is no knowledge of the distribution of systematic errors so a constant \( \sigma \) is chosen approximately equal to the noise level in the data.
From comparison of equations 3.1 and 3.6 it can be seen that $K_b T$ in MMC and $\sigma$ in RMC are equivalent so $\sigma$ may be used to raise the 'temperature' of the model and shake it up if convergence at a local minimum is suspected.

In this work we found the global minimum to be fairly broad and little manipulation of $\delta$ or $\sigma$ was necessary to reach it. A constant value of $\sigma = 0.01 \text{ Å}$ was adopted.

3.4 Analysis of Structural Models

When a simulation is complete the information contained within a model must be retrieved. RMC writes out the final $g^c_{ab}(r)$'s enabling the position of each coordination shell, $R_j$, to be read directly from the data. The standard deviation of this value, $\sigma_j$, can be obtained by inspection although it will suffer from large error as we expect a value for $\sigma_j$ of the order $0.1 \text{ Å}$ but measured with a resolution of $0.05 \text{ Å}$.

Other properties are measured in the form of distributions. Because we know where each type of atom is relative to another we can obtain these in terms of partial distributions.

Average coordination distributions, $C_{ab}(n)$ and from these, average coordination numbers, $\bar{N}_{ab}$ were obtained for the first shell using the program NEXTTO by averaging several configurations. There is a potential problem here in that it is hard to define the first coordination shell if $g^C_{ab}(r)$ does not go to zero, i.e. the 1st and 2nd shells overlap. Most of our samples showed this feature so a check of the significance of this error was thought necessary.

We assumed a Gaussian distribution of atoms (which proved to be correct) to fit the first peak in $g^C_{ab}(r)$:

$$g^{\text{attnsl}}_{ab}(r) = \frac{\exp \left[ -\frac{(r-R_{ab})^2}{2\sigma_{ab}^2} \right]}{2\pi \sigma_{ab}^2 N_{ab}}$$

(3.14)
Since the peak position, $R_{p}$, and the standard deviation of the peak, $\sigma_{p}$, were known there was only one variable, $N_{p}$, the number of atoms within the peak. This quantity was adjusted until $g_{\text{meas}}^{\text{meas}}(r)$ overlayed $g_{\text{c}}^{\text{c}}(r)$ and the value compared with that found using NEXTTO. For each sample tested it was found that these two values agreed to within error so all values of $N_{p}$ are found using this program.

Potentially, bond angle distributions may be found by defining a bond to exist between two atoms whose centres lie within the distance given by the first minimum in their partial RDF's. This is a purely geometric definition with no implication of chemical bonding.

3.5 RMC vs. EXCURV92

Both techniques have a lot to offer the field of structural analysis within EXAFS so perhaps they should not be set in competition with each other but rather the strengths of one be used to enhance the other. It is useful then to point out the merits of each in the context of the general limits of EXAFS itself.

1. Assumptions - EXCURV92 is built upon a theory which approximates many aspects of the solid. If a sample contains a non-Gaussian distribution of atoms then EXCURV92 will not achieve a satisfactory fit. RMC however assumes nothing about the structure being modelled except the concentration of each element and the microscopic density.

   It should be noted that the density of amorphous thin films is difficult to determine experimentally and is often taken as 10% less than the crystal density found using crystallographic data. It is possible to use RMC to determine density by using it as a parameter of simulation. A detailed method is given in section 3.6.

2. User Friendliness - EXCURV92 is a fast algorithm needing a minimum of setting up to gain a feel for the atomic structure. In this respect it is a useful tool to
have during experimental work as a means of checking the quality of data being collected. RMC must be carefully set up as simulations can take between 1 and 10 hours to converge.

EXCURV92 is a relatively easy program to master so that results can be obtained after a few days of learning whereas RMC has many aspects that need to be understood. It is in its infancy so a certain amount of code familiarity is therefore required for debugging.

3. Efficiency - EXCURV92 gradually builds up a structural picture from defined features of the data which means that not all of the information present is being used.

RMC uses every data point in the data range in a quantitative rather than qualitative way.

4. Consistency - EXCURV92 is applied to each absorption edge in turn and the results checked for consistency, for example to make sure that $R_{ab} = R_{ba}$. This can be a useful way of using strong data from one edge to unravel information in weaker data from the other edge. The errors associated with this approach are minimised by RMC because data from both edges are used simultaneously to calculate $\chi^2$; therefore consistency between edges is automatic.

5. Depth of Information - RMC models a three-dimensional structure therefore $g(r)$ must correspond to a possible physical structure which implies information on the partial RDF's is available.

6. Accuracy of Distances - EXCURV92 scores highly on this point as it can determine interatomic distances to within an error of ± 0.01Å. This is because within the EXAFS function (equation 2.6) used by EXCURV92, three of the processes involve $R_n$, which makes it highly sensitive to interatomic distances.

RMC does not possess this degree of accuracy because of the resolution of $g(r)$ is usually in the range 0.05-0.1Å.
7. Accuracy of Coordinations - RMC is however more useful in determining coordination numbers because of the density constraint. Coordination numbers can be found for each atom type and from this an average coordination number to within ±5%. EXCURV92 has a higher error of ±10% because N is strongly correlated to another fitting parameter, the Debye-Waller factor (see section 2.2.1). Also, N is related to the amplitude of the EXAFS signal which is attenuated by inelastic scattering processes to an uncertain degree.

8. Speciality - Whereas RMC is superior in that it can simultaneously model data from different experiments, EXCURV92 has the aesthetic advantage that it was designed specifically for EXAFS data. EXCURV92 will not become obsolete in the face of RMC as the coefficient files which form the core of the RMC EXAFS analysis are themselves calculated using EXCURV92.

EXAFS is a probe of short range order where data contains information out to 10Å at most. Modelling an extensive structure on this amount of information is challenging. The method may be significantly enhanced by simultaneously modelling complementary data from, for example, neutron diffraction data.

3.6 Choosing a Density

The microscopic number density of scattering centres, \( \rho \) is a key quantity in any structural study. The RDF, the primary source of real space information, is dependant on density, therefore everything derived from \( g(r) \) depends on this parameter.

The quantity is easy to measure for bulk solids and liquids but for the sputtered samples used in this thesis of \(-1\mu m\) thick, experimental determination of \( \rho \) is very difficult. An alternative method was therefore employed.

The assumption was made that RMC will show a minimum in \( \chi^2 \) when the correct density is chosen. This is based on previous experience and that of Gereben and Pusztai et al.

To test the assumption, data from a neutron scattering experiment on a-Ge was chosen (Etherington et al.) as the density and local structure are known. This was
applied to a configuration of 512 atoms, less than Pusztai's system of 1720 atoms but again \(g(r)\) was unity at \(r = 10\AA\) so this was deemed appropriate. The actual length of the box was varied to give a variation in density between 0.037 and 0.047 \text{Atoms/\AA}^3, ±10% of the latest value reported in the literature of 0.043 \text{Atoms/\AA}^3.

It is clear from figure 3.1 that \(\chi^2\) reaches a minimum at 0.045 \text{Atoms/\AA}^3, the 'correct' value of \(\rho\). The dip in \(\chi^2\) is shallow in comparison to Pusztai's data. This reduced sensitivity to \(\rho\) is probably due to the use of a small configuration of atoms: density is set over a medium range whereas our configuration only allows short range correlations to exist.

From these findings it was proposed that this method may be used to select \(\rho\) for related low density materials such as our samples, with the density calculated from crystallographic data used as a starting point.

Figure 3.1  Plot showing the relationship between the fit index, \(\chi^2\) and density as an input parameter for the neutron data taken from a-Ge by Etherington et. al.\textsuperscript{34}. Results of Pusztai et. al.\textsuperscript{5,13} are shown as circles and those from a 512 atom configuration as crosses.
3.7 References

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Chapter 4

The Origins and Properties of Samples

4.1 Introduction

The objective of this thesis is to understand the structural properties of amorphous films with respect to the metal-insulator transition. By observing the relationship between (a) the atomic to mid-range structure and (b) the optical absorption with composition, further insight may be gained into the mechanism of the MIT in disordered materials. In order to study these properties, good quality amorphous alloys of known composition and conductive state are required. In the first section of this chapter, we indicate the various methods of fabrication available and justify our use of RF sputtering. This is followed by a description of the method.

We have measured the optical absorption of our samples and from this, calculated the band gap; samples were assumed to be semiconducting if a gap was measured and metallic if not. The latter half of this chapter relates to the theoretical, experimental and analytical techniques involved.

4.2 Preparation of Samples

The main requirement of the samples was, of course, that they be amorphous which is achieved by choosing an appropriate fabrication technique of which there are many. This section describes some of these, concentrating on RF sputtering, adopted by the group as the preferred method of fabrication.
4.2.1 Fabrication Methods

There are a great variety of preparation methods used in the production of amorphous materials and even a moderately detailed description of each is beyond the scope of this work so a discussion of only the basic processes is given here with references to more detailed accounts.

Most preparation techniques are variations of a few basic schemes:
1. Production by quenching,
2. Deposition by chemical processes,
3. Surface or bulk amorphisation,
4. Deposition by atomisation.

4.2.1.1 Quenching Methods

A melt is formed of the required composition by one of the usual heating methods; resistive, electron-beam, laser, induction or plasma jet and then rapidly cooled by either bringing the melt into contact with an external cooling medium (in which case a bulk or powder form of the material will be produced) or the bulk solid can act as a coolant, resulting in a modified surface layer.

Bulk materials are often referred to as glasses, a form which is usually limited to a few pure elements, high metal content alloys and chalcogenides because of the limited cooling rates available (< 10^7 Ks^-1). The melt must be cooled fast enough to prevent crystallisation.

There are three types of quenching method in use; sealed melt quenching, rapid quenching and surface melting. Sealed melt quenching involves heating an evacuated tube containing the required proportions of high purity elements to a temperature of about 1000 °C for tens of hours and then cooling in air or water to room temperature. This method can yield up to tens of grams of material but the slow cooling rate means only a limited range of glasses can be produced.
Rapid quenching involves changing the shape of the melt to give the maximum possible contact area with the cooling medium. 'Splat' quenching has cooling rates of $10^8$ Ks$^{-1}$ but produces uneven shapes and more importantly uneven thickness which is not useful for measuring electrical or mechanical properties. Melt-spinning techniques, whereby a continuous ribbon of constant dimensions is produced, overcomes this problem but cooling rates of $10^9$ Ks$^{-1}$ must be tolerated.

Melted surface layers can be produced using directed energy beams (lasers, electron beams) which provide the heat and the bulk acts as the heat sink giving cooling rates up to $10^{10}$ Ks$^{-1}$. A particularly successful technique is that developed by von Allmen$^{44}$ where alternating layers of the desired alloy constituents of about 15nm thick are built up using conventional techniques. Upon irradiation with a laser pulse a homogeneous melt is produced which cools to form an amorphous alloy layer. This technique has obvious applications in device manufacture.

4.2.1.2 Deposition by Chemical Processes

Although a large variety of chemical deposition processes exist most can be excluded from this discussion because a) Si cannot be deposited from solution and b) equilibrium reactions cannot produce amorphous materials, only stoichiometric crystalline compounds. This leaves two methods; chemical vapour deposition (CVD) and plasma deposition. Both methods require suitable gases to be decomposed into thin films which is a major limitation of the technique especially as any film will contain contaminants from the carrier gas, for example H, F and Cl. This means that for example a-Si:H can be made but not pure a-Si or associated alloys.

CVD$^4$ is a 'gentle' method offering the advantage of no X-ray or ion damage to the film. It involves passing the reactive gas containing the required elements over the substrate which can be at room temperature or cooled to prevent the loss of H from the a-Si:H film. Alternatively the gas can be dissociated using optical light. Mercury is often added to the gas to assist in the dissociation process.

Plasma enhanced CVD$^5$ or glow discharge deposition systems involve using the plasma to decompose gases flowing over the substrate. This method is used
because of the wide range of properties that can be imparted to the film. It is not easily scaled up to industrial levels however.

4.2.1.3 Amorphisation

This is a relatively new technique where an amorphous material is created by either modifying a crystal structure or a the mixing of a material without melting.

Ion implantation has been used to dope semiconductors for some time but has recently been used to mix layers of a-Si and Ni producing an effect rather like that of laser quenching.

The newest technique is that of fast neutron irradiation of a bulk crystal which can amorphise the entire sample.

4.2.1.4 Deposition by Atomisation

These processes are based on the condensation and solidification of an atomised solid. In analogy to the quenching process cooling rates are large (10³ Ks⁻¹) because the largest possible surface area is presented. The difference between techniques under this heading lies in how the solid is atomised.

Evaporation of bulk alloy material is achieved by heating crystalline compounds or sintered mixtures with an electron beam or resistive source. Different final compositions to the evaporant material are to be expected possibly resulting in compositional grading. Methods have been developed to overcome this problem but tend to be outrageously violent such as the ‘exploding wire’ technique, flash evaporation or arc discharge from electrodes composed of the desired alloy constituents.

Ion beams can be used to place material directly onto a substrate with a large degree of control especially if the beam is composed of the material one wishes to deposit. If the ions are not composed of the sample material but are being used to displace material from a target the technique is called sputtering. If the ions are produced and controlled by a plasma oscillating at radio frequencies the technique is called RF Sputtering. It was the method used by the Leicester group to fabricate the
samples used in this thesis so as a technique merits more detail than those previously mentioned.

4.2.2 RF Sputtering

This is a method for producing amorphous materials in thin film form. It was chosen because of its particular suitability in alloy formation. No modification to the system is necessary when swapping between pure samples and binary or ternary alloys.

For the purposes of this study, ‘thin’ means about 1μm or 3000 atomic thickness so that the films can be considered as representative of the bulk.

4.2.2.1 The Sputtering Process

Heavy ions formed inside a plasma are accelerated towards a target consisting of the alloy components where they impact upon the surface ejecting target atoms which are then deposited elsewhere in the form of a thin film.

For conductive targets a negative DC bias will accelerate the positive ions but for semiconducting samples this is not possible. Instead, the target is fed with a 13.5 MHz signal (the radio frequency slot allocated to industry) which attracts ions on the negative half-cycle and electrons during the positive half-cycle. Due to the difference in mobility between electrons and ions a negative bias builds up on the target surface, known as the plasma ‘sheath’, which serves to further accelerate ions which bombard the target and eject material. Once ejected, this material travels through the plasma to adhere to the substrate. Several processes work in opposition to the film growth; the ejected material may be scattered by ions during its passage, or re-emission from the substrate may occur by ions accelerated across a thin substrate sheath. To reduce the effects of the latter process, a DC bias is applied to the substrate electrode.

Sputtering yield is defined as the ratio of the number of atoms ejected from the target surface to the number of ions. The term defines the erosion rate but not necessarily the deposition rate, because of the non-deposition related processes outlined above. The deposition rate can be enhanced by positioning a permanent...
magnet behind the target. This will help to contain the primary ionising electrons within the region of the target, reducing the number lost to the walls of the chamber. This technique is known as magnetron sputtering.

The plasma is supported by low pressure Ar gas which provides the bombarding ions. This gas was chosen because of its large atomic weight and chemical neutrality because its presence must be expected in the finished samples.

Films can be expected to grow at a rate of about 1000Å per hour although different materials will be deposited at different rates which can cause problems predicting the composition of alloys.

4.2.2.2 The Sputtering System

All the films in this study were prepared by RF co-sputtering using a Nordiko NM-2000-T8-SE1 sputtering system (Nordiko Ltd., Havant).

A stainless steel vacuum chamber, 56cm in diameter and 40cm high contained a multi-electrode turret, a substrate electrode to which a 20cm oxygen-free copper substrate plate was fixed, 5.5cm above the target surface. The substrate electrode could be cooled by either water or liquid nitrogen or heated up to 400 °C. To ensure good electrical and thermal contact thin copper gaskets were inserted between electrode and substrate plate. A manually operated shutter was positioned just below the level of the substrate to allow sputter-cleaning of the target before deposition.

The chamber was pumped by a Varian VHS-250 mm oil diffusion pump with a liquid nitrogen cold-trap. A water-cooled baffle below this trap helped to reduce the diffusion of pump-oil vapour into the chamber. The diffusion pump was backed by a Leybold-Heraeus D30A direct-drive rotary pump. In order to reduce the backstreaming of oil from the rotary pump into either the diffusion pump or the chamber, a foreline trap was located between the two pumps.

Pressure below 2x10⁻⁷ Torr in the main chamber could be achieved when a Meissner coil located around the substrate electrode was used.

The RF power was supplied by a 1.25 kW, 13.56 MHz generator. A matching unit was employed between generator and target electrode to reduce reflected power.
4.2.2.3 Preparation Conditions

Each analytical technique required the sample to be mounted on a specific substrate material;

- EXAFS measurements: Station 7.1 - Mylar is used as it is an organic polymer that displays no significant absorption within the energy range used on this station. It may be folded, allowing the sample thickness to be optimised.
  
  Station 3.4 - A good conductor is required to obtain the total electron yield, therefore samples are grown on Cu foil. Thickness is not important here because X-rays of the energy used on this station only penetrate the top 100Å of the sample.

- SAXS measurements: Thin Al foil is employed because it produces a featureless scattering pattern at low angles (<1°). Samples may be folded to give the required thickness.

- Composition analysis: A conductive substrate is required for the SEM measurements, therefore a thick Al foil is used.

- Optical measurements: Optically pure Corning 7059 glass is used.

- Thickness determination: Samples are grown on a microscope slide which provides a smooth surface.

Each substrate was cleaned with soap solution, methanol and an ultrasonic process to ensure good adhesion of the sputtered material. To ensure consistency, samples of the same composition were grown on the various substrates simultaneously.

Target material consisted of a 10cm diameter crystal of Si or Ge mounted on a copper plate which was screwed onto the target electrode. On top of the semiconductor a number of Ni or Ti squares (0.5cm x 0.5cm) were uniformly arranged to give a homogeneous distribution at the substrate.

The chamber was pumped overnight to a pressure < 6 x 10⁻⁷ Torr and the Meissner coil filled to achieve a base pressure of < 3 x 10⁻⁷ Torr. The chamber was then filled with 99.998% purity Ar gas via a Vacuum General 78-7 flow control unit.
which allowed a constant pressure of 3.5 mTorr to be maintained during the eight or so hours of sputtering.

A plasma was struck with the shutter in place and the RF power, matching unit and target bias were set to 200 Watts, <1 Watt and 700V respectively. After about 40 minutes the shutter was removed and the substrate exposed for deposition. No substrate heating was employed. The plasma was extinguished by shutting off the Ar supply and the chamber allowed to pump down to $10^{-6}$ - $10^{-7}$ Torr again to remove any dangerous vapours. The samples were removed and stored in non-scratch plastic bags inside an evacuated desiccator until required.

### 4.3 Characterisation of Samples

The nature of the sputtering method does not allow the exact parameters of samples to be chosen, at least not without involved monitoring techniques. However, for this work, specification of individual sample properties was not necessary. What was demanded was a set of samples of uniform thickness with composition ranging from low to high metal content spanning the metal-insulator transition. The detailed properties could then be pinned down after fabrication using techniques described in the following sections.

#### 4.3.1 Composition

Careful and clean sample preparation means that only four components should be detectable in the sample; the substrate material (aluminium), the sputtering gas (argon) and two target materials. Consequently, energy dispersive X-ray analysis could be used to determine the composition of each sample. This involved placing samples in a DS130 scanning electron microscope and measuring the characteristic X-ray yield of each element. The SEM focuses on a few square $\mu$m so yields were taken across the sample and averaged to allow for local fluctuations in composition. All samples showed little variation in composition confirming their homogeneity.
Also present in each sample is a small quantity of argon (about 2%) believed to be held inside nanometre scale voids (see Chapter 2).

4.3.2 Film Thickness

The study undertaken on the structure of amorphous materials demands that the films be thick enough to represent the bulk state, when surface effects are negligible. This is satisfied when the film thickness is of the order of a micron. Knowledge of the thickness is also essential when determining the optical properties of a material (Section 4.3.3).

A mechanical method was used in this thesis involving amplification of a stylus' motion across the sample/substrate boundary which meant the profile of the sample edge could be seen. This was performed using a Rank-Taylor Hobson Talysurf which gave readings to an accuracy of 0.05 μm. The technique is limited by its localisation, i.e. measurements are taken from a small fraction of the sample and must be averaged to gain a fair idea of the overall thickness. Alternatively the average thickness can be calculated using the optical method outlined in Section 4.3.3.4.

4.3.3 Conductive State

A goal of this work is to establish a relationship between the structural makeup and electronic properties of the samples; does a metal-like sample have different physical features to an insulating sample?

This section will deal with how electronic properties were quantified, followed by a description of the theory and experiment. Results are presented in the appropriate experimental chapters.
4.3.3.1 Probing The Band-Gap With Light

Electrical insulation is usually ascribed to the energy gap between filled valence states and an empty conduction band. This is by no means always the case; for example, the SiP system contains shallow states that allow thermally induced tunnelling at 0.01% P causing conduction while still having a broad optical gap between valence and conduction bands\(^4\) (see Figure 4.1(b)).

However, it has been found in previous studies\(^4\)\(^4\) that for SiNi and other Si:Transition-metal alloys\(^4\)\(^4\) the size of the optical gap is a good indication of the conductive state of the material. In this study it is assumed that the a-Ge:Ni,Ti systems display similar behaviour (i.e. the transition from insulator to metal is accompanied by the closure of the optical gap) because previous studies\(^4\)\(^4\) have given this event to occur also for metal contents of 10-20% rather than the fraction of a percent range.

How then do we determine whether or not we have a gap between the two bands?

The valence band/conduction band gap is of the order of eV, approximately the energy of visible light. Absorption will occur when the energy of this light, \(h\omega\), is greater than the energy of the gap, \(E_g\) (known as the optical gap), as an electron is stimulated from one band to the other.

In theory then, the absorption spectrum will contain information on the electronic structure of the sample.

4.3.3.2 The Optical Gap

Transitions from the top of the valence band to the bottom of the conduction band are stimulated when an incident photon has an energy in the range 1-3 eV. It is the absorption behaviour in this energy range which reveals the characteristics of the density of states around the gap. To calculate the expected absorption, the density of states is usually assumed to obey a power law\(^1\)\(^7\)
Dangling Bonds

Au Impurity Band

Figure 4.1(a) The standard model of the Density of States at the conduction and valence band edges, after Tauc. The thin lines represent band tailing due to distortions in bond angle associated with amorphous materials.

Figure 4.1(b) Density of States for a-Si:P, 0.01% P showing the shallow induced states consisting of two impurity bands, each containing one state per donor centre. Electrons in the \( e_2 \) band travel through the solid by means of thermally induced tunnelling while those in \( e_1 \) occupy extended states giving the usual band mechanism. This illustrates how in some instances conduction takes place while a finite optical gap can be detected.

Figure 4.1(c) Density of states for a-Si: Au with <14% Au, after Morigaki showing the introduction of mid-band impurity hopping states and a large degree of band tailing, eliminating any clearly defined band gap. Also shown are states induced by dangling bonds associated with voids.
where energies are measured from the valence band, so that $E_o$ represents the magnitude of the mobility gap.

Under the assumption that the material is highly disordered so that there is no phase correlation between electron wavefunctions at atomic sites, the relationship between the absorption coefficient, $\alpha(E)$, and mobility gap is given by

$$\alpha(E) \propto (\hbar \omega - E_o)^{x/y}$$  \hspace{1cm} (4.2)

Tauc$^{4,15}$ assumed a parabolic form of the band edges (i.e. $x = y = 1/2$), illustrated in Figure 4.1(a), so that a plot of $(\alpha(E))^{1/2}$ vs. $\hbar \omega$ should be linear and more importantly an extrapolation to the $x$-axis will yield a value for the optical gap, denoted by $E_{\text{tqc}}$

However, there is usually a large degree of similarity between amorphous and crystalline materials over a short range which weakens the random phase approximation and calls into question the validity of $E_{\text{tqc}}$ as a measure of the optical gap. Further errors are introduced if the band edges are not truly parabolic. Unfortunately the form of the density of states at the band edges is not well understood; states are known to protrude into the gap, and this ‘tailing’ of states arises through fluctuations in short range order such as bond angle distortions. This could be minimal, as shown in Figure 4.1(b), or could, in the extreme case follow the Cohen-Fritzsche-Ovshinsky$^{4,16}$ model, where tails from either band actually overlap so that there is no clear gap, merely a minimum in the density of states. SiAu exhibits a non-zero density of states$^{4,14}$ as the gap contains deep states due to the Au atoms, and is illustrated in Figure 4.1(c). In this case $E_{\text{tqc}}$ would certainly not be a good measure of the gap, so an alternative method, proposed by Stuke$^{4,18}$ is to take the energy where the absorption coefficient reaches some value, usually $10^3$ cm$^{-1}$. The optical gap is then conventionally denoted by $E_{\text{o}}$. 

\[ N_c(E) \propto E^y \quad \text{for} \quad E < 0 \]
\[ N_c(E) \propto (E - E_o)^y \quad \text{for} \quad E > E_o \]  \hspace{1cm} (4.1)
4.3.3.3 Evaluation of $\alpha(E)$

The absorption coefficient can be found by measuring the transmittance, $T(E)$, and reflectance, $R(E)$, of light directed at a sample and using the relationship:

$$T(E) = \{1 - R(E)\}e^{-\alpha(E)d}$$  \hspace{1cm} (4.3)

where $d$ is the thickness of the sample. For a non-absorbing material, $T(E) + R(E) = 1$ but as soon as any absorption takes place, the transmission becomes attenuated by the exponential factor seen on the right hand side of equation 4.3.

However, Equation 4.3 ignores the boundary condition imposed by the sample surfaces, both the air and the sample/substrate interface as depicted in Figure 4.2. When the multiple internal reflections caused by these effects are taken into account the considerably more complex expression below is arrived at:

$$T = \frac{(1 - R_2)(1 - R_3)\{1 - R_2(1 - R_3)\}e^{-\alpha d}}{(1 - R_2R_3)\{1 - (R_2R_3 + \frac{(1 - R_d)R_3}{1 - R_2R_3})e^{-2\alpha d}\}}$$  \hspace{1cm} (4.4)

where $R_1$ is the reflection forwards from the sample, $R_2$ is the reflection coefficient and $R_3$ is the reflectivity from the substrate and is for most glasses $= 4.5\%$. We also have the relation

$$R_2 = \frac{(R_3 - R_1)}{(1 - 2R_3 + R_2R_3)}$$  \hspace{1cm} (4.5)

where $R_0$ is the measured reflection from the substrate side of the sample.
Figure 4.2  Schematic showing the components of equation 3.4 where all boundary conditions are taken in account.

Figure 4.3  A-Si optical spectra clearly showing the interference fringes due to multiple internal reflections. The dashed boxes enclose the usable data range.

The effect of the reflections within the sample is to superimpose interference fringes onto the T(E) and R(E) data, as illustrated in Figure 4.3, which must be
averaged out before equation 4.4 can be applied. This was achieved by fitting a suitable equation to the relevant part of the data, i.e. when $T(E) > 1\%$ or above the noise level up to the last extrema in the interference oscillations. These limits are defined by the box in Figure 4.3.

The oscillations are not entirely unwanted as they contain information about the thickness of the sample.

4.3.3.4 Optical Thickness

As mentioned earlier, optical thickness, $d$, is the average thickness of the sample and can be calculated from the condition for a maximum or minimum to occur:

$$4nd = m\lambda_m$$  \hspace{1cm} (4.6)

where $n$ is the refractive index at $\lambda_m$, the wavelength at the $m$th maxima or minima. For films more reflective than the substrate (e.g. all films studied in this thesis) $m$ will be odd for maxima and even for minima. From equation 4.6 we have that:

$$\frac{m}{m+1} = \frac{\lambda_m}{\lambda_{m+1}}$$  \hspace{1cm} (4.7)

Assuming $n$ does not change rapidly from one extremum to the next, $m$ is found by dividing $\lambda_m$ by $\lambda_{m+1}$ and estimating the fraction, $m/m+1$, that this represents, e.g. $4/5, 5/6$ etc. From here it is easy to check that the fringes have been correctly labelled.

The refractive index, $n$, can be calculated using:

$$n = \left\{n \cdot \frac{(1 - R_m^{1/2})}{(1 + R_m^{1/2})}\right\}^{1/2}$$  \hspace{1cm} (4.8)

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where $R_{\text{max}}$ is the reflectivity at the first complete maxima and $n$ is the refractive index of the substrate. The method was applied to the a-Si sample and a thickness of 0.55 µm was returned, comparing well with the 0.50 µm measured with the Talysurf device.

4.3.3.5 Experimental Detail

Films were sputtered onto optically pure Corning 7059 glass, obtained from Gooch and Horsego, which has a refractive index of 1.53.

Transmission and reflection data were collected on a Perkin Elmer 330 double beam spectrophotometer which possesses a large near infrared - ultraviolet wavelength range of 2500nm - 187nm (0.5eV - 6.5eV).

This machine was calibrated in reflection mode using a standard Aluminium mirror with a known absolute reflectivity profile, $R_{\text{refl}}(E)$. This profile should be unity at all wavelengths but in reality has a certain wavelength dependence. The output data contains this unwanted spectrum in the form $R(E)/R_{\text{refl}}(E)$, which must be removed during data analysis.

Data collection was facilitated by an interfaced 486 DX100 PC running a simple collection code written within the Leicester University Physics Department. Data was collected at a speed of 200nm/min in steps of 2nm resulting in a file containing approximately 1500 points.

Data was analysed using EXCEL under Windows following the steps below;

1. Reflectivity from the front, $R_f$, and rear, $R_r$, of the sample must be multiplied by the response of the standard mirror, $R_{\text{refl}}$. $R_{\text{refl}}$ is usually applied in the form of an equation.

2. For highly absorbing samples, interference effects are minimal, but for some samples, significant fringing occurs. Any fringing effects must be averaged out (they are a function of film dimension and not the intrinsic absorption of the sample) by fitting a suitable equation through the interference maxima and minima. At present this is done by eye, but it is hoped a more efficient, automatic routine will be developed in the future to improve accuracy and speed. A suitable form for these averaging equations was found to be
R, & R_b = Ae^{-B\lambda} + C \quad (4.9)

T = D - \frac{D}{\exp\left[\frac{E(\lambda^2 - F)}{(GA - H)^2}\right] + 1} \quad (4.10)

where \( \lambda \) is the wavelength and the constants are of the order

A \sim 10; \quad B \sim 10^3; \quad C \sim 10; \quad D \sim 10; \quad E \sim 10^7; \quad F \sim 10^6; \quad G \sim 1; \quad H \sim 10^5

The form of these equations can be seen in Figure 4.4(a)(b).

3. The average values of reflectivity and transmission are then put into Equation 4.4 and wavelengths converted to eV to obtain a plot of \( \alpha(E) \) vs. photon energy, where the value \( E_{\text{abs}} \) can be easily obtained. An example is shown in Figure 4.4(c), where \( \alpha(E) \) reaches \( 10^4 \text{ cm}^{-1} \). In the most highly absorbing samples, it was necessary to extrapolate the absorption coefficient to \( 10^6 \text{ cm}^{-1} \) to obtain an estimate for \( E_{\text{abs}} \).

4. \( E_{\text{true}} \) may be obtained by plotting \( \{\alpha \times \alpha(E)\}^{1/2} \) vs. energy and extrapolating the straight line section to the abscissa, as shown in Figure 4.4(d).

\( E_{\text{abs}} \) is usually found to be larger than \( E_{\text{true}} \).
Figure 4.4 (a) Optical transmission spectrum of an a-Ge film. Interference fringes at large wavelengths are clearly visible, dependent on extrinsic properties of the sample i.e. film thickness. Parameters of Equation 4.10 are chosen so as to pass evenly through the maxima and minima to obtain the intrinsic transmission characteristics of the sample. The average transmission is represented as a dashed line, and is used in Equation 8.4 to calculate the absorption coefficient. (b) Corrected reflectivity of the same a-Ge sample, where similar fringing is observed. The average reflectivity is shown as the dashed line and takes the form of Equation 8.9. (c) The absorption coefficient, \( \alpha(E) \), of a-Ge, calculated using Equation 8.4. (d) A Tauc plot of the absorption coefficient, where an extrapolation of the straight line section to the x-axis gives a value for the band gap. In this case, \( E_{\text{tauc}} = 0.58 \) eV and \( E_0 = 0.70 \). The band gap in c-Ge is 0.70 eV.
4.4 References

4.11 J.M.E. Harper in ref. 3.5, p175
Chapter 5

Short And Medium Range Order In Amorphous Ge_{1-x}Ti_x

5.1 Introduction

To our knowledge, this work is the first structural study of the a-Ge_{1-x}Ti_x system embracing a large composition range. There is, of course, data on the crystalline phases of this compound\textsuperscript{3,4}, which has been used in the Discussion section of this chapter for comparison purposes, but information on the amorphous phase appears to be lacking. There is a significant body of work on related systems, however, undertaken in an effort to unite the observed metal-insulator transition (MIT) and the structural data.

Two modes of thought exist at present as to how the MIT should be modelled. The usual assumption is that the metal atom is included homogeneously in an a-Ge network, either interstitially or substitutionally. Conduction then occurs, according to Anderson\textsuperscript{5,2}, when electron states become delocalised. Alternatively, interconnecting conducting phases may play an important role. Recent structural investigations of a-Ge_{1-x}Mo_x by both EXAFS\textsuperscript{5,3} and anomalous SAXS\textsuperscript{5,4} have shown that the incorporation of metal atoms can produce regions of a conducting phase, suggesting that a percolation theory should be applied as a model for the MIT. Work done by Edwards et. al.\textsuperscript{5,5} using EXAFS data from the a-Ge_{1-x}Au_x system also supports the idea of separation into different phases.
Wright\textsuperscript{1,6} has studied the electronic properties of the \textit{a}-Ge\textsubscript{1-x}Ti\textsubscript{x} system and has reported a range of Ti compositions (3-6 at.\% Ti) at which the metal-insulator transition occurs, corresponding to a range of analytical techniques. He reports that 6 at.\% Ti is a good estimate for the position of the MIT in RF sputtered samples. Optical spectroscopy has been used in this work to identify the concentration at which the MIT occurs in our samples.

Other related work includes a comprehensive review of the structure of binary metallic glasses by Steeb and Lamparter\textsuperscript{5,7} containing results obtained with techniques besides EXAFS and gives an idea of the extent of interest in such materials.

This chapter contains structural parameters obtained using the techniques of EXAFS and SAXS. EXAFS data is resolved using two methods of data analysis: the curve fitting approach of EXCURV92 and atomic simulation by RMC. Guinier analysis\textsuperscript{5,21} is used to interpret the SAXS data. It is hoped that this work will serve a dual purpose, firstly as an investigation into the structure of the system, contributing original data to the study of amorphous metal-metalloid alloys and secondly to illuminate the mechanisms of the MIT.
5.2 Data Analysis

5.2.1 EXCURV92

Ge and Ti K-edge data were of a high standard, enabling a relatively large data range of 1-15 Å⁻¹ to be used for all compositions. The amplitude factor, AFAC, which corrects for events such as multiple excitations was fixed at 1.0 and 0.8 for Ge and Ti data respectively. Hedin-Lundqvist exchange potentials were used.

A two shell fit was appropriate for samples in the range 0.22 ≤ x ≤ 0.51 for Ge edge data and 0.42 ≤ x ≤ 0.70 for Ti edge data. This was judged according to the criteria that a reduction in the fit index of 10% by using two shells, with respect to a single shell fit, is significant.

5.2.2 RMC

A configuration size of 512 atoms was chosen, allowing structure to be modelled to a maximum r of 10 Å. This relatively small array was deemed appropriate as the Fourier transform of the EXAFS data showed structure out to a maximum of 6 Å. The statistical uncertainty associated with this small size was reduced by averaging over five configurations, each one collected after convergence of χ² and separated by 5x512 accepted moves.

Density was fixed using the method described in Section 4.6 and found to be 0.050 Atoms/Å³ and invariant with composition. This is 10% lower than the crystalline GeₓTi₁₋ₓ value of 0.055 Atoms/Å³.

Cut-off distances for the nearest neighbour coordination were set at 2.1 Å, 2.3 Å and 2.5 Å for Ge-Ge, Ge-Ti and Ti-Ti distances respectively. The experimental error, σ, was set at 0.0001 which gave a χ² of the order 10-30 at convergence.
5.3 Results

5.3.1 Ge K-edge data

An example of Ge K-edge EXAFS data is given in Figure 5.1 above along with the Fourier transform, representing the radial distribution function. The data for samples where \(0.22 < x < 0.51\) was good enough to fit a two shell model using EXCURV92 with Ge in the first shell and Ti in the second. The two samples at the composition extremes could only be realistically modelled with a single Ge shell for \(x = 0.12\) and a single Ti shell for \(x = 0.77\). The amplitude factor, AFAC, was set at 1.0 for all Ge K-edge data, this value being chosen using an a-Ge sample. A value of unity indicates the absence of any secondary photoelectron effects after the ejection of the K-shell electron other than those included in the Hedin-Lunqvist description.

![Figure 5.1](image)

Figure 5.1 (a) The EXAFS spectrum for a-Ge\(_{0.77}\)Ti\(_{0.23}\) (solid line) and the theoretical fit using EXCURV92 (dashed line). The data was taken on the Ge K-edge and weighted with \(k^2\) to emphasise the high k region. The abscissa is the wavevector, \(k\), in units of Å\(^{-1}\). (b) The Fourier transform of the EXAFS data (solid line) and the theory (dashed line). There is clearly no structure past the first coordination shell, so this sample is truly amorphous.

Partial and total coordination numbers are shown in Figure 5.2 where EXCURV92 results show that Ge maintains a total coordination of 4 for \(x \leq 0.51\) so that the structure around Ge is still tetrahedral. RMC results indicate a slightly higher coordination of 5 but are still consistent EXCURV92 results within error. The \(x=0.77\)
sample shows a slight trend towards higher coordinations, bringing it into agreement with the RMC coordination of 5.

![Figure 5.2 plots showing the coordination numbers for a-Ge_{1-x}Ti_x. Crosses indicate results from EXCURV92 analysis. Circles represent those obtained through analysis using RMC. a) Total coordination, b) Partial Ge-Ge coordination. Also shown are the predicted coordinations from the CBN model (solid line) and the RBN model (dashed line). c) Partial Ge-Ti coordination with the theoretical curves also shown.]

These observations are consistent with the crystalline structure of Ge_{1-x}Ti_x obtained by X-ray diffraction. The RMC values agree with those found using EXCURV92 within error but are consistently higher. This could be due to the way coordinations are calculated when using a configuration of atoms. Particles are counted within a sphere whose radius is defined by the minimum in the RDF after the first peak. If this minimum is non-zero then atoms from the next shell are included too.
Partial coordination numbers provide a way of identifying the bond network present. At present, two models are used, an Ordered Bond Network (OBN) where Ge-Ti bonds are favoured over Ge-Ge or Ti-Ti bonds and the Random Bond Network (RBN) where no bonds are favoured (see Appendix 1 for full description). Figure 5.2 shows the theoretical partial coordinations expected for each model and how the experimental results compare. The RMC coordinations clearly follow the RBN at all compositions with a tendency for Ge atoms to remain 4-fold coordinated as Ti content increases. This randomness in bonding is to be expected from the RMC results as the nature of the simulation causes the most disordered structure consistent with the data to be returned. EXCURV92 results indicate the presence of a partially ordered network.

The Debye-Waller factors, $\sigma^2$ or the degree of variation in bond lengths, are shown in Figure 5.3 for each analytical method. There is consistency between the RMC and EXCURV92 values of $\sigma^2$; both are $60 \times 10^{-4}$ Å$^2$. Using the Einstein model of atomic interactions, the contribution of thermal vibrations to this value can be calculated. Using a stretch frequency of 280 cm$^{-1}$ from Elliott, the room temperature thermal contribution to $\sigma^2$ is 0.0044 Å$^2$ indicating that most of the observed disorder is due to thermal vibration as opposed to static disorder in the network. Under the assumption that the Ge-Ti bond will display a similar degree of thermal vibration, EXCURV92 results show a large amount of static disorder in this bond, with a $\sigma^2$ of 0.010 Å$^2$ at all compositions. The RMC values for this bond start high and decrease to below the EXCURV92 values with increasing concentration; such behaviour would be consistent with Ti atoms having more freedom to move about their atomic positions when there are less of them.
Figure 5.3 Debye-Waller factors for a-Ge$_x$Ti$_{1-x}$ data. Circular markers represent results obtained using RMC and crosses for EXCURV$92$. (a) shows the Ge-Ge factors while (b) shows Ge-Ti. Also shown on this plot are the values obtained for Ti-Ge, marked with squares. The consistency between data from the two edges can be clearly seen. (c) Ti-Ti Debye-Waller factors.

Figure 5.4 shows the distances of the first and second coordination shells from the central Ge atom. Both the EXCURV$92$ and RMC values for the Ge-Ge bond length agree with the crystal value$^{5,10}$ of 2.45Å at low x. The data suggests that as Ti content increases the distance becomes slightly larger, the effect being enhanced for RMC values. The dilation of this bond could possibly be attributed to charge transfer from Ti atoms to the more electronegative Ge atoms (Pauling electronegativities of 1.5
and 2.0 respectively) causing electrostatic repulsion between Ge atoms and pushing them apart as the Ti concentration increases.

The Ge-Ti bond length corresponds well with the sum of the covalent radii\(^5\), indicating covalent bonding. This length is invariant with composition.

![Graphs showing interatomic distances for a-Ge\(_x\)Ti\(_{1-x}\).](image)

Figure 5.4 Plots showing the interatomic distances for a-Ge\(_x\)Ti\(_{1-x}\). Again, the circles denote results obtained using the RMC method while crosses denote EXCURV92 data. (a) Ge-Ge distances, compared with the crystalline value of 2.45\(\text{Å}\) (dashed line). (b) Ge-Ti distances (crosses), Ti-Ge distances (squares) and the calculated distance assuming a covalent bonding between the two atom types of 2.68\(\text{Å}\) (dashed line). (c) Ti-Ti distances. The dashed line is the crystalline Ti-Ti distance of 2.91\(\text{Å}\). All distances are due to Wyckoff\(^6\).  

Chapter 5: Structure in a-Ge\(_x\)Ti\(_{1-x}\)
5.3.2 Ti K-edge Data

All Ti K-edge EXAFS spectra were fitted with a first shell of Ge atoms whereas only the three samples with \( x \geq 0.42 \) could be fitted with a second Ti shell. This reflects the bias towards low Ti content samples.

Distances are shown in Figure 5.4. The Ti-Ge bond remains constant over the entire composition range and averages 2.64 Å, displaying a consistency with the Ge K-edge data to within experimental error. The value returned by EXCURV92 for the Ti-Ti bond length is also found to be consistent with the crystal value\(^5\) of 2.91 Å, with the large spread of points reflecting the errors associated with fitting a second shell. The RMC results cannot be supported by any such argument as they are on average 0.1 Å below that expected. The algorithm has tried to bring the partial RDF's together, i.e. increase the Ge-Ge distance and decrease the Ti-Ti distance with more emphasis on the latter. This could be due to the two atom types being partially indistinguishable resulting in a mild averaging of the two species' positions.

The Debye-Waller factor for the Ti-Ti bond is \( 60 \times 10^{-4} \text{ Å}^2 \), shown in Figure 5.3(c) where it can be seen that RMC and EXCURV92 values agree within error. Using the Debye model\(^2,11\) to calculate the thermal contribution to \( \sigma^2 \) with a Debye temperature of 428 K\(^3,12\), we obtain a value \( 40 \times 10^{-4} \text{ Å}^2 \). It is apparent that this bond is similar to the Ge-Ge bond in that disorder is largely due to thermal effects. Figure 5.3(b) shows very good agreement between the Debye-Waller factors of the Ge-Ti bond from both edges analysed with EXCURV92. Good consistency between edges is an important check on the validity of results. This, of course, does not apply to the RMC method as consistency is automatic.

Total Ti coordination varies little with composition from a value of 4, suggesting that the tetrahedral network of a-Ge is maintained. Again, the RMC results for partial coordinations obey the RBN model for both Ge and Ti shells, while EXCURV92 results tend to follow a partially ordered model, although the wider scatter of data points in this instance prevents a more conclusive judgement.

Chapter 5: Structure in a-Ge\(_{1-x}\)Ti\(_x\)
Table 5.1 Partial and total coordination numbers for Ge and Ti K-edge data. X denotes results obtained using EXCURV92, R denotes results obtained from RMC.

<table>
<thead>
<tr>
<th>Ti Content at.% Ti</th>
<th>$N_{\text{Ge-Ge}}$ ±0.5</th>
<th>$N_{\text{Ge-Ti}}$ ±1.0</th>
<th>$N_{\text{Ti-Ge}}$ ±0.5</th>
<th>$N_{\text{Ti-Ti}}$ ±1.0</th>
<th>$N_{\text{Ge-Total}}$ ±2.0</th>
<th>$N_{\text{Ti-Total}}$ ±2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.3 4.4 - - - -</td>
<td>0.6 3.5 4.8 2.3 4.3</td>
<td>0.5 2.3 3.7 - -</td>
<td>2.1 4.5 5.3 3.2 4.8</td>
<td>0.5 2.3 3.7 - -</td>
<td>2.1 4.5 5.3 3.2 4.8</td>
</tr>
<tr>
<td>12</td>
<td>2.1 4.1 2.0 1.0</td>
<td>3.8 3.5 - 1.0</td>
<td>4.1 5.1 3.8 4.5</td>
<td>4.1 5.1 3.8 4.5</td>
<td>4.1 5.1 3.8 4.5</td>
<td>4.1 5.1 3.8 4.5</td>
</tr>
<tr>
<td>33</td>
<td>2.9 4.0 1.7 1.3</td>
<td>3.2 2.7 - 2.1</td>
<td>4.5 5.3 3.2 4.8</td>
<td>4.5 5.3 3.2 4.8</td>
<td>4.5 5.3 3.2 4.8</td>
<td>4.5 5.3 3.2 4.8</td>
</tr>
<tr>
<td>42</td>
<td>1.0 4.0 2.4 1.9</td>
<td>3.7 2.6 0.3 2.2</td>
<td>3.4 5.9 4.0 4.8</td>
<td>3.4 5.9 4.0 4.8</td>
<td>3.4 5.9 4.0 4.8</td>
<td>3.4 5.9 4.0 4.8</td>
</tr>
<tr>
<td>51</td>
<td>0.8 3.1 3.0 2.3</td>
<td>3.3 2.3 0.8 2.6</td>
<td>3.8 5.4 4.1 4.8</td>
<td>3.8 5.4 4.1 4.8</td>
<td>3.8 5.4 4.1 4.8</td>
<td>3.8 5.4 4.1 4.8</td>
</tr>
<tr>
<td>70</td>
<td>- 1.1 5.3 4.7</td>
<td>2.6 2.0 1.1 3.6</td>
<td>5.3 5.8 3.7 5.6</td>
<td>5.3 5.8 3.7 5.6</td>
<td>5.3 5.8 3.7 5.6</td>
<td>5.3 5.8 3.7 5.6</td>
</tr>
</tbody>
</table>

Figure 5.5 Coordination numbers for a-Ge$_x$Ti$_{1-x}$ calculated using EXCURV92 (crosses) and RMC (circles) for Ti K-edge data. (a) Total Ti coordination. (b) Ti-Ti partial coordination. Predictions of the OBN model (solid line) and RBN model (dashed line) are included for comparison. (c) Ti-Ge partial coordination, also with predicted coordination from the bond models.
It is useful to check the consistency of the coordinations, obtained from the number of Ge-Ti bonds, using the relationship

\[(1-x)N_{\text{Ge-Ti}} = xN_{\text{Ti-Ge}} \]  \hspace{1cm} (5.1)

where \(N_{\text{Ge-Ti}}\) is the number of Ti atoms around each Ge atom and \(N_{\text{Ti-Ge}}\) is the number of Ge atoms around each Ti. The results can be seen below in Table 5.2.

<table>
<thead>
<tr>
<th>conc. of Ti (x)</th>
<th>EXCURV92</th>
<th>RMC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((1-x)N_{\text{AB}})</td>
<td>(xN_{\text{BA}})</td>
</tr>
<tr>
<td>0.12</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>0.22</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>0.33</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td>0.42</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>0.51</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>0.70</td>
<td>1.6</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 5.2: Numerical representation of the degree of consistency between data from each edge. Type A represents Ge and type B Ti.

The table shows very good consistency within the RMC results, although theoretically they should be identical. The slight deviations are probably due to a non-zero partial \(g(r)\) after the first coordination shell. EXCURV92 results from each edge agree very well, particularly at higher Ti contents. Deviations here are because EXCURV92 tends to miss weaker shells.
5.3.3 SAXS

The Small-Angle spectra for all samples display a single maximum at 0.08 Å⁻¹ with an intensity decaying to a smooth background from the substrate. This background was used to normalise the spectra, enabling the relative maximum intensities to be observed. The maximum intensity is a function of the density of scattering particles within a sample. Inspection of Figure 5.6 shows significant differences in these relative peak heights with no clear trend with composition. This points toward the fabrication process as the origin of the inhomogeneities.

![Figure 5.7 Plot showing the Small-Angle intensity distribution for samples of Ge₁₋ₓTiₓ, all of which exhibit the single maximum associated with widely dispersed scattering centres. Note the intensity of this maximum is independent of composition and is therefore probably a function of deposition conditions. The average Rₐ is 13Å, or features measuring 35Å across. Plots have been offset for clarity.](image)

It is interesting to note that the a-Ge sample displays a maximum in the SAXS pattern and must therefore contain inhomogeneities. This sample cannot be phase separated, which leads to the conclusion of voids as the origin of this scattering peak, introduced during the sputtering process. Deviations in bond length and bond angles cause a certain degree of strain energy to build up during fabrication which is alleviated...
by the formation of a network of voids containing the sputtering gas argon. This is supported by the 10% density deficit with respect to the crystal noted during RMC analysis. If voids are present in this sample, it is fair to assume they are responsible for the observed peak in spectra from the other samples.

Guinier analysis was used to calculate the dimension of these voids and the results are shown in Table 5.3 below. There is no variation of dimension with metal content, as expected. Each sample contains voids of a size close to the average of 35Å.

<table>
<thead>
<tr>
<th>x</th>
<th>$R_g$ ± 3Å</th>
<th>Radius ± 4Å</th>
<th>Size ± 8Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>0.12</td>
<td>15</td>
<td>19</td>
<td>39</td>
</tr>
<tr>
<td>0.22</td>
<td>17</td>
<td>22</td>
<td>43</td>
</tr>
<tr>
<td>0.33</td>
<td>10</td>
<td>13</td>
<td>26</td>
</tr>
<tr>
<td>0.42</td>
<td>16</td>
<td>21</td>
<td>41</td>
</tr>
<tr>
<td>0.51</td>
<td>16</td>
<td>21</td>
<td>41</td>
</tr>
<tr>
<td>0.70</td>
<td>13</td>
<td>17</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 5.3 Dimension of scattering centres in a-Ge$_{1-x}$Ti$_x$ calculated using the Guinier analysis described in Section 2.3.1.1. The size, or diameter, of the particle is calculated from the Radius of Gyration using $2R_g(5/3)$. The Guinier condition that $R_g/kT > l$ is met, albeit by a narrow margin.

5.3.4 Optical Study

By observing the absorption characteristics of samples at optical wavelengths, the extent of the band gap can be determined and hence the metal content at which the MIT is induced can be identified. For samples with $x \geq 0.12$, transmission was zero, implying the non-existence of a band gap and metal-like behaviour. The a-Ge and lowest metal content sample, however, display an absorption edge and their absorption profiles are shown in Figure 5.8(a). A shift towards lower energy on addition of metal can be clearly seen, indicating the narrowing of the optical band gap with the introduction of impurity states. The width of the gap can be quantified in one of two ways;
(i) The energy when $\alpha(E)$ drops to some specified value, usually taken as $10^4$ cm$^{-1}$ and conveniently denoted $E_{\text{opt}}$. Values obtained are $0.7 \pm 0.2$ eV for a-Ge, which compares well with the crystalline value of $0.7$ eV$^{3,22}$, and $0.3 \pm 0.2$ eV for $x=0.06$. The data range was not large for this latter sample because of the increased absorption associated with a smaller band gap. This required the extrapolation of the curve to $10^4$ cm$^{-1}$.

(ii) By assuming parabolic band edges, Tauc showed that the absorption coefficient was related to the photon energy by

$$\alpha(E) = (\hbar \omega - E_{\text{Tauc}})^{1/2}$$

(5.2)

where $E_{\text{Tauc}}$ is the magnitude of the band gap (see Section 3.3.3.2). A plot of $(\alpha(E))^{1/2}$ vs. E will give a straight line, where $E_{\text{Tauc}}$ is found from the intercept of the line with the x-axis. Such a plot is shown in Figure 5.8(b) for the two absorption curves in (a). Again, the shift to lower energies upon addition of any metal is apparent. Values for $E_{\text{Tauc}}$ were found to be in agreement with $E_{\text{opt}}$ at $0.6 \pm 0.2$ eV and $0.2 \pm 0.2$ eV for a-Ge and a-Ge$_{0.94}$Ti$_{0.06}$ respectively. It is often found that the assumption of a parabolic band edge does not hold for amorphous samples because of disorder induced tails in the density of states which protrude into the gap. However, the agreement between $E_{\text{opt}}$ and $E_{\text{Tauc}}$ suggests either method is a suitable indication of the state of the gap.

Figure 5.8(c) illustrates the relationship between the $E_{\text{opt}}$, $E_{\text{Tauc}}$ and composition, and shows the steady closure of the gap as metal is introduced. A lack of samples exhibiting an absorption edge makes it difficult to ascribe a form to this behaviour. However, if a linear relationship is assumed, a continuum arises at $10 \pm 2$ at.% Ti which we take as the onset of metallic behaviour.
Figure 5.8  
(a) Absorption curves for samples of a-Ge$_{1-x}$Ti$_x$. The dashed line represents the value $E_{\text{gap}}$, the energy at an arbitrary value of $\alpha(E)$, intended as a measure of the band gap energy. (b) Tauc plots for the spectra in (a), where $\alpha(E)$ represents $(\alpha xx E)^{1/2}$, measured in units of cm$^{-1}$eV$^{-1}$. The intercept of the curve and the x-axis give values for $E_{\text{gap}}$. (c) Relationship between the band gap energy and metal content, $x$, of the sample. By assuming a linear relationship, the MIT is seen to occur at -10 at.% Ti.
5.4 Discussion

Studies performed on a-Ge using EXAFS, neutron and X-ray diffraction generally agree that the structure can be characterised by a tetrahedral random network (TRN), with an average first coordination number of around 4.51. The total coordination numbers of our samples show four-fold coordinated Ge and Ti atoms for 0 ≤ x ≤ 0.51, indicating that this TRN persists into the metal-rich composition range with Ti atoms substituting for Ge atoms in the network. The a-Ge₀.₃₀Ti₀.₇₀ sample is the only exception to this view as it shows an increased Ge coordination of 5. This could be a result of Ti atoms clustering around Ge, as reported for Au atoms by Edwards et. al. in the a-Ge₁₋ₓAuₓ system. Alternatively, the tetrahedral covalent bonds may be changing to higher coordinated metallic bonds; Hayes et. al. report Ge atoms surrounded by 8.6 Pd atoms for an a-Ge₀.₂₂Pd₀.₇₈ sample. In our samples, the increase in Nₘₙₘₚ is unaccompanied by a change in Ti coordination, so it is most likely that a move towards a denser structure is taking place. The interatomic separations of our amorphous samples also reflect those of their crystalline counterparts across the composition range, alerting us to the possibility of micro-crystallites in our samples. However, the lack of any structure beyond the first maximum in the RDFs confirms that all the samples are amorphous. (See, for example Figure 5.1(b)).

The bond preference in this system is not readily definable. EXCURV92 results point toward the Ge-Ti bond as favoured but not conclusively, while RMC results conclusively show that the bonding is random, but this could be a product of the method and not the structure. The most believable answer is that the structure is a combination of both types of bonding. Harris et. al. working with EXAFS data from sputtered a-Fe₁₋ₓTb, noted a preference for Fe-Tb bonding in the growth direction while like-like bonds were favoured for the in-plane direction, putting forward the idea that the bond ordering is dependent on the fabrication conditions. The possibility exists, therefore for both types of bonding to exist in the same sample.

Many a-Ge:M films where phase separation has been reported, e.g. for M=Fe³⁺, Mo⁵⁺, Au⁵⁺, W⁵⁺, display a characteristic composition dependant second maximum in the SAXS pattern (see Section 2.3.1.2). There is no such evidence in our a-Ge₁₋ₓTiₓ samples, so the assumption is made that phase separation is not present.
This is not to say that a-Ge:Ti does not phase separate since, as Bienenstock et. al. have noted, medium range structure is highly dependent upon deposition conditions. Our samples are not homogeneous however, as there is a measurable Guinier peak in each spectrum at low k, revealing the presence of inhomogeneities of approximately 35Å in size. The heights of the Guinier peaks show that these particles vary in number from sample to sample, with no apparent compositional trend and are found even in the a-Ge sample. These observations can be accounted for by assuming inclusions of neutral voids containing Ar sputtering gas introduced during the fabrication process. It is unlikely that these scattering centres are chemical inhomogeneities, but conclusive results can only be obtained using the anomalous-SAXS technique.

It is well known that two samples of the same composition can display a metal-insulator transition at widely differing metal concentrations, seemingly dependent on the fabrication technique. For instance, Massenet et. al. cite a transition composition of 25 at.% Fe for co-evaporated a-Ge1-xFe_x while Lorentz et. al. find it at 15 at.% Fe for triode-sputtered material. Regan and Bienenstock suggest that the latter is separated into conducting and non-conducting phases so that the metallic state occurs when a percolation threshold is reached, which naturally requires less Fe than if the whole sample is to become conductive.

We report a metal-insulator transition occurring at 10 at.% Ti for a-Ge1-xTi_x, perhaps lower than expected in the light of the SAXS results as phase separation cannot be invoked as an explanation of the low Ti threshold. This value is, however, consistent with the conductivity work undertaken by Wright, who reports an MIT at 6 at.% Ti. We report no structural changes taking place around this composition, but there is a distinct lack of data in this composition range.
5.5 Conclusion

We have set out to characterise the short and medium range structure of RF sputtered a-Ge$_x$Ti$_{1-x}$ thin films in relation to the metal-insulator transition. Optical spectroscopy was used to determine the presence of an energy gap between conduction and valence bands, $E_g$, which was found to decrease constantly from 0.7eV for a-Ge to zero at 10 at.% Ti.

Two analytical techniques, EXCURV92 and RMC, were used to determine coordination numbers, interatomic distances and variations therein, from EXAFS data. Results from both techniques were found to be in agreement but distances were judged to be more reliable from EXCURV92 as RMC can only resolve distances to 0.05Å while RMC results offered more conclusive coordination numbers as EXCURV92 tends to overlook weak peaks. The Ge-Ge bond length was found to be 2.45Å at low Ti content, in agreement with the crystal value, rising slowly across the composition range to 2.48Å at $x = 0.70$ with a constant Debye-Waller factor associated with this bond of 0.006 Å$^2$. The number of these bonds steadily decreased from 4 as Ti was added, while the number of Ti atoms around each Ge increased in such a way as to keep the Ge atoms four-fold coordinated across the composition range. The same effect was observed for Ti K-edge data, Ti atoms remaining four-fold coordinated in total as Ti-Ge bonds were swapped for Ti-Ti. RMC results suggest this was done in a random way but there is evidence from EXCURV92 that some ordered bonding was present. The Ti-Ge and Ge-Ti bond lengths were found to be consistent at 2.68Å, with an associated $\sigma^2$ of 0.010 Å$^2$. A Ti-Ti distance of 2.91Å was found using EXCURV92 which is the same as the crystal value. The mean square deviation in this bond was also 0.010 Å$^2$. Inspection of the results show no obvious structural changes around the 10 at.% Ti composition but this must be taken with the knowledge that only 3 samples exist within the range $0 \leq x \leq 0.22$.

SAXS experiments revealed that our samples contain inclusions of Ar sputtering gas, approximately 35Å across and in varying amounts, independent of composition. The samples display no evidence of phase separation.
5.6 References

5.2 Mott, N., 1974, "Metal-Insulator Transitions", Taylor & Francis Ltd., London
5.6 Wright, T., 1996, PhD Thesis, Cavendish Laboratory, University of Cambridge
5.11 As 5.8, p.209
5.12 As 5.8, p.219
Chapter 6

Short And Medium Range Order In Amorphous
Si$_{1-x}$Ti$_x$

6.1 Introduction

The transition from semiconducting to metallic behaviour of certain alloys has been the subject of much interest from both a fundamental and technological point of view. Of special interest is the heavy doping of Si with transition metals because of the application to the microelectronics industry. The degree of control over conductivity in such materials has led to their application as components in integrated circuits$^4$. By varying the metal content of these alloys it is possible to fabricate either metals or insulators, with the transition from one state to another (the MIT) occurring across a narrow threshold, usually at a metal content of around 15 at.

The mechanism of the MIT was originally thought to be electronic in origin, the alloying producing impurity levels deep within the intrinsic band gap inducing an Anderson type transition$^5$. Recent structural reports, however, suggest that metallic behaviour occurs when regions of conducting material embedded in a non-conducting phase become large enough to percolate through the entire structure$^6$. Without a more detailed knowledge of the short and medium range order, the MIT cannot be fully understood, yet few structural studies have been undertaken on these materials, and to our knowledge there have been no investigations into the structure of a-Si$_{1-x}$Ti$_x$. We present here then just such an investigation.
6.2 Analytical Details

The package EXCURV92, available at the SRS, Daresbury Laboratory, was used to analyse EXAFS data. A standard Ti foil was used to determine the amplitude factor (AFAC) to be used during analysis of Ti K-edge data: this was found to be 0.8. AFAC for the Si K-edge was found to be 0.9 using the a-Si sample, where a coordination of 4 is expected, as a standard. The Hedin-Lundqvist exchange potential and von-Barth ground state potential were used to calculate the phase-shifts for both edges. The energy difference, $E_0$, between vacuum zero and the edge being worked on, $E_f$, was found to remain constant at $-11 \pm 1$ eV across the composition range for the Ti edge data while Si edge data displayed an $E_0$ of $-15 \pm 3$ eV.

An attempt was made to apply the Reverse Monte Carlo method to the data, without success. The poor quality Si K-edge EXAFS data allowed atoms to move into unphysical positions and atomic types became confused. The resulting distances and coordinations obtained from the RMC were put into EXCURV92 and good fits were obtained for these ‘wrong’ values, proving that the problem did not lie with the algorithm but within the data itself. For an account of the limits of RMC, see Section 3.7.
6.3 Results

An example of Ti K-edge EXAFS data is shown in Figure 6.1. For each data set, a two shell fit with Si in the first shell and Ti in the second was found to be appropriate. Good quality data extending from 1-12 Å⁻¹ for all spectra meant a Fit Index of around 10-20 could be expected.

![Figure 6.1](image)

(a) The EXAFS spectrum for a-SiₓT𝑖ₓ (solid line) and the theoretical signal calculated using EXCURV92 (dashed line). The data has been weighted by \( k^3 \) to increase the amplitude of the high \( k \) signal. (b) The Fourier Transform of the data (solid line) and theory (dashed line).

The Si K-edge data, not shown, was of considerably lower quality than Ti K-edge data, due in part to the drain-current method (see Section 2.2.4.2). Analysis was hampered by a short data range of 1-9 Å⁻¹, hence Fit Indices of 30-50 were typical.

Despite the shortcomings of the data, a two shell fit was found to be appropriate, i.e. fitting a second shell reduced the Fit Index by 10% or more, with the exception of the \( x = 0.26 \) sample where only a single Si shell could be fitted.
6.3.1 Coordination Numbers

<table>
<thead>
<tr>
<th>Ti Content, at. % Ti</th>
<th>$N_{Si}$ $\pm 0.5$</th>
<th>$N_{SiTi}$ $\pm 1.0$</th>
<th>$N_{TiSi}$ $\pm 0.5$</th>
<th>$N_{TiTi}$ $\pm 0.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>2.9</td>
<td>0.3</td>
<td>9.1</td>
<td>1.7</td>
</tr>
<tr>
<td>16</td>
<td>2.9</td>
<td>1.9</td>
<td>9.5</td>
<td>2.6</td>
</tr>
<tr>
<td>19</td>
<td>2.2</td>
<td>2.5</td>
<td>9.3</td>
<td>2.2</td>
</tr>
<tr>
<td>26</td>
<td>2.1</td>
<td>-</td>
<td>9.5</td>
<td>1.9</td>
</tr>
<tr>
<td>44</td>
<td>0.8</td>
<td>4.1</td>
<td>9.3</td>
<td>1.5</td>
</tr>
<tr>
<td>51</td>
<td>1.3</td>
<td>3.8</td>
<td>8.8</td>
<td>1.9</td>
</tr>
<tr>
<td>54</td>
<td>1.2</td>
<td>4.0</td>
<td>8.3</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 6.1 shows the partial coordination numbers for Si and Ti K-edge data. The large error in $N_{SiTi}$ reflects the poor quality of the EXAFS data for the Si K-edge.

Equation 6.1 was applied to the relevant columns of Table 6.1 and the LHS and RHS plotted on the same axis, as shown in Figure 6.2(a). The two curves are consistent to ~30 at. % Ti. The consistency curve (dashed line in the figure) is chosen to run between the error bars of each coordination curve, ensuring that the average is weighted towards the most reliable data set.

Having obtained $N_{Conscem}$, the consistent partial coordinations are calculated at each composition thus

$$N_{SiTi} = \frac{N_{Conscem}}{1-x} \quad (6.2)$$
The results can be seen in Table 6.2 and are plotted in Figure 6.2(b). Values for Ti are relatively unchanged while Si coordinations at high Ti content have been shifted upwards, the bias reflecting the large degree of inaccuracy associated with this data set.

Table 6.2 The complete set of coordination numbers for a-Si<sub>x</sub>Ti<sub>1-x</sub> EXAFS data where N<sub>s</sub> and N<sub>t</sub> have been corrected to induce consistency. The final column shows the trend towards bond ordering with increasing x.
Also shown, in the right most column of Table 6.2, are the results from a numerical test for the degree of chemical order within each sample. The difference in bond energy for each atomic species, $\Delta E$ can be calculated using the expression

$$e^{-\Delta E/k_BT} \frac{N_{Si}N_{Ti}}{N_{Si}N_{Ti}}$$

(6.4)

For $e^{-\Delta E/k_BT} = \infty$, $\Delta E = -\infty$ and the Si-Ti bond is preferred, i.e. chemical ordering. For $e^{-\Delta E/k_BT} = 0$, like-like bonds are preferred. If the exponential is unity, the bonding is random. Appendix 2 covers the theory behind Equation 6.4 in more detail. The tabulated results show a clear trend of increasing order with increasing Ti content.

Figures 6.3(b) and (c) show the partial Si coordination numbers, where it can be seen that pure Si is surrounded by four other Si atoms. As Ti is added, the number of Si atoms fall, replaced by Ti atoms, probably substituting into the network at first because the total coordination remains at approximately four fold. This value rises more quickly above 20 at.% Ti indicating interstitial occupancy.

The Si-Ti partial coordination rises steeply for metal contents greater than 30 at.% Ti, so that at 50 at.% Ti, Si is eight-fold coordinated giving rise to the speculation that Si becomes close packed at very high Ti content. Indeed, this idea is supported by work done on the bulk a-Si$_x$Pd$_{1-x}$ glass where at $x = 0.84$, Si is surrounded by 9 Pd atoms. This allows us to extrapolate the total Si coordination across the entire composition range (shown as the bold line in Figure 6.3 (a)), from which expected partial coordinations from two bond order models can be calculated. These are the Ordered Bond Network (OBN), where Si-Ti bonds are favoured and the Random Bond Network (RBN) where no bond has a preference.
Figure 6.3 (a) Total Si coordination. The bold line drawn through the data points and extrapolated to high x represents the values used to calculate the bond affinities. (b) Partial Si-Ti coordination. The expected coordinations if the bonding is chemically ordered (OBN) are shown as the solid line while the RBN predictions are marked with a dashed line. The two circles represent the SiTi coordination in the two known crystal phases, TiSi and TiSi$_2$. (c) Partial Si-Si coordinations, with OBN (solid line) and RBN (dashed line) predictions shown.

The equations governing the behaviour of the partial coordinations under each model are outlined in Appendix 1 and the results shown in Figure 6.3(b) & (c). It is apparent from the figure that at high Ti content, $N_{SiTi}$ and $N_{TiSi}$ tend to follow the OBN model while at lower metal concentration the ordering is not as clear. This is in agreement with the bond energy calculations performed above.

Ti partial and total coordinations are shown in Figure 6.4. It can be seen that Ti is close packed for $x \leq 0.26$, surrounded by 10 Si atoms and 2 Ti atoms.
The number of Si atoms falls to 8 at higher Ti content while the number of Ti atoms remains at 2. This apparently high number of Si atoms is in agreement with data from the crystal TiS12 where $N_{TISi} = 10^{6.6}$.

The extrapolation to higher Ti compositions has a higher confidence level in this case as Ti metal is known to be 12 fold coordinated. The expected partial coordinations from the OBN and RBN were calculated using a smooth line drawn through the data points (solid line in Figure 6.4(a)) and plotted in Figure 6.4 (b) and (c). From this data, the change from random to chemical ordering with increasing Ti content can be clearly seen.
6.3.2 Interatomic Distances

Atoms of Si in the crystal are reported to be 2.34 Å apart. The value for amorphous Si is 2.35 Å. Figure 6.5 represents the interatomic distances found using EXCURV92 where it can be seen that at all compositions, the Si-Si bond in a-Si<sub>Ti</sub> remains at approximately this length to within experimental error. The Ti-Ti bond was found to be lower than the value of 2.91 Å for metallic Ti<sup>67</sup> at 2.80 ± 0.01 Å, invariant across the composition range.

The Si-Ti bond length also remained constant in all samples but was found to be slightly higher when viewed from Ti atoms (2.66 ± 0.01 Å) than when measured with respect to Si (2.61 ± 0.02 Å), probably due to a slight mismatch in the calculation of phaseshifts at each edge. The actual bond length can be taken as a weighted average of the two, i.e. 2.64 ± 0.02 Å. This value compares well with the sum of the covalent radii, 2.63 Å<sup>67</sup>, indicating covalently bonded Si and Ti.
6.3.3 Debye-Waller Factors

The Debye-Waller factors, \( \sigma^2 \), for our samples are shown in Figure 6.6. Values obtained from the Si absorption edge are clearly less reliable than their Ti edge counterparts, which is to be expected considering the relative quality of each raw data spectrum. A certain degree of fluctuation is noted in the mean-square interatomic distances for like-like bonds. However, a straight, flat line can be drawn through the error bars of all data points at \( \sigma^2_{\text{Si-Si}} = 45 \times 10^{-4} \text{ Å}^2 \) and at \( \sigma^2_{\text{Ti-Ti}} = 130 \times 10^{-4} \text{ Å}^2 \).
The room temperature thermal contribution to $\sigma_{\text{si}}^2$ is known to be $40 \times 10^{-4}$ Å$^2$ (see reference 6.8) indicating that there is little static disorder in this bond for our samples. It must be noted however that the total electron yield measurements only probe the top 50-100 Å and therefore the effect may be confined to the surface.

Using the Debye model$^5,9$ of atomic vibrations with a Debye temperature of 428K for Ti$^{4+}$$^{10}$ to calculate the thermal contribution to the Ti-Ti bond, we find that $\sigma^2 = 40 \times 10^{-4}$ Å$^2$. When compared with the experimental value of $130 \times 10^{-4}$ Å$^2$, it can be inferred that the disorder arises from static disorder rather than thermal effects.

Values of $\sigma^2$ for Ti-Si are constant across the composition range at $190 \times 10^{-4}$ Å$^2$ and the values obtained from the Si K-edge are consistent with these, albeit with large errors. Under the assumption that the Ti-Si bond will behave thermally in a similar manner to the homopolar bond, we expect the deviation in the Si-Ti bond length associated with thermal vibrations to be approximately $40-45 \times 10^{-4}$ Å$^2$, indicating that the large observed Debye-Waller factor is due to static disorder.
6.3.4 SAXS

Due to excessive noise on some of the a-Si$_x$Ti, SAXS spectra, it was only possible to accurately analyse data on three out of the seven samples. These samples, however, span the composition range from 4 at.% to 54 at.% Ti giving a reasonable picture of the behaviour of medium range structure with composition. The three curves, normalised and background subtracted, are shown in Figure 6.7.

![Figure 6.7 SAXS spectra taken on Station 8.2 at the Daresbury Laboratory SRS. The data has been normalised to an arbitrary value, common to each sample, enabling comparison of peak heights. A constant has been added to each successive spectra for clarity.](image)

The main feature of each spectra is the large peak at 0.08 Å$^{-1}$, with a sharp cut off at 0.05 Å$^{-1}$ due to the beam stop. The peaks are of approximately equal amplitude and shape, indicating that the inhomogeneities present occur in the same quantities and are of the same size, independent of Ti content. This provides evidence in favour of voids as the origin of the observed scatter as they can be introduced during sample fabrication in the form of bubbles of Ar sputtering gas. Their characteristics will be a function of sputtering conditions rather than chemical composition$^8$$^{11}$.

Guinier analysis$^9$$^{12}$ (see Section 2.3.1.1) performed on the trailing edge of this peak shows the dimension of the voids to be about 35±2 Å.
The two samples containing 4 at.\% and 19 at.\% Ti display a weak second peak at 0.24 Å⁻¹ while the sample containing 54 at.\% Ti does not. This signals the presence of non-disperse regions of differing electron density. Coupled with the compositional dependency, we could be seeing the manifestation of phase separation. In fact, Gong et al. have calculated the Gibbs free-energy for each type of bond within the a-Si₁₋ₓTiₓ matrix and concluded that for 0.0 ≤ x ≤ 0.23 a two-phase mixture of an a-Si₄Tiₓ alloy and c-Si is more likely than the pure amorphous alloy. For x ≥ 0.23, only the amorphous alloy is expected to occur; the absence of a second maximum in our data for the a-Si₀.₄₆Ti₀.₅₄ sample is consistent with this.

6.3.5 Optical Studies

Measurement of the optical absorption properties of a sample indicates the extent of the band gap and hence whether the material is metallic or semiconducting. It was found that all samples where x ≥ 0.16 were highly absorbing, indicating metallic behaviour. Figure 6.8(a) shows the absorption coefficients measured for the a-Si and x= 0.04 samples, where it can be seen that the addition of metal causes a shift to lower energies and a flattening of the curve, associated with the closure of the band gap as states within the gap become filled. A standard measure of the gap is taken as the energy where α(E)= 10⁴ cm⁻¹, denoted Eₐₐ. This was found to be 1.4 ± 0.2 eV, somewhat higher than the crystalline value of 1.2 eV. This is surprising because the band gap is expected to be smaller in amorphous materials due to the disorder induced effect of band tailing into the gap. This observation may reflect the fact that Eₐₐ is not a measure of the true gap, but of the energy separation of states higher in the valence and conduction bands. Eₐₐ for the sample where x= 0.04 was found to be 0.5 ±0.2 eV.

Results of a Tauc analysis (see Section 3.3.3.2) are shown in Figure 6.8(b). The shift to lower energies in the plot on addition of Ti represents a decrease in the width of the band gap, E₉₉, from 1.3 ± 0.2 eV for a-Si to 0.3 ± 0.2 eV for a-Si₀.₆₆Ti₀.₃₄. The theory behind Tauc analysis assumes parabolic band edges, which
may not be the case. For this reason we have adopted $E_{\text{oa}}$ as a measure of the band gap.

Figure 6.8(c) is intended to show the composition dependence of the band gap, but is hampered by a distinct lack of data points. However, by assuming a linear relationship, it appears that the gap closes at $-6 \pm 2$ at.\% Ti. We take this value as the critical concentration at which the MIT occurs.

![Graphs showing absorption coefficient, Tauc plot, and band gap vs. composition](image)

Figure 6.8  (a) Absorption coefficient for a-Si and a-Si$_{x}$Ti$_{1-x}$ where the decrease in dependence on photon energy with the addition of Ti can be seen. The short absorption curve must be extrapolated to obtain $E_{\text{oa}}$ which is measured at $\alpha(E) = 10^{4}$ cm$^{-1}$ (dashed line). (b) Tauc plot of the absorption coefficient, where $\alpha(E) = (\alpha_{0}E)^{1/2}$ with units of cm$^{-1}$eV$^{-1/2}$. Extrapolation of the line to the x-axis gives a measure of the band gap, $E_{\text{Tauc}}$ which is seen to decrease on addition of Ti. (c) Plot showing $E_{\text{oa}}$ (crosses) and $E_{\text{Tauc}}$ (diamonds) vs. composition, showing the closure of the band gap on addition of metal and hence the apparent MIT at 6 at.\% Ti.
6.4 Discussion

Inspection of the total Si coordination appears to show two distinct types of behaviour.

i) Si in the composition range \(0 \leq x \leq 0.19\) is clearly four-fold coordinated, by Si at low \(x\), to be replaced by Ti as the Ti content rises. This indicates either substitution of the Si atoms by Ti atoms to create an amorphous SiTi alloy with the tetrahedral random network (TRN)\(^6\) of a-Si, or pure a-Si may be present at all \(x\) in this range with distinct phases of an a-SiTi alloy slowly appearing. The latter argument is supported by the SAXS study which reveals the presence of a small degree of phase separation while the Si is four-fold coordinated. Further evidence for an a-Si, a-SiTi mixture is provided by Gong et. al.\(^4\) in their study of the Gibbs free-energy (\(\Delta G\)) of the Si-Ti system where they report that there are three distinct regions in the \(\Delta G\) vs. \(x\) curve. The first, for \(0 \leq x \leq 0.23\) is where a mixture of crystalline Si and an amorphous alloy has a lower \(\Delta G\) than a single-phase amorphous alloy (although EXAFS data from the Si K-edge show little structure beyond the first maximum in the RDF, indicating that there is no crystalline phase present). For \(0.23 \leq x \leq 0.83\), a single phase should be a more stable state. Indeed, our sample containing 54 at.% Ti shows no phase separation. For \(0.83 \leq x \leq 1.0\), a mixture of crystalline Ti and an amorphous alloy has a lower \(\Delta G\) and should therefore be more stable. Unfortunately we do not have samples in this composition regime.

It should be stressed that there is only a small amount of evidence for phase separation, only present in two samples (\(x = 0.04\) and \(x = 0.19\)) which somewhat restricts any firm conclusions.

ii) In the range \(0.19 \leq x \leq 0.54\), total Si coordination rises constantly with Ti content from 4 up to around 9. Results from a similar system, i.e. a-Si\(_{60}\)Pd\(_{40}\) suggest that a-Si\(_{1-x}\)Ti\(_x\) will become close-packed at higher \(x\)\(^4\). Data from the crystal phases, TiSi\(_2\) and TiSi\(_6\)\(^6\) agree well with these coordination numbers and support the idea of a close-packed alloy.

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Chapter 6: Structure in a-Si\(_{1-x}\)Ti\(_x\)
In comparison to the Si environment, Ti remains in a remarkably constant state across the composition range. At low x, Ti is certainly involved in a close-packed alloy with Si as the Ti-Si partial coordination is so high. The total Ti coordination drops to 10 in the range 0.44 ≤ x ≤ 0.54, in line with the crystal data, but then must rise again as Ti metal is 12 fold coordinated.

The idea that the Ti environment remains close-packed while Si evolves from 4 to 10 or 12 fold coordinated suggests that there is indeed a pure a-Si phase with an increasing proportion of an amorphous SiTi alloy forming as Ti content increases. The same behaviour has been noted by Edwards et. al. in the a-SiNi:H system\(^6\)\(^6\). However, it is not possible to describe the behaviour of these phases with composition in any detail without more samples to fill in the gaps in the composition range. Samples are required in the important 0.10 < x < 0.15 region where the two phases are expected to occur in similar quantities and hence give the largest possible second maximum in the SAXS spectrum.

Guinier analysis of SAXS data also revealed the presence of widely separated inhomogeneities, of approximately 35Å in size with characteristics invariant across the composition range. This leads us to attribute the scattering in the Guinier region to neutral inclusions of Ar atoms introduced during the sputtering process, as opposed to chemically dependant inhomogeneities such as phase segregation. Conclusive results can only be obtained by performing anomalous-SAXS\(^6\)\(^7\) which scans the energy of the incident X-ray beam through an absorption edge, allowing the contribution of each element to the scattering pattern to be identified.

A study of the chemical ordering of our samples using two methods yielded positive results. The first method used partial coordination numbers to calculate bond energies (Equation 6.4) in such a way that no assumptions need be made about the total coordination. It was found that in the Si rich regime there is probably no chemical ordering and the bonding is essentially random. As Ti is added, the bonds become more polarised with the Si-Ti bond favoured. This transition appears to happen quite smoothly.

The second method used total coordination numbers to set up two bond-order models; total ordered bonding and total random bonding. The resulting partial coordinations were plotted on the same axis as the experimental results for
comparison. The above observation of increasing chemical order with increasing $x$ was confirmed. It is easiest to spot a trend in bonding from a plot of the Ti partial coordinations because the expected values from the bond models have their largest difference where most of our samples are, i.e. at low Ti content. It can be seen that there is a gradual shift from random to ordered bonding with increasing $x$. It is worth noting that the crystals tend towards ordered bonding, as expected, which is a useful check on the validity of our models.

The above results are perhaps surprising in that the degree of chemical order usually decreases with metal content because the increased number of free electrons should act to screen the Coulomb potential of individual atoms. There is obviously another bonding mechanism involved in this $\text{a-Si}_{1-x}\text{Ti}_x$ system.

We report a metal-insulator transition occurring at around 6 at.% Ti for $\text{a-Si}_{1-x}\text{Ti}_x$. This is much lower than the critical concentration ($N_c$) found in other similar systems, e.g. $\text{a-SiAu}$ where $N_c = 14$ at.% Ni$^{14}$, $\text{a-SiMn}$ has an $N_c$ of 17 at.% Mn$^{19}$ and $\text{a-SiFe}$ is reported to undergo the MIT at 16 at.% Fe$^{20}$. This discrepancy is probably due to the errors associated with the lack of data points in our optical study. It is worthy of note, however, that a MIT induced when regions of a conducting phase reach a percolation threshold is likely to occur at a lower concentration than would otherwise be expected.

We have found no variation in bond length in $\text{a-Si}_{1-x}\text{Ti}_x$ to correlate with this change in electronic state. We have, however, found a change in Si coordination number around this composition, consistent with the appearance of conducting pockets of an amorphous Si-Ti alloy embedded in a semiconducting a-Si phase. The conjecture is that the MIT in our samples occurs when these pockets interconnect at a percolation threshold. This argument is discussed in depth by Regan and Bienenstock$^{6,4}$ who invoke a percolation argument rather than an Anderson transition model to explain the MIT transition in samples of $\text{a-Ge}_{1-x}\text{Fe}_x$. 

Chapter 6: Structure in $\text{a-Si}_{1-x}\text{Ti}_x$
6.5 Conclusion

We have set out to characterise the short and medium range structure of a-Si$_{1-x}$Ti$_x$ and in so doing perhaps arrive at a better understanding of the metal-insulator transition. An attempt was made to use the atomic simulation code, RMC, but failed because of weak data allowing the 'atoms' to move to unphysical positions. Analysis of structural data has therefore been exclusively carried out using EXCURV92.

Optical spectroscopy was used to determine the critical metal content at which the MIT occurs and was found to be at 6 at% Ti.

The Si-Si bond length was found to be 2.35Å with an associated Debye-Waller factor of $45 \times 10^{-4} \text{Å}^2$, in agreement with crystal data. Both the Si-Ti and Ti-Ti bond exhibit a large degree of static disorder with Debye-Waller factors of 190 and $130 \times 10^{-4} \text{Å}^2$ respectively. Chemical order was found to increase from a random system at low Ti content to a state where the Si-Ti bond is highly favoured at higher $x$.

We report that Ti atoms are surrounded by 2 Ti atoms at 2.80Å and between 8 and 10 Si atoms at 2.64Å across the composition range. Therefore, Ti exists only as a close-packed alloy within our samples. The Ti-Si bond length is equal to the sum of the covalent radii and was found to be consistent with Si edge data.

Si is four-fold coordinated at low Ti content ($x \leq 0.19$), rising slowly to 9 fold at $x = 0.54$ and potentially becoming close-packed at metal-rich compositions. This indicates that Si co-exists as a tetrahedral random network and as an a-SiTi alloy, the former in diminishing quantities as Ti is added. This idea is supported by results from our SAXS experiments where evidence indicating the presence of two phases at low Ti content was found. If this is the case then a percolation theory of interconnecting conducting regions of a-SiTi would have to be considered as a model of the MIT.
6.6 References


6.9 As 6.7, p209

6.10 As 6.7, p219


Chapter 7

Short And Medium Range Structure In Amorphous
$\text{Si}_{1-x}\text{Ni}_x$

7.1 Introduction

Transition metal silicides have been studied in depth to enhance the understanding of the metal to insulator transition (MIT) and because of their potential device application. As device dimensions decreased, it became clear that the resistance of conductors fabricated from polycrystalline silicon would become too high. The resistivity of pure silicon can be varied across a large range, however, by progressively adding metal and hence the tailoring of its conductive properties becomes possible.

The electronic behaviour of the $\text{a-Si:}\text{Metal}$ system has been studied in depth, although ideas about the mechanism of the MIT are changing and the value of critical metal content, $N_c$ at which it occurs, is not well defined. Under the condition that metal atoms substitute randomly into the tetrahedral random network (TRN) of amorphous silicon, the MIT can be thought of in terms of the extension of the extension of localised states. It was originally assumed that these amorphous materials were structurally homogeneous but recent investigations have shown that inhomogeneities exist, upsetting the idea of a random distribution and hence a percolation theory may be more appropriate to model the MIT.

Studies performed on $\text{a-Si}_{1-x}\text{Ni}_x$ generally agree that the MIT occurs at between 10 and 20 at.% Nickel, although Rogachev et. al. has noted a dramatic decrease in the width of the optical band gap after addition of only 5 at.% nickel.
Investigations into the atomic structure have been carried out by two groups\textsuperscript{7,8}, both of whom find that the inclusion of Ni into a-Si leads to local re-ordering of the TRN and suggest clusters of a separate NiSi\textsubscript{2} phase form within a-Si\textsubscript{1-x}Ni\textsubscript{x}:H, implying that a percolation model would indeed be an appropriate description of the transport behaviour. This conclusion has been reinforced with SAXS experiments performed on the same system\textsuperscript{9}.

Originally, a detailed understanding of the local atomic structure of a material was necessary to fathom the MIT. It now looks as though an understanding of the mid-range structure is equally important. It is with this in mind that we present here the combined results from EXAFS and SAXS experiments performed on a series of a-Si\textsubscript{1-x}Ni\textsubscript{x} samples, where 0.12 \( \leq x \leq 0.74 \).

### 7.2 Data Analysis

#### 7.2.1 EXCURV92

Ni K-edge data was of a high quality, with a large k-range of 1-15 Å\textsuperscript{-1} for all samples, enabling two coordination shells to be reliably fitted to the data. EXAFS spectra taken from each sample for this edge are shown in Figure 7.1. It is worth noting that the phase and amplitude of the EXAFS signal is constant across the composition range, indicating an unchanging Ni environment. Fit indices of 25 were not uncommon. The amplitude factor, AFAC, which corrects for events such as multiple excitations, was fixed at 0.8 by assuming four-fold coordination in the a-Si sample. Hedin-Lundqvist exchange potentials were used.

Si K-edge data was of considerably poorer quality, probably due to the surface sensitive total electron yield method used on Station 3.4, so that the working k-range was, on average, 1-11 Å\textsuperscript{-1}. Fit indices of around 45 were normal. Despite the poor data, a two shell fit was found to be appropriate for all but two samples: \( x=0.12 \) and 0.22. AFAC was set at 0.9 and Hedin-Lundqvist exchange potentials were used.
Figure 7.1 Ni K-edge EXAFS signal from each of the a-Si<sub>1-x</sub>Ni<sub>x</sub> samples studied (solid line). The theoretical fit is shown as a dashed curve. Of note is the similar phase and amplitude between spectra, suggesting an unchanging Ni environment across the composition range.

7.2.2 RMC

A configuration size of 512 atoms was chosen, allowing structure to be modelled to a maximum \( r \) of 10Å. This relatively small configuration gave convergence times of the order of 3 hours but necessitated averaging of ten converged configurations, separated by 512 accepted moves, to compensate for the associated increase in statistical uncertainty.

The standard experimental error, \( \sigma^2 \), was used to reflect the relative qualities of each data set, allowing the partial \( \chi^2 \) to reach equal magnitudes. Hence a \( \sigma^2 \) of 0.1 and 1.0 was used for Si and Ni edge data respectively. The Ni edge \( \sigma^2 \) was reduced to 0.1 to achieve final convergence.

The density was chosen using the minimum \( \chi^2 \) method described in Section 4.6. The results are presented in Figure 7.2 and show that the density increases from 0.065 to 0.075 atoms/Å\(^3\) with increasing metal content.
Cut-off distances were set at 2.3, 2.1 and 2.4 Å for Si-Si, Si-Ni and Ni-Ni nearest neighbour coordinations respectively.

Analysis via the RMC method could only be successfully performed on samples within the composition range $0.12 \leq x \leq 0.28$ i.e. low metal content. This is probably because atoms find it hard to move past each other at the higher densities. It is also likely that the degree of bond ordering plays a part; RMC produces configurations with the maximum degree of disorder consistent with the data and therefore finds it difficult to introduce chemical order.
7.3 EXAFS Results

7.3.1 Coordination Numbers

<table>
<thead>
<tr>
<th>Ni content, at.% Ni</th>
<th>N_{SiNi} ± 0.5</th>
<th>N_{NiSi} ± 1.0</th>
<th>N_{NiNi} ± 0.5</th>
<th>N_{SiSi} ± 0.5</th>
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</thead>
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<td>0.3</td>
<td>5.5</td>
<td>4.8</td>
<td>6.2</td>
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</table>

Table 7.1 Partial coordination numbers for Si and Ni K-edge data. The large error for N_{SiSi} reflects the lower quality EXAFS data for the Si edge.

Partial coordination numbers obtained from EXCURV92 analysis are shown in Table 7.1. The number of Si-Ni bonds should be the same whether viewed from a Si or a Ni atom, i.e. the coordination numbers should be consistent, after taking account of the relative concentration of each atomic species so that (1-x)N_{SiNi} = xN_{NiSi}. These values were therefore plotted (Figure 7.3) to check the consistency between edges; this appears to worsen with increasing metal content, but is generally acceptable.

Figure 7.3 Plot of the values (1-x)N_{SiNi} (crosses) and xN_{NiSi} (circles). The dashed line represents the set of values consistent with both data sets, biased towards the stronger Ni edge data.
The Ni edge data follows a well defined curve while Si coordinations are erratic, probably due to the short range and poor quality of the Si edge data. By employing the method outlined in Section 6.3.1, the stronger Ni edge data can be used to suggest values for $N_{\text{SiNi}}$. The results of these calculations are shown below in Table 7.2.

<table>
<thead>
<tr>
<th>Ni content, at.% Ni</th>
<th>$N_{\text{SiSi}}$ ± 0.5</th>
<th>$N_{\text{SiNi}}$ ± 1.0</th>
<th>$N_{\text{NiSi}}$ ± 1.0</th>
<th>$N_{\text{SiNi}}$ ± 0.5</th>
<th>Total $N_{\text{Si}}$</th>
<th>Total $N_{\text{Ni}}$</th>
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<td>6.2</td>
<td>9.1</td>
<td>9.3</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 7.2 Consistency corrected coordinations. The final column shows results from a bond energy calculation, where increasing values with increasing metal content indicate chemical ordering is taking place.

Also shown, in the right most column of Table 7.2, are the results from a numerical test for the degree of chemical order within each sample.

The difference in bond energy for each atomic species, $\Delta E$ can be calculated using the expression

$$e^{-2\Delta E/k_BT} = \frac{N_{\text{SiSi}}N_{\text{NiNi}}}{N_{\text{SiSi}}N_{\text{NiNi}}} \quad (7.1)$$

For $e^{-2\Delta E/k_BT} = \infty$, $\Delta E = \infty$ and the Si-Ni bond is preferred, i.e. chemical ordering is complete. For $e^{-2\Delta E/k_BT} = 0$, like-like bonds are preferred because the change in bond energy is unfavourable. If the exponential is unity, the bonding is random. The theory behind Equation 7.1 is explored in Appendix 2. The tabulated results show a clear trend of increasing AB order with increasing Ni content.
Partial and total Si coordinations are plotted in Figure 7.4 with the theoretical values obtained from the ordered and random chemical bonding models described in Appendix 1.

Total Si coordination remains four-fold for $0.12 \leq x \leq 0.28$, indicating the presence of a tetrahedral random network (TRN) where Ni substitutes for Si in the matrix. Above this composition regime the total Si coordination jumps to around 8, remaining at this value for all subsequent samples. By inspection of Figure 7.4(b), it is clear that this is due to the Si-Si partial coordination rising to four-fold again at $x = 0.42$ while $N_{\text{SiNi}}$ continues rising to $8.0 \pm 2.0$, implying a close-packed structure. Asal et al. have found that $N_{\text{SiNi}}$ reaches no higher than four in the a-Si$_x$Ni$_y$ system.
By comparison with the bond order models, it appears that the samples are partially chemically ordered.

Figure 7.5 Coordination numbers from Ni K-edge EXAFS data. (a) Total Ni coordination. The solid line represents coordination used to calculate bond order models. (b) Ni-Si partial coordination. (c) Ni-Ni partial coordination. Ordered (solid line) and random (dashed line) bonding models are shown in (b) & (c). Also shown are results from RMC (circles).

Figure 7.5 shows total and partial Ni coordination numbers. As anticipated from the pure EXAFS signals from this edge (see Figure 7.1), the Ni environment changes little over the entire composition range. Significant change is only observed in the most Ni rich sample. For $0.12 \leq x \leq 0.61$, each metal atom has approximately 7 nearest neighbours of Si and 2 Ni near neighbours. This high figure suggests that Ni exists within a close-packed structure, possibly an amorphous Ni-Si alloy.
Bond preference clearly moves from random to ordered with increasing $x$, supporting the results from the bond energy calculations performed above.

The RMC method was successfully applied to the three samples where $x \leq 0.28$. Coordination numbers for these samples generally agree well with the EXCURV92 results (with the exception of $N_{\text{SiSi}}$ at $x = 0.12$): $N_{\text{SiNi}}$ and $N_{\text{NiNi}}$ values found via RMC are identical to those found using EXCURV92. A slight discrepancy is noted between values of $N_{\text{NNi}}(\text{RMC})$ and $N_{\text{NNi}}(\text{EXCURV92})$ for $0.12 \leq x \leq 0.28$; the former increases steadily from $1.0 \pm 0.5$ to $2.0 \pm 0.5$, while the EXCURV92 result remain constant at $2.0 \pm 0.5$. The values do lie within each others error regime, however.

The RMC method successfully modelled samples that were known to be randomly bonded, understandable in that configurations are generated through a random selection process which maximises the disorder within the confines of the data. Difficulties were encountered when analysing partially ordered samples. An inherent limitation of the algorithm appears to be an inability to introduce chemical order, at least when EXAFS data is being modelled alone.

### 7.3.2 Interatomic Distances

Inspection of Figure 7.6 shows that the Si-Ni bond length is consistent between edges, indicating that the appropriate atom has been chosen under EXCURV92 analysis. This bond was found to be a constant length across the composition range at $2.34 \pm 0.01 \text{ Å}$, in good agreement with Asal et. al. who report a value of $2.33 \text{ Å}$ for this bond in the a-Si$_{1-x}$Ni$_x$H system and also with Edwards et. al. who find $R_{\text{SiNi}}$ to be $2.35 \pm 0.02 \text{ Å}$ for the same system. It must also be noted that the Si-Ni bond length in c-NiSi$_2$ is quoted as $2.34 \text{ Å}$ and that the Si-Ni bond length is similar in c-NiSi at $2.29 \text{ Å}$.

The Ni-Ni bond was found to be $2.54 \pm 0.02 \text{ Å}$ for $x \leq 0.28$, slowly decreasing to $2.47 \pm 0.02 \text{ Å}$ at $x = 0.56$, which is comparable to the metallic Ni value of $2.49 \text{ Å}$. This is in agreement with Asal et. al and Edwards et. al. For greater metal concentrations, however, we find this bond length returns to $2.54 \text{ Å}$ while Asal et. al.
report that it maintains a value characteristic of metallic Ni. This discrepancy could be
due to the presence of a different phase.

Figure 7.6 Interatomic distances in a-Si$_x$Ni$_{1-x}$ determined via EXCURV92. Si-Si distances are
marked with crosses, Si-Ni with triangles, Ni-Si with squares and Ni-Ni with diamonds.

The Si-Si bond length was found to increase steadily for $0.12 \leq x \leq 0.28$ from
$2.32 \pm 0.01$ Å (c.f. $R_{\text{Si-Si}}$ in a-Si of 2.34 Å) to $2.44 \pm 0.01$ Å. For $x > 0.28$, $R_{\text{Si-Si}}$
remains constant at 2.44 ± 0.01 Å. These results are entirely consistent with those
reported by Asal et. al. and Edwards et. al. The unusual behaviour of this bond may
be understood in terms of electrostatic repulsion of Si atoms if charge transfer from Ni
occurs. Alternatively, an a-Si$_x$Ni alloy with a larger Si-Si interatomic distance may be
appearing. Evidence to support the latter argument is provided by the SANS results.

7.3.3 Debye-Waller Factors

The mean square deviations in the nearest-neighbour distances, $\sigma^2$, are shown
in Figure 7.7. The Si-Si Debye-Waller factor increases from $60x10^4$ Å$^2$ to $140x10^4$
Å$^2$ within the composition range 0.12 $\leq x \leq 0.28$ and decreases to a constant $30x10^4$
Å$^2$ for $x \geq 0.48$. A room temperature thermal contribution to the Si-Si Debye-Waller
factor of $40x10^3$ Å$^2$ [17][12] suggests that there is a large degree of static disorder at low
metal content, while thermal effects dominate at metal rich compositions.

The Si-Ni Debye-Waller factor remains constant at $100x10^4$ Å$^2$ across the
composition range, with consistency between values obtained from both edges. The
room temperature thermal contribution to $\sigma^2$ for the Si-Ni bond, as calculated using a
method proposed by Cyrin\textsuperscript{7.13} with a stretch frequency of 680 cm\textsuperscript{-1}, is equal to 30\times10^{-4} \text{Å}^2, indicating a significant degree of static disorder in this bond.

Using the Debye theory\textsuperscript{7.14} to calculate the room temperature thermal contribution to $\sigma^2$ for the Ni-Ni bond, with a Debye temperature of 450 K\textsuperscript{7.15}, we arrive at a value of 42\times10^{-4} \text{Å}^2. We measured the mean square deviation in this bond to be 150\times10^{-4} \text{Å}^2, indicating a large degree of static disorder.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{debye_waller_factors}
\caption{Debye-Waller factors for a-Si\textsubscript{x},Ni\textsubscript{1-x}.}
\end{figure}
7.3.4 Small-Angle X-Ray Scattering Results

Figure 7.8(a) shows the background subtracted, normalised SAXS profile from seven of the samples studied, all of which display a large peak at \( k = 0.030 \, \text{Å}^{-1} \), truncated at low \( k \) by the beam stop.

The relative amplitude of this Guinier peak gives an idea as to the relative number of scattering bodies incorporated in each sample. This is independent of composition suggesting the presence of voids introduced during fabrication, as void characteristics are a function of deposition conditions rather than chemical composition. Guinier analysis\(^7\)\(^6\) show these inhomogeneities to have a radius of \( 45 \pm 5 \, \text{Å} \), for all compositions.

Samples in the range \( 0.12 \leq x \leq 0.48 \) also show a second peak at higher \( k \). This is caused by interference of X-rays scattered from non-disperse regions of contrasting electron density, e.g. between void and matrix or between regions of different phase. The relative amplitude of the observed second peak is composition dependent, suggesting that separation of the sample into distinct phases is taking place.

The chemical composition of each phase can be inferred from an end-point analysis (see Section 2.3.5.1), shown in Figure 7.8(b). The peak at 20-30 at.\% Ni indicates the presence of two phases in similar quantities, while the disappearance of the peak at \( \sim 50 \) at.\% Ni points towards a single phase of a-NiSi. These results suggest the co-existence of a-NiSi and a-Si in the composition range \( 0.12 \leq x \leq 0.48 \).

The angular position of the second peak, \( k_p \), is related to the correlation length, \( L_c \), of the scattering bodies by \( L_c = 2\pi/k_p \). This distance moves abruptly from \( 0.19 \, \text{Å}^{-1} \) to \( 0.16 \, \text{Å}^{-1} \) between samples containing 22 and 28 at.\% Ni respectively, corresponding to a change in correlation length from 33Å to 40Å. However, the shift is so small that it would be tenuous to link it to a physical event.
Figure 7.8 (a) SAXS pattern from samples of a-Si$_x$Ni$_{1-x}$ mounted on aluminium foil. Data has been background subtracted and corrected for the detector response. The sample where $x = 0.61$ has been divided by a factor of 4, for clarity. (b) End-point analysis of second peak in (a), where height is plotted against composition. The curve reaches zero at $x = 0.50$, suggesting that the samples contain a-NiSi alloy.

7.3.5 Optical Studies

We have measured the optical absorption spectrum of all samples with the aim of identifying the concentration at which a-Si$_x$Ni$_{1-x}$ ceases to be semiconducting and becomes metallic, recognised as the point at which the optical band gap closes. By measuring the absorption at optical wavelengths, the size of the band gap can be characterised; an absorption edge indicates the presence of a gap whereas constant absorption in this range implies a continuum and hence metallic behaviour. Two samples were found to display absorption edges, a-Si and the sample containing 12 at.% Ni, while flat, featureless curves were observed for all samples where $x \geq 0.22$. This implies that samples at and above 22 at.% Ni are metallic. The position of the MIT can be found by quantifying the gap in one of two ways;
The energy when \( \alpha(E) \) falls to a value of \( 10^4 \text{ cm}^{-1} \) is taken, denoted by \( E_\alpha \). This is shown as the dashed line in Figure 7.9(a) and gives values of \( 1.4 \pm 0.2 \text{ eV} \) and \( 0.1 \pm 0.2 \text{ eV} \) for a-Si and a-Si\(_{10.8}\)Ni\(_{0.12}\) respectively. The gap in crystalline Si is usually quoted as \( 1.2 \text{ eV} \), in agreement with that found for a-Si, although a slightly smaller band gap is expected in amorphous solids in relation to their crystalline counterparts because of disorder induced tailing of states into the gap.

Figure 7.9  
(a) Absorption coefficient vs. energy for the two samples where transmission was non-zero. \( E_\alpha \) is shown as the dashed line which intercepts the curve at 1.4 eV. The curve for \( x = 0.12 \) is extrapolated to \( 10^4 \text{ cm}^{-1} \) to obtain an \( E_\alpha \) of 0.1 eV. (b) Tauc plot of absorption coefficients showing the shift to lower energies on addition of metal. (c) Plot of energy gap vs. composition (\( E_\alpha \) as crosses, \( E_{\text{ex}} \) as diamonds). The lack of data points makes the relationship between the two difficult to predict. Under the assumption of a linear decrease in energy, the gap appears to close at \( x = 0.13 \pm 0.02 \).
(ii) Tauc analysis can be applied (see Section 3.3.3.2), where \((\propto x(E))^2\) vs. \(E\) is plotted, so that the intercept on the x-axis gives a value, \(E_{\text{tuc}}\), for the gap. This was found to be 1.3 ± 0.2 eV and 0.2 ± 0.2 eV for a-Si and a-Si$_{0.88}$Ni$_{0.12}$ respectively. The theory behind the Tauc gap assumes parabolic band edges, which may not be the case, especially when the band is very narrow so that band tails may overlap. For this reason, \(E_{\text{ad}}\) is preferred as a measure of the band gap. Values of the band gap are plotted in Figure 7.9(c) against composition in order to determine the position of the MIT. If a linear dependence of \(E_{\text{ad}}\) on \(x\) is assumed, the MIT is expected to occur at 13 ± 2 at.% Ni. More data points are necessary if the error is to be reduced.

7.4 Discussion

Ni K-edge data show that Ni atoms are surrounded by 7.0 ± 0.5 Si atoms at 2.34 ± 0.01 Å and 2.0 ± 0.5 Ni atoms at 2.54 ± 0.02 Å. These high coordination numbers imply that Ni does not substitute into the tetrahedral random network of a-Si as previously thought but exists only within the close packed structure of an amorphous Ni$_x$Si$_{1-x}$ alloy. However, Si K-edge data show Si as being four-fold coordinated at low metal content, consistent with the idea of a tetrahedral random network. These observations can be reconciled by invoking the idea of a two-phase system, with an a-Si: Ni alloy growing within an a-Si matrix. This idea is supported by results from the SAXS study which clearly show the presence of two non-disperse scattering media, of which one steadily increases in abundance until it dominates the sample at \(x = 0.50\). This behaviour would be exhibited by samples containing regions of the phase NiSi within an a-Si network. Crystalline NiSi alloys have been observed to form from the melt\(^{2,17}\). We found no evidence of crystallisation (i.e. no second peaks in the Fourier transform of the EXAFS spectra) at any composition, confirming that all phases present are amorphous.

Another group (Edwards et. al.\(^{7,17}\)) working with the a-Si$_{1-x}$Ni$_x$:H system have observed the clustering of Ni atoms in the form of an amorphous Ni:Si alloy and find
strong evidence to suggest this alloy is a-NiSi₂. We report similarities in bond length and coordination number with those reported by Edwards et. al. and with the tabulated values for c-NiSi₂:

<table>
<thead>
<tr>
<th></th>
<th>c-NiSi₂ (^{7,10})</th>
<th>Edwards et. al.(^{7,11})</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Si bond length</td>
<td>2.34 Å</td>
<td>2.34 Å</td>
<td>2.34 Å (extrapolated to 33 at.% Ni)</td>
</tr>
<tr>
<td>Si-Ni coordination</td>
<td>4</td>
<td>-</td>
<td>2.5 (for 0.12 ≤ x ≤ 0.14)</td>
</tr>
<tr>
<td>Ni-Si coordination</td>
<td>8</td>
<td>8.3 (≈ 29 at.% Ni)</td>
<td>7.0 (for 0.12 ≤ x ≤ 0.14)</td>
</tr>
</tbody>
</table>

This alerts us to the possibility that an a-NiSi₂ phase may exist in our samples.

The above discussion gives two (rather simplistic) models for the chemical homogeneity of our samples; a) that there are a-NiSi regions present within a bulk a-Si network at all compositions, or b) that regions of a-NiSi₂, a-NiSi and a-Si exist in various quantities at appropriate compositions.

Both models are illustrated in Figure 7.10.

Figure 7.10 Representation of two possible models of the chemical homogeneity in samples of a-Si\(_{1-x}\)Ni\(_x\). The vertical scale represents the relative quantity of each phase.
The change in correlation length of the scattering bodies observed between the $x = 0.28$ and $x = 0.42$ samples may be associated with the change in composition of the Ni containing phase at 33 at.% Ni if model (b) is adopted.

Model (a) can be tested against experiment through bond energy calculations. Under the assumption of complete phase separation into a-Si and a-NiSi, the relative quantity of each phase at a given composition, $x$, is expressed as

\[
\begin{align*}
\text{Si} &= (1-2x) \\
\text{NiSi} &= x
\end{align*}
\]

for $x < 0.5$

Hence the expected partial coordinations are obtained

\[
\begin{align*}
N_{\text{SiSi}} &= \frac{4(1-2x)+2x}{1-x} \\
N_{\text{NiSi}} &= \frac{8x}{1-x} \\
N_{\text{NiNi}} &= 2
\end{align*}
\]

These partial equations substitute into Equation 7.1 to give

\[
e^{-\frac{2ME}{k_BT}} = \frac{64x}{8-12x}
\]

When these values are compared with the experimental values shown in Table 7.1, good agreement between the two data sets is observed, as shown in Figure 7.11. This implies that the coordination numbers are consistent with the idea of phase separation of our samples into a-Si and a-NiSi for compositions of less than 50 at.\% Ni.
Figure 7.11 Experimental and theoretical bond energy calculations. The y-axis represents the exponential term in Equation 7.1 and reflects the preference for the Si-Ni bond. The crosses show the trend in bond preference from random towards chemical ordering with increasing metal content in samples of a-Si$_{1-x}$Ni$_x$. The solid curve shows the expected value of the exponential if partial coordinations are calculated from a completely phase separated model. The clear similarity shows that the experimental partial coordinations uphold the idea of the coexistence of a-Si and a-Ni$_x$Si$_{1-x}$ for $x \leq 0.05$.

It is not clear how the presence of phase separation will affect the MIT. We observe this event at 13 at.% Ni, in good agreement with the work of Dammer et. al., on the same system, who report a transition at 18 at.% Ni. No significant structural changes were observed around this composition range, expected if a traditional model of the MIT is applicable, although the lack of data points around this highly significant composition prevents a concrete conclusion from being drawn.
7.6 Conclusion

We have used optical spectroscopy to measure the extent of the band gap in a series of a-Si<sub>x</sub>Ni<sub>y</sub> samples and found that around 13 at.% Ni was enough to induce a MIT. An EXAFS study undertaken on these samples show an increase in the Si-Si bond length from 2.34Å to 2.44Å across this composition range (0 ≤ x ≤ 0.28). We attribute this to the appearance of a discrete a-Si:Ni phase rather than the interstitial occupancy or substitution of Si atoms by Ni in a TRN. Evidence is provided by a high Ni coordination, suggesting that Ni exists only in a close-packed alloy of Si-Ni, and a Si-Ni distance characteristic of this bond in c-NiSi<sub>2</sub>. Further evidence is supplied by a complementary SAXS study which reveals the presence of two phases, possibly a-Si and a-NiSi<sub>2</sub>. Evidence for two phases in the a-Si<sub>x</sub>Ni<sub>y</sub>H system has been reported by Edwards et. al. Other reports suggest that the MIT occurs at a higher metal content if there is no separation of phase.

These results suggest that a percolation theory describing the connectivity of regions of a conducting a-Si:Ni alloy within an a-Si matrix is a more appropriate model of the MIT than the traditional Anderson model.

Results from bond energy calculations and fits to bond order models indicate a shift from random to chemically ordered bonding with increasing Ni content and are consistent with values expected if two distinct phases of a-Si and a-NiSi coexist in the material. Chemical ordering at metal rich compositions is probably why an RMC analysis failed in this composition range.
7.7 References

7.1 Morigaki, K., 1980, Phil. Mag. B., 42, 979
7.5 Dammer, U., Adkins, C.J., Asal, R. & Davis, E.A., XX
7.9 Rigden, J.S. & Newport, R.J., Unpublished
7.11 As 7.10, 15, 107
7.15 As 7.14, p219
Chapter 8

A Structural Study Of Amorphous Ge$_{1-x}$Ni$_x$

8.1 Introduction

Amorphous metal-germanium films have been the subject of much interest recently, not only because of the potential technological applications but also to gain an understanding of the metal-insulator transition (MIT) that is known to occur in such systems$^{1,2}$. The MIT can be induced by increasing the proportion of metal in the sample above a certain critical limit, the exact composition depending on the structure of the system. Many view these materials as homogeneous, undergoing a continuous structural transition as the proportion of metal atoms is increased, allowing the MIT to be described in terms of an Anderson transition where electrons at the Fermi level become delocalised and extended state conduction can occur. In contrast Regan et. al.$^{3,4}$ have presented ASAXS observations that indicate the MIT in metal-germanium films proceeds by the percolation of an intermetallic phase. Kortright and Bienenstock$^{5,6}$ have inferred from a structural study of a-Ge$_{1-x}$Mo$_x$ that their films are not homogeneous but consist of a Mo modified germanide phase within an a-Ge matrix. An EXAFS study of a-Ge$_{1-x}$Au$_x$ films undertaken by Edwards, Fairbanks and Newport$^{7,8}$ indicates the presence of a Ge-Au alloy embedded in an amorphous Ge host network for x < 0.20 and these authors suggest that the conductivity of the
sample is best interpreted using a percolation theory. They have recently confirmed
their results with a SAXS study of the same system.5

To illuminate further the structural changes accompanying and mechanisms
responsible for the MIT, we present a study of the short and medium range structure
present in RF sputtered samples of a-Ge<sub>x</sub>Ni<sub>y</sub> for 0 ≤ x ≤ 0.67, using the techniques of
EXAFS and SAXS. This system was the subject of an EXAFS investigation by
Oyanaki, Tsuji and Hosaya in 1980 using a laboratory source to probe the Ge K-
edge only. They also present neutron diffraction results to complement this study,
which will be used for comparison purposes later in this chapter. A conductivity study
of the system has been undertaken by Wright who estimates that the MIT occurs at
8-10 at.-% Ni.

8.2 Details of Analysis

The similarity of Ge and Ni scattering factors presents serious difficulties in
analysing EXAFS data from this system. Near-neighbours are identified, in theory, by
the characteristic phaseshift of the photoelectron as it passes through the potential of
the atom. In practice, phaseshifts can only be reliably resolved if the difference in
atomic number, Z, between two species is greater than -10, and becomes almost
impossible for ΔZ < 5. ΔZ for Ge-Ni is 4. The problem is compounded by the similar
covalent radii (1.23Å and 1.25Å for Ge and Ni respectively). These difficulties can
be overcome by careful observation of interatomic distances and coordination
numbers.

8.2.1 EXCURV92

Typical Ge and Ni K-edge EXAFS spectra, accompanied by their phase-
corrected Fourier transforms are shown in Figure 8.1. Data from both edges was of
good quality, extending over the range 1-15 Å<sup>-1</sup> for all samples. A Ni foil was used to
estimate AFAC for Ni as 0.8 and this value was applied during the analysis of other Ni
K-edge spectra. The a-Ge samples was used to fix AFAC at 1.0 for Ge K-edge
calculations by assuming a near-neighbour coordination of four. (For the definition of
AFAC, see Section 2.2.3.1.) Hedin-Lundqvist exchange potentials were used during analysis of both edges.

Figure 8.1 (a) EXAFS spectrum, with $k^2$ weighting, taken from the Ge K-edge of a-Ge$_{1-x}$Ni$_x$, where $x=0.39$, with the phase corrected Fourier transform shown in (b). (c) & (d) show the EXAFS signal and Fourier transform from the Ni K-edge of the same sample. The larger amplitude of the Ni edge EXAFS spectrum means Ni probably has a higher total coordination than Ge. The dashed line in each figure represents the theoretical fit to the data using EXCURV92. The lack of a second peak in (b) and (d) confirms the amorphous nature of our samples.

Because of the difficulty in distinguishing Ge and Ni atoms, data from the Ge edge of low metal content samples were fitted first so that interatomic distances could be used to suggest a shell composition. A single shell with a characteristic Ge-Ge distance was found to be appropriate for $0 \leq x \leq 0.12$. For $0.14 \leq x \leq 0.33$, two shells were identified by interatomic distance, one of Ge and the other Ni. (For this reason, bond lengths are presented first in this chapter.) The criterion used for a two-shell fit was that a second shell must decrease the fit index by 10% or more for it to be meaningful. Consistency between Ge-Ni and Ni-Ge bond lengths assisted the fitting of Ni K-edge data, where a two shell model of Ni coordinated by Ge and Ni atoms was appropriate for all samples. The number of Ge-Ni and Ni-Ge bonds in this composition range was used to check the validity of our assumption. Bond...
consistency was then used to fit Ge edge data for the remaining samples where \( x \geq 0.39 \).

### 8.2.2 RMC

![Graphs showing comparison of Ge and Ni edge EXAFS signals and radial distribution functions](image)

Figure 8.2  (a) Comparison of the Ge K-edge EXAFS signal (solid line) of a-Ge\(_{1-x}\)Ni\(_x\), where \( x = 0.39 \), with the spectrum obtained from RMC using a 512 atom configuration (dashed line). (b) Ni K-edge EXAFS signal from experiment (solid line) and RMC (dashed line). (c) Radial distribution functions obtained from the configuration of atoms produced by RMC. The high noise level is attributable to the relatively small number of atoms used in the simulation.

The RMC method was successfully applied to all samples, probably because good quality data was available for both edges. RMC should experience less difficulty in distinguishing Ge and Ni atoms than EXCURV92 because data from both edges is used simultaneously. It was also found that the majority of samples tended to be randomly chemically ordered, a feature which is particularly suited to the method as this random element is at the heart of the algorithm.

A configuration size of 512 atoms was used. This required ten converged configurations, separated by 512 accepted moves, to be averaged to reduce statistical
uncertainty. A standard error, $\sigma^2$, of 0.1 was used for both edges, reflecting the high quality of data. Closest approach values of 2.25Å, 2.2Å and 2.35Å were used for Ge-Ge, Ge-Ni and Ni-Ni interactions respectively. A typical fit to the data is shown in Figure 8.2.

![Figure 8.2](image)

A typical fit to the data is shown in Figure 8.2.

![Figure 8.2](image)

The RMC method requires a value for the density as a parameter of the fit. This quantity is difficult to obtain experimentally for thin films, so RMC itself was used to calculate a value using the method of Gereben and Pusztai. Figure 8.3 shows the effect on the fit index, $\chi^2$, as the density is varied. A clear minimum is observed in each curve and this is taken as the 'correct' value.

8.3 Results

8.3.1 Interatomic Distances

Figure 8.4(a) shows the presence of a constant bond length of 2.46 ± 0.01 Å for $x \leq 0.33$, obtained using the RMC and EXCURV92 methods of data analysis. Oyanagi et al. report a Ge-Ge bond of this length in samples of a-Ge$_x$Ni$_{1-x}$, and many other authors report a similar distance in samples of a-Ge. We therefore infer that
this shell is composed of Ge atoms. For compositions greater than 33 at.\% Ni, EXCURV92 did not detect a Ge-Ge bond, consistent with the fact that no Ge is observed in the first coordination shell of any of the known crystalline germanide phases.\textsuperscript{8,11} The RMC method predicts a short Ge-Ge distance of $2.35 \pm 0.05 \text{\AA}$ for $x \geq 0.33$ which supports the EXCURV92 results and gives an important insight into the RMC algorithm itself; Ge is defined in the configuration of atoms used by RMC. When given data which suggests that Ge is not present, the algorithm tries to reduce the calculated EXAFS signal from these atoms by concealing them within the Ni shell at $2.35 \text{\AA}$.

![Figure 8.4](image)

(a) Ge-Ge bond lengths calculated with EXCURV92 (crosses) and RMC (circles). (b) Ni-Ni bond lengths from EXCURV (crosses) and RMC (triangles). Ge-Ni interatomic distances are shown as diamonds (EXCURV92) and circles (RMC). Ni-Ge values are marked with squares.

A shell of atoms at $2.41 \pm 0.005 \text{\AA}$ from the Ge central atom (for all compositions) can be identified as Ni because of the similarity with the Ge-Ni bond length of $2.42 \text{\AA}$ in c-NiGe.\textsuperscript{8,12} A similar distance is observed in Ni K-edge data (also at all compositions), identifying this shell as Ge.
8.3.2 Coordination Numbers

EXCURV92 results in Figure 8.5(a) show the Ge environment as generally four-fold coordinated for $x \leq 0.39$, indicating the persistence of a tetrahedral random network (TRN) throughout this composition range. Figures 8.5 (b) & (c) reveal that this overall coordination is composed of Ge and Ni atoms in changing quantities. Ni coordination of Ge increases as $N_{\text{GeNi}}$ decreases, suggesting the substitution of Ni atoms for Ge into the TRN. Above 39 at.% metal, the coordination rises slightly to six-fold at $x = 0.53$. RMC results agree well with EXCURV92 for the total coordination number. The values are slightly higher than expected, due to the

![Figure 8.5](image)

Figure 8.5  (a) Total and partial coordinations (b,c) calculated from Ge K-edge EXAFS data using EXCURV92 (crosses) and RMC (circles). The expected partial coordinations from an ordered bonding model (solid line) and a random bonding model (dashed line) are shown.
The analytical methods differ, as expected, in the number and type of nearest neighbour. RMC suggests that partial coordinations are directly related to the quantity of Ni present, i.e. random bonding, whereas EXCURV92 indicates that Ni is surrounded by 5 Ge and 2 Ni atoms for all samples where $x \leq 0.53$. If the latter model is to be believed, this would point towards the clustering of Ni atoms in some form of Ge-Ni alloy.
The solid line in Figures 8.5(a) and 8.6(a) can be extrapolated to 12-fold coordination at very high metal content \(x = 1.0\), enabling the bond order models, described in Appendix 1, to be applied over the entire composition range. It appears that chemical ordering of bonds is predicted by EXCURV92 analysis, whereas random ordering is predicted by RMC.

<table>
<thead>
<tr>
<th>Comp. , (x)</th>
<th>(N_{GGe} \pm 0.3)</th>
<th>(N_{GeNi} \pm 0.3)</th>
<th>(N_{NGe} \pm 0.3)</th>
<th>(N_{NNi} \pm 0.3)</th>
<th>(N_{GGe Total} \pm 0.6)</th>
<th>(N_{Ni Total} \pm 0.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.1 (5.0)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.1 (5.0)</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
<td>2.3</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>0.08</td>
<td>3.2 (3.8)</td>
<td>- (0.5)</td>
<td>5.1 (6.0)</td>
<td>2.1 (0.2)</td>
<td>3.2 (4.3)</td>
<td>7.2 (6.2)</td>
</tr>
<tr>
<td>0.12</td>
<td>3.1 (3.3)</td>
<td>- (0.7)</td>
<td>5.3 (5.3)</td>
<td>1.6 (0.6)</td>
<td>3.1 (4.0)</td>
<td>6.9 (5.9)</td>
</tr>
<tr>
<td>0.14</td>
<td>2.3 (3.2)</td>
<td>0.3 (0.9)</td>
<td>4.2 (4.2)</td>
<td>1.2 (0.6)</td>
<td>2.6 (4.1)</td>
<td>5.4 (5.8)</td>
</tr>
<tr>
<td>0.33</td>
<td>1.8 (2.5)</td>
<td>2.4 (2.2)</td>
<td>5.4 (4.6)</td>
<td>1.7 (1.8)</td>
<td>4.2 (4.7)</td>
<td>7.1 (6.4)</td>
</tr>
<tr>
<td>0.39</td>
<td>-</td>
<td>4.1 (2.5)</td>
<td>5.7 (3.9)</td>
<td>2.5 (2.3)</td>
<td>4.1 (2.5)</td>
<td>8.2 (6.2)</td>
</tr>
<tr>
<td>0.53</td>
<td>-</td>
<td>6.5 (3.5)</td>
<td>5.5 (3.0)</td>
<td>1.3 (4.0)</td>
<td>6.5 (3.5)</td>
<td>6.8 (7.0)</td>
</tr>
<tr>
<td>0.67</td>
<td>-</td>
<td>5.4 (4.6)</td>
<td>2.7 (2.3)</td>
<td>3.6 (4.9)</td>
<td>5.4 (4.6)</td>
<td>6.3 (7.2)</td>
</tr>
<tr>
<td>1.00</td>
<td>-</td>
<td>-</td>
<td>12.0</td>
<td>-</td>
<td>12.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.1 Complete set of coordination numbers for a-Ge\(_x\)Ni\(_y\), calculated with EXCURV92. RMC coordinations are shown in brackets.
8.3.3 Debye-Waller Factors

Figure 8.7 shows the Debye-Waller factors for the various bonds in the samples. We report a value of 100x10^4 Å^2 for the Ge-Ge bond, which is twice the room temperature thermal contribution (RTTC), suggesting a large degree of static disorder in this bond. The same is true for the Ge-Ni bond where the RTTC is expected to be ~ 30x10^4 Å^2, compared with the experimental value of 100x10^4 Å^2. The Ni-Ni Debye-Waller factor exhibits a large spread about 60x10^4 Å^2, indicating a relatively small variation in this bond above the thermal vibration.

---

Figure 8.7 (a) Ge-Ge Debye-Waller factors (EXCURV92; crosses, RMC; circles). (b) Ge-Ni Debye-Waller factors calculated with EXCURV92 are shown as crosses, Ni-Ge as triangles. RMC values are marked with circles. (c) Ni-Ni Debye-Waller factors.
8.3.4 Small-Angle X-ray Scattering

Figure 8.8 (a) Normalised and background subtracted SAXS patterns from samples of a-Ge$_{1-x}$Ni$_x$, offset for clarity of presentation. For $x = 0.39, 0.53, 0.67$, spectra have been multiplied by 0.5, 0.05 and 0.2 respectively. (b) End-point analysis, where the amplitude of the second peak in (a) is plotted against composition.

Figure 8.8(a) shows the scattering profile of each sample in the small-angle region. Each spectra contains a Guinier peak at 0.03 Å$^{-1}$, one side sharply cut off by the beam stop, the other decaying exponentially to zero (indicating a satisfactory background subtraction). Widely dispersed particles are responsible for this low-k scattering and Guinier analysis$^{8,13}$ reveals the presence of particles with a radius of approximately $65 \pm 10$Å at all compositions. These particles are observed in the a-Ge sample so are likely to be strain-relieving voids introduced during fabrication. It is
impossible to quantify the extent of void content because the SAXS intensity is not absolute. The relative amplitude of the Guinier peak, however, indicates an increase in the number of voids with increasing metal content, possibly because of the increased strain associated with metallic bonding.

Samples in the range $0.05 \leq x \leq 0.33$ also display a second maximum, at $k=0.20 \text{ Å}^{-1}$, attributable to correlations between non-dilute regions of contrasting electron density of approximately $30\text{Å}$ in size ($2\pi/k_{\text{max}}$). More information is probably available from the peak width, shape etc. but the absence of a theory to model these features prohibits a deeper analysis. We do know that the amplitude of this peak is related to the difference in electron density and to the volume ratio of each region. An end-point analysis of this second maximum (see Figure 8.8(b)) suggests that the abundance of the regions is compositionally dependent, indicative of phase separation. End points at 0 at.% and ~40 at.% Ni suggest that the samples are separated into a-Ge and Ge$_3$Ni$_2$ phases. The presence of a deep eutectic in the phase diagram of GeNi at this composition has been observed$^{8,14}$, indicating that this alloy is energetically favourable.
8.3.5 Optical Results

Measurement of the optical absorption gives an idea as to the size of the band gap. The composition at which the gap closes is taken to be the composition of the MIT. Absorption curves characteristic of a finite band gap were observed for samples where $x \leq 0.08$, shown in Figure 8.9(a). A gradual shift with rising Ni content to lower energies can be seen, accompanied by a reduction in the energy dependence of the absorption coefficient. A standard measure of the band gap is taken as the energy when $\alpha(E) = 10^4 \text{ cm}^{-1}$, denoted by $E_{\text{opt}}$. This was found to be $0.70 \pm 0.2 \text{ eV}$ for a-Ge, in agreement with the crystalline Ge value. As samples become more absorbing, the data range shortens so that extrapolation of the curve is necessary to obtain a value for $E_{\text{opt}}$. This was performed for $x= 0.05$ and 0.08, where $E_{\text{opt}}$ was found to be 0.30 and 0.14 eV respectively.

The absorption has been shown to take the form

$$\alpha(E) = (h\omega - E_g)^{x+y+1}$$

where $E_g$ is the magnitude of the band gap. Tauc has shown that for parabolic mobility edges, $x = y = 1/2$, so that a plot of $(\alpha(E))^{1/2}$ vs. $E$ will yield a straight line, where the x-axis intercept represents a value for the band gap, denoted by $E_{\text{Tauc}}$. Such a 'Tauc' plot is shown in Figure 8.9(b). Again, the steady decrease in energy of the gap is observed. Values of $E_{\text{Tauc}}$ are 0.58, 0.20 and $0.05 \pm 0.2 \text{ eV}$ for a-Ge, $x= 0.05$ and $x= 0.08$ samples respectively. These are consistently less than the $E_{\text{opt}}$ values, as expected. Because parabolic band edges are assumed under Tauc analysis, $E_{\text{Tauc}}$ may not offer the most reliable indication of band gap energy.

Figure 8.9(c) shows the relationship between the band gap energy and composition. The steady closure of the gap can be seen, but the lack of data points makes it difficult to ascribe a form. If a linear relationship is assumed, the gap has vanished by $10 \pm 2$ at.% Ni, suggesting that all samples above this composition are metallic. This compares well with the composition reported by Wright of 9 at.% Ni.
Figure 8.9 (a) Absorption coefficient from three samples of a-Ge$_{1-x}$Ni$_x$. The shift of the spectrum to lower energies with rising Ni content can be clearly seen. $E_{\text{ex}}$ is measured at $10^5$ cm$^{-1}$, shown as the dashed line. (b) Tauc plot of the absorption values in (a), where $\alpha(E)$ has units of cm$^{-1}$eV$^{-1/2}$ and represents $(\alpha(E))^1/2$. Extrapolation of the line to the x-axis gives a measure of the band gap, $E_{\text{gap}}$, which is seen to decrease with increasing Ni content. (c) Plot of $E_{\text{ex}}$ (crosses) and $E_{\text{gap}}$ (diamonds) vs. composition, clearly showing the steady closure of the band gap with increasing metal content.
8.4 Discussion

Some difficulty was experienced during analysis of EXAFS data due to the close similarity of Ge and Ni atoms. By employing the better defined Ge K-edge results from low Ni content samples during analysis of Ni edge data and reversing the procedure for the remaining Ge K-edge data, sensible results were obtained. The approach appears to have been successful in that good consistency between Ge-Ni and Ni-Ge interatomic distances and partial coordination numbers is observed. Published data from a crystalline sample of GeNi also lends weight to our findings; at $x = 0.53$, we note that Ge is coordinated by $6.6 \pm 0.2$ Ni atoms at $2.41 \pm 0.005\text{Å}$ and Ni by $5.5 \pm 0.3$ Ge atoms at $2.41 \pm 0.005\text{Å}$. In c-GeNi, $N_{\text{GeNi}} = 6$ and $N_{\text{NiGe}} = 6$ at $2.422\text{Å}$. We are confident that our samples do not contain crystalline regions because of the lack of any structure in the Fourier transform beyond $3\text{Å}$.

A combined neutron diffraction and EXAFS study by Oyanagi, Tsuji and Hosoya of RF sputtered $a$-$\text{Ge}_{1-x}\text{Ni}_x$ films suggests a value of $2.41 \pm 0.03\text{Å}$ for the Ge-Ni bond length, agreeing well with our value. They report a slowly increasing $N_{\text{GeNi}}$ from $0.5$ at $x = 0.10$ to $4.0$ at $x = 0.55$ (taken from neutron diffraction data), which is in agreement with our results. However, they also report an $N_{\text{NiGe}}$ of $4.0$ (from EXAFS data) at all compositions, in contrast to our slowly decreasing Ge-Ge partial coordination. This discrepancy is probably due to the difficulty in distinguishing Ge and Ni atoms. (It must be noted that the EXAFS measurements of Oyanagi et. al. were undertaken on a laboratory source, probably responsible for the large errors in their reported bond lengths.) For this reason, it is perhaps sensible to draw conclusions from total coordination numbers only.

Ge K-edge results show that Ge is essentially four-fold coordinated within the range $0 \leq x \leq 0.40$. This would imply the persistence of the $a$-Ge tetrahedral random network throughout this composition range, with the substitution of Ni for Ge atoms taking place. Outside this composition range, total Ge coordination increases, tending towards a close packed structure. Ni K-edge results seem to exhibit a contradictory behaviour, in that Ni-Ge and Ni-Ni partial coordinations are high at $5.0 \pm 0.5$ and $2.0 \pm$
0.5, even at low metal content, showing no signs of tetrahedral bonding. The total Ni coordination of 7.0 ± 1.0 throughout the composition range, suggests a reasonably close-packed structure. Evidence for the existence of Ni in a close-packed form alongside tetrahedral Ge is provided by SAXS data, which exhibit a second maximum behaviour, characteristic of phase separated samples. The amplitude of the peak displays a chemical dependence, increasing to a maximum at 15 ± 5 at.% Ni and decreasing to zero at 40 ± 5 at.% Ni, suggesting these are phases of a-Ge and a-Ge,Ni. Although no crystalline phase of Ge,Ni has been recorded, the phase diagram of the Ge:Ni alloy displays a deep eutectic at 40 at.% Ni, suggesting an alloy of this composition would be favoured. The hypothesis of phase separated samples can reconcile observations from both edges and is supported by work from studies on similar materials.\textsuperscript{4,2,8,15,8,16} If we now consider the material as a two-phase system consisting of an a-Ge TRN containing regions of an amorphous conducting Ge:Ni alloy, any MIT will occur when the regions of alloy interconnect, at some percolation threshold. This is likely to be at a lower concentration than would otherwise be expected.

RMC results generally support those from EXCURV92. For instance, the Ge-Ge bond lengths calculated by both methods were consistent at 2.46 ± 0.01Å for 0 ≤ x ≤ 0.33. Outside this composition, Ge atoms are not thought to exist in the first coordination shell (consistent with crystal data in this composition range\textsuperscript{8,12}) as EXCURV92 favoured a single Ni shell fit. RMC reacted to this feature of the EXAFS data by drastically reducing the Ge-Ge distance to 2.35 ± 0.005Å, in line with the Ge-Ni distance, in effect hiding the presence of Ge atoms not allowed by the data. Total coordination numbers from the RMC method agree well with those obtained from EXCURV92. These observations lead us to conclude that the converged configurations of atoms produced by RMC for x ≤ 0.33 are acceptable representations of the structure of our samples to within experimental error, and are suitable for further analysis such as bond angle calculations and percolation studies.

Partial coordinations obtained from EXCURV92 and RMC differ to a certain extent, in line with expectations. The theory-based method tends to display ordered bonding characteristics, while the simulation approach suggests random chemical bonding takes place. We therefore infer the presence of a partially ordered network.
The behaviour of the optical absorption coefficient reveals the presence of a band gap in the three samples where $x \leq 0.09$. $E_{oa}$, as expected, is larger than $E_{bc}$ because the latter measures the gap deep inside the density of states. It is known that the density of states in a-Ge cannot be described by a power law, reducing our confidence in $E_{bc}$. For this reason, we have adopted $E_{oa}$ as a measure of the band gap, which we find to be 0.7 eV for a-Ge, in agreement with the crystalline value\[^{4,17}\]. This is perhaps surprising as the tailing of states into the band gap noted in disordered materials usually means a smaller gap than is to be found in their crystalline counterparts. The optical gap steadily decreases in magnitude until it disappears at $\sim$ 10 at.% Ni. We conclude that the MIT occurs at this composition in our samples of a-Ge$_{1-x}$Ni$_x$, which is in good agreement with Wright\[^{19}\]. This transition does not appear to be accompanied by the structural changes predicted by the traditional models, which supports a percolation model of the MIT.
8.6 Conclusions

We report a total Ge coordination of $4.0 \pm 0.5$ and a total Ni coordination of $7.0 \pm 1.0$ across a large extent of the composition range, which suggests the coexistence of an a-Ge TRN and a close-packed Ge:Ni alloy. This idea is supported by SAXS data which displays a chemically dependent second maximum with characteristics suggesting the presence of both an a-Ge and a-Ge$_2$Ni$_3$ phase. Evidence for a two-phase model has been reported for similar systems $^{8,15,8,16}$. We report the onset of a MIT at 10 at.%Ni, consistent with other work$^8$, but find no evidence for structural changes on the atomic scale around this composition. This would suggest that the percolation of regions of a conducting phase in an insulating matrix would be an appropriate model of the MIT, rather than the traditional Anderson model$^8$. SAXS studies also reveal the presence of voids of $-130\AA$ across, introduced during fabrication.

We find that the Ni atoms are coordinated by $5.0 \pm 0.5$ Ge atoms at $2.41 \pm 0.005\AA$ and $2 \pm 0.5$ Ni atoms at $2.60 \pm 0.005\AA$, within the composition range $0 \leq x \leq 0.53$. Ge atoms are coordinated at $2.46 \pm 0.01\AA$ by $4.1 \pm 0.3$ Ge atoms at $x=0$, decreasing to zero at $x=0.33$, while the Ge-Ni partial coordination increases steadily, maintaining a constant separation of $2.41 \pm 0.005\AA$. Debye-Waller factors indicate appreciable static disorder in the Ge-Ge and Ge-Ni bond.

Confidence in the partial values is not high because of the inherent risk in confusing atomic species during analysis.

We report the successful application of RMC to the analysis of a-Ge$_{1-x}$Ni$_x$, confirming the role of good data if a satisfactory fit is to be obtained. The method is fundamentally weakened, however, by the limited information content of EXAFS data.
8.6 References

8.1 Morigaki, K., 1980, Phil. Mag. B., 42, 979
8.7 Wright, T., 1996, PhD Thesis, Cavendish Laboratory, University of Cambridge
8.12 As 1.11, 13, 28
Chapter 9

Conclusion

As with many other scientific works, this thesis has addressed certain questions, yet in doing so has posed many more. For instance, we have found evidence for phase separation in certain samples. Why is this seen in some samples and not in others? Does the presence of this structure affect the MIT? If so, how should the transition be modelled? The role of this concluding chapter is to outline some of the answers that have been found and tie the more disparate elements together, while giving some idea as to how the new questions arising from this work may be answered.

Over the course of this work, the atomic and medium range structure in a number of amorphous metal-metalloid alloy systems was investigated. A good understanding of the way the coordination numbers and interatomic distances vary with composition has been obtained as well as an indication of the general degree of homogeneity of our samples. These data have great relevance to the elucidation of a mechanism for the MIT.

The main experimental tool used in this thesis was the EXAFS technique. The first part of Chapter 2 was devoted to the theory behind the method, with details presented on the execution of an experiment, from data collection to reduction. The latter part of the Chapter addressed the SAXS technique in similar depth.

Chapter 3 was used to discuss the relatively new ab initio atomic simulation of the Reverse Monte Carlo method, as applied to the interpretation of EXAFS data from certain samples.

Chapter 4 addressed the fundamental issue of sample fabrication and covered other relevant properties, such as film composition, thickness and optical
characteristics. This latter category was described in some detail because an optical study was performed to locate the MIT.

The main emphasis of this thesis was on experimental results and discussions, which were presented in Chapters 5 to 8. Summarised below are some of the main features of this work.

(i) All MIT’s were found to occur in the 0-20 at.% metal composition range. The transition in the a-Si$_{1-x}$Ti$_x$ series occurred at 6 at.% Ti, rather lower than the 15 at.% previously reported for this system. This may be because the assumption of a linear decrease in band-gap with increasing metal content is incorrect or that perhaps a different mechanism is responsible for the MIT, but the lack of semiconducting samples has seriously restricted any further speculation. The a-Ge$_{1-x}$Ti$_x$, a-Ge$_{1-x}$Ni$_x$, a-Si$_{1-x}$Ni$_x$ series display a MIT at 10 at.% metal and a-Si$_{1-x}$Ni$_x$ at 13 at.% Ni, all consistent with values reported elsewhere. The error in these results was estimated to be around ± 2 at.% but may be higher if the band-gap does not close linearly with metal content.

(ii) Much evidence was found to suggest the presence of phase separation in all but the a-Ge$_{1-x}$Ti$_x$ system. Initially, EXAFS results from Ni K-edge data from the a-Si$_{1-x}$Ni$_x$ system pointed towards the clustering of Ni atoms within a close-packed alloy; Ni atoms were found to be surrounded by 7.0 ± 0.5 atoms of Ni at 2.55 ± 0.02 Å and 2.0 ± 0.5 Si atoms at 2.34 ± 0.01 Å across a large part of the composition range, including the sample containing only 12 at.% Ni. This was noted while the Si remained four-fold coordinated at low (x ≤ 0.28) metal content, suggesting the presence of a TRN. Interestingly, the Si-Si bond length was found to increase steadily from the approximately crystalline value of 2.32 ± 0.01 Å to 2.44 ± 0.01 Å over this composition range, meaning either the extension of this bond due to charge transfer or perhaps the more realistic idea that EXCURV92 is averaging the lengths of a short Si-Si bond in the TRN and a longer Si-Si bond in a Si:Ni alloy.

This evidence would be tenuous if taken alone, but it is strongly supported by results from the SAXS study. Scattering of X-rays from these samples of a-Si$_{1-x}$Ni$_x$ into the small angle region display a second maximum caused by interference between non-disperse inhomogeneities. The amplitude of this maximum is chemically dependent, a characteristic of phase segregated samples associated with the change in scattering contrast as the proportion of each phase increases or decreases with metal...
content. From the height of this peak, we have determined that the samples are probably a mixture of a-Si and a-NiSi with the possible presence of a-NiSi$_2$ (both of these alloys are known to form from the melt). Bond energy calculations show that the partial coordinations obtained from the EXCURV92 analysis are consistent with total phase separation into a-Si and a-NiSi.

Similar results were obtained for the a-Ge$_{1-x}$Ni$_x$ and a-Si$_{1-x}$Ti$_x$ systems, although they were somewhat less reliable; partial Ge and Ni coordinations may be confused because of the similar scattering factors of the two atoms, and there was limited SAXS data from a-Si$_{1-x}$Ti$_x$ samples. However, by judicious use of consistency conditions while analysing the a-Ge$_{1-x}$Ni$_x$ system, we reasoned that Ni atoms were surrounded by 5.0 ± 0.3 Ge atoms at 2.41 ± 0.005 Å and 2.0 ± 0.3 Ni atoms at 2.62 ± 0.005 Å across the composition range, while the total Ge coordination remained at 4.0 ± 0.3 for x ≤ 0.33, implying the co-existence of the TRN of a-Ge and a Ge:Ni alloy. An end-point analysis of SAXS data pointed towards a-Ge$_3$Ni$_2$ as the alloy.

Ti atoms in a-Si$_{1-x}$Ti$_x$ were noted as being 12-fold (metal-like) coordinated for 0.04 ≤ x ≤ 0.26. This shell was composed of 10.0 ± 0.5 Si atoms at 2.66 ± 0.01 Å and 2.0 ± 0.5 Ti atoms at 2.80 ± 0.01 Å. The total Si coordination was 4-fold until x = 0.19 and steadily increased from 4 to 8-fold in the composition range 0.19 ≤ x ≤ 0.55. Again, this suggests the presence of two distinct compounds, one semiconducting and the other metallic. Evidence from the SAXS study showed that phase separation may be taking place, but a lack of samples in the crucial composition range hinders a complete conclusion.

(iii) In theory, structural changes should be observed when a material undergoes a MIT, which could give an insight into the mechanism of this process. A metallic sample has free electrons which act to screen atomic potentials, although it is not clear what effect this will have on the separation of atoms. It is possible that charge transfer between atoms would serve to increase the A-A or B-B bond length while the A-B bond remains unchanged (if one atom type increases in size the other must reduce), but the effect is likely to be small. The requirement that the free electron density remains uniform, however, means a close-packed structure is favoured over the gap-ridden network of a tetrahedral structure (hence the close-packed nature of metals).
No significant changes in interatomic distance were observed across the MIT in any of the four series of samples, although a conspicuous absence of data at the low metal concentrations makes it difficult to be sure of this conclusion. The change in bond length associated with charge relocation may be small in comparison to the error levels. Metal-metal distances remained constant throughout the composition range; Ti-Ti at $2.80 \pm 0.01\,\text{Å}$ in a-Si$_{1-x}$Ti$_x$ and $2.91 \pm 0.01\,\text{Å}$ in a-Ge$_{1-x}$Ti$_x$. The Ni-Ni bond length was found to be $2.54 \pm 0.02\,\text{Å}$ in a-Si$_{1-x}$Ni$_x$ for $x < 0.28$ and $2.62 \pm 0.005\,\text{Å}$ in a-Ge$_{1-x}$Ni$_x$ for $x < 0.33$ (note the shorter metal-metal bond in the Si compounds).

Metal atoms in all but the a-Ge$_{1-x}$Ti$_x$ system were found to have high coordination numbers, even at compositions below the MIT, suggesting they exist only in a conducting, close-packed structure. The implication is that isolated regions of this conducting phase must be locked within a (tetrahedral) semiconducting matrix in samples below the MIT to prevent the entire sample from conducting. This would suggest that the MIT occurs when conducting regions interconnect at some percolation threshold, a mechanism recently proposed by other groups. The a-Ge$_{1-x}$Ti$_x$ system, however, appears to contradict this conclusion; the semiconducting TRN persists throughout the composition range and there is no evidence of phase separation, yet the MIT occurs at approximately the same composition as in the other systems.

(iv) The atomic simulation algorithm, Reverse Monte Carlo, was applied to the analysis of EXAFS data from all samples, with partial success. Good results were obtained for the a-Ge$_{1-x}$Ti$_x$ and a-Ge$_{1-x}$Ni$_x$ systems, where coordination numbers and interatomic distances were in agreement with the results obtained from EXCURV92. Results from EXCURV92 suggested that there were no Ge atoms present as first neighbours in the a-Ge$_{1-x}$Ni$_x$ system when $x \leq 0.39$, reflected by RMC as a large drop in the Ge-Ge bond length to the Ge-Ni distance of $2.35 \pm 0.05\,\text{Å}$, in effect ‘hiding’ the Ge atoms: EXAFS data does not contain the second neighbour information needed by RMC to place the Ge atoms at the ‘correct’ distances in the configuration.

Coordination numbers returned by RMC distinctly follow a random bonding model, where there is no bond preference and the number of A-A, A-B and B-B bonds are determined by statistical considerations. This is in agreement with EXCURV92 results at low $x$, but for higher metal content the theory-based method anticipates a
shift towards bond ordering. This contrast is probably due to the combined effect of
the individual characteristics of each method; RMC returns the most disordered
structure consistent with the data while EXCURV92 tends to miss weak shells.

The RMC method failed to model a-Si_{x}Ti_{y} data and only satisfactorily fitted
Ni K-edge data from two samples in the a-Si_{x}Ni_{y} system. This was probably because
of the poor Si K-edge EXAFS data. In conclusion, RMC is a suitable analytical tool
for this type of work if 'clean' EXAFS data is used from samples that are known to be
randomly chemically bonded, and can offer otherwise unobtainable information (partial
radial distribution functions).

Naturally the scope for further work is large, as this thesis is intended as a link
in a chain that will perhaps run into the distant future. However, the more immediate
issues that should be addressed are as follows;
(i) We have fabricated four series of samples over a broad composition range and
have obtained a good idea as to how the structure changes over this range. This has
been achieved at the expense of the sample density around the MIT, leaving this
significant composition regime with relatively few data points. It would be of
considerable benefit if more samples containing 0-20 at.% metal were fabricated so
that the proposed models could be evaluated and perhaps even a definitive model
identified.
(ii) A percolation model of the MIT has been suggested, arising from evidence
indicating the presence of distinct regions of a conducting phase. This model needs to
be investigated in some detail, with the aim of predicting a metal composition at which
these regions interconnect. Agreement between this theoretical value and the observed
position of the MIT would give considerable weight to the percolation model. This
task is non-trivial, however, because depletion regions are expected to occur between
the two phases.
(iii) The SAXS patterns observed in phase separated samples contain information
that we are unable to access because of the lack of a suitable theory. We have
extracted phase composition and correlation lengths from peak height and position, but
the medium range structure responsible for the width and shape of the peak remain to
be identified.
Although we are confident that we have correctly identified voids as the origin of the Guinier peak observed in all SAXS data, and phase separation as the cause of the second maximum in certain spectra, there must always remain a little doubt. By performing anomalous-SAXS, where the X-ray energy is not fixed but is scanned across an absorption edge of an element of the sample, the scattering component from each atomic species may be identified and all doubt as to the peak origin removed. Unfortunately ASAXS facilities do not exist at Daresbury Laboratory so measurements would have to be performed outside the UK.

There is room for further development of the RMC algorithm. The most pressing demand is to investigate why the method failed to model certain samples. We suspect that this may be related to the ordering of bonds because the simulation of randomly bonded samples was far more successful than for chemically ordered samples. If this is so, a way must be found to introduce chemical order into a configuration. This may take the form of randomly switching atoms, which would allow the configuration to undergo major structural changes. It must be said though that the method is inherently weak because of the use of EXAFS data alone, which only contains structural information to first neighbour, possibly second neighbour distances. Stronger models would be obtained from the combination of EXAFS, neutron and X-ray scattering data. Indeed, the RMC algorithm is specifically designed to simultaneously model data from a variety of experimental techniques.

Finally, it is hoped that this work has contributed to the field of amorphous materials and that the results contained herein will shed light on the mechanism behind the phenomenon of the MIT.
Appendix 1:

Bond Ordering

The preferential ordering of bonds in covalent alloys is a significant parameter of the short range order but can have an influence on the medium-range order. For instance, favouring of A-A and B-B bonds within an A,B alloy would mean the separation of the material into two distinct phases. The degree of chemical order gives an idea as to the relative strengths of bonds and is therefore usually calculated from partial nearest-neighbour coordination numbers, obtained from EXAFS or diffraction experiments. The limiting possibilities are ordered bonding where the A-B interaction dominates and random bonding where the distribution of bond types is purely statistical. The first possibility implies that only A-A and A-B bonds are allowed for A-rich compositions while the second admits A-A, A-B and B-B bonds are present at all compositions except x = 0 and 1. The exact proportions expected from both models can be calculated from the constancy conditions

\begin{align*}
N_A &= N_{AA} + N_{AB} \\
N_B &= N_{BA} + N_{BB} \\
(1-x)N_{AB} &= xN_{BA}
\end{align*}

where \(N_A\) is the total coordination of A atoms and \(N_{AB}\) is the partial coordination of A atoms by atoms of type B. We have then

(i) The Ordered Bond model for preferential A-B bonding where

\begin{align*}
N_{AB} &= N_A \\
N_{BA} &= N_B \\
N_{AA} &= 0 \\
N_{BB} &= 0
\end{align*}

at the appropriate compositions, which can be found from Eqn. A1.1c.
This only holds for $xN_b \geq (1-x)N_A$ as $N_{bb}$ cannot be negative. Outside this range, $N_{bb}$ is zero. We are then able to write a set of equations that govern the partial coordination numbers, in terms of total coordination number, across the composition range.

\[
N_{aa} = N_a - \frac{1-x}{x}N_s
\]

(A1.2)

The Random Bond model assumes a no bond preference so that a statistical method can be used to calculate the coordination numbers.

If any coordination is equally likely, then the probability of an AA coordination is

\[
P_{AA} = \frac{(1-x)N_A}{(1-x)N_A + xN_B}
\]

(A1.3)

from which the partial coordination is immediately obtained by multiplying by $N_A$. At all compositions then, the partial coordinations are given by

\[
N_{ab} = \frac{xN_aN_b}{N} \quad (A1.4a) \quad N_{ba} = \frac{(1-x)N_aN_b}{N} \quad (A1.4b)
\]

\[
N_{aa} = \frac{(1-x)N_A^2}{N} \quad (A1.4c) \quad N_{bb} = \frac{xN_B^2}{N} \quad (A1.4d)
\]
Appendix 2

Bond Ordering Energy

The bond ordering energy, $\Delta E$, controls the degree of chemical order present in the sample - hence its name. The observed partial coordination numbers will be related to this energy; bond ordering (accompanied by the associated coordination numbers) will occur if the change in energy when different atomic types form a bond is favourable.

For a binary alloy, $A_xB_{1-x}$, it is defined as

$$\Delta E = E_{AB} - 1/2(E_{AA} + E_{BB})$$

(A2.1)

where $E_{AB}$ is the energy associated with the A-B bond.

The object of this appendix is to define a relationship between $\Delta E$ and partial coordination number.

We assume that the observed structure is that with the minimum Gibbs Free energy, given by $G = E - TS + pV$. We neglect the $pV$ term since volume effects are small in solids. We take the internal energy as arising only from the bond energy, $E_b$, and the entropy as entirely due to the configurational entropy. $T$ represents the fixed glass transition temperature; as we cool the sample, the structure becomes 'frozen-in' at this temperature and no structural changes occur as we further cool.

We take each $A$ atom as having a coordination $N_A$ and each $B$ atom a total coordination $N_B$, with the total number of atoms in the sample as $N$. We define $v_j$ as the number of units centred on an $A$ atom and having $j$ A-B bonds in a particular arrangement. The number of arrangements is given by $P_j = N_A!/((N_A-j)!j!)$. Similarly, $\mu_j$
is the number of B centred units with I B-A bonds in a particular arrangement. Q, is the number of arrangements.

The number of different possible arrangements of the (1-x)N A units is given by

\[ \Gamma_A = \frac{((1-x)N)!}{\Pi_j (v_j)!^j} \]  

(A2.2)

There will be a similar expression for the arrangements of B units. Combining the two gives the total number of arrangements and hence the configurational entropy.

\[ S = k \ln(\Gamma_A \Gamma_B) \]
\[ = k \left\{ \ln((1-x)N)! - \sum_j P_j \ln(v_j) + \ln((xN)! - \sum_i Q_i \ln(\mu_i) \right\} \]  

(A2.3)

We define unit proportions \( n_j \) and \( m_i \) to substitute into A2.3 as these are accessible to experiment.

\[ n_j = \frac{P_j v_j}{(1-x)N}, \quad \sum_j n_j = 1 \]
\[ m_i = \frac{Q_i \mu_i}{xN}, \quad \sum_i m_i = 1 \]  

(A2.4)

The partial coordination numbers, \( N_{ij} \), may be written in terms of these proportions:

\[ N_{AA} = \sum_j n_j (N_A - j) \quad \quad N_{AB} = \sum_j j n_j \]
\[ N_{BB} = \sum_i m_i (N_B - i) \quad \quad N_{BA} = \sum_i i m_i \]  

(A2.5)

After substitution of these proportions, A2.3 becomes

\[ S = -kN \left\{ (1-x)\sum_j n_j (\ln n_j - \ln P_j) + x \sum_i m_i (\ln m_i - \ln Q_i) \right\} \]  

(A2.6)

The bond energy can be written as
Thus we have the Gibbs Free Energy in terms of the unit proportions, \( n_j \) and \( m_i \). The minimisation is carried out with respect to these variables on the function

\[
G = (1-x)N\Delta E \sum_j n_j + xN\Delta E \sum_i m_i
\]

\[
+ kT N \left( (1-x) \sum_j n_j (\ln n_j - \ln P_j) + x \sum_i m_i (\ln m_i - \ln Q_i) \right)
\]

\[
+ \lambda_1 \left[ 1 - \sum_j n_j \right] + \lambda_2 \left[ 1 - \sum_i m_i \right] + \lambda_3 \left[ (1-x)N \sum_j n_j - xN \sum_i m_i \right]
\]

(A2.8)

the three \( \lambda \) being Lagrange multipliers. We may then differentiate with respect to \( n_j \) and \( m_i \) to obtain the two equations

\[
\frac{\partial}{\partial n_j} = (1-x)N\Delta E_j + kT(1-x)N(\ln n_j - \ln P_j) + 1 \lambda_1 + \lambda_3 (1-x)N_j = 0
\]

\[
= xN\Delta E_i + kTx(\ln m_i - \ln Q_i) + 1 \lambda_2 - \lambda_3 xN_i \quad (A2.8)
\]

To eliminate the three Lagrange multipliers we select the equations for \( n_0 \), \( m_0 \) and \( n_i \). We know that \( P_0 = Q_0 = 1 \) and \( P_i = N_i \). We therefore arrive at expressions

\[
n_j = n_j P \left( \frac{n_j}{n_0 N_i} \right) = n_j P^j \alpha^j
\]

\[
m_i = m_i Q \left( \frac{n_0 N_i}{n_i} \right) \exp \left( \frac{-2\Delta E}{kT} \right) = m_i Q^i \beta^i \quad (A2.9)
\]

These equations define the two variables \( \alpha \) and \( \beta \). Each \( n_j \) is given by a term in the expansion of \((1+\alpha)^N\), similarly for \( m_i \). From A2.4, we have

\[
\sum_j n_j = n_0 (1+\alpha)^N
\]

\[
\sum_i m_i = m_0 (1+\beta)^N \quad (A2.10)
\]
from which $n_a$ and $m_b$, and hence all of the unit proportions, may be obtained in terms of $\alpha$ and $\beta$. To link the two sets of proportions we use the bond consistency condition $(1-x)N_\alpha = xN_\beta$, to obtain

$$(1-x)N\sum_j n_j\alpha_j = xN\sum_i m_i\beta_i \quad (A2.11)$$

Each sum may be written as a derivative to remove the $j$ and $i$ multipliers, and then summed using A2.10. The results put into A2.5 to obtain the partial coordination numbers in terms of total coordination numbers and the variables $\alpha$ and $\beta$.

$$N_{AA} = N_\alpha \frac{1}{1+\alpha} \quad N_{AB} = N_\alpha \frac{\alpha}{1+\alpha}$$

$$N_{BB} = N_\beta \frac{1}{1+\beta} \quad N_{BA} = N_\beta \frac{\beta}{1+\beta} \quad (A2.12)$$

By writing the partial coordination numbers in the form of a ratio to remove the total coordination dependence, we arrive at

$$\frac{N_{AB}N_{BA}}{N_{AA}N_{BB}} = \alpha\beta = \exp\left(\frac{-2AE}{kT}\right) \quad (A2.13)$$

This important result allows the partial coordinations to be obtained from the bond ordering factor or vice versa.
I was unable to concentrate on my work. In a dream-like state I left for home, where an irresistible urge to lie down overcame me.

- Dr. Albert Hofmann