The analysis of local structural effects in alloys using total scattering and reverse Monte Carlo techniques

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This thesis has two dedications; first to all those who have looked after me, encouraged and pushed me over the years; secondly, to my grandfather who did not get to see this thesis finished.
There are only patterns, patterns on top of patterns, patterns that affect other patterns.

Patterns hidden by patterns.

Patterns within patterns . . .

What we call chaos is just patterns we haven’t recognized.

What we call random is just patterns we can’t decipher.  

- Chuck Palahniuk
Preface

This dissertation is submitted for the degree of Doctor of Philosophy at the University of Cambridge. The work described herein was carried out in the Department of Materials Science and Metallurgy at the University of Cambridge and the ISIS Neutron and Muon Source between Oct 2013 and September 2017 under the supervision of Dr. Howard Stone, Dr. Matthew Tucker and Dr. Helen Playford. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text. It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree or diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. I further state that no substantial part of my dissertation has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text.

It does not exceed the prescribed word limit from the Degree Committee for the Faculty of Physics and Chemistry.

Parts of this dissertation have already been published:


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Glossary and abbreviations

APB - Anti-phase boundary

bcc - Body centred cubic

ccp - Cubic close packed

DAWN - Data Analysis WorkbeNch

DSC - Differential Scanning calorimetry

EDX - Energy dispersive X-ray spectroscopy

EPSR - Empirical pair structure refinement

EXAFS - Extended X-ray absorption fine structure

EXPGui - Graphical user interface to GSAS

fcc - Face centred cubic

GSAS - General structure analysis system

hcp - Hexagonal close packed

HEA - High entropy alloys

ILL - Institut Laue-Langevin

IMC - Inverse Monte-Carlo

LRO - Long-range order

Mantid - Manipulation and Analysis Toolkit for Instrument Data

MC - Monte-Carlo

NMR - Nuclear magnetic resonance

partials - Partial pair distribution functions

PDF - Pair distribution function

RMC - Reverse Monte-Carlo

SEM - Scanning electron microscopy

SRO - Short-range order

StoG - $S(Q)$ to $G(r)$ programme

TEM - Transmission electron microscopy

TOF - Time of flight

WC - Warren-Cowley

XRD - X-ray diffraction

XRF - X-ray fluorescence
Abstract

Over the years ‘short-range order’ (SRO), whereby the local atomic arrangement differs from that of a random distribution, has been used to explain physical phenomena such as thermodynamic discontinuities, increased strength, anomalous electrical resistivity and magnetic variations in a host of alloys. However, due mainly to experimental difficulties and the complexity of the calculations required for the analysis of diffuse scattering, such work has been largely abandoned and hence quantification and assessment of SRO is notably sparse in the literature. The recent development of reverse Monte-Carlo (RMC) methods for the analysis of total scattering data has opened a promising route for the assessment of a material’s local environment and has already provided important insights into a host of complex chemical systems, including liquids, network glasses, nano-materials, functional oxides and metal organic frameworks.

The work presented in this thesis focuses on the development of a new methodology for the analysis of local structural effects in metallic systems using total scattering, and the first systematic application to the study of alloys. The simulation of total scattering data from a range of model structures is used to show that the information content of total scattering functions, in particular the pair distribution function (PDF), is sufficiently high to allow the assessment of different types and degrees of short-range order. This is supported by a demonstration of how such orders can be quantified from large box models, produced by fitting total scattering data using the RMC algorithm, with the mathematical analyses outlined. This culminates in a proposed methodology for the analysis of SRO in alloys.

Having developed this analytical methodology it is subsequently applied to a number of interesting alloy systems. To demonstrate the efficacy of this methodology it was first applied to the study of a sample of Cu$_3$Au - the classically cited case example of a system demonstrating SRO prior to an ordering transition. This experiment provides new insight into this well characterised transition, and also demonstrates the significance of data processing errors on the generation of artefacts in large box modelling. The technique is also applied to the study of the industrially important family of nickel superalloys, assessing ordering in the gamma-phase alloy Ni-Cr and the sublattice orderings occurring in L1$_2$ alloys.

Next, the use of the technique for the analysis of local strains exhibited in a lattice is presented. A series of models is used to demonstrate how the PDF is expected to change under variations in local strain caused by increased concentration of atomic substitution and variation in atomic radii. This is subsequently used to study the characteristic high-entropy alloy (HEA) CrMnFeCoNi. Through analysis of the PDF, it is demonstrated that the level of local strain exhibited in this alloy is not significantly different from those of other related compositionally simpler alloys. This result is highly significant as it challenges one of the core principles of
the field - that the lattices of HEAs are necessarily highly strained. Finally, the energetics of ordering reactions are briefly considered and used to justify some of the observed transformations presented in the earlier work.

Together, the body of work in this thesis shows how the total scattering technique can be used to provide valuable insight into a host of interesting local phenomena occurring in alloy systems. It is hoped that this will open up a new field of study into these effects, and ultimately guide the creation of new alloys based on these structure-property relationships.
Chapter 1

Background

1.1 Short-range order

Ordering transitions are common in alloy systems. At high temperatures it is often found that the constituent elements mix together throughout the alloy structure to form a random solid solution. At these high temperatures the thermal energy overcomes any favourable enthalpic interaction and the system is dominated by entropy. Conventionally, metallurgy assumes that these solid solutions are completely statistically random.

As the temperature of the system is reduced, it may reach a transition state, where the atomic species order themselves, resulting in the formation of a long-range ordered (LRO) structure. The thermodynamics of the system shift from being dominated by entropy to by enthalpy. A two-dimensional schematic of such a transition is shown in Fig. 1.1. These types of transitions are common in alloy systems and are often predicted and shown in phase diagrams as sharp transitions, with no indication any intermediate state. The state, where locally the system may exhibit order, but overall the system is still considered ‘random’ is known as short-range order (SRO).

![Figure 1.1: Schematic of a typical ordering transition as temperature is varied. At high temperatures (left) the thermal energy overcomes the favourable enthalpic interactions and the system is dominated by entropy forming a random solid solution. At low temperatures (right) the enthalpy dominates over the entropy and the system forms an ordered state. Short-range order is the intermediate state between these two end members.](image_url)

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Chapter 1. Background

It has been observed [1] that there persists some degree of order above the transition temperature, in the solid-solution, which may or may not be related to the LRO structure. Atoms may have preference for like or unlike neighbours at certain distances that are substantially different to that expected by a simple probabilistic distribution. Close to a solvus of a system a higher degree of short-range order is apparent; whilst as the temperature of the solid solution increases and approaches the solidus, the system approaches a random solid solution.

Whilst it is known that changes in ordering in a system can strongly affect its physical properties, the effect of short-range order is currently not well understood. If a link is ultimately to be made between alloy structure and properties, the nature and consequences of short-range order need to be clarified.

1.2 Order and alloy strength

1.2.1 Solid-solution strengthening

The effect of atomic substitution on the strength of an alloy has long been established. The introduction of atoms of different size into a lattice creates a local strain field around the substitution. The interplay of this field with a dislocation leads to a decrease in the motion of the dislocation and a corresponding increase in the observed strengthening of the material. If the substitution results in no observed change in symmetry of the unit cell, it is commonly assumed that such ‘solid-solutions’ are statistically random. The formation of solid solution by substitution was originally noted and described by Hume-Rothery [2], who presented a series of rules to suggest whether a particular substitution may be possible in a system:

- Extensive substitution may occur if the relative difference between the atomic radii ($r$) of the two elements is less than 15%, i.e. for solid solubility:
  \[
  \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \leq 0.15 \tag{1.1}
  \]
  Conversely, if the difference is greater than 15%, solubility is generally limited.

- Crystal structures of the two elements must be identical for appreciable solid solubility.

- Solute and solvent atoms should typically have the same valency in order to achieve maximum solubility. For different valencies, a metal will dissolve a metal of higher valency to a greater extent than one of lower valency.

- Electronegativities need to be similar for maximum solubility, i.e. a solute and solvent should be close in the electrochemical series. When the difference in electro-negativities increases, intermetallic compounds tend to form rather than substitution solid solutions.

These rules are, however, limited and do not account for deviations from the assumed random structure, such as the formation of intermetallic long range ordered structures, or short range ordered structures. Indeed, it is common in conventional metallurgy to make the assumption that solid-solutions are statistically random when creating models linking structure and observed physical phenomena.
In addition to the strengthening provided by local strains, the bond energies across the plane of a dislocation will be different in a substituted alloy compared with that of a pure metal. The energy penalty required to move a dislocation (bonds broken vs. bonds made) will be different from the pure element, and this may also result in a change to the observed strength. Models of dislocation motion in metals have been developed [3]; however, these often consider simply the average composition of the metal across the plane of the dislocation and do not consider the effect of ordering across a dislocation. If the distribution of bond types across this plane change from the nominal average, there will be a corresponding change in the strength of the material. Both Fisher [4] and Flinn [5] highlighted that there should be a difference in dislocation motion in structures with and without short-range order (SRO), which were subsequently confirmed in studies of Cu₃Au alloy [6]. Flinn proposed a simple model to account for the variation in strength caused by the change in interactions across the dislocation plane. However, the model was limited to a description of changes in the first nearest neighbouring shells only, and so was found to systematically underpredict the effect of ordering on the dislocation motion.

Roth [7] calculated empirical strengthening coefficients for solid solution substitutions into nickel using the model proposed by Gypen [8], using:

$$\Delta \sigma = \left( \sum_{i} k_i^{n_i} c_i \right)^n$$

where $\Delta \sigma$ is the change in shear stress, $k_i$ the strengthening coefficient for element $i$ and $c_i$ the concentration of the element in the alloy. For the Feltham model, $n = \frac{1}{2}$. Fig. 1.2 shows the coefficients calculated by Roth plotted against the percentage difference in atomic size to nickel. Although there is a general trend of increasing strengthening with atomic size, there is considerable scatter on the graph. The reason for this scatter is currently not known, but may, in part, be attributable to the different SRO ordering occurring in the different systems.

### 1.2.2 Ordering in nickel based superalloys

In the end-member case of a long-range ordered structure, dramatic increases in the strength may be observed compared with the corresponding random structures. Nickel based superalloys are currently used extensively in the aviation industry to cope with the operating temperatures and stresses required in the jet turbine engine. The strength of the superalloys is derived from the presence of the ordered L1₂ $\gamma'$ phase within the random A1, face centred cubic (fcc), structure of the $\gamma$ matrix. These structures, along with the ordered D0₂₂ $\gamma''$ structure, that can form on substitution of certain atomic species such as Nb, are shown in Fig 1.3.

For A1 structures, the close packed planes are the {111}, see Fig. 1.4a. The Burgers vector of a perfect dislocation in the $\gamma$ structure is $\frac{a}{2}(110)$. In the L1₂ structure the $\frac{a}{2}(110)$ vector is no longer a lattice vector, see Fig. 1.4b; instead $a(110)$ is the shortest lattice vector in the {111} plane. The motion of a $\frac{a}{2}(110)$ dislocation will leave an anti-phase boundary in the system, see Fig. 1.4c. Therefore, a second dislocation will be required in order to remove the unfavourable anti-phase boundary (APB) formed by the motion of a single dislocation. Hence, dislocations move through the structure in pairs, explaining the very high creep resistance. Similar arguments can be made for the ordered D0₂₂ structure.
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Figure 1.2: Change in the observed Feltham strengthening coefficient upon substitution into nickel lattice, with the change in atomic radius relative to nickel (radii taken from [9]).

Figure 1.3: The $\gamma$ (A1), $\gamma'$ (L1$_2$) and $\gamma''$ (D0$_{22}$) structures of superalloys. The purple circles indicate that atoms of either type may occupy this position. Blue and red circles show the A and B atoms respectively in the ordered structures, both of which have the composition A$_3$B. $\gamma$, $\gamma'$ and $\gamma''$ is the nomenclature used by the superalloy community, whilst A1, L1$_2$ and D0$_{22}$ are Strukturbericht notation.

Typically elements such as Cr, Mo and W are used to provide solid-solution strengthening effects to the gamma matrix. The effect of solid solution strengthening is currently explained only by a difference in size and the resulting variation in strain of the lattice, without considering any effect from short-range ordering. However, studies of the Ni-Cr, Ni-Mo and Ni-W systems [10–12] have all shown evidence of different degrees of short-range order and therefore this effect must be considered. Further, it is currently assumed that the substitution into the L1$_2$ structure may occur on either the Ni site or the Al site, or across both. However, it is assumed that there will be no preference for the X atoms to be adjacent to other X atoms or other Al atoms.

Much of the interest driving this PhD project is in relating short-range ordering processes to
1.3 Analysis of short-range order in metals

Thus far, only the influence of short-range order on strength of the materials has been discussed. However, it should be noted that short-range order has been associated with variations in many other physical properties. Thermodynamic discontinuities in nickel chromium alloys [13], along with observed anomalies in electrical resistivity [14,15] have led to the description of a Komplex (K-) state containing a different order to that expected for a random solid solution. Similarly, changes in magnetic properties, such as an increase in the observed spin wave stiffness of Ni$_3$Mn [16], provide evidence for short-range ordering. Likewise, more recently, the change in radiation damage in Ni-Co-Cr alloys and high entropy alloys (HEAs) [17] with short-range order has been suggested.

The short-range order has often been inferred in alloys from the change in the physical properties of the material but has not been quantified. In spite of this influence on numerous materials properties, the study of short-range ordering in alloy systems has been largely abandoned over the last 20 years or so. This is due mainly to the lack of experimental evidence available from conventional diffraction experiments and the difficulties associated with the calculation of the ordering parameters from the diffuse scattering observed in single crystal experiments. To consider the origin of the observed diffuse scattering, it is worth reviewing some basic scattering theory.
1.3.1 Basic scattering theory

Consider an object being irradiated by an incident beam \( \bar{s}_0 \) as shown in Fig. 1.5a. The beam is scattered off both P and P', producing two parallel waves \( \bar{s} \), that have an introduced path difference \( \delta = QP + PR \). If the angle \( P'PR = \eta \) and \( P'PX = \eta' \) we can write:

\[
\delta(r) = |\bar{r}| \cos(\eta) - |\bar{r}| \cos(\eta')
\]

where \( \bar{r} \) is the vector from P to P'. This corresponds to a phase difference in the waves of:

\[
\Delta(\bar{r}) = \left( \frac{2\pi}{\lambda} \right) \left[ |\bar{r}| \cos(\eta) - |\bar{r}| \cos(\eta') \right]
\]

where \( \lambda \) is the wavelength of the incident wave, To simplify further, note the relationship shown between the incident beam \( (\bar{s}_0) \), diffracted beam \( (\bar{s}) \) and scattering vector \( (\bar{S}) \) shown in Fig. 1.5b. Hence:

\[
\Delta(\bar{r}) = 2\pi(\bar{r}, \bar{S})
\]

It is also apparent from the diagram in Fig 1.5c that:

\[
S = \frac{2 \sin \theta}{\lambda}
\]

where \( \theta \) is the scattering angle. Therefore the diffracted amplitude, which is given as the sum of these two waves, is given as:

\[
\Psi(\bar{S}) = \sum \psi_0(r) dV_r \exp(2\pi i \bar{r} \cdot \bar{S})
\]

where \( \psi_0(r) \) is the transmission function at the point P' and dV_r is the volume element at P'.

This is the nomenclature commonly used by X-ray researchers. An alternative, and entirely equivalent, normalisation is often used by Neutron researchers removing the factor of \( 2\pi \), i.e. \( \bar{k} = 2\pi \bar{s}, \bar{k}_0 = 2\pi \bar{s}_0 \) and \( \bar{Q} = 2\pi \bar{S} \), simplifying the expression to:

\[
\Psi(\bar{Q}) = \sum b_j \exp \left[i(\bar{k} - \bar{k}_0) \cdot \bar{r}_j \right]
\]

where \( b_j \) is the neutron scattering length of species \( j \). Equation 1.7 may be rewritten as:

\[
Q = \frac{4\pi \sin \theta}{\lambda}
\]
1.3. Analysis of short-range order in metals

The measured intensities in the diffraction pattern are then given as:

\[ S(Q) = \frac{1}{N} |\Psi(Q)|^2 \]  
\[ = \frac{1}{N} \sum_{j,k} b_j b_k \exp [i\hat{Q}.(\vec{r}_j - \vec{r}_k)] \]  

where \( N \) is the number of irradiated scattering objects and \( j \) and \( k \) are atomic labels.

(a)

(b)

(c)

Figure 1.5: Diffraction from a general object. a) The diffraction of incident radiation of a general object, b) Vector diagram of the incident and scattering vectors, c) Rotated form of b) demonstrating that \(|\vec{s}| = |\vec{s}_0|\) for an elastic collision.

1.3.2 Bragg scattering

If the object on which the radiation is incident is crystalline, then by definition the atoms in the structure will occupy a discrete set of atomic coordinates. Mathematically, the position of atoms within the periodically repeating unit cell are given as \( \vec{r}_n = x_n\vec{a} + y_n\vec{b} + z_n\vec{c} \), where \( \vec{a}, \vec{b} \) and \( \vec{c} \) are the lattice vectors of the crystal. Consequently, constructive interference will only occur at a set of discrete positions where \( \hat{Q}.\vec{r} \neq 0 \). This corresponds to wavevectors satisfying the equation \( \hat{Q} = h\vec{a} + k\vec{b} + l\vec{c} \). The values \( \vec{a}, \vec{b} \) and \( \vec{c} \) correspond to vectors in reciprocal space, and define the reciprocal lattice of the structure. The vectors have the relationship \( \vec{a}.\vec{a} = \vec{b}.\vec{b} = \vec{c}.\vec{c} = 2\pi \) and \( \vec{a}.\vec{b} = \vec{a}.\vec{c} = \vec{b}.\vec{c} = \vec{c}.\vec{a} = \vec{c}.\vec{b} = 0 \). The position of these diffracted intensities
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in reciprocal space is therefore directly determined by the scattering planes, and hence atomic positions and unit cell, in real space.

This type of scattering was first noted and described by Bragg [18] and is the basis of nearly all structural determination methods. Bragg noted that for a crystalline structure, maxima in diffracted intensity in a 1D diffraction pattern would occur at angles satisfying the condition:

\[ \lambda = 2d \sin \theta \] (1.14)

where \( d \) is the interplanar spacing, \( \lambda \) the incident wavelength and \( \theta \) the scattering angle. Standard diffraction experiments, particularly of powder samples, derive structural information from this characteristic Bragg pattern. Inherently, this analysis provides information about the long-range average structure and yields a crystallographic description of the material, in terms of the unit cell dimensions, angles and the atomic coordinates. However, information on the short-range ordering that may be present in the system is lost.

1.3.3 Diffuse scattering

Consider a structure where atoms are displaced from the idealised atomic positions, such that the atomic position \( \vec{r} = \vec{r}_0 + \vec{u} \), where \( \vec{r}_0 \) is the nominal site position and \( \vec{u} \) the displacement. From equation 1.10 it follows that:

\[ \Psi(\vec{Q}) = \sum_j b_j \exp[i\vec{Q} \cdot (\vec{r}_0 + \vec{u})] \] (1.15)

Expanding the exponential we can write:

\[ \Psi(\vec{Q}) = \sum_j b_j (1 + i\vec{Q} \cdot \vec{u} \ldots) \exp[i\vec{Q} \cdot \vec{r}_0] \] (1.16)

The first term of this equation will yield the Bragg scattering term that has already been discussed. All contributions from subsequent terms in the expansion will yield some additional diffracted intensity that is distinct from the observed Bragg scattering, and is denoted as diffuse scattering and corresponds to local variations in the system. Considering the second term in the expansion, if the \( \vec{u} \) displacement were the same in every direction then this function, when spherically averaged, would be zero. However, if the motion is correlated in any way, then this term will be non-zero and will produce observed scattered intensity. Here only the contribution from the first term has been described, but additional contributions will also arise from the higher order terms in the expansion and result in observed scattered intensity, although they will have a weaker contribution than the first term.

Importantly, unlike the Bragg scattering that produces discrete points corresponding to specific values of \( |\vec{Q}| \) satisfying the Bragg condition, the diffuse scattering will be produced across a range in \( |\vec{Q}| \). Consequently, the diffuse scattering intensity will be comparatively weak compared with the Bragg scattering and, therefore, can be lost in the noise of the background. It is partly for this reason that the study of diffuse scattering is often neglected, as the signal to noise ratio is often insufficient to allow the accurate determination of the diffuse scattering.
Here, only the diffuse scatter produced by correlated motion has been examined; however, any local change in the structure will also produce a variation in the observed diffuse scattering.

In 1947 Huang [19] examined the effect of static site displacement resulting from atomic substitution, in dilute solid solutions, by considering the distortion of the lattice by an atom of a different size. A static displacement parameter was created analogous to the Debye-Waller factor for thermal displacements; the presence of diffuse scattering peaks was also noted, with maxima coincident with the Bragg peaks. This theory was later extended by Warren et al. [20] who noted a modulation in the period of the diffuse scattering with atomic size. Indeed, Von Laue [21] had already noted that random solid solutions would yield a constant diffuse scattering corresponding to local chemical inhomogeneity in the system. Cowley [1] developed this idea, considering local structure due to preferential correlations between atom types in solid solutions, resulting in modulation of the period of the diffuse scattering. Inherent in the analysis was the assumption that the atoms occupied idealised lattice positions.

Several mathematical methods for the treatment of diffuse scattering have been suggested. Krivoglaz [22] provided a numerical description to discuss deviations of the crystal away from an idealised average ‘grey atom’ structure considering the scattering amplitude as:

\[ [p_A^m b_A + (1 - p_A^m)b_B] \exp [i \bar{Q}.(\bar{r}_m^0 + \delta_m)] \]  

(1.17)

where \( p_A^m \) is the probability of finding atom A at the position \( m \), rather than the expected concentration of A. \( \bar{r}_m^0 \) is the nominal site location of atom \( m \), and \( \delta_m \) the offsite displacement. The ‘grey atom’ lattice being described as:

\[ [c_A b_A + c_B b_B] \exp (i \bar{Q} \bar{r}_m^0) \]  

(1.18)

where \( c_A \) and \( c_B \) are the concentrations of A and B respectively. The linear expansion of this yields two terms for the diffuse scattering: one that is affected by the atomic displacements, and a second dependent on the short-range order in the system. N.B. Each of these terms corresponds to a Fourier series sum.

A further extension to this was carried out by Borie and Sparks [23, 24] who considered the relative displacement between two atoms, expanding the displacement term to include the quadratic terms, in addition to the linear term included by Krivoglaz. This expansion results in 6 terms from the linear displacement term and an additional 18 terms from the quadratic. Neither of these methods took account of the static Debye-Waller factor, corresponding to the time averaged thermal displacements in the system. This effect was subsequently accounted for in the two methods through extensions made by Fenz and Moss [25], and Hayakawa [26].

Experimentally, therefore, to accurately determine the short-range order parameters, the diffuse scattering needed to be accurately measured from 25 positions in a single crystal pattern, to have enough data to solve the system of equations that arises. Some simplifications of the mathematics were suggested. Gragg [27] reduced the number of parameters to 10, by assuming that the atomic displacements are the same for all atomic species. Inherent in the analysis was the assumption that the form factors remained constant with \( Q \), and so was only applicable to neutron methods. For X-rays, Georgopoulos and Cohen [28,29] suggested an alternative method,
exploiting the reduced number of parameters required for lines and planes passing through the origin (e.g. $h00$) and using an optimisation method to minimise the standard deviation of the calculated and observed values. The $3\lambda$ approach [30,31], used three distinct wavelengths chosen such that certain terms in the system of equations would become negligible and hence could be ignored.

Owing to the large number of data points required, or the need to use multiple wavelengths, it can be seen that these experiments were laborious. To gather a sufficient number of single crystal diffuse patterns, in a large volume of reciprocal space, is time consuming. Consequently, it was often unfeasible to collect data, and hence analyse the order of an alloy whilst holding the system at elevated temperatures, *in situ*. Instead, alloys were normally heat treated prior to the experiment, *ex situ*, quenching the sample to ‘freeze’ the order into the system. This assumed that quenching had no effect on the SRO of the system, although experiment suggested that this was not the case in some systems [11]. If a sufficient number of measurements of high enough quality were made, the analysis and calculation of short-range order parameters from the system of equations was complex, and could contain large errors. Consequently, the study of short-range order through the analysis of diffuse scattering from single crystals has largely been abandoned over the years.

1.3.4 Total scattering

The study of amorphous materials, which by definition lack the long-range order that leads to Bragg peaks, motivated the development of the total scattering technique, in which the Bragg and diffuse scattering from a sample are measured and analysed simultaneously. The technique has, more recently, been applied with great success to study many crystalline and disordered-crystalline systems [32], providing insight into local deviations from the average structure. The basic scattering function for neutrons [33] is given as:

$$S(\bar{Q}) = \frac{1}{N} \sum_{i,j} \langle b_i b_j \exp i\bar{Q} (\bar{r}_i - \bar{r}_j) \rangle$$  \hspace{1cm} (1.19)$$

where $i$ and $j$ are atomic labels, $\bar{r}$ the instantaneous position of an atom, $b$ the atomic scattering length, $N$ the number of atoms and $Q$ the magnitude of the scattering vector $\bar{Q}$ i.e. the momentum transfer of the incident radiation. An equivalent expression for X-rays can be derived, replacing the neutron scattering length $b$ with the $Q$-dependent atomic form factor. For a periodic crystal this equation simplifies to the Bragg condition. For any sample, amorphous or crystalline, this spherically averaged expression is given as:

$$\langle \exp i\bar{Q} (\bar{r}_i - \bar{r}_j) \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \exp (i|\bar{Q}| |r_{ij}| \cos \theta)$$  \hspace{1cm} (1.20)$$

$$= \frac{1}{2} \int_0^\pi \sin \theta \exp (i|\bar{Q}| |r_{ij}| \cos \theta) d\theta$$  \hspace{1cm} (1.21)$$
where $\theta$ and $\phi$ are the polar coordinate angles, and $\vec{r}_{ij}$ is the vector between atoms $i$ and $j$. Making the substitution $x = \cos \theta$, and hence $dx = \sin \theta \, d\theta$:

$$\langle \exp i\vec{Q} \cdot (\vec{r}_i - \vec{r}_j) \rangle = \frac{1}{2} \int_{-1}^{1} \exp (i|\vec{Q}| |\vec{r}_{ij}| x) \, dx$$

$$= \frac{\sin |\vec{Q}| |\vec{r}|}{|\vec{Q}| |\vec{r}|}$$

Hence, we can write:

$$S(|\vec{Q}|) = \frac{1}{N} \sum_{i,j} \vec{b}_i \vec{b}_j \sin \left( \frac{|\vec{Q}| |\vec{r}_i - \vec{r}_j|}{|\vec{Q}| |\vec{r}_i - \vec{r}_j|} \right)$$

separating the self-scattering components:

$$S(|\vec{Q}|) = \frac{1}{N} \sum_i \vec{b}_i^2 + \frac{1}{N} \sum_{i,j} \vec{b}_i \vec{b}_j \sin \left( \frac{|\vec{Q}| |\vec{r}_i - \vec{r}_j|}{|\vec{Q}| |\vec{r}_i - \vec{r}_j|} \right)$$

Defining $Q = |\vec{Q}|$ and $r = |\vec{r}_i - \vec{r}_j|$ this can be recast in the form:

$$S(Q) = F(Q) + \sum_i c_i \vec{b}_i^2$$

where $c_i$ is the concentration of species $i$ and the total scattering function, $F(Q)$, is given by:

$$F(Q) = \rho \int_0^\infty 4\pi r^2 G(r) \frac{\sin Qr}{Qr} \, dr$$

in which $\rho_0$ is the average density of the structure and:

$$G(r) = \sum_{i,j} c_i c_j \vec{b}_i \vec{b}_j \left( g_{ij}(r) - 1 \right)$$

where the $g_{ij}(r)$ terms are the partial pair distribution functions. The function $G(r)$ is often known as the pair distribution function (PDF). The inverse Fourier transform of Eq. 1.27, used for the calculation of a PDF, is given by:

$$G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 F(Q) \frac{\sin Qr}{Qr} \, dQ$$

Alternative normalisations of the PDF are sometimes used for convenience, to emphasise specific features of the function related to the properties and length-scales of interest. A more complete descriptions of alternative forms and normalisations of the total scattering functions can be found in Chapter 2. Unless otherwise stated, the terms $G(r)$ and PDF will be used interchangeably.

The partial PDFs (referred to as partials) are described mathematically as:

$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 \rho_0 \, dr}$$

where $n_{ij}(r)$ is the number of atoms lying within $r$ and $r + dr$, and $\rho_i = c_i \rho_0$, where $\rho_0$ is the density of the substance and $c_i$ the concentration of species $i$. Critically, this description is as
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applicable to periodic crystals as to amorphous materials.

The PDF, is a weighted histogram of the distribution of distances between atoms in the structure. A peak in the pair distribution function gives information about pairwise atomic positions, thermal effects and also the number and type of atoms at a given distance simultaneously. The position of a peak will be indicative of the average ‘bond length’ in the structure. The width of the peak is indicative of the variations of bond length across the structure, and from this information about thermal vibrations and/or static displacements can be extracted. It is important to note that the peak width is also affected strongly by the $Q_{\text{max}}$ used for the Fourier transformation. Finally, the area of the peak gives the coordination number of the particular pair interaction it is assigned to; simply, the number of neighbouring atoms found at a certain distance. An example of a PDF calculated from a 2-D square lattice can be seen in Fig. 1.6

Whereas Bragg analysis provides a description of the average structure of a material, total scattering provides a view of the local structure. As an illustrative example, consider the case of variation in bond length of quartz with temperature. A unit cell of the structure may be derived from fitting of the Bragg data, or by projecting the atomic positions from a large box model back onto a single unit cell. From this the bond distance between the average position of the atoms, $\langle \text{Si} \rangle - \langle \text{O} \rangle$, can be calculated. It is found that this distance decreases as the temperature increases (Fig. 1.7). The increase in the temperature causes an increase in the bond oscillation in an arc, such that the distance between average positions of the atoms decreases as the length of the arc increases. In contrast, the PDF reveals an average of the instantaneous Si-O distances, $\langle \text{Si-O} \rangle$, which increases with temperature, as would be expected.

Both X-ray and neutron total scattering experiments are possible, and are highly complementary. The need for data measured over a broad $Q$-range, necessitates the use of spallation neutrons or high-energy X-rays, for which there are optimised instruments available e.g. Polaris and I15/XPDF. As is apparent from Eq. 1.27 and Eq. 1.29, the PDF and $F(Q)$ are different representations of the same information (both contain the local structural information lacking in the Bragg peaks alone). Whilst other local structural probes exist, such as EXAFS and NMR
spectroscopy, they are of limited use for the analysis of short-range order in alloys systems, owing to the fact that EXAFS and NMR provide information for only the first couple of shells, whilst the PDF is capable of describing much longer correlations.

Whilst it is straightforward to achieve a qualitative understanding of the information provided by a PDF, producing accurate structural models is more involved.

### 1.3.5 Reverse Monte Carlo and ‘real-space Rietveld’ techniques

Traditionally, analysis of total scattering data involved visual inspection of the scattering functions and the use of peak fitting to obtain information about the arrangement of the first few coordination shells. It is also common to use molecular dynamics or Monte Carlo to obtain structural models, from which theoretical total scattering functions can be calculated and compared with the observed data. Only if the two are found to be in good agreement can the models provide useful information about the system. The tuning of initial potentials to create a structural model that more accurately reflects the data is theoretically possible, but the direct effect of the potentials on the diffuse scattering is often difficult to quantify and the process of fine-tuning is laborious. Recently, the analysis of total scattering in the literature has become separated into two distinct methods: small and large box modelling.

#### Small box modelling - PDFgui

Small box modelling, or real-space Rietveld as it is sometimes referred, uses the refinement of a crystallographic unit cell to fit input total scattering functions. An initial structure for a material is proposed and a pair distribution function of the structure calculated. This is done by assuming infinite translational symmetry, as in a traditional Rietveld refinement. The delta functions produced by the structure are convoluted with Gaussian functions to model thermal
oscillations in the system. A least squares minimisation is then applied to a series of refineable parameters (e.g. cell size, atomic position, site occupancy, instrumental parameters, thermal displacements etc) to obtain the best fit to the system. Most commonly, this least squares fitting process is carried out using the PDFgui software [35]. This technique is very powerful and has been used to gain insight into a number of interesting systems. However, such methods are fundamentally limited by the definition of a single unit cell of the material, which ultimately produces a crystallographic description of a structure, albeit one that is biased towards the local, rather than the average, structure. As such, it is unsuitable for the analysis of metallic systems containing short-range order, where the variation over the period of a number of shells needs to be considered.

One advantage of small box modelling is the capability of handling multiple phases. Multiple unit-cells reflecting all of the phases in the material can be input into the system and refined simultaneously. This effectively assumes that the phases in the material are mutually exclusive and the surface effects of the interface between them is negligible. Currently such methods are not employed in large box modelling.

Large box modelling - EPSR and Reverse Monte Carlo methods

A more viable alternative for the study of SRO in alloys is large box modelling. This field is divided into two main methods. The empirical potential structure refinement (EPSR) technique [36] combines direct Monte Carlo simulations with the refinement of an empirical potential in order to obtain calculated scattering functions that are in good agreement with the observed data. This technique was developed for analysis of liquid systems and is extensively used to extract information from data sets that lack defined Bragg data. This method relies on an accurate calculation and understanding of the energetics of the system, particularly the intermolecular pair interactions of the system. For solid systems, such interactions are often not well defined and so the method cannot be used. In contrast, the reverse Monte Carlo (RMC) technique [37] is an iterative process in which goodness-of-fit parameters, that describe the statistical quality of the agreement between the model and the experiment, are minimised.

In the RMC method, an initial arrangement of atoms is created that reflects the average structure of the system, as determined by analysis of the Bragg diffraction data. The PDF calculated from this will consist of a series of delta functions, as every atom will be on its ideal position, with no allowance made for positional variations associated with thermal vibrations. However, a more realistic initial model can be obtained by applying small off-site displacements to each atom according to a pseudo-random Gaussian distribution generated using the Box-Muller method [38]. From this, a number of scattering functions may then be calculated and compared with the experimental data. In general, the quality of the fit is defined by an agreement factor, $\chi^2$, which is calculated as follows:

$$
\chi^2 = \sum_j \frac{(y_{j}^{\exp} - y_{j}^{\text{calc}})^2}{\sigma_j^2}
$$

(1.31)

where $j$ indicates a data point, $y_{j}^{\exp}$ the experimental value at that point, $y_{j}^{\text{calc}}$ the value calculated from the refined box and $\sigma_j$ the weighting factor for an individual data set. The $\chi^2$
1.3. Analysis of short-range order in metals

parameters for different data sets are then summed as follows:

\[ \chi^2_{\text{RMC}} = \chi^2_{F(Q)} + \chi^2_{G(r)} + \chi^2_{\text{Bragg}} + \chi^2_{\text{potentials}} + \ldots \]  

(1.32)

Any number of data sets can be summed, allowing the independent fitting of multiple different data sets simultaneously. The implementation of constraints (e.g. \(\chi^2_{\text{potentials}}\)) helps to ensure physically and chemically realistic results are obtained from the refinement.

The algorithm makes random atomic translations and swaps and calculates the change in the scattering functions that result. Changes that lower \(\chi^2_{\text{RMC}}\) will be automatically accepted, whilst those that increase \(\chi^2_{\text{RMC}}\) by \(\Delta \chi^2_{\text{RMC}}\) will be accepted with a probability of:

\[ P = \exp \left( -\frac{\Delta \chi^2_{\text{RMC}}}{2} \right) \]  

(1.33)

By accepting a certain number of ‘bad’ moves, the system may be prevented from becoming stuck in false minima. The result of the RMC refinement is an atomistic model that adequately fits all datasets and obeys all applied constraints. A schematic of the RMC algorithm is shown in Fig. 1.8

![Flowchart of the RMC algorithm](image)

Figure 1.8: Flowchart of the RMC algorithm.

The RMC algorithm has been implemented in a number of software packages (for example [36,39–41]) for the analysis of local structure and disorder. However, for accurate analysis of the structure of crystalline alloy systems, it is necessary to explicitly fit the Bragg pattern as well as the total scattering data. The RMCPProfile [39] code, which incorporates this functionality, is therefore optimised for studies of this nature, and has been used to provide insight into a host of interesting materials systems [32]. Large box modelling is arguably better suited for the analysis of ordering in alloy systems as it is unconstrained by symmetry and produces large (> 10,000 atoms) models that provide the ability to probe the ordering across appropriate length scales. Consequently, this work will focus primarily on the use of the RMC algorithm. However, some
use will be made of small box techniques where appropriate.

It should be noted that the RMC method currently does not contain the capability of handling multiple phases. An open question remains about the best method to combine them - whether to build a large box containing both phases and limit the refinement moves to prevent the breakdown of the phases, or combine multiple large box models akin to the summation of PDFs carried out in PDFgui. An exception to this, however, is when one structure is a superstructure of the other, i.e. the two phases are distinct only in the ordering that is observed within them, whilst the lattice motif remains fixed. This exception enables us to use the RMC method for the analysis of these ordering transitions and the intermediate short-range order stages without the need to implement descriptions of both of the phases separately.

1.4 Outline of work

Ultimately, it is hoped that a link can be made between an alloy’s observed physical properties and the underlying structure, accounting for the local effects in the material. However, in order to achieve this, new techniques are required in order to measure, assess and quantify the effects of short-range order and local distortions in the lattice. This thesis presents work undertaken to make the total scattering technique and large box modelling suitable for such analyses. Chapter 2 will introduce some of the standard methods that will be used in this thesis.

Firstly, the viability of the method for the analysis of short-range order needs to be assessed and a robust methodology for the assessment and quantification of such order needs to be established. Chapter 3 presents theoretical work undertaken to demonstrate that the PDF contains the information content required to distinguish between different types of order present in the system. It also outlines a suitable methodology for experiments and protocols for providing a numerical description of short-range order. A demonstration of this methodology is presented in Chapter 4, with a case study of analysis of ordering in the classic system Cu$_3$Au. Chapters 5 and 6 will discuss the ongoing attempts made to apply this technique to the study of nickel based superalloys.

As already discussed, the justification of much of the strengthening observed in alloy solid solutions is linked to the discrepancies in atomic radii. A direct evaluation of these local strains in alloys using PDF techniques has not previously been carried out. Chapter 7 will present arguments for the use of PDF as a means of directly assessing these strains. An application of this to a controversial problem in the field of high entropy alloys (HEAs) is presented in Chapter 8.

Chapter 9, will present a brief discussion of the energetics of a system. In this chapter the enthalpic effects are considered, focussing on the necessary adaptations that will need to be made to create better models for strength and for the calculation of more accurate phase diagrams. In addition, a suggestion is made as to how the entropy of the system may be calculated for short-range ordered systems.

Finally, the thesis will conclude with a brief look at potential areas of future study that naturally lead on from the work already undertaken.
Chapter 2

Experimental and analytical methods

This chapter presents some of the techniques and methodologies have been used throughout this thesis.

2.1 X-ray and neutron sources

When performing scattering experiments there are two methods that can be employed for structure determination based on whether the source is monochromatic or polychromatic. Recall Bragg’s law states that:

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

(2.1)

where \( d \) is interplanar spacing, \( \lambda \) the wavelength and \( \theta \) is the scattering angle. To determine \( d \), both \( \lambda \) and \( \theta \) are required. Either \( \lambda \) is fixed and \( \theta \) is varied, or \( \theta \) is fixed and \( \lambda \) can be varied.

In a lab environment, X-rays are generated by colliding a metallic target (anode) with fast moving electrons. The collision results in an electronic transition in the structure, with a resultant emission of X-rays as the electron relaxes back to the ground state. Monochromatic X-rays are therefore released corresponding to the specific electronic transitions used to generate them.

Synchrotron facilities generate X-rays by the acceleration of electrons, maintaining them in a circular orbit through guiding dipole magnets. As the electrons are moving in a circular orbit, they are continually accelerating and so emit X-ray radiation tangentially to the orbit. Typically the electrons are separated into packets during the acceleration process, resulting in the generation of a pulsed X-ray beam. Owing to the nature of the formation mechanism of the X-rays, synchrotron radiation is necessarily polarised. The intensity of the beam will be dependent on the number of electrons in the packet and is many magnitudes more intense than a lab source. This enables fast collection of data sets and the possibility of performing time-resolved studies. The radiation produced is a white-beam. However, specific wavelengths can be easily selected using monochromators or mirrors.

There are commonly used methods for the generation of neutrons: Nuclear reactors and spallation sources. Nuclear reactor neutron sources produce a range of neutron wavelengths by the process of nuclear fission. Often, however, these beams are monochromated and then used
Chapter 2. Experimental and analytical methods

with angular dispersive diffractometers, and so reactor sources are often regarded as monochromatic sources. Reactors produce a very high-flux of neutrons, distributed with a Maxwellian distribution. Nuclear reactor sources are obviously problematic due to the requirements for nuclear fuel, the relatively slow reaction shut down time and the removal of nuclear waste.

Spallation sources produce neutrons as the result of collisions of fast moving protons with a heavy metal target. Historically targets were made of uranium; however, due to the background caused by natural nuclear decay and the harmful waste products, it is now more commonly tungsten or tantalum. Whilst the total flux of neutrons produced by a spallation source is lower than a nuclear reactor source, the energetic distribution of neutrons produced can be more favourable as it produces a higher flux of higher energy neutrons.

For both sources, it may be necessary to slow down the neutron to be useful for experiments, a process called ‘moderation’. Typical moderators are water and liquid methane, and produce a energy spread of neutron wavelengths. Spallation sources are designed to either operate continuously, where the target is continuously bombarded and neutron production is continuous, or pulsed, where protons are accelerated in packets creating a series of collision events in which all neutrons are produced simultaneously. For the latter case, experiments are carried out using the ‘time-of-flight’ method.

For any diffractometer at a pulsed spallation source the detector to source distance can be measured. Each detector measures counts as a function of time after the collision pulse. From the time and the distance, the velocity and, hence, momentum of the neutron can be calculated. Using the De Broglie relationship this, in turn, allows calculation of the wavelength of the neutron. As the angle of the detector relative to the sample is also known, the interplanar spacing $d$ can be calculated. This is only possible due to the pulsed nature of the neutrons producing neutrons at a singular event. For continuous sources, the time of flight method can be employed if pulsed events are created by the introduction of a chopper. However, it is often more common to used the ‘white-beam’ or select a single wavelength using a monochromator.

For total scattering experiments there are two key requirements for a choice of source. Owing to the low intensity of the diffuse scattering signal, compared with the much stronger Bragg peaks, high intensity data across a broad $Q$-range are required to obtain a statistically significant measurement of the diffuse scattering in a total scattering experiment. High intensity sources, synchrotrons and neutron sources, are better suited than lab X-ray sources owing to the much higher signal to noise ratio. The POLARIS instrument, at the ISIS neutron and muon source, is additionally optimised through the containment of the sample and detectors within a vacuum tank. This further reduces the background and allows a more accurate measurement of the diffuse scattering.

Secondly, as mentioned in Chapter 1, a broad $Q$-range is required to provide the most accurate calculation of the PDF. It can be seen from Eq. 1.29, that the integral should be calculated over an infinite $Q$-range, and while this is obviously not achievable experimentally, as wide a $Q$-range as possible is required for obtaining a high-quality PDF. Since the magnitude of $Q$ is given by $Q = \frac{4\pi \sin \theta}{\lambda}$ (where $\theta$ is the diffracted angle and $\lambda$ the incident radiation wavelength) it can be seen that the use of short-wavelength incident radiation is desirable. A typical laboratory X-ray diffractometer operating with Cu Kα radiation can achieve a $Q_{\text{max}} \sim 6 \text{Å}^{-1}$, while a
specialised instrument with an Ag source can achieve $Q_{\text{max}} \sim 18$-20 Å$^{-1}$. Likewise, as nuclear reactor sources produce very few high energy, low wavelength, neutrons the accessible $Q_{\text{max}}$ range available from such sources is necessarily limited. Superior data may be obtained at high-energy synchrotron X-ray and spallation neutron sources, which can achieve a $Q_{\text{max}} > 30$ Å$^{-1}$.

The choice between synchrotron X-ray and neutron radiation, should be made based on the specific system of interest, and will be dependent on the relative concentrations of the atomic species and their scattering lengths and form factors. For X-rays, which scatter from the electronic cloud, the magnitude of the scattering is roughly proportional to the atomic number of the species. Neutrons scatter from the nucleus and their scattering length is a function of nuclear energies, which can vary considerably between neighbouring species. A schematic illustration of the variation in the scattering lengths and form factors for the first row transition metals is shown in Fig. 2.1. As can be seen, whilst for X-rays these elements would be difficult to distinguish, for neutrons there are large differences. With neutrons, it is possible to have both positive and negative scattering lengths. Positive scattering lengths represent a phase change in the wave of 0 and those with a negative scattering length a phase change of $\pi$. For studies of short-range order, the radiation should be chosen so as to maximise the difference in the scattering between the random and ordered structures. For example, the study of Cu-Au alloys with neutrons is unfeasible due to their almost identical neutron scattering lengths, whereas X-rays show a large difference in their relative form factors.

Figure 2.1: X-ray form factors and neutron scattering lengths for the 3d transition metals. The radius of the circle indicates the magnitude of the form factor or scattering length. For neutrons, blue indicates positive scattering lengths and red negative scattering lengths.

### 2.2 Powder metallurgy

Total scattering is an extension of traditional powder diffraction and so requires samples that are crystallographic powders. Therefore, when studying engineering materials and alloys the issue of crystallographic texture inherited from prior processing must be considered. Whilst the effect of texture on Bragg data is well documented in the literature, the effect of texture on a PDF is not well understood. Hence, collected total scattering data must be as free from textural effects as possible, and the Bragg intensities should, therefore, be carefully assessed for discrepancies.

In addition to issues associated with the sample texture, the experimental set up should seek to maximise the number of crystallites illuminated by the incident radiation. For neutrons:

\[ ^* \text{An exception to this is magnetic scattering of neutrons from magnetic samples. In this case neutrons scatter from the electron cloud and exhibit a similar } Q \text{-dependant form factor to X-ray scattering} \]
rons, a large sample volume makes this relatively straightforward. However, with X-rays the irradiated volume is much smaller, and care must be taken during sample preparation to minimise crystallite size. For metals produced by either arc-melting or vacuum induction melting (VIM) techniques, the grains can easily grow to the mm lengths scale, and often larger. Thermo-mechanical processing is commonly used to reduce grain size but can result in strong crystallographic textures.

Consequently, an atomisation technique (either water or gas) is required. In gas atomisation, the alloy is heated until molten and sprayed with argon to produce spherical droplets of powder. Water atomisation is similar but relies on a jet of water rather than argon, resulting in a greater variation in particle size and morphology. A schematic illustration of the typical setup used in such experiments is shown in Fig. 2.2. Typical cooling rates of these processes are on the order of 100 K s\(^{-1}\) or higher and, as such, should produce a random quenched sample from the melt. In spite of this fast cooling rate, gas atomisation is known to produce solidification induced micro-segregation textures in the produced powder, so samples must be subsequently heat-treated in the single-phase field (solid solution) in order to remove multiple phases with different compositions and ensure a homogenous random sample is ultimately achieved. The powders made in this manner can subsequently be heat-treated at the temperature of interest to allow ordering to develop in the sample. Heat-treatments for the powders examined in this thesis will be discussed with the specific experiment.

### 2.3 2D diffraction data and DAWN

Fig. 2.3 shows the setup used on the I15 and I15-1 beamlines at the Diamond light source for the collection of 2-D diffraction data. The sample is a crystallographic powder and so contains crystals in all orientations. When the sample is irradiated by the X-ray beam, it scatters the X-rays producing cones of diffracted intensity. Placing a 2-D flat plate detector in the path of these beams results in circular rings of intensity (shown in the schematic illustration). If the sample does not represent a true powder average these rings are observed as spotty or incomplete, due to scattering occurring more strongly in certain orientations compared with others.

The DAWN software is designed for processing the data and reducing them from the observed 2-D diffraction pattern to the more familiar 1-D diffraction pattern in terms of the scattering angle 2\(\theta\). A calibrant of known structure and cell parameters is initially loaded into the experimental apparatus. The energy of the beam is known and controlled through the use of monochromating crystals. Using the calibrant, the precise sample to detector distance is calculated. The calibrant also allows the determination of the precise beam centre on the detector plate and any tilt angles.

For data collection carried out on the instrument, a background, or dark-field correction, is taken before each sample. The DAWN software first performs a subtraction to remove the dark field image, caused by electronic noise in the detector. Using the calculated sample to detector distance and detector tilt angles, the distance from the beam centre to the diffraction rings is converted to a 2\(\theta\), Q or S scale as required. The data are then azimuthally integrated to produce a 1-D diffraction pattern.
2.3. 2D diffraction data and DAWN

Figure 2.2: Schematic illustration of water atomisation apparatus.

Figure 2.2: Schematic illustration of water atomisation apparatus.
Chapter 2. Experimental and analytical methods

2.4 Mantid

The Mantid software is the data processing and analysis toolbox used on all instruments at the ISIS neutron source, and at other neutron facilities, to initially process data produced on the different instruments. Every instrument is designed for different measurements and has different detector geometries. A schematic illustration of the POLARIS diffractometer at ISIS is shown in Fig. 2.4

POLARIS contains 3008 individual detector tubes, grouped into 5 detector banks. These banks nominally sit at angles of 10°, 26°, 52°, 92° and 146°. However, in actuality the banks will cover an angular range, with each of the detectors having a unique diffraction circle source to detector distance. At the start of each operational cycle, calibrations are carried out to calculate the sample to detector path length for every detector and any additional required zero-offsets. The Mantid software uses this calibration information to merge the detectors into the desired banks according to similar angles. Mantid also uses a recorded Vanadium sample to place the data of each bank on an absolute scale. Vanadium has a negligible coherent scattering length, so is dominated by single atom scattering. It also has a well known density, attenuation and capture profiles and can easily be formed into rods that do not require a container. Consequently, it can be used to normalise the data, place them on an absolute scale and subsequent allow fitting of the data and allow determination of the lattice constants.

A routines also exists within Mantid to correct for sample absorption, assuming a simple cylindrical sample geometry. The absorption coefficients are calculated externally, from sample composition and geometry information, and input into Mantid software. Finally, Mantid outputs a 1D diffraction pattern for each of the detector banks, as well as the necessary files to perform a Rietveld refinement in the GSAS software.

Figure 2.3: Schematic illustration of basic 2-D setup for a synchrotron diffraction experiment.
2.5 GSAS

The success of the method proposed by Rietveld [42] for the analysis of diffraction data, can be seen by the almost universal application of the method. The General Structure Analysis System (GSAS) is one of a host of programmes that uses this method to gain crystallographic information about a material from diffraction data. The Rieveld method refines a given structure, using a least squares minimiser, to fit the observed Bragg diffraction data. It should be noted that the Rietveld method is a structural refinement method, rather than a structural solution method - i.e. some knowledge of the phases is required initially in order to allow the refinement to proceed.

Data are loaded into GSAS along with an instrument parameter file. This instrument parameter file is made by Rietveld refining a standard, the lattice parameters of which are known and fixed, to yield the diffractometer constants. Data collected at ISIS are recorded in time of flight (TOF) and the programme requires the diffractometer constants to allow conversion between the units of TOF, d-spacing and Q. The refinement of the calibrant also provides an initial mathematical description of the peak profile likely to be observed on the diffractometer used, as it is assumed to exhibit no sample related broadening.

An initial crystal structure is provided, from which the expected peak positions are calculated using Braggs law. Each of these delta functions is then convoluted with a peak shape, the profile for which is initially set to that calculated from the calibrant. Additional corrections for absorption, texture and thermal decay are also applied. If there are a number of phases these
are then summed, along with an input background function, and scaled to yield a calculated diffraction pattern.

Parameters that can be refined include the crystal parameters (unit cell dimensions, composition, site occupation, and atomic positions), peak shape, diffractometer constants (zero correction, DIFA and DIFC - discussed in greater detail in Chapter 5), thermal parameters, background, phase quantities and texture. Rietveld refinement is therefore invaluable as it provides information on the average crystallographic unit of the material, directly providing unit cell dimension, phase quantities, atomic coordinates, composition and textural effects. In addition, further calculations can allow the determination of bond lengths, bond angles, microstrain and crystallite size.

The GSAS code is also capable of implementing Le Bail fits. These are similar to Rietveld fits, but provide an arbitrary scaling for each individual peak, rather than for the pattern as a whole. In addition it assumes that, where peaks are coincident or overlap, that the constituent peaks provide an equal contribution to the overall sum. Consequently, any physical information that will affect only the intensity of the peak will necessarily be lost using this method. This includes phase information, composition, absorption, texture and thermal oscillations. Although a lot of physical information is lost, it yields a much simpler refinement process with a smaller calculation matrix and can, therefore, be performed much faster. It is primarily used for initial fits when less is known about the structure of the sample.

For the work carried out here, a high quality Rietveld refinement demonstrates that the sample represents a true crystallographic powder, and is not textured, and hence suitable for analysis as a total scattering dataset. The refinement also provides information about the crystal structure of the material, necessary for constructing a suitable supercell for RMC refinements. It also yields the Bragg data and peak profile information, that is used by the RMCProfile code for refinement of the Bragg data, ensuring the average structure of the material is maintained.

## 2.6 Gudrun software

The Gudrun software has become an essential tool in the processing and analysis of total scattering data. For the full use and methodology of the Gudrun software, the manual should be consulted. Here, a brief summary of the main processes and utilities of the software is provided. There are two programmes, GudrunN and GudrunX [43, 44], developed for the processing of neutron and X-ray data respectively. Many of the features are applicable to both pieces of software but, where specified, some features apply only to one programme.

### 2.6.1 Data processing

**Deadtime corrections**

This function exists only in GudrunN and accounts for the time taken for each detector to refresh before the next measurement can be taken.
Normalisation - beam count and vanadium

To allow the merging of different spectra and data banks, the data from the detectors need to be placed on the same scale. The data therefore needs to be normalised by the number of neutrons. This is accomplished by using an either an incident beam monitor that counts the number of neutrons produced by the spallation source, or from the measured µamps of the accelerated proton beam. The detectors, therefore, may be normalised by dividing by the number of neutrons measured by the beam monitor, placing measurements on the same scale, irrespective of counting time or number of neutrons produced. For neutrons, the normalisation can be taken a step further, with the data being placed on an absolute scale. A vanadium sample is run for a similar collection time as that required for the experiment. By processing this standard, the neutron data can be placed on an absolute scale and allow comparison between data collected on different instruments or under different experimental set-ups.

For X-rays there are no similar non-coherent scatterers or incident beam monitors, so placing the system on an absolute scale is difficult. Instead, numerical methods are used that iteratively refine a scaling constant based on the amount of scattering that is expected to be produced by the sample.

Attenuation and multiple scattering

Attenuation of the beam may be caused by both the sample and container. Often for neutrons it is standard to use a vanadium can, that scatters only incoherently, to minimise the attenuation effect on the sample. However, for some samples, and for X-rays, this may not be possible and so the attenuation will need to be considered. Likewise, the effect of multiple scattering occurring both within the sample and the container are approximately calculated and accounted for.

Background and containers

In any experiment some scattering will be produced from objects in the beam other than the sample, such as molecules in the air, sample containers or sample environments (e.g. furnaces, cryostats etc). This additional scattering will have to be subtracted from the raw data to separate the sample dependent scattering. Data sets for the background, sample containers and sample environment are recorded. These are normalised, corrected for attenuation and multiple scattering and subtracted from the similarly corrected experimental data.

Self-scattering

Recall from Chapter 1, that the collected raw data, $I(Q)$ are given as:

$$I(Q) = F(Q) + \sum_m c_m \bar{b}_m^2$$  \hspace{1cm} (2.2)

where $F(Q)$ is the inter-atomic scattering and $\sum_m c_m \bar{b}_m^2$ is the self-scattering component, with $c_m$ being the concentration of species $m$ and $\bar{b}_m$ the scattering length. Gudrun will subtract this component from the system during the correction process.
2.6.2 Post-processing

Detector bank merging

The GudrunN software was developed at ISIS specifically for the analysis of spallation source total scattering data. A typical diffractometer will have several thousand individual detector elements recording data during the course of an experiment. Although these are often grouped into angular banks, with similar positions, each tube will have a unique angle and flight path length. The Gudrun software takes account of these individual lengths to ensure each individual spectrum lines up and calculates the scattering pattern produced by each detector bank in terms of the scattering vector $Q$. The software also assesses the detector counts and removes any detectors that are not performing properly. These detector banks are then further merged to yield the total-scattering function $F(Q)$. For X-rays this function is not normally used as normally there will only be a single detector.

Polarisation, Bremsstrahlung, Fluorescence and Compton corrections

For X-rays some additional effects need to be accounted for. The polarisation of the incident beam will affect the observed scatter and will be source dependent. Likewise there may be additional Bremsstrahlung scattering from a lab source, the result of background radiation caused by retarded electrons in the anode material. Fluorescence may also occur, where an excited electronic transition will generate an X-ray of a different wavelength to the incident beam. Finally Compton corrections, to account for variations in the scattering due to the electronic recoil caused by a previous scattering event - essentially inelastic scattering produced by the sample.

Top hat function

If, for whatever reason, the data processing results in a structure factor with a $Q$-dependent background that has not be accounted for, it is possible to remove this using the top-hat function. The data are convolved with a square top-hat function, which effectively smoothes out the data across the region, resulting in a background function. This can then be subtracted from the data to remove the effect, prior to the Fourier transformation.

Minimum radius correction

The pair distribution should be flat in the region below the shortest nearest neighbour distance. It can be useful to enforce this constraint during processing. This is achieved by the subtraction of a background function from the $F(Q)$ prior to transformation. The background function is calculated so as to flatten the the low-\(r\) region in real space.
Lorch function

This commonly used function is often applied to remove the effects of truncation ripples on a Fourier transform. The original Lorch function [45] is given as:

\[ L_0(Q, \Delta_0) = \frac{\sin Q \Delta_0}{Q \Delta_0} \] (2.3)

\( \Delta_0 \) is chosen such that the data decays to a value of zero at \( Q_{\text{max}} \). Consequently, it removes the effect of high-frequency noise in real space, but at the expense of a reduction in the peak resolution. In fact the Gudrun code typically uses a revised Lorch function of the form:

\[ L_1(Q, \Delta_1) = \frac{3}{(Q \Delta_1)^3} (\sin Q \Delta_1 - Q \Delta_1 \cos Q \Delta_1) \] (2.4)

If applied, the user can specify the desire value of \( \Delta_1 \), based on the choice of \( Q_{\text{max}} \), and the Lorch function is applied to the total scattering function prior to transformation.

2.7 \( S(Q) \) to \( G(r) \) - StoG

The StoG utility is distributed as part of the RMCPProfile code to perform the Fourier transform from reciprocal to real space. The Fourier transform can also be carried out in the Gudrun codes, but is typically done using StoG as it produces the exact file formats required for use with RMCPProfile. As well as performing the required Fourier transform, there are a couple key inputs that are worth noting in the StoG programme.

StoG input files

StoG typically takes the corrected total scattering function Gudrun output files as an input file. The output file is normally the \( F_{\text{norm}}(Q) \) - normalised by either the sum of the Faber-Ziman coefficients (Neutrons), \( \langle b \rangle^2 \), or the self-scattering (X-rays) \( \langle b^2 \rangle \). Depending on which function is used, different values will be required for the final scaling of the Fourier transformed file.

y-offset and scale

Note the definition of \( S(Q) \) as:

\[ S(Q) - 1 = \frac{F(Q)}{(\sum_{i=1}^{n} c_i b_i)^2} \] (2.5)

StoG allows a user input y-offset and scale. The y-offset is normally set = 1 \(^\dagger\) to allow the first file that is plotted to be the \( S(Q) \). As part of the routine, the Fourier transform necessarily subtracts 1 from all of the y-values, so this offset is necessary. An arbitrary y-scale value is also provided as an option. This function is available in case there has been a miscalculation of the density and/or packing of the structure in Gudrun. The normal method is to apply this scale to bring a known low-\( r \) value to the correct value - often the flat region between the first and

\(^\dagger\)y-offset is set to a value such that \( S(Q) \rightarrow 1 \) at high \( r \), typically y-offset = 1
second peaks in a system (if they are sufficiently resolved). The scale factor \( \frac{1}{y_{\text{scale}}} \), where \( y_{\text{scale}} \) is the value input in the programme, is applied prior to the \( y \)-offset.

\( Q_{\text{min}} \)

It is common to cut the lowest-\( Q \) data out of the calculation when performing the transform. The Fourier transform in StoG is designed to implement the following sin Fourier transformation:

\[
G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 F(Q) \frac{\sin (Q r)}{Q r} dQ
\]

(2.6)

However, as is typical, if the following transform is performed:

\[
G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_{Q_{\text{min}}}^\infty 4\pi Q^2 F(Q) \frac{\sin (Q r)}{Q r} dQ
\]

(2.7)

This is equivalent to performing the more complete transform shown in 2.6, but on the function:

\[
F_{\text{mod}}(Q) = \begin{cases} 
0 & Q < Q_{\text{min}} \\
F(Q) & Q_{\text{min}} \leq Q 
\end{cases}
\]

(2.8)

This is not true for the \( F(Q) \) which should tend to a known non-zero value at low-\( Q \) and will lead to a discrepancy in the data. Therefore, a correction for this lost \( Q \)-region must be applied. The simplest method for correction is to extrapolate the low-\( Q \) region back to the origin with a linear interpolation. In fact, to reduce the computation time, this is calculated in StoG, but adding a function to the transformed \( G(r) \) that corresponds to the Fourier transform of the linear correction that would need to be applied to correct the \( F(Q) \) function. \(^\dagger\)

### 2.8 Total scattering functions and PDFs

The term ‘Pair Distribution Function’ is an encompassing term that covers a large number of equations with alternative normalisations and scalings. Starting with the definition of \( F(Q) \) as:

\[
I(Q) = F(Q) + \sum_m c_m \bar{b}_m^2
\]

(2.9)

where \( I(Q) \) is the scattering function of the compound, where \( c_m \) is the concentration of atom \( m \), and \( \bar{b}_m \) is the average scattering factor for atoms of type \( m \). \( r \) is the interatomic distance, and \( Q \) the magnitude of the scattering vector. Most of the PDFs are then simply normalisations, scaled by \( r \), offset or Fourier inverse forms of the \( F(Q) \) (or indeed a combination). Table 2.1 outlines the relationship between these functions and their limiting cases as \( Q \) and \( r \) tend to 0 and \( \infty \) where \( \rho \) is the atomic density of the sample and

\(^\dagger\)There is a slight error in the calculation of this correction depending on the normalisation used. The StoG code linearly interpolates the data back to a y-intercept = -1. This will only be the case if the \( \langle b^2 \rangle \) normalisation is used (see Table 2.1). The discrepancy between these values is likely to be small, but the correction should be taken into account.
2.8. Total scattering functions and PDFs

Table 2.1: Reference table for the different total scattering functions and PDFs.

<table>
<thead>
<tr>
<th>Function</th>
<th>Normalised form of</th>
<th>$r$-scaled form of</th>
<th>Offset form of</th>
<th>Fourier Transform</th>
<th>$\lim_{r\to0}$</th>
<th>$\lim_{Q\to\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F(Q)$</td>
<td>-</td>
<td>-</td>
<td>$G(r)$</td>
<td>$- \langle b^2 \rangle$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$S(Q)$</td>
<td>-</td>
<td>$F_{\text{norm}}(Q)$</td>
<td>-</td>
<td>$- \langle b^2 \rangle + \langle b \rangle^2$</td>
<td>$\langle b \rangle^2$</td>
<td></td>
</tr>
<tr>
<td>$G(r)$</td>
<td>-</td>
<td>$G'(r)$</td>
<td>$F(Q)$</td>
<td>$- \langle b \rangle^2$</td>
<td>0</td>
<td>$\langle b \rangle^2$</td>
</tr>
<tr>
<td>$G'(r)$</td>
<td>-</td>
<td>$G(r)$</td>
<td>-</td>
<td>0</td>
<td>$\langle b \rangle^2$</td>
<td></td>
</tr>
<tr>
<td>$D(r)$</td>
<td>-</td>
<td>$G(r)$</td>
<td>$T(r)$</td>
<td>$- 4\pi \rho \langle b \rangle^2$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$T(r)$</td>
<td>$G'(r)$</td>
<td>$D(r)$</td>
<td>-</td>
<td>0</td>
<td>$4\pi \rho \langle b \rangle^2$</td>
<td></td>
</tr>
<tr>
<td>$F_{\text{norm}}(Q)$</td>
<td>$F(Q)$</td>
<td>$S(Q)$</td>
<td>$G_{\text{norm}}(r)$</td>
<td>-1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$S_{\text{norm}}(Q)$</td>
<td>$S(Q)$</td>
<td>-</td>
<td>-</td>
<td>1 $\frac{\langle b^2 \rangle}{\langle b \rangle^2}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$G_{\text{norm}}(r)$</td>
<td>$G(r)$</td>
<td>$G_{\text{norm}}'(r)$</td>
<td>$F_{\text{norm}}(Q)$</td>
<td>-1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$G'_{\text{norm}}(r)$</td>
<td>$G'(r)$</td>
<td>$G_{\text{norm}}(r)$</td>
<td>-</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$D_{\text{norm}}(r)$</td>
<td>$D(r)$</td>
<td>$D_{\text{norm}}(r)$</td>
<td>$T_{\text{norm}}(r)$</td>
<td>-</td>
<td>$-r$</td>
<td>0</td>
</tr>
<tr>
<td>$T_{\text{norm}}(r)$</td>
<td>$T(r)$</td>
<td>$T_{\text{norm}}'(r)$</td>
<td>$D_{\text{norm}}(r)$</td>
<td>-</td>
<td>0</td>
<td>$r$</td>
</tr>
</tbody>
</table>

* The low $Q$-limit shown here is correct, but differs from that presented by Keen [46].

\[
\langle b^2 \rangle = \sum_j c_j \bar{b}_j^2
\]  
(2.10)

i.e. the self-scattering component of atoms in the compound and

\[
\langle b \rangle^2 = \left( \sum_j c_j \bar{b}_j \right)^2
\]  
(2.11)

i.e. the sum of the Faber-Ziman partials.

Here the ‘normalisations’ referred to are generally calculated by dividing through with the sum of the Faber-Ziman partials i.e. $\langle b \rangle^2$. This is conventional for Neutron scattering experiments. Historically, however for X-rays the $\langle b^2 \rangle$ normalisation has been used, and care should be taken over which normalisation is being used (see the note on StoG input files and low-$Q$ corrections).

For more information about these formalisms and alternative representations of the PDF, see Keen [46].

\[ L. \ Owen \]
2.9 Conclusions - General sample preparation and data processing methodology

In this chapter the various standard techniques and methods used for the processing of total scattering data have been presented. The necessity for a powder samples requires the generation of metal powders via an atomisation route. It has been shown how the choice of source is important for the quality of the data, and should be based on the relative scattering powers of the constituent components. The programmes used for processing and reduction of data have been presented, and their functionalities described. The various normalisations and forms of the total scattering functions have also been included for reference. Taken together, the following methodology is suggested for the preparation, collection and processing of total scattering data for metallic samples:

1. Alloy powder produced by gas or water atomisation.
2. If required, alloy powder heat treated at desired temperature to yield a homogenous random sample.
3. Powder sample prepared and loaded into sample container required for experiment.
4. Total scattering quality data of the sample, along with necessary calibrants, gathered at X-ray synchrotron or neutron spallation source.
5. DAWN or MANTID software used to reduce data to 1-D powder diffraction pattern.
6. Rietveld fit carried out in GSAS software to yield crystallographic information about the sample.
7. Total scattering data processed in GudrunN or GudrunX software.
8. PDFs and total scattering functions calculated using the StoG programme.

This is the standard sample preparation and data processing methodology that will be used in all experiments. Where necessary, and important to the subsequent discussion, additional details of the experiment and the processing parameters, such as the $Q_{\text{max}}$, will be provided.
Chapter 3

Methodology for the analysis of short-range order in alloys

3.1 Introduction

Historically, analysis of short-range order has been carried out by the assessment of diffuse scattering from single crystal experiments. Such data are often complex to analyse and laborious to collect. The PDF technique has now been used in a number of different systems of chemical insight to provide local structural information on the material. However, to date, it has not been systematically applied to the study of alloys. This chapter will seek to answer two key questions as to the use of the technique for the study of alloy systems. First, is the information content of the PDF sufficiently high to be able to determine whether short-range order is occurring within a system and distinguish between different types of ordering. Second, if such order is present, how can the amount and nature of the order be measured and quantified.

In this chapter, a methodology is presented by which total scattering techniques may be used for the direct observation of short-range order in crystalline alloy systems. Simulated supercells based on the face-centered cubic (fcc) structure, containing various types and degrees of short-range order, are used to explore the information content of pair distribution functions. The methods through which the type and nature of the order may be determined and quantified are discussed.

3.2 Short-range order in binary alloy systems

3.2.1 Super-lattice structures in binary alloys

The phase diagrams of many alloy systems show regions where long-range ordered structures form, that differ from the disordered parent phases only in that the atoms are not randomly distributed but occupy specific lattice sites, either within a single cell or a super-cell of the parent phase. This results in the breaking of the symmetry of the parent structure and the appearance of super-lattice peaks in the diffraction pattern. A simple example of this is shown in Fig. 3.1

To demonstrate the efficacy of analysing short-range order though characterisation of pair distribution functions, the super-lattice structures of the face centred cubic (fcc) lattice have been
Chapter 3. Methodology for the analysis of short-range order in alloys

Figure 3.1: Simulated neutron diffraction pattern of Ni$_3$Al for random (A1) and ordered (L1$_2$) arrangements of atoms. The superlattice peaks are indicated by the arrows.

considered, but the analyses carried out could equally be extended to other structural families. Owing to the common occurrence of certain long-range ordered structures, Strukturbericht notation is normally adopted for ease of reference. For example, the L1$_2$ structure (A$_3$B) is based on the face centred cubic structure, but with atoms of type A on the faces and atoms of type B on the corners. The case example for this type of ordering is Cu$_3$Au [47]. However, it is common in other systems such as Ni$_3$Al [48] (this structure may be seen in Fig. 1.2, Fig. 3.1 and Fig 3.4).

3.2.2 Short-range order in binary alloys

As discussed previously, the presence of short-range order has historically been inferred from the change in the observed physical properties of a system, or by the presence of diffuse scattering wings in single crystal diffraction patterns. Single crystal experiments often involved attempts to quantify and describe the nature of such ordering, whilst those based solely on physical inference merely noted the presence of order and relative increases or decreases. There are, however, different types and ways that short-range order could develop within a system.

There are three main types of short-range order (shown in Fig. 3.2): statistical order, the disperse model and the micro-domain model.

- **Statistical order** is akin to the ordering observed in some glasses, where the proportion of atoms in a given coordination shell differs from that of the nominal stoichiometry. The statistical ordering model describes a homogenous order throughout the sample.

- **Disperse order** refers to a form of ‘two-phase’ short-range order model; dispersely distributed particles of a long-range ordered phase exist in a random (or weakly ordered) matrix.
Evidence of a Komplex state (or K-state) in some compounds has shown the validity of this model [13]. For systems such as Cu-Al [49], the ordered regions are observed to be of a different stoichiometry to that of the bulk material, with the matrix compensating accordingly - an example of the disperse model. This model also describes clustering of atoms, such as that observed in the Cu-Ni system [50].

- **Microdomain order** refers to another version of a ‘two-phase’ short-range order model; where the structure contains micro-precipitates within a matrix. In this model it is assumed, however, that the compositions of the precipitates, or in this case micro-domains, and the matrix are the same and it is only the level of order that creates a difference between the two.

The latter two models are perhaps more familiar when it comes to considering the formation of an ordered precipitate, as they more closely resemble a crystallisation model of a solid from a liquid, however are possibly more problematic when considering the end member long-range order state. A question that persists in the community, is the point at which short-range order becomes long-range order. The distinction made is one based solely on technique and experimental observation. If Bragg superlattice peaks are observed, the system is long-range ordered, whilst diffuse scattering suggests short-range order. Numerically this is impossible to quantify and will be entirely system dependant. For example, whether the ‘micro-domain’ model should be called the ‘nano-domain’ model could be debated. If this type of order does occur in the system, then it will be necessary to provide a quantification as to the size of the domain. It is this type of order that is most commonly investigated using high-resolution electron microscopy.

It is worth noting that a fourth model is sometimes proposed, the ‘Defect model’, where nucleation of order occurs due to either point defects, vacancies or substitutions, or higher order defects such as dislocations. This model is distinct from the others as it is more concerned with the causality of order, as opposed to the nature of the order itself and, as such, will not be considered during the course of this analysis.

Whilst the formation of a random solid solution is driven by entropic effects, long-range ordered structures are driven by the favourable enthalpy of forming like or unlike bonds in a given coordination shell. Short-range order exists between these two extremes as a balance.
between increased enthalpy of forming certain favoured bonds and the loss in entropy caused by doing so. Therefore, it is necessary to consider both of these end member states in any future analyses in order to understand the intermediate short-range ordered systems.

### 3.2.3 Quantitative descriptions of short-range order

In order to link the short-range order of a system to its observed physical properties, quantitative descriptors of the ordering occurring in the system are required. This section outlines two of the main methods by which this is typically achieved. The way they can be related to large box models, is discussed in Section 3.3.

**Warren-Cowley parameters**

The Warren-Cowley parameters [1,51] are one of the simplest and oldest methods of describing short-range order in a system and are most closely linked to the statistical model of short-range order. They describe how the observed occupation of a coordination shell differs from that of the nominal stoichiometry.

They are defined as:

\[
\alpha_{mn}^{AB} = 1 - \frac{P_{lmn}^{AB}}{c_B} = 1 - \frac{P_{lmn}^{BA}}{c_A}
\]

(3.1)

where \(P_{lmn}^{AB}\) is defined as the probability of finding a B atom at position \(r_{lmn}^* = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3\) (where \(\vec{a}_1, \vec{a}_2\) and \(\vec{a}_3\) are lattice vectors, and \(l, m\) and \(n\) are fractional coordinates) from an origin placed on an A atom, and \(c_A\) and \(c_B\) are defined as the atomic fractions of A and B respectively in the alloy. For a random distribution of atoms in an alloy, \(\alpha_{000}^{AB} = 0\), with the exception that, by definition, for any system \(\alpha_{000}^{AB} = 1\). Positive values (to a maximum of 1) suggest a preference for like atom coordination in the system; conversely negative values (to a minimum value of \((c_A - 1)c_A\) when measured around B, and \((c_B - 1)c_B\) when measured around A) indicate a preference for unlike atom coordination.

Whilst for a random structure all \(\alpha^{AB}\) parameters will tend to zero, for long-range ordered structures, \(\alpha^{AB}\) will oscillate in a predictable manner through the coordination shells. Historically, experimental \(\alpha\)-parameters were calculated using either the Borie-Sparks [24], Georgopolous-Cohen [28] or 3\(\lambda\) methods [30], from single crystal diffuse scattering patterns. These reported values are the average \(\alpha\)-parameter of the sample. It is the Warren-Cowley parameters that Flinn used to incorporate the effect of short-range order into his proposed model for solid solution strengthening.

Whilst the preceding description applies only to binary alloy systems, extensions have been made for ternary or higher systems. For higher-dimensional systems, ordering parameters analogous to the Warren-Cowley parameters are possible, such as the pairwise multicomponent short-range order (PM-SRO) parameters [52], which are defined as:

\[
\alpha_{m}^{AB} = \frac{p_m^{AB} - c_B}{\delta^{AB} - c_B}
\]

(3.2)

where \(\delta^{AB} = 1\) if \(A = B\) and zero otherwise, \(p_m^{AB}\) is the probability of finding a B-type atom around an A type atom, in shell \(m\). This parameter reduces to the Warren-Cowley parameter for
a binary alloy. More complex formulations, such as the generalised multicomponent short-range order (GM-SRO) parameters [53], also exists that can describe interactions of multiple species.

The Warren-Cowley parameters are useful but are limited, as their description of the system is based solely on a consideration of pairwise interactions. Current developments in the modelling of system energetics, for example the Cluster variation model [54], have moved away from these pairwise interactions and consider the higher order triplet, quadruplet etc. interactions. Consequently, it may be useful to consider alternative parametric forms based on structural motifs.

Clapp configurations

Although they provide useful information about the hallmarks of short-range order in a system, the Warren-Cowley parameters do not provide an exact description of local atomic arrangements within an alloy. As an alternative description, Clapp [55] published a complete list of the 144 possible arrangements of the 12 nearest neighbour atoms in an fcc lattice. The number of configurations is reduced from the theoretical maximum of 4096 by the removal of any orientation basis of the configuration. The labelling convention used by Clapp may be found in Fig. 3.3.

Complete tables can be drawn up to describe the possible arrangements of these twelve atoms around an atom of a given type. The complete table of Clapp configurations for an fcc structure may be found in Appendix B. The numbering in Fig. 3.3a and Fig. 3.3b denote which atomic positions are occupied by unlike atoms, as found in the table in Appendix B. Clapp also performed a similar analysis for the eight nearest neighbours in a body centred cubic (bcc) structure, Fig. 3.3b and Appendix B. Note that each configuration has a multiplicity $W_k$ associated with it, due to the symmetry operations in a cube, which make some configurations equivalent. The labelling convention of the configurations is such that the configurations with negative numbers contain the inverted arrangement of the twelve nearest neighbours to the positive configurations. This is demonstrated in Fig. 3.3c.

An alloy with a random distribution of atoms will occupy many Clapp configurations, whereas a long-range ordered structure will occupy only a limited number of very specific configurations that are necessary structural motifs for the building of the structure. Fig. 3.4 shows three common long-range ordered structures and the associated Clapp configurations from which they are made.
Figure 3.3: The Clapp numbering convention used in the a) fcc and b) bcc lattices. The numbers correspond to which positions are occupied, as denoted in the table in Appendix B. (c) The labelling convention used by Clapp. Note that if all the atom types are inverted, the same configuration label is used. However, if only the 12 nearest neighbour atom types are inverted, but the central atom remains unchanged, then the sign of the Clapp configuration label changes.

Figure 3.4: Some typical long-range ordered structures and the Clapp configurations occupied by the atoms in the structure. Filled circles indicate atoms of type A and empty circles atoms of type B. L1₀ has stoichiometry AB, whilst L1₂ and D0₂₂ are both A₃B.
3.3 Information content of the PDF

3.3.1 Calculated PDFs of long-range ordered structures

For all of the proposed models of short-range order in alloy systems, the limiting cases for ordering in structures are the random distribution and long-range ordered structures. A comparison between the theoretical PDFs of these structures can be used to demonstrate the level of information available in a PDF, and what may be observed in short-range ordered systems.

To illustrate this, $20 \times 20 \times 20$ supercells of the face-centred cubic (fcc) structure (with lattice parameter $a = 3.55\,\text{Å}$) were created to reflect possible structures of the Cu$_3$Au alloy at high temperature (atoms randomly distributed across all sites in the fcc) and low temperature (forming the L1$_2$ structure). A random displacement was applied to the atom positions to yield a Gaussian distribution that mimics the effect of thermal motion using the gaussdist programme distributed in the RMCProfile package. This uses the Box-Muller method to create a normally distributed set of random offsite displacements (see Appendix 1).

The same Gaussian displacement was applied to both structures, the situation reflecting different degrees of order frozen into the structure at the same temperature by quenching. PDFs were calculated for these structures, as if the sample were an alloy of copper and gold scattering X-rays and are shown in Fig. 3.5. It is common in the analysis of X-ray total scattering data to use an average atomic form factor as a simple method to account for the $Q$-dependency of X-ray scattering [56]. As such this effectively approximates the system as a series of point-scatterers, equivalent to the scattering of neutrons. Therefore, in this study the PDFs have been calculated using a $Q$ independent X-ray scattering length equivalent to the atomic number, $Z$, to weight the contributions of each pair of atoms.

From Fig. 3.5 it can be seen that, whilst there is an apparent change in the area of the peaks on ordering, there is no shift in the peak position in the PDF. This contrasts with other systems more typically studied with total scattering, which more commonly show a variation in the peak position under an applied stimulus, or the appearance of new features in the PDF. The change in area of the peaks reflects alterations in the occupation of different coordination shells (see Eq. 1.30). Identifying which peaks change, and the extent of the change, can provide information about the type of ordering occurring in the system. This can be demonstrated by a consideration of a host of long-range ordered structures.

The number of long-range ordered structures is a countable infinity; however, here the consideration is restricted to a subset of structures, those with 4 atoms or fewer in the unit cell. Hart [57] suggested that there are only 17 binary supercells modelled on a fcc structure that fulfil this criterion and listed those that have been observed and those that have yet to be observed in the literature. For reference, images of these structures can be found in Appendix. C. The D1$_a$ structure is also included for consideration, as it is part of a family of structures commonly observed in short-range ordered systems.

Many of the structures demonstrate a simpler unit cell than that shown in the appendix. However, these structures are shown and displayed in this manner owing to their nature as supercells of the fcc lattice. As previously discussed, analysis of the PDF by the RMC method is currently limited in the assessment of multiple phases. However, an exception to this is when
Figure 3.5: Calculated PDFs for a random Cu$_3$Au alloy (solid line) and an ordered L1$_2$ (dotted line) structure. The offset line indicates the calculated difference.

one phase may be considered as a supercell of the other; in which case a single simulation box that reflects both structures can be used.

To examine the sensitivity of the PDF to different types of ordering, 24 × 24 × 24 face-centred cubic (fcc) supercells were created of the eighteen long-range ordered structures of interest, in a similar manner to that outlined previously (for the D1a a 25 × 25 × 25 box was used owing to the dimensions of the D1a supercell). PDFs were calculated in the same manner as previously. The atomic arrangement was randomised using unconstrained Monte Carlo swapping and the normalised PDF calculated for the random structure. The difference between the ordered structure PDF and that of the randomised box was calculated, and these difference PDFs, which represent the maximum differences that can be expected to occur, are shown in Fig. 3.6.

From this figure it is apparent that different orderings will produce different and distinguishable changes in the PDF. Each structure produces a sequential series of increases or decreases in area, of varying magnitude, that corresponds to the ordering occurring. Interestingly, the difference pattern for the L1$_0$ and L1$_2$ structures are similar, producing an alternating pattern of decreased and increased intensity, suggesting that the ordering is driven by a similar cause, and the difference between the two structures is the result of the concentration. For panels (c) and (d) the most commonly observed structures are shown at the top, with predicted structures at the bottom. As can be seen the variations in the theoretical structures are comparatively weaker than the observed structures, which could explain practically why they are not as common in the literature.

It is important to note that the predicted difference PDFs shown in Fig. 3.6 represent the
3.3. Information content of the PDF

differences between long-range order and no order. As such it represents the bounds on what might be expected to be observed in a complete ordering transition from the perspective of the PDF. It is of course expected that the complete transition would normally be followed by the appearance of the superlattice peaks, that would allow the calculation of the new unit-cell of the material and the long-range ordered structure it would form.

Figure 3.6: Predicted difference PDFs for some long-range ordered binary alloy structures. The panels reflect long-range ordered structures of the same stoichiometry: (a) A_4B, (b) A_2B, (c) A_3B and (d) AB. The structures are those described by Hart [32] and the D1_a structure. Images of all the structures can be found in the Appendix A for reference. Structures indicated by * have been predicted to exist in the system they are named after, but as yet have not been physically observed. Structures indicated ** have been neither predicted nor observed. These are named after the family of planes in which there is an observed oscillation in the type of atom occupying the plane. Otherwise structures are named after with the standard Structurbericht notation, or the case example system in which they are observed to exist.
3.3.2 Calculated PDFs of short-range ordered structures

To extend this analysis to the study of short-range order, it is necessary to consider if and how the PDF would vary depending on the different types and amounts of short-range order that could occur.

To compare the different models of short-range order a series of short-range ordered boxes of size $20 \times 20 \times 20$ were created as follows:

1. Statistically ordered boxes with $\alpha_{AB}^1 = -\frac{0.3333n}{20}$ and $\alpha_{AB}^2 = \frac{n}{20}$, where $n = 0, 1, \ldots, 20$

2. Disperse boxes containing a domain of $L1_2$ of size $n \times n \times n$, where $n = 0, 1, \ldots, 20$

3. Microdomain boxes containing a domain of $L1_0$ of size $m \times m \times m$, where $n = 0, 1, \ldots, 20$ and $m = 0, 1 \ldots, 15$

All of the boxes were made of copper and gold atoms in a ratio of 3:1. The $L1_0$ and $L1_2$ structures were chosen due to their common occurrence in metal alloy systems and due to the fact the structures have the same Warren-Cowley parameters $\alpha_{2q+1}^{AB} = -\frac{1}{3}$ and $\alpha_{2q}^{AB} = 1$ for all positive integer values of $q$. The Warren-Cowley parameters of the statistical boxes were chosen for the same reason, so that in the case where $n = 20$, $\alpha_{1}^{AB}$ and $\alpha_{2}^{AB}$ are the same for the statistical and $L1_2$ microdomain cases.

The statistically ordered boxes were created by means of a Monte Carlo refinement. A programme was written that calculates the Warren-Cowley parameters from a large box model up to a number of specified nearest neighbour shells. A goodness of fit parameter is used to determine the difference between the calculated $\alpha$ parameters and the input parameters to fit to. Pairs of atoms are chosen at random and allowed to swap. The swap is accepted if it brings the box closer to the desired statistical order. As with the RMC algorithm, a certain number of ‘bad’ moves are also accepted, to prevent the system from falling into a false minimum. The resultant box contains the level of statistical order of interest. In this case the refinement was carried out restricting only the first two nearest neighbours, with the remaining shells being unrestrained.

Software was also written to generate supercells containing different size domains of long-range ordered structures, to create the microdomain and disperse-model based systems. The programme generates an $fcc$ supercell of a given size (i.e. number of cells), dimension and stoichiometry. The option is then provided to create an ordered domain within the structure. The programme then generates the domain of the LRO structure, of a size specified by the user. The remaining atoms are distributed randomly through the remainder of the supercell.

As with the LRO structures, Gaussian displacements are applied, the PDFs calculated and compared with random configurations. Given that the change in area of the peaks is of greatest interest, as previously mentioned, the integral of the PDFs is calculated and the difference from a random arrangement of the same nominal stoichiometry plotted, Fig. 3.7.

Whilst for the statistical and microdomain models the difference integral PDF oscillates close to the base line, for the disperse model there is a notable increase in the base line with size of domain. This is due to differences between the local concentration and the nominal stoichiometry of the system. Oscillations on this curved background are also visible that have
3.3. Information content of the PDF

Figure 3.7: Difference integrated PDFs for a series of boxes containing different types and amounts of short-range order. The panels are as follows: (a) Statistical order with different magnitudes of Warren-Cowley parameter for the first two shells (created by a Monte Carlo simulation). (b) Microdomain order - containing cubic domains of the L1₀ structure of different sizes. (c) Disperse order - containing cubic domains of the L1₀ structure of different sizes. In panels (a) and (b) the difference integral PDFs are offset for ease of viewing.
Chapter 3. Methodology for the analysis of short-range order in alloys

a similar damping to that observed in the microdomain case. For the statistically ordered case, it can be seen that the oscillations are limited to the first few nearest neighbour shells. As the amount of order in the box increases, so does the magnitude of the difference, but there is relatively little extension out in \( r \).

By contrast, the heterogeneously ordered systems show a difference that gradually grows out in \( r \) as the domain grows to fill the box. One factor not accounted for in these simulations, is the distance between the microdomains and, hence, the relative concentration of domain and matrix. If the domain were to be of a similar size to those shown here, but the volume of the matrix were to increase (and so too the distance between the domains), there would be a reduction in the magnitude of these oscillations. Importantly however, it should not change the length in \( r \) over which the difference is observed.

As it is qualitatively possible to tell the difference in these types of order from the PDF, it demonstrates that the information content of the PDF is sufficient to assess and distinguish between these different types and degrees of order. A mathematical fitting algorithm, such as the RMC code, should then be able to fit these different types of order.

3.4 Extracting short-range order parameters from structural models

Having demonstrated that the PDF is capable of observing a difference between different states of known order, RMC simulations should be able to replicate this order. However, in the cases previously described, the type and amount of order was known quantitatively. To provide a meaningful understanding of the type of order taking place, a method of description is required that will enable the extraction of the required information about the nature and degree of order. It is therefore necessary to consider the descriptors of short-range order and how these can be used in conjunction with large-box modelling.

3.4.1 Warren-Cowley extension to large box models

Warren-Cowley parameters can be extracted directly from an atomistic model, by averaging the Warren-Cowley parameter calculated for every individual atom. From the set of long-range ordered structures used to simulate the PDFs in Fig. 3.6 it is possible to calculate how the Warren-Cowley parameters oscillate through the co-ordination shells. The calculated \( \alpha_{\text{AB}} \) parameters for some standard structures are shown in Table 3.1.

Similarly, the Warren-Cowley parameters for the short-range ordered boxes generated previously can be calculated. A selection of these, corresponding to both the disperse and microdomain cases, are shown in Fig. 3.8. It can be seen that the magnitude of the oscillation changes as expected. However, it is difficult to assign any meaningful interpretation to the oscillations.

More usefully, by using a large box method it is possible to extract additional information about the system by a consideration of the distribution of the Warren-Cowley parameters within a given shell, and not simply the average value for each shell for the entire box. For a random box, whilst on average \( \alpha = 0 \) for all shells, there will be a distribution of \( \alpha \) values for each of the different atoms in the system due to local random variations in the box. This can be seen...
### 3.4. Extracting short-range order parameters from structural models

Table 3.1: Warren-Cowley parameters $\alpha^{AB}$ for the first 10 coordination shells in some standard long range structures based on the fcc lattice. The table is grouped according to the stoichiometry of the alloys. Going down the table a) A$_4$B, b) A$_3$B, c) A$_2$B and d) AB.

<table>
<thead>
<tr>
<th>Shell</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
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<td>0.1667</td>
<td>-0.25</td>
<td>-0.04167</td>
<td>-0.25</td>
<td>0.1667</td>
<td>0.1667</td>
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<td>1</td>
<td>-0.33333</td>
<td>1</td>
<td>-0.33333</td>
<td>1</td>
<td>-0.33333</td>
<td>1</td>
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<td>0.11111</td>
<td>-0.33333</td>
<td>-0.33333</td>
<td>0.11111</td>
<td>1</td>
<td>-0.33333</td>
<td>0.55556</td>
</tr>
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<td>-0.33333</td>
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<td>1</td>
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<td>-0.33333</td>
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<tr>
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<td>-0.33333</td>
<td>-0.33333</td>
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<td>0.11111</td>
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<td>1</td>
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</tr>
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<td>1</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
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<td>-0.33333</td>
<td>0.33333</td>
<td>-0.33333</td>
<td>1</td>
<td>0.33333</td>
<td>0.33333</td>
<td>0.33333</td>
</tr>
<tr>
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<td>-0.33333</td>
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<td>1</td>
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<td>-1</td>
<td>0.05556</td>
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</tbody>
</table>

Figure 3.8: Calculated Warren-Cowley parameters ($\alpha^{AB}$) for simulated boxes with different types and levels of short-range order. (a) Different size of disperse domain of the L1$_0$ structure, (b) different size of microdomain of the L1$_2$ structure.
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In Fig. 3.9, where the $\alpha$-parameter measured around A and B atoms respectively in a series of random $A_{(1-x)}B_x$ configurations are recorded. The theoretical distribution of the Warren-Cowley parameters in a given shell may be calculated by a simple application of binomial theorem.

For a given atom the probability, $P(n_A)$, of it having $n_A$ neighbouring atoms of type A, in a coordination shell containing $d$ atoms is given as:

$$P(n_A) = \frac{d!}{n_A!(d - n_A)!} c_A^{n_A} c_B^{(d-n_A)}$$

(3.3)

where $c_A$ and $c_B$ are the concentration of A and B respectively. For a given value $n_A$ the Warren-Cowley parameter can then be calculated as:

$$\alpha_{AB} = 1 - \frac{n_B}{dc_B}$$

(3.4)

For every atom in the model, the Warren-Cowley parameter may be calculated and so the distribution of the number of atoms with a given parameter plotted. By comparing these observed distributions, in a given shell, with those predicted by the binomial distribution above, information about the nature and magnitude of order in the box may be extracted.

The distributions of Warren-Cowley parameters from different models of short-range order can be calculated using the same simulated boxes as previously. Fig. 3.10 shows the first shell Warren-Cowley parameters for the random case and the different simulated types of short-range order.

The observed Warren-Cowley parameters in the random case (a) can, as expected, be seen to agree well with those predicted using the binomial theorem. In the statistical case (b) it can be seen that, while the general shape has been maintained, the maximum of the distribution has shifted. This reflects the fact that, on average across the box, A atoms tend to form more A-B bonds in their first coordination shell than would be expected based on the stoichiometry alone. In the microdomain box (c), the contribution of the random matrix (dotted line) has

Figure 3.9: Warren Cowley $\alpha$-parameters recorded for the a) A and b) B atoms in a 20x20x20 supercell representing random alloys $A_{(1-x)}B_x$ with varying $x$. 
3.4. Extracting short-range order parameters from structural models

Figure 3.10: The distribution of Warren-Cowley parameters for the first coordination shells ($\alpha_1$) in generated supercells of size $20 \times 20 \times 20$ and stoichiometry $A_3B$. The short range order present is as follows: (a) random, (b) statistical order created using a Monte Carlo simulation with a preference for unlike nearest-neighbour bonds (average $\alpha_{AB}^1 = -0.0417$ and $\alpha_{AB}^2 = 0.1250$), (c) an L1_2 microdomain of size $10 \times 10 \times 10$ unit cells and (d) an L1_0 disperse domain of size $10 \times 10 \times 10$ unit cells. In all cases, the solid black line with markers indicates the observed values around A atoms ($\alpha_{AB}^1$). The solid red line with markers indicates the observed values around B atoms ($\alpha_{BA}^1$). For panels (a) and (b) the dotted lines indicate the contribution of the random matrix distribution predicted by Eq. 3.3 and Eq. 3.4. For panels (c) and (d) the dotted lines indicate the random distribution for the matrix contribution, as predicted by Eq. 3.3 and Eq. 3.4 and accounting for the change in local concentration of the matrix and size of the matrix compared with the size of the domain. In panels (c) and (d) an increase in occupation of a specific $\alpha_{AB}^1$ and $\alpha_{BA}^1$ are indicated by vertical dashed lines.
been scaled by a factor of 0.875 to reflect the proportion of the box it occupies, and this reveals a clear increase in the number of atoms (both A and B) with $\alpha_1 = -0.3333$, corresponding to the atoms in the L1$_2$ microdomain region. Finally, in the L1$_0$ disperse box (d), increases in different parameters for the two atom types ($\alpha^{AB} = -1.6667$ and $\alpha^{BA} = 0.1111$) are apparent, which is indicative of the stoichiometry of the domain being different to that of the box. In this case, the matrix contribution was scaled for both the proportion of the box it occupies and the difference in concentration caused by the disperse domain.

By working out the concentration at which $\alpha^{AB} = \alpha^{BA}$ for the parameters with increased occupation, the concentration of the ordered domain, $c_{A,\text{dom}}$, can be calculated. i.e.

$$c_{A,\text{dom}} = \frac{(1 - \alpha^{BA}_{\text{obs}})c_{A,\text{obs}}}{(1 - \alpha^{BA}_{\text{obs}})c_{A,\text{obs}} + (1 - \alpha^{AB}_{\text{obs}})c_{B,\text{obs}}}$$

(3.5)

where $\alpha^{AB}_{\text{obs}}$ and $\alpha^{BA}_{\text{obs}}$ are the increased Warren-Cowley parameters in the observed distribution, and $c_{A,\text{obs}}$ and $c_{B,\text{obs}}$ are the nominal stoichiometry of the box. This can then be used to fit the remainder of the pattern with a matrix of the correct size and concentration, and thus estimate the size of the domain. When performed on the L1$_0$ disperse box considered previously, this calculation yields a domain size of approximately $9 \times 9 \times 10$ unit cells, very close to the correct value of $10 \times 10 \times 10$.

Whilst in these cases it is possible to see the increase in the number of atoms with an $\alpha$ corresponding to that of the ordered domain, as the domain size reduces, it becomes almost impossible to see this increase. For a $5 \times 5 \times 5$ unit cell domain, i.e. 1.5625% of the volume of the sample, it is no longer possible to see this increase and extract information about the system. The exact percentage at which this increase would not be visible is dependent on both the stoichiometry of the overall system and the local concentration in the domain.

Although here only the first shell has been considered, a similar analysis could be performed in all shells and the nature of ordering occurring in the microdomain extracted.

### 3.4.2 Clapp Configurations from large box models

As noted previously, for a random alloy a variety of the Clapp configurations would be expected to be occupied. Fig. 3.11 shows the occupied configurations found in a series of random boxes of varying stoichiometry. At low substitutions, the low numbered configurations are the most likely to be occupied. As the concentration of the substituting species increases, so does the occupation of the higher configurations, until the configurations are more equally occupied. However, the configurations are not uniformly occupied owing to a larger multiplicity of some configurations compared with others. Recall that the orientational basis for configuration was removed and, therefore, some arrangements of atoms will exist in the same configuration and so the different configurations will have different multiplicities based on their symmetry relative to the cubic symmetry. These multiplicities are listed in the table in Appendix B.

Accounting for these multiplicities and re-normalising produces Fig. 3.12. The occupation of these configurations now has a stepped profile. This is due to the the way the configurations are numbered, with those closest to zero having the largest number of like nearest neighbours i.e. $C1$ - 12 like atoms, $C2$ - 11 like, 1 unlike atoms, $C3$-$C6$ - 10 like, 2 unlike atoms etc. This
3.4. Extracting short-range order parameters from structural models

Figure 3.11: Probability of Clapp configurations being occupied recorded for a series of $20 \times 20 \times 20$ supercells representing random alloys $A_{(1-x)}B_x$ with varying $x$.

Figure 3.12: Probability of Clapp configurations being occupied, weighted by the multiplicity, recorded for a series of $20 \times 20 \times 20$ supercells representing random alloys $A_{(1-x)}B_x$ with varying $x$. 

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demonstrates that, as might be expected, the occupation of a given Clapp configuration in a random alloys is again dependant on the stoichiometry and so can be theoretically calculated for any binary alloy system.

In a large box model that represents an alloy with no long- or short-range order, the occupation of a given Clapp configuration will depend only on the stoichiometry of the alloy, the number of like atoms in the box and the multiplicity of the configuration. The theoretical probability of a given Clapp configuration, \( a \), existing in a face centred cubic alloy \( \text{A}_x \text{B}_{(1-x)} \) (around either atom type A or B) can be calculated using the binomial theorem and is given by:

\[
p_a = m_a[x^n(1-x)^{13-n} + x^{13-n}(1-x)^n]
\]

where \( n \) is the number of unlike atoms amongst the 12 nearest neighbours, \( m_a \) is the multiplicity of the configuration and \( x \) is the concentration of species A.

Comparing this theoretical distribution with several random super-cells, the model is found to be in good agreement. The variation in occupation of a given configuration between the simulated random box and the values calculated from Eq. 3.6 should be within the statistical variation of the distribution. As such, it is essential to obtain some measure of this statistical noise, in order to separate the real enhancements from the random fluctuations of the box. Considering only one Clapp configuration and arguing that either an atom exists in this configuration, or does not, a second application of the binomial theorem states that the mean (\( \bar{n}_a \)) and standard deviation (\( \sigma_{n_a} \)) in occupation of the configuration (\( n_a \)) will be given by:

\[
\bar{n}_a = p_a N
\]

\[
\sigma_{n_a} = \sqrt{p_a(1-p_a)N}
\]

where \( p_a \) is as defined in Eq. 3.6 and \( N \) the number of atoms in the box.

An enhancement factor \( \beta_a \) for configuration \( a \), may then be defined as follows:

\[
\beta_a = \frac{n_a - \bar{n}_a}{\sigma_{n_a}}
\]

where \( n_a \) is the observed number of configurations \( a \) existing in the refined box and \( \bar{n}_a \) and \( \sigma_{n_a} \) are defined by Eq. 3.7 and 3.8. The central limit theorem indicates that for a large number of iterations of a probability distribution, the distribution will tend to a normal distribution. The number of atoms in a large box model is sufficient to satisfy this condition. Consequently, the probability of a certain range of values of enhancement factors is that of a normal distribution.

It follows that if, in a structural model, a configuration has an enhancement factor \( \beta_a \geq 3 \), this configuration is enhanced due to some ordering effect and not merely the result of statistical noise in a random box. An enhancement in specific configurations can then indicate that the ordering is tending towards a certain long-range ordered structure. Reference tables of long-range ordered structures, and the Clapp configurations from which they are made, can be drawn up (see Table 3.2).

The application of these enhancement factors to the analysis of order in a system can be demonstrated using the same simulated boxes as for the Warren-Cowley analysis (Section 3.4.1).
3.4. Extracting short-range order parameters from structural models

Table 3.2: Some classic long-range ordered structures and the Clapp configurations from which they are made.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Formula</th>
<th>Clapp Configurations</th>
</tr>
</thead>
<tbody>
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<td>111_A2B2</td>
<td>AB</td>
<td>15</td>
</tr>
<tr>
<td>331_A2B2</td>
<td>AB</td>
<td>-42</td>
</tr>
<tr>
<td>L10</td>
<td>AB</td>
<td>-16</td>
</tr>
<tr>
<td>L11</td>
<td>AB</td>
<td>82</td>
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<tr>
<td>NbP</td>
<td>AB</td>
<td>-17</td>
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<td>AgZr</td>
<td>AB</td>
<td>79</td>
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<td>A3B</td>
<td>1, 15, 82</td>
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<td>Pt3Tc</td>
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<td>-16, 1, 32</td>
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The results are shown in Fig. 3.13. In the random case (a) the fluctuations are well within the bounds predicted probabilistically. For the statistically ordered case (b) a range of significant enhancements, both positive and negative, are observed. In contrast, with the micro-domain (c) and disperse models (d) there are massive enhancements in the configurations corresponding to the domains of the L12 (C-1 and C16) and L10 (C-16) structures respectively. The Clapp configuration enhancement factors also identify enhancements even with the 5 × 5 × 5 domain structures, making it an apparently more sensitive probe of the order present in the box than the Warren-Cowley parameter distributions.

If, as has been previously described, short-range order is considered to be an intermediate state between disorder and long-range order, there is likely to be much interest in the processes through which order develops. As the atoms diffuse through the solid forming the ordered structure it may be expected that not only the Clapp configurations present in the final structure will be enhanced, but also those that are structurally related. This may in turn highlight key structural motifs that are important to the process of formation of the final structure.

An understanding of the relationship between the Clapp configurations is fairly easy to develop. For each configuration a consideration is made as to how the structure would be affected by either the addition, or removal, of certain atomic types. This creates a degradation pathway that describes how the configurations would develop as the local composition of the...
Figure 3.13: Enhancement factors for generated supercells of size $20 \times 20 \times 20$ and stoichiometry A$_3$B. The short range order present is as follows: (a) random, (b) statistical order created using a Monte Carlo simulation with a preference for unlike nearest-neighbour bonds (average $\alpha_{AB}^1 = -0.0417$ and $\alpha_{AB}^2 = 0.1250$), (c) an L1$_2$ microdomain of size $10 \times 10 \times 10$ unit cells and (d) an L1$_0$ disperse domain of size $10 \times 10 \times 10$ unit cells. The dashed lines indicate the bounds of the region $|\beta_a| \leq 3$ in which the enhancement may be due to random statistical fluctuations of the box rather than from ordering in the box.
3.4. Extracting short-range order parameters from structural models

box changes. In addition, many phase diagrams often identify a region containing a long-range ordered structure that extends beyond the ideal stoichiometry of the ordered structure. In these off-composition alloys cases, the degradation pathways can also be used for identifying the type of ordering that might be present. Fig. 3.14 shows the degradation pathways related to the $C16$ configuration, an essential component of the $L1_2$ structure. Returning again to Fig. 3.13 in the microdomain case (c), the enhancement in the $C34$ configuration can now be understood due to its degradation relationship to the $C16$ structure, as seen in Fig. 3.14. The full degradation pathway diagram for all the structures derived from a face centred cubic structure can be found in Fig. 3.15.

![Degradation Pathway Diagram](image)

Figure 3.14: Degradation pathways for the $C16$ structure as concentration of B atoms (filled) in the structure is either increased or decreased. Numbers indicate the Clapp configuration.

So far, only binary alloys have been considered in this analysis. Extensions of the Warren-Cowley parameters to multicomponent systems have already been discussed. The Clapp configurations, unfortunately, may not be extended to higher order alloy systems so easily. Whilst for a binary alloy the number of arrangements of two atom types in a face centred cubic lattice may be reduced by symmetry to the 144 already discussed, for a three-component system the same symmetry reduction yields 12,111 configurations. It is proposed, therefore, that Clapp configurations are only likely be of practical use if combinations of atoms are used to reduce the system to a pseudo-binary system. This will often make chemical sense due to the natural partitioning of elements onto specific sites during ordering transitions. An example of this is discussed in detail in Chapter 6.
Figure 3.15: Diagram of all degradation pathways for the Clapp configurations in \textit{fcc} systems. Configurations on the same level contain the same local concentration of atom types. A step down a level in the diagram indicates a decrease in the number of like atoms in the surrounding shells, whilst a step up indicates an increase in the number of like atoms. The tree is effectively symmetrical and is the same for the negative configurations. If you decrease the concentration of the C58 to C87 configurations the configuration becomes one of the C-34 to C-57 level.
3.5 Proposed method for the analysis of short-range order in alloys

It is clear from the preceding sections, and discussions in previous chapters, that total scattering provides valuable insight into the structure and properties of many complex alloy systems demonstrating local structural phenomena. To increase confidence in the results obtained in such a manner, it is essential to establish a systematic methodology for the collection and analysis of data.

The following method for the analysis of total scattering data from an alloy is proposed:

- Samples should be prepared in a manner which produces an adequate powder average.
- High quality total scattering data should be obtained using X-ray synchrotron and/or spallation neutron sources.
- Atomistic models representative of the long- and short-range order of the alloy, should be produced using appropriate simulation and/or refinement techniques, guided by the total scattering data.
- Short-range order in the system should then be determined, quantified and described by the methods outlined in this chapter:
  - Difference PDF plots: suggest the model for order occurring in the system - i.e. micro-domain, disperse, statistical
  - Warren-Cowley distributions: to demonstrate the type and magnitude of order occurring in the system.
  - Clapp Configuration enhancement factors: to identify the local arrangement of atoms.
  - Degradation pathways: to identify the key structural motifs and related LRO structures.

3.6 Conclusions

Theoretical work has suggested the use of the total scattering technique may provide new insight into ordering transitions and short-range ordering occurring in alloy systems. In the examples considered, the simulated boxes containing different types and amounts of short-range order have been used to show that PDFs contain the necessary level of information to understand and differentiate between the different short-range order models. In addition, developments to the quantitative descriptions of short-range order used historically have extended their applicability to the analysis of order in large box models, such as those obtained from RMC refinements. Using a combination of Warren-Cowley parameter distributions, Clapp configuration enhancement factors and degradation pathways, a quantitative description of the ordering in the system can be provided. This level of quantitative information is required if models are to be developed to explain the link between the observed order and physical properties such as resistivity or strengthening.
Chapter 3. Methodology for the analysis of short-range order in alloys
Chapter 4

Short-range order in Cu$_3$Au

4.1 Introduction and Background

The Cu-Au alloy system is often used as a case example of ordering transitions in metal alloys and of short-range order in a solid solution. At higher temperatures, a complete solid solution is observed across the full compositional range, which has the A1 face centred cubic (fcc) structure. Below a critical temperature, $T_c$, the Cu-Au alloys are known to form two long-range ordered cubic structures: L1$_0$ (CuAu, $T_c \approx 410^\circ$C [58]) and L1$_2$ (Cu$_3$Au, $T_c \approx 390^\circ$C and CuAu$_3$, $T_c \approx 240^\circ$C [58]). The phase diagram for this system can be found in Fig. 4.1.

![Figure 4.1: Phase diagram for the Cu-Au system (from the ASM Phase diagram database [59]).](image)

Analysis of ordering in Cu$_3$Au was first carried out in the seminal work of Cowley [1]. Since then, it has been used as a benchmark for comparison of analysis techniques due to the presence of diffuse scattering both pre- and post-ordering. Indeed, Clapp [55] used the Cu-Au system to demonstrate the use of probabilistic analysis and his description of short-range ordering in a material.
Roberts and Vineyard [60] extended the Cowley analysis, using the same sample as previously investigated and demonstrated the coexistence of long range and SRO at a temperature $T_c \approx 0.995$. In a study by Borie [61] a change in the diffuse scattering close to the (300) reflection of a sample of Cu$_3$Au was reported when the sample was quenched from above 600°C, compared with quenching from below this temperature. However, it was also noted that this may not simply indicate the presence of a greater degree of SRO above 600°C, as the effect of quenching on the SRO was not fully understood. A proposed explanation for the change at 600°C was the existence of micro-domains in the region $T_c < T < 600$°C. An initial investigation into the CuAu$_3$ alloy was carried out by Batterman [62], calculating the Warren-Cowley parameters at 250°C and 320°C; thereby demonstrating analogous SRO behaviour to the Cu$_3$Au alloy and suggesting microdomain sizes of around 50Å.

Walker and Keating [63] re-evaluated the original results of Cowley in order to take into account developments in diffuse scattering theory to include thermal vibrations and static displacements. Largely these effects made little difference to the calculated $\alpha$-parameters [1, 51], except for the two nearest neighbour terms. Similarly Moss [64] re-evaluated the original Cowley data extending the result to a calculation of the $\alpha$-parameters for the first ten co-ordination rings of the system. Moss and Clapp [65] carried out an analysis on CuAu$_3$ and Cu$_3$Au using their thermodynamic approach to calculate the pair-potentials from the extracted $\alpha$-parameters. Through this they identified a longer-range pair potential effect that extends to at least the third nearest neighbours.

A more systematic X-ray diffraction study of Cu$_3$Au across the temperature range $T_c < T < 930$°C was carried out on a single crystal using a lab based Cu-Kα source by Bardhan and Cohen [66]. Close to $T_c$, diffuse scattering was observed at the $[1\frac{1}{2} 0]$ position, which was believed to indicate the presence of domains of both the D0$_{22}$ and L1$_2$ structures. As the temperature was increased the observed D0$_{22}$ pattern disappeared, whilst a $[\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ diffuse maximum became apparent, not previously reported in the literature. Calculation of the $\alpha$-parameters agreed well with previous results. Computer simulations based on the diffuse data gathered suggested that the specific heat anomaly present at 600°C is due to the loss of D0$_{22}$ micro-domains in the alloy; whilst that at 850°C is due to the development of L1$_1$ regions. The consensus from these studies is that the ordering transition is preceded by a region ($T_c < T < 600$°C) in which SRO is observed, related to either the L1$_2$ and D0$_{22}$ structures, with the system becoming a solid solution above $\sim$ 600°C.

A re-evaluation of the Cu$_3$Au system above the critical temperature (using Co Kα radiation on a single crystal) was carried out [67] using the Georgopolous-Cohen [28] method for separation of the SRO effects and treating the atomic displacements observed in the system explicitly (rather than applying an approximation, as had been done previously). The results agreed well with those from previous studies and identified (through computer simulations) the presence of micro-domains up to 10 unit-cells in length. The measurement of diffuse scattering from Cu$_3$Au using X-ray synchrotron radiation [68] demonstrated that the distance between peak maxima in the diffuse peaks should increase with temperature, but is hidden by the broadening of the peaks. For off-stoichiometric alloys, evidence was provided by Kuhlmann et al. [69] for the presence of LRO at Cu-10at.%Au, this was subsequently refuted by Schönfeld et al. [70].
4.2 Experimental details

Whilst most of these studies were based on traditional single crystal experiments, more recently Proffen et al. [71] recognised the potential of total scattering for the analysis of ordering in alloy systems. X-ray total scattering data were collected from two samples of polycrystalline Cu₃Au manufactured by grinding a cast ingot, one ordered and one disordered. However, no data were obtained in their study on the intermediate ordering states. From fitting of these data with a reverse Monte Carlo (RMC) refinement, implemented within the DISCUS software [72], α-parameters for the completely ordered and disordered systems were calculated.

Owing to the extensive interest in this system it provides an ideal case example for the demonstration of the total-scattering technique for the analysis and determination of short-range order. A systematic measurement of the short-range order in Cu₃Au has been made using in situ X-ray total scattering. This chapter presents the analysis of these data using the RMC method and represents the first application of the method outlined in the previous theoretical work (Chapter 3) [73] to real experimental data and demonstrates the potential of total scattering to provide a better understanding of ordering occurring in metallic systems beyond analyses based on Warren Cowley α-parameters alone.

4.2 Experimental details

A powder sample of Cu₃Au (i.e. Cu-25at.%Au) was produced by water atomisation and sieved to yield a particle size < 45 µm to ensure that a powder average would be obtained when the sample was illuminated by the X-ray beam. The powder was loaded into a 0.5 mm diameter silica glass capillary and placed on the I15 beamline at the Diamond Light Source Ltd, Didcot, UK. The instrument was set up to record diffraction data in transmission geometry with a Perkin-Elmer flat plate 1621EN detector, with a sample to detector distance of ∼ 210 mm. This enabled scattering data to be acquired across an angular range from 2 < 2θ < 42°. A CeO₂ sample was used for calibration of the sample to detector distance using a fixed energy E = 75.534 keV. Total scattering data were gathered of the ‘as-received’ sample at room temperature prior to heating. The sample was subsequently heated using a Cyberstar gas blower apparatus to 900°C. The system was stepped down in temperature in 100°C steps over a series of hours until ordering occurred and superlattice peaks appeared in the diffraction pattern. At each step, total scattering data were acquired. The system was then held at this temperature for a second hour to allow further ordering to occur. The temperature was then raised to 500°C and subsequently reduced in smaller 10°C increments in the region close to the critical temperature and the ordering transition. The temperature profile of the data with time is shown in Fig. 4.2.

The X-ray data were subsequently reduced and corrected using the DAWN software package [74]. Rietveld refinements [42] were carried out using the GSAS [75] software package. The total scattering data were processed and corrected for self-scattering and sample container scattering using GudrunX [43, 44], to yield total scattering functions. Notes on these techniques can be found in Chapter 2. Subsequent Fourier transforms, to yield PDFs, were carried out using the StoG routine, distributed as part of the RMCProfile package [39], using a Qmax = 26 Å⁻¹. Neutron total scattering data of the as-received powdered Cu₃Au sample were also measured at room temperature on the Polaris diffractometer at the ISIS Neutron and Muon Source, Didcot, UK. The data were corrected, normalised and collated using the Mantid software [76] and the
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Figure 4.2: Temperature profile of the sample with time. Points marked with cross represent the total scattering datasets.

total scattering functions processed using the GudrunN software [43].

4.3 Data processing and analysis

4.3.1 The RMC algorithm and data processing errors

As previously discussed the RMC algorithm is driven by the reduction of a goodness of fit parameter, creating a fit that best reflects the data input into a system. Whilst this is incredibly powerful, it can be problematic if the refinement methodology is unrestricted, or if there are inherent errors in the data. The algorithm will make moves that improve the fit to the data, irrespective of physical sense. The extent to which unrealistic moves are accepted can be minimised by the introduction of physical constraints (e.g. minimum bond distances). However, data that contain errors from incorrect collection or processing methods will still be fitted by the algorithm and may result in configurations that reflect these processing artefacts rather than any real information contained within these data sets.

It is, therefore, essential to consider such artefacts and ensure the data have been correctly processed, prior to fitting, to ensure that the configurations produced by the fitting are representative of the order in the system and not merely an artefact produced by incorrect handling of the data.

Instrument resolution function

A resolution function is used to describe the way that instrumental parameters affect the data. The function itself, which may consist of a complex mixture of exponentials, Gaussian and Lorentzian terms, is convoluted with every point in the gathered reciprocal space data. In its most simple and basic form this function may be approximated as a Gaussian function, with a $Q$-independent width. For X-ray synchrotron data acquired using a flat-plate detector, such as the one used in this experiment, this is a reasonable approximation. Consequently, the
corresponding effect on the PDF will be a decay envelope of the form

\[ S(r) = \exp\left(-\frac{(\Delta Q)^2 r^2}{2}\right) \] (4.1)

where \( \Delta Q \) can be estimated from the observed full width half maximum of peaks in the total scattering function \( F(Q) \) and \( r \) is the distance in real space. The \( S(r) \) can be be used to correct the PDF for the instrumental resolution, by dividing through by this function. A subsequent reverse Fourier transform can be used to obtain a resolution corrected \( F(Q) \). An equivalent result could also be obtained by convolving the original data set with a resolution function, however, this is more computationally expensive.

**Incorrect lattice parameter measurements**

Normally the lattice parameters used to generate the initial atomic model for the RMC refinement are obtained from the Rietveld analysis of the Bragg data. However, care is required as any inconsistencies in calibration during the processing of the Bragg and total scattering data are likely to compromise the integrity of the atomic model produced. Errors can arise due to conversion between units (e.g. \( 2\theta \) to \( Q \)) or from systematic offsets in the data (e.g. differing descriptions of bins in different programmes).

**4.3.2 Simulation of data processing errors**

To assess the effect of these potential data processing errors on atomistic models produced by RMC fitting, the calculated PDFs were artificially altered in the following ways:

- damping by multiplying by the scaling function \( S(r) \) with \( \Delta Q = 0.031 \text{ Å}^{-1} \). This \( \Delta Q \) value is representative of the instrumental broadening observed in the experimental data (measured from the peak width).

- offsetting the data by 0.02 Å (a typical histogram bin width), using the box used to generate the data as a starting configuration.

These PDFs, representative of different processing errors, were subsequently fitted using the atomistic models that had been used to generate the datasets. A third simulation was carried out using the calculated dataset, but fitting with an atomistic model with a lattice parameter 0.1% larger than that used to simulate the original data set, representative of an error in the third decimal place of the calculated lattice parameter. The theoretical dataset was also fitted using a starting model with all atoms on their idealised lattice sites to provide a reference. The simulations were run allowing both swaps and translations to occur in a ratio of 1:3.

The atomistic models obtained from the fitting, along with these models collapsed back onto a single unit cell, are shown in Fig. 4.3. The data processing error datasets and the PDF fits before and after refinement are shown in Fig. 4.4. As can be observed, in spite of the deliberately introduced discrepancies between the datasets and boxes used in the fitting process, an excellent fit was obtained using the RMC algorithm.
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Figure 4.3: Output supercell boxes and versions collapsed back onto a single unit cell from RMC runs fitting data with different processing errors. Red spheres represent gold atoms, yellow spheres copper atoms. (a) and (e) are from fitting to calculated data (with no errors) with an idealised random box. (b) and (f) are the outputs fitting a dataset damped by an instrumental resolution function $S(r)$ with $\Delta Q = 0.031 \text{Å}^{-1}$. (c) and (g) are the outputs from fitting a calculated dataset with a box with a 0.1% error in the lattice parameter. (d) and (h) are the outputs from fitting calculated data with a systematic shift in $r$ of 0.02Å.

Considering the output configurations, Fig. 4.3, a region of deformation can be observed in the middle of the supercell in all three examples, with that resulting from the instrumental resolution effect, Fig. 4.3b, being particularly obvious. What is more striking, for the exponential decay fitting, is considering the result when the atoms were condensed back onto a single unit-cell, as shown in Fig. 4.3f. From Fig. 4.3f it is apparent that the distribution of the atoms in the supercell is no longer describing the expected ellipsoidal shape, but instead show regions of deformation. Such results are physically unrealistic and the presence of such offsite displacements in an RMCProfile output for a crystalline alloy system are likely to be indicative of incorrectly processed data. Some deformation of the thermal ellipsoid and offsite displacement can also be observed in the other processing errors, but they are less significant.

The Warren-Cowley $\alpha$-parameters and Clapp configuration enhancement factors, are shown in Fig. 4.5. Fitting the datasets, representative of the artificially applied processing errors, there is a large enhancement in the $C1$ and $C2$ configurations in all boxes, again with the exponential decay box showing a much larger effect. The $C1$ configuration describes atoms surrounded by atoms of the same type. This has not been observed in the Cu-Au system and indeed is shown through this case example to be an artefact of fitting to incorrectly processed data. There are also large enhancements in the Clapp configurations $C2$, $C6$, $C15$ and $C33$, as well as many of the Clapp configurations containing roughly equal numbers of copper and gold atoms ($C70-87$). These enhancements are what would be expected for a cluster of like atoms - $C1$ configurations occupy the centre of the cluster and $C70-87$ at the edge. Similar to the effect on the observed Clapp configurations, there is a clear difference between the random and
4.3. Data processing and analysis

Figure 4.4: PDF $T(r)$ datasets and fits for runs with shifts in lattice parameter (both $r$ dependent and independent). Points indicate the data sets for fitting, red lines the RMC fit and the blue line the difference between the data set and the fit. (a) and (b) show the ‘instrumental resolution’ datasets with the calculated $T(r)$ before and after refinement respectively. (c) and (d) show the fitting with a box with a 0.1% change in the lattice parameter with the calculated $T(r)$ before and after refinement respectively. (e) and (f) show the data set with the systematic shift of 0.02 Å with the calculated $T(r)$ before and after refinement respectively.

observed Warren-Cowley parameters for the first 10 shells, as can be seen in Figs. 4.3e and 4.3f.

Given an awareness of these problems, appropriate steps were taken during data processing to ensure they did not lead to erroneous results in this study.
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Figure 4.5: Enhancement factors, $\beta$, and Warren Cowley parameters, $\alpha$, for the boxes shown in Fig. 4.3. The enhancement factors for the different simulated data sets are (a) fitting ideal calculated data with a random box, (b) fitting a dataset damped by an instrumental resolution function $S(r)$ with $\Delta Q = 0.031 \text{ Å}^{-1}$, (c) fitting a calculated dataset with a box with a 0.1% error in the lattice parameter, and (d) fitting calculated data with a systematic shift of 0.02 Å. The dotted lines in these plots indicate the bounds between which random fluctuations in the box are expected. Panels (e) and (f) show the Warren-Cowley parameters for the outputs. The dashed line shows the predicted L1$_2$ structure and the dotted line the idealised random value. In (e) the red line indicates the results of fitting the unaltered dataset and the blue line the instrumental dampened dataset. In (f) the red line indicates results from fitting the dataset with percentage change in the lattice parameter and the blue line the shifted dataset.
4.4 Results and discussion

4.4.1 Raw data

The raw X-ray diffraction patterns collected during the experiment are shown in Fig. 4.6. A slight shift in the position of the Bragg peaks with temperature is apparent in these data, corresponding to the lattice parameter change associated with thermal expansion. Likewise, there is the expected increase in the observed Debye-Waller factor.

Figure 4.6: Experimental diffraction patterns as a function of temperature. The data has been truncated in the y-axis, to focus on the changes in the diffuse scattering signal closer to the baseline space. The temperature increases from top to bottom. Datasets labelled in italics were gathered during heating of the as-sprayed sample, those in plain text were obtained during the first cooling ramp and those in bold during the second cooling ramp (see Fig. 4.2).

Three of the data sets (300°C and two at 400°C) show evidence of L1₂ super-lattice peaks. Careful inspection at low 2θ, also identified an apparent increase in the diffuse scattering signal (increased curve to the background at the location of the super-lattice peaks) as the temperature was reduced towards the ordering temperature (Tₓ ~ 400°C). It should be noted that there are additional small peaks present at 2θ ≈ 3.7°. These peaks correspond to Cu₂O, that is likely to have formed during the water atomisation process. Fitting the data using a Rietveld refinement, the phase fraction of this impurity was estimated to be ≈ 1.2%, which will have no measurable contribution to the PDF.

The change in lattice parameter with temperature is shown in Fig. 4.7. Overall, the variation with temperature is linear. However, there are notable discrepancies in the 300°C and 400°C datasets, and a gradual shift away from the trend in the samples between 410°C and 500°C. This reduction of the lattice parameter on ordering is to be expected, as in the L1₂ structure the Au atoms are surrounded only by Cu atoms, removing the larger Au-Au correlations and
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Figure 4.7: Change in lattice parameter of the copper gold alloy with temperature. The black crosses indicate lattice parameters obtained from the Rietveld fits with a random structure and the circles are the lattice parameters obtained from the ordered L1₂ structure.

allowing the lattice to contract.

4.4.2 RMC fitting - random box, translations only

RMC fitting was carried out using large box models representing \(20 \times 20 \times 20\) supercells of the unit cells obtained from Rietveld refinement (32,000 atoms). The data were corrected for the instrumental resolution, as described previously, using the \(S(r)\) function with \(\Delta Q = 0.031\ \text{Å}^{-1}\), calculated from a consideration of the full width at half-maximum of the peaks in the \(F(Q)\).

RMC refinements were initially carried out using boxes containing a random distribution of atoms, allowing only translational moves and fitting the \(r\)-range to the maximum value possible in \(~75\ \text{Å}\) supercells (i.e. \(~37.5\ \text{Å}\)). This procedure means that any remaining discrepancies between data and model must be caused by changes in site occupancy, i.e. chemical ordering in the system. The difference between the experimental PDFs and the calculated values is shown in Fig. 4.8. From this figure it is immediately obvious that the largest discrepancy is in the 400°C samples. This is unsurprising given that these are two of the three samples that have superlattice Bragg peaks corresponding to the L1₂ structure. Comparing these two difference PDFs to that of the 300°C sample it is interesting to note that they appear similar up to around 22-23Å. As noted in the Bragg data, the 300°C data show small superlattice peaks that suggest the formation of the L1₂ superstructure. This difference PDF suggests that these domains of L1₂ are no more than around 2.5nm in size in the 300°C sample.

In the other datasets, there is little appreciable difference beyond c. 17Å. The low \(r\) region does, however, suggest a systematic change with decreasing temperature. This is apparent in the relative magnitudes of the two peaks in the doublet at 3-4 Å and subsequently in the doublet at 7-8Å. The development of short-range order into long-range order is likely to proceed in one of two ways. First, a statistical model can be proposed whereby order forms homogeneously throughout the structure, resulting in a change in the observed local concentration in a specific coordination shell compared with the nominal stoichiometry. In this case, order would be limited to only a few correlation shells and exhibited as a difference in the low \(r\)-region of the PDF.

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Figure 4.8: Plot of the difference $T(r)$s after fitting the data with $20 \times 20 \times 20$ supercells containing a random configuration of atoms using the RMCProfile algorithm, allowing translations only. Datasets labelled in italics were gathered during heating from the as-sprayed sample, those in plain text were obtained during the first cooling ramp and those in bold during the second cooling ramp (see Fig. 4.2).

Only. Alternatively, micro-domains of an ordered phase can form that gradually grow through the structure. It is likely that such domains would be larger than the typical RMC box size. Consequently, changes will occur across the whole $r$-range typically used in PDF fitting, with the magnitude of the difference in the PDF increasing with the volume fraction of the material occupied by the domain. The difference PDFs, therefore, suggest that this type of short-range order is better described by a statistical growth model as opposed to a micro-domain growth model.

Fig. 4.9a shows the final $\chi^2$ values from the same fits used to generate the difference PDFs shown in Fig. 4.8. The differences in these $\chi^2$ values show the quality of the fits under the restriction of randomly distributed atom types in the structure. Therefore, these $\chi^2$ values can be used as indications of the level of chemical short-range order present in the structure at different temperatures, as the quality of the fit should not be temperature dependent if the system has been run for a sufficiently long time to allow convergence.

From this graph, the clear additional order present in the structures with identifiable superlattice peaks can be seen by the comparatively large $\chi^2$ value. Above $600 \, ^\circ C$ the fits have the same $\chi^2$ value, suggesting that above this temperature the sample is indeed random. A line has been added to the graph to indicate this ‘random’ baseline, as indicated by the $\chi^2$. Interestingly, there does appear to be some order present in the low-temperature samples ($<300 \, ^\circ C$). The room temperature sample is the as-sprayed sample and the order present in the sample must therefore be representative of a melt quenched sample of Cu$_3$Au. This itself is a significant result as it indicates that either some level of ordering must exist in the melt (less likely owing to the
lack of order present in the sample close to melting at 900°C), or that the ordering transitions occur fast enough for limited local order to develop during the melt quenching process. As the temperature is increased the comparative level of order reduces, prior to the formation of the superlattice peaks.

Data acquired from the sample at 500°C suggest some level of order exists at this temperature, although possibly different levels of order due to the previous heating regime. The second 500°C measurement was made after the sample was reheated above $T_c$ following the formation of the ordered structure. Therefore, it may be the case that the formation of the additional order at 500°C is due to the fact that the sample was not heated sufficiently to allow the sample to fully randomise. There is also an increase in the level of ordering on cooling between 500°C and 410°C, prior to the appearance of superlattice peaks, suggesting the formation of short-range order in this temperature region, as has been suggested in the literature.

### 4.4.3 RMC fitting - translations and swaps

The $\chi^2$ values obtained following RMC fitting, allowing atom types to swap, are given in Fig. 4.9b. The results show no significant difference in the $\chi^2$ values, which suggests that the system has converged and the additional chemical order has been accounted for. Fig. 4.10 provides a more detailed comparison of the partial correlation functions obtained from the boxes fitted to the data acquired at 900°C (Fig. 4.10a) and the 400°C 2nd hour (Fig. 4.10b), which exhibits the highest level of order. The configurations from which these partials are calculated can be found in Fig. 4.11. Comparing the two configurations, it is apparent that ordering has occurred in the system. It is important to note, however, that the ordered structure formed in Fig. 4.11(b) is not an ordered domain, as is expected, but is occurring throughout the system. Owing to the inherent random nature of the RMC algorithm, the result of such a refinement is likely to be the least ordered configuration that best represents the data, assuming multiple configurations.
that yield the same level of fit exist. Consequently, it is highly unlikely to produce an ordered micro-domain in the simulation, and will favour instead configurations more representative of statistical order. Therefore, conclusions of this nature must be drawn from the difference plots (as already discussed) and not on the basis of the large box models.

Figure 4.10: Partials from the output of RMC fits, allowing both translations and atomic swaps, carried out on the data collected at (a) 900°C and (b) 400°C (2nd hour). The red line indicates the Cu-Cu partial, the green line the Cu-Au partial and the blue line the Au-Au partial. Dotted lines indicate the expected peak positions from the lattice parameters. The inset in panel (a) shows how the expected peak positions relate to the lattice parameter in an fcc lattice.

In Fig. 4.10a there is an apparent difference in the maximum of the partials in the first coordination cell. A closest approach constraint, preventing atoms from forming correlations at shorter distances than a given value, was set in the system at 2.2 Å, but crucially this was the same for all atom types, and no other distance window constraints were applied to the system. As such, this difference in bond length is believed to be real and not a result of the
fitting constraints used. This is seen in the data acquired at all temperatures and is as would be expected from a hard sphere model considering the relative atomic radii of the Cu ($\sim 1.28 \, \text{Å}$) and Au ($\sim 1.44 \, \text{Å}$) atoms. Moving to higher shells, there is little difference in the maxima of these peaks and instead average values determined by these bond lengths are observed.

Importantly, the difference in atomic size is likely to cause local strain within the lattice. At higher temperatures the lattice is given more vibrational energy and the system is observed to expand. This may offset the disparity in atomic size and relieve some of the strain in the system. At lower temperatures ordering occurs in the system, with the gold atoms becoming surround by copper atoms ($C\text{-}1$ Clapp configuration). This is apparent in Fig. 4.10b where a reduction in the Au-Au partial is observed. This will result in a concomitant reduction in the lattice strain and a decrease in the lattice parameter, as observed in Fig. 4.7. Other energetic effects, such as the relative change in bond energies on the formation of more Cu-Au bonds and reduction in Au-Au bonds may also contribute to this ordering effect, but the decrease in local lattice strain is likely to be a strong contributing factor.

As will be discussed in Chapter 7, the level of lattice strain in an alloy can be inferred from a consideration of the FWHM of the PDF peaks. Fig. 4.12 shows a plot of the calculated FWHM for the first peak in the PDF with temperature. As expected, increasing the temperature leads to an increase in the observed peak width, as the dynamic displacements in the structure increase. However, the increase is not linear. The discrepancy must be due to an accompanying change in the static displacements with temperature. Therefore, it appears that the system orders in such a way as to reduce the level of local lattice strain in the structure. What is more striking is the resemblance of this graph to the variation of the lattice parameter shown in Fig. 4.7. Taken together this suggests that the reduction in the lattice parameter, and ordering occurring within the system, are likely associated with the removal of unfavourable Au-Au interactions that cause high levels of local strain in the structure.

![Figure 4.12](image.png)

Figure 4.12: Variation in the observed FWHM of the first peak in the PDF of Cu$_3$Au with temperature.
4.4.4 Neutron data

Neutron total scattering data were collected from the room-temperature as-sprayed Cu₃Au powder. For X-ray data the scattering strength is roughly proportional to the atomic number, Z. As such there is a large scattering contrast between Cu (Z = 29) and Au (Z = 79) atoms. For neutrons, the scattering lengths are \( \bar{b}_{\text{Cu}} = 7.718 \text{ fm} \) and \( \bar{b}_{\text{Au}} = 7.63 \text{ fm} \) [77]. Consequently, the Cu and Au atoms are essentially indistinguishable. It is therefore expected that the level of ordering in a Cu-Au alloy would be essentially invisible in neutron data. As such, neutron scattering provides a method by which it is possible to confirm that the ordering observed in the system from fitting to X-ray data is real, and not merely a consequence of the RMC fitting algorithm.

A comparison of the room temperature fitted datasets using X-ray and neutron radiation are shown in Fig. 4.13. In the X-ray data there are notable differences in the areas of the partials that make up the later peaks, whilst there are distinct differences in the positions of the peak maxima in the different partials, corresponding to changes in the interatomic distances. In contrast, the partials calculated from the neutron data show no obvious differences. This confirms that the order observed in the box fitted to the X-ray data is likely to be real and not merely an artefact of the fitting algorithm. Similarly, it should be noted that during the 12 hours of fitting the X-ray data the total number of accepted swaps quickly plateaus to a value on the order of 5,000 - 10,000. Fitting the neutron data, however, the atoms were continuously swapped, with a similar number of swaps being performed approximately every 15 minutes, showing that swapping had no effect on the goodness-of-fit.

![Figure 4.13: Partials from the RMC fits to data acquired from the room temperature as-sprayed sample allowing both translations and swaps for the X-ray and neutron data. The red line indicates the Cu-Cu partial, the green line the Cu-Au partial and the blue line the Au-Au partial. The dotted lines indicate the expected peak positions from the lattice parameters. The inserts show the number of swaps as a function of time for the fitting of the two data sets respectively.](image)
4.4.5 Warren-Cowley parameters and Clapp configurations

The output boxes from the RMC runs were analysed using the methods described in Chapter 3, calculating the enhancement factors and Warren-Cowley parameters for these systems. The Warren-Cowley $\alpha$-parameters for the first ten co-ordination shells, obtained using this method, are shown in Fig. 4.14a. It can be clearly seen that the $300 \, ^\circ\mathrm{C}$ and $400 \, ^\circ\mathrm{C}$ data all contain the oscillations that would be expected with L1$_2$ ordering of the material. At many of the other temperatures it appears that the sample is random. However, there is a distinct change in the first couple of coordination shells.

As discussed in Chapter 3, the Warren-Cowley parameters average some of the finer information in the system and are often less sensitive descriptors of the ordering present in the box. As such, it is perhaps unsurprising that the oscillations dampen faster than might be expected from observation of the difference PDFs. Even so, it is again important to note that there appears to be no systematic increase in all of the coordination shells, but rather an initial increase in the closest coordination shells, providing further indication that the order forming is statistical, as opposed to microdomain. However, as already noted when considering the output configur-
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ations, this may be the result of the random nature of RMC algorithm, and such conclusions should therefore be treated with caution.

The Clapp configuration enhancement factors, $\beta$, were calculated for a series of boxes run with both translations and swaps fitting the X-ray PDF data. An example of the enhancement factors calculated from the 900 °C data is shown in Fig. 4.14b. All the enhancement factors are within the bounds of statistical noise, suggesting that the sample is truly random. In comparison, the data obtained from the sample at 400 °C (2nd hour), Fig. 4.14c, shows a distinct pattern of enhancements in specific Clapp configurations. A series of refinements were also run including the Bragg data, which added the additional constraint that the obtained model must agree with the long-range average structure as well as with the short- to mid-range structure described by the PDF. Fig. 4.15 shows the enhancement factors (for all datasets) for those configurations that are most enhanced and some of the other configurations of interest. For many of the samples, there is a reduction in the $C1$ Clapp configuration, panel (b). This indicates that the lattice parameters used in the simulation are correct and the correction for the instrumental resolution has been carried out successfully.

The L1$_2$ structure is made from only two Clapp configurations: the $C16$ and $C-1$. These configurations do show significant enhancement in the data obtained from the sample at 400 °C (2nd hour), Fig. 4.14c. However, several other Clapp configurations also show significant enhancements, which can be rationalised by considering the degradation tree from the Clapp configurations, Fig. 4.16a. Fig. 4.16a shows the small portion of this tree for the configurations that are observed to be enhanced in this system. The $C16$ configuration contains four unlike atoms arranged in a planar configuration, Fig. 4.16b. The $C34$ and $C7$ configurations are then structurally related, and hence connected by a degradation pathway: the $C34$ is similar to the $C16$ Clapp configuration with an additional out-of-plane unlike atom, whilst the $C7$ is similar to the $C16$ with one of the in-plane unlike atoms replaced by a like atom. For a key structural motif, such as the $C16$ configuration in the L1$_2$ structure, enhancements in the related configurations ($C7$ and $C34$) are also to be expected, and indeed are observed in our atomistic models.

It is possible that these enhancements in the $C7$ and $C34$ configurations are responsible for the additional diffuse scattering that has been reported to exist in conjunction with the ordered structures in some of the early studies on this system [60]. By comparing the data acquired from the sample at the low temperatures, $<300$ °C, with those obtained at room temperature it is apparent that there is an increase in some of the observed Clapp configurations. The data correction for this sample is the same as for the other samples, and consequently it is believed that these enhancements are likely to be real. This sample is in the ‘as-sprayed’ condition i.e. water-quenched from the melt, and therefore these results suggest that the rate of formation of the L1$_2$ may be sufficiently fast to occur during the quenching process. It is also possible that this effect has occurred as a consequence of incomplete mixing in the melt. However this would be expected to give rise to a similar level of order in the 900 °C sample, which in fact exhibits lower enhancement factors. Therefore, it is more likely to be attributable to ordering during quenching, although, further experiments would be needed to confirm this hypothesis. This also raises questions about the assessment of order in this system in previous ex situ studies, where
Figure 4.15: Clapp configuration enhancement factors, $\beta$, from the output boxes from the RMCProfile fits to total scattering data recorded at different temperatures. The dotted lines indicate the upper and lower bounds expected due to statistical variation. The different panels represent specific Clapp configurations a) C-1, b) C1, c) C7 d) C16 e) C17 and f) C34.
4.4. Results and discussion

Figure 4.16: (a) Degradation tree for the 400 °C (2nd hour) sample (Clapp configuration enhancement factor, $\beta$, shown in italics) with the configurations where $\beta \geq 3$. The dominant pathway, apparent from the enhancements in the data, has been highlighted by the solid line (b) Clapp configurations for the dominant pathway shown in (a).

the observed order may be the result of rapid formation during the quenching process.

As the temperature decreased from 500 °C to the transition, there was a systematic increase in the $C-1$ and $C16$ configurations (and related $C7$ and $C34$). This can be explained as an increase in the short-range order in the system related to the L1$_2$ structure and is as expected. From the enhancement factors, there is also a notable difference in these configurations between the datasets acquired at 500 °C and 600 °C, but the difference between the two 500 °C datasets is comparatively less than that expected from the $\chi^2$ values.

Some earlier experiments on the Cu$_3$Au system have suggested that the D0$_{22}$ structure may form during the ordering process to the L1$_2$ structure. Indeed, if the ordering is in response to the strain of the large Au-Au bond distance and occurs entirely to remove this strain by surrounding Au atoms by Cu atoms, then in a Cu$_3$Au alloy the energetics of the L1$_2$ and D0$_{22}$ structures would be the same. The D0$_{22}$ is formed by the $C-1$, $C16$ and $C17$ so can be distinguished from the L1$_2$ structure by the presence of the $C17$ configuration. This is shown in panel e) of Fig. 4.15, in which there is an observed increase in the $C17$ configuration at all temperatures, apart
from after the appearance of the superlattice peaks at 400°C. It should also be noted that, whilst the C17 configuration increases as the temperature is cooled from 900°C to 500°C, there is little variation in the region 500°C to 410°C.

Based on these conclusions it is possible to suggest the ordering that now may be occurring in the ‘solid-solution’ region of the Cu₃Au phase diagram. Fig. 4.17 shows a schematic illustration of the ordering that occurs during the cooling process for a sample of Cu₃Au. Close to 900°C the system is thought to be at the most random. However, even at this temperature enhancement factors outside the bounds of the statistical random are calculated. Likewise, there was still an observed change in the bond distributions of the partials at 900°C. If the local strain caused by these partials is indeed the driving force of the ordering, then this difference in the partials is likely like create some order, even at this elevated temperature. Between 900°C and 500°C there is an increase in the observed order, particularly in the C-1, C16 and C17 configurations, which suggest the formation of order tending towards both the D0_{22} and L1₂ LRO structures. Below 500°C the number of C17 configurations remains constant, whilst the C16 continues to increase. Finally at 400°C the system completely orders to L1₂ and the C17 configurations are removed.

![Figure 4.17: Schematic of the ordering that occurs during the cooling process for a sample of Cu₃Au cooled from 900°C to room temperature. Au atoms are shown in red, Cu atoms in yellow and orange spheres represent a mixture of atom types.](image)
4.5 Conclusions

In the previous chapter, the methodology and analytical methods for the assessment of short-range order in alloys were presented and discussed. The data presented here, on the Cu₃Au system, have demonstrated the efficacy of this technique for the analysis of subtle variations of order in metallic systems using a combination of pair distribution functions and RMC techniques. The generation and fitting of simulated datasets highlighted potential artefacts in obtained models that could result from incorrect data processing. Avoiding such errors is of vital importance if a correct determination of the order present in the system is to be successfully accomplished.

Cu₃Au was observed to undergo an ordering transition, to the L₁₂ structure at $\sim 400$ °C, in agreement with values from literature. This transition was apparent both in the appearance of superlattice peaks in the Bragg data and the change in the area under the peaks in the PDF. Prior to the transition, different levels of short-range order were also apparent, evidenced by changes in the PDFs, demonstrating the high-level of information content available through this methodology. By considering the Clapp configuration enhancement factors and the fitting $\chi^2$ values, a systematic increase in the ordering was identified in the temperature range $400 < T < 500$ °C. The order identified confirms previous reports of the existence of short-range order in the region $400 < T < 600$ °C. By evaluating the Clapp configuration enhancement factors, the increased configurations (C-1, C7, C16, C34) clearly identify the type of ordering as being related to the L₁₂ formation. The presence of C17 configurations in the output revealed the presence of some D₀₂₂ type ordering, which forms as a precursor to the long-range ordered L₁₂ structure, and is removed upon long-range ordering.

The identification of order in the melt-quenched sample suggested that local-ordering in this system may occur much faster than previously expected. Many of the previous studies on this system have identified order in ex situ samples. Given the rate at which order forms in this sample, it is possible that these previously measured levels of order could be the result of ordering during the quenching process, as opposed to the thermodynamically stable state at the quenching temperature. The identification of different levels of order at 500 °C, could suggest that the system was not sufficiently randomised prior to the second total scattering measurement; hence the order exhibited in the region prior to the transition could be growth of an ordered region that was nucleated at a lower temperature. Further in situ studies are required to identify the true level of order that is thermodynamically stable in this crucial region.

Examination of the partials PDFs calculated from the RMC-obtained models, revealed differences in the relative bond length distributions for the different bond types at all temperatures. This is as expected from the relative sizes of the atomic radii of Cu and Au. These difference were not seen in the model obtained from fitting to neutron total scattering data; the neutron scattering lengths of Cu and Au are similar enough to render them indistinguishable. This further illustrates the impressive level of information available from the PDF. The datasets exhibiting superstructure peaks show a distinct decrease in the occupation of the Au-Au partial in the first coordination shell, resulting in a reduction of the largest interatomic distances and hence a contraction in the observed lattice parameter and a decrease in local lattice strain. Finally a comparison of the difference plots obtained from fitting the data with a random atomistic configuration, suggested that the formation of the order in this structure occurs continuously.
throughout the system, rather than in the growth and expansion of ordered micro-domains. This was also confirmed by the observed fluctuations in the Warren-Cowley parameters and further supports that this is the mechanism through which order develops in Cu$_3$Au.
Chapter 5

Ordering in Ni-based superalloys - $\gamma$ phase

5.1 Nickel-Molybdenum and Nickel-Tungsten alloys

Ni-Mo is one of the family of so-called $(1 \frac{1}{2} 0)$ scatterers (see Appendix C), so named due to the presence of superlattice peaks at this position. The phase diagram for the Ni-Mo system is shown in Fig. 5.1. Below around 875 $^\circ$C, alloys of composition Ni-20at.%Mo have been observed to undergo an ordering phase transition from the disordered A1 alpha-phase to the ordered beta-phase D1$_a$ Ni$_4$Mo structure (tetragonal). The transition is accompanied by a hardening in the system, suggested to be the result of the formation of small domains of the $\beta$-structure within the host $\alpha$-lattice. However, the use and necessity of a micro-domain model, for describing SRO, is under much debate in the literature, with the Ni-Mo system often cited as one of the most contentious cases. The alignment of the two lattices has been observed experimentally [11] to occur in six distinct orientations.

A neutron diffraction study [11] identified SRO present in compositions of 10.7-at.% Mo and 20.0-at.%Mo at various temperatures above the ordering transition. The observed SRO seemed to be analogous to the LRO structure that forms at low temperatures, suggesting disperse particles of the long-range ordered structure might be forming, with an estimated dimension equivalent to 10 unit cells, the same dimension predicted for maximum order hardening [79]. Variations in SRO with quenching conditions were also noted, although there was no obvious correlation between the quenching temperature and the observed degree of SRO. Early electron diffraction studies [80] suggested that the ordering transition occurred by the growth of the micro-domains, present in the SRO alloy, into the LRO structure observed. This has been supported by subsequent experiments [81,82], which concluded that the diffuse scattering observed at $(1 \frac{1}{2} 0)$ is due to a combination of micro-domains of the D1$_a$ structure, observed in a mixture of the 6 possible orientations in which it can exist, and the hypothetical Ni$_2$Mo structure, analogous to the Pt$_2$Mo structure. Theoretical calculations carried out by Clapp and Moss [83] suggested that the formation of micro-domains was unlikely, and that a simple statistical order model was sufficient to explain the experimental observations in the literature. Chakravarti et al. [84] suggested that the increase in domain size with annealing observed in a sample of c. 18.9-at.%Mo could be directly responsible for the increase in yield stress and strengthening of
the system. Further studies [85] by the same authors indicated a preference for a rod-like morphology in the formation of the micro-domains of the Ni$_4$Mo, due to a suggested preference for a Mo atom to be surrounded by unlike neighbours. This particular morphology has also been noted in Ni-W alloys [12, 86].

The Ni$_3$Mo structure is orthorhombic and analogous to the D0$_{22}$ (Cu$_3$Ti) structure (see Fig. 6.2). The process of the formation of the structure, which is related to a hexagonal close packed structure rather than an fcc structure, has also lead to some debate in the literature. Das and Thomas [87] used electron microscopy techniques to show the formation of Ni$_2$Mo and Ni$_4$Mo as metastable phases during the ordering that occurs in Ni$_3$Mo. Work done by van Tendeloo [88] suggested that the D0$_{22}$ structure formed as a precursor to the formation of the Ni$_4$Mo (D$_{1a}$) and Ni$_2$Mo (Pt$_2$Mo).

The phase diagram for the Ni-W system is shown in Fig. 5.2. At low tungsten concentrations, nickel tungsten forms an analogous D1$_{3a}$ structure, Ni$_4$W, to that observed in the Ni$_4$Mo. Ammons and Spruill [12] noted SRO occurring in Ni-10at.%W by X-ray diffraction and used this to explain electrical resistivity anomalies observed in the system. An electron diffraction study by Mishra and Ranganathan [86] of Ni-15at.%W and Ni-20at.%W suggested that both formed ordered microdomains of Ni$_2$W and Ni$_3$W, whilst in the single phase fcc region. The Ni$_3$W structure is D0$_{22}$ and the Ni$_2$W has the Pt$_2$Mo structure, analogous to the Ni$_2$Cr structure.

Given the extensive use of Mo and W as solid solution strengthening alloying elements in the gamma phase of nickel based alloys, an understanding of the ordering occurring in these systems would be valuable to an evaluation of the strengthening observed in the systems. Due to the large difference in atomic number, and thus the magnitude of the form factors, these alloys are suitable for an X-ray total scattering study.
5.1. Nickel-Molybdenum and Nickel-Tungsten alloys

5.1.1 Experimental details

An experiment was proposed and carried out on the Diamond I-15 beamline, to investigate ordering occurring in samples of Ni-15at%Mo (referred to as Ni-Mo) and Ni-15at%W (referred to as Ni-W) under in situ heat treatments. To fully randomise these samples it is required to raise the temperature to nearly 1500°C. This was well above the temperatures accessible using the hot gas blower, and therefore a different experimental setup to that used for the Cu₃Au investigation was required. It was proposed to use a portable Linkam furnace, which has a nominal maximum operating temperature of 1500°C. The furnace heats a small sample in an alumina crucible, holding the sample in position with a wire. The furnace has silica windows on either side and a hole in the base of the crucible. Aligned correctly, it should be possible to pass the beam through this hole, to reduce any additional background from the crucible. The furnace operates under flowing argon, and is water cooled on the exterior.

For this apparatus, samples are required in a small pellet geometry. It was attempted to make such pellets by pressing the powder using a pellet press and die apparatus. However, owing to the highly spherical nature of the atomised powder particles, it was found that insufficient force could be applied to successfully form a powder pellet by this method. Instead, it was proposed to form the samples by sintering the powders. Gas atomised powder samples of the alloys were sealed in quartz tubes under argon and heat treated to allow sintering. The resultant sintered bars were cut with an Accutom to form small pellets. For the Ni-Mo pellets of 1mm thickness were cut, whilst for Ni-W, 0.5mm pellets were cut. Ideally, the sample should be as thick as possible to maximise the incident number of crystals in the beam. However, this also reduces the transmission of the beam, and therefore a thickness must be chosen that balances these two counteracting effects.

In addition, a number of other samples were prepared in the fine quartz capillaries typically...
used in these experiments for ex-situ heat treatments. Unfortunately, many of these samples softened and deformed during the heat treatment process, and resulted in an unusable sample geometry. Of greater concern was an obvious blotchy discolouration on the surface of the Ni-Mo samples, then indicated that the samples had undergone a reaction with the silica. The potential result of the silica ingress on the samples was unknown, and consequently the samples were treated with caution.

Having loaded the pellet samples into the Linkam furnace a number of additional problems were faced. The most notable one was the quality of the data that was produced. There was difficulty in aligning the apparatus, so the beam passed cleanly through the set-up. In many instances it resulted in an absorption shadow pattern on the detector, showing the internal heating element structure of the furnace crucible. With correct alignment, it was possible to collect data. However, even with correct alignment there were concerns about the background caused by the silica windows of the apparatus.

More significant was the quality of the data produced. The highly scattering nature of the materials resulted in ghosting on the detector, which meant the time between measurements had to be dramatically increased. In addition, it became apparent in the post-processing of the data that the top of the most intense Bragg peaks were flat. This suggested that the scattering of the sample was so strong and the intensity of the peak so high, that it reached the maximum value recordable by the detector. Consequently, any such irradiated pixels will read out the maximum value, resulting in a flat top or ‘clipping’ of the peak. Unfortunately data sets that demonstrate such a clipping are of limited use, as the resultant effect on the total scattering functions is not known.

Further, as the sample geometry was now a flat pellet, the sample remains in a fixed orientation throughout the experiment (i.e. spinning is not possible). The quality of the data is therefore reliant on a sufficiently large number of crystallites in a random orientation to produce a crystallographic powder average. Unfortunately, it was found that this was not the case, as the pellets demonstrated a very spotty powder pattern and overall produced low quality total scattering data.

In addition, both samples showed pronounced discolouration after the heating process, suggesting oxidation of the samples - that was also observable in the Bragg pattern. Although the system was being held under argon, commercially available argon contains a small contamination of oxygen. As there is a continuous flow of Argon during the experiment, this actually results in the sample being exposed to an appreciable partial pressure of oxygen, which at the high temperatures at which the sample is held does result in significant oxidation. The Rietveld fits of the Bragg data demonstrated that the Ni-Mo had oxidised to MoO$_2$ and the Ni-W to the unusual W$_5$O$_{14}$ - a distinct purple oxide that coated the surface of the pellet. For the Ni-W case, literature [89] suggested that the formation of the oxide may be catalysed by the presence of nickel or iron. The unit cell of this oxide is shown in Fig. 5.3. One possible explanation for the formation of this oxide may in fact be the presence of an ordered structure in the alloy. By forming SRO this could create a patterned template for the W atoms from which the oxide can grow. However, further experimentation would be required to validate this hypothesis.

Finally, there was a question about the quality of the thermal contact between the sample and
the furnace, and the temperature actually achieved by the sample. The Linkam was originally calibrated offline using both a thermocouple and pyrometer, and found to be relatively accurate. However, an experiment being run concurrently with this experiment using the same apparatus, suggested that the Linkam was not achieving the required temperatures (by comparing a known transition temperature to the transition temperature observed when heating in the Linkam). It is thought that this may have been due to a combination of poor thermal contact when the apparatus was in a vertical geometry on the beamline and a decaying heating element (that had to be subsequently replaced).

Owing to the experimental issues encountered, the data obtained from this experiment were unfortunately of insufficient quality to accurately determine any order occurring within either system. It should be stated that the Linkam furnace is used for a number of diffraction experiments at Diamond and is still an invaluable piece of equipment for in-situ heating experiments. However, owing to the requirements for low background and texture free data, it is not currently ideally suited for the collection of total scattering X-ray data \textit{in situ}. It is hoped that this experimental set-up could be revisited in the future as it could provide an important method of accessing the higher temperatures, required in such alloy systems, unavailable with current experimental setups. In addition the Ni-Mo and Ni-W still provide interesting cases of short-range order that could provide fertile ground for study.
5.2 Nickel-Chromium alloys

Of the elements added to nickel-based alloys, chromium is particularly important as it provides both solid solution strengthening and improved environmental resistance. In addition, Ni-Cr alloys are used extensively in the manufacture of thermocouples, and are found to demonstrate a drift in electrical resistivity over their lifetimes that could be attributable to the formation of SRO. The phase diagram for the nickel-chromium alloy system is shown in Fig. 5.4. For nickel-rich compositions at high temperature an $fcc$ solid solution is observed; whilst at the chromium-rich end of the compositional range a $bcc$ structure is formed. At low temperatures in the nickel-rich end the Ni$_2$Cr structure has been observed in X-ray [90] experiments. A significant degree of undercooling is often required for nucleation of this long-range ordered phase (up to 40 K below the 845 K transition temperature at stoichiometric composition). The relation of this structure to the parent $fcc$ lattice is shown in Fig. 5.5. This structure is the same long range ordered structure observed in Pt$_2$Mo and is one member of the family of $(1 \frac{1}{2} 0)$ SRO structures (see Appendix C).

![Figure 5.4: Binary phase diagram for Ni-Cr taken from [91].](image)

![Figure 5.5: Theoretical ordered Ni$_2$Cr structure. Blue dotted lines show the unit cell of the material, red dotted lines indicate the relationship of this structure to the $fcc$ lattice. Grey spheres represent nickel atoms and green spheres represent chromium atoms.](image)
5.2. Nickel-Chromium alloys

Anomalies in the physical properties of nickel-chromium alloys, such as electrical resistivity [14] and specific heat [13], have been attributed to short range ordering in the system. The observed increase in electrical resistivity upon ageing and reduction of resistivity on cold working suggested the existence of the so-called Komplex (K-) state [92] in the high Ni-content alloys. The exact nature of the K-state is the matter of some controversy in the literature. Some sources [93] attribute the specific heat anomalies to micro-domains of an ordered structure existing in a partially ordered matrix; although these results have subsequently been refuted by several others [94,95] who proposed instead that the K-state exhibited statistical order. Whilst the K-state leads to an increase in resistivity, precipitation of the Ni$_2$Cr structure at higher Cr concentrations leads to a decrease in the resistivity. The K-state at Ni-33at.\%Cr has been observed to undergo a distinct lattice contraction upon annealing, unobserved in Ni-25at.\%Cr. Work carried out by Popov et al. [96] suggested that dislocations would move in triplets through the Ni$_2$Cr; later identified in electron microscopic observations [94].

Specimens close to the Ni-33at.\%Cr composition, investigated by electron diffraction [94], showed that, whilst the structure is analogous to the Pt$_2$Mo structure, the type of rhombic splitting characteristically observed in the Pt$_2$Mo structure was not seen in these specimens. The study also suggested that the size of the micro-domains could be up to several hundred Angstroms. Pair potentials and SRO parameters were calculated, from diffuse scattering peaks at (1 1 2 0) in single crystal samples of Ni-20at.\%Cr recorded at different temperatures using constant wavelength neutron diffraction at the ILL, Grenoble [10]. The study confirmed preference for opposing nearest-neighbors in the system, that was corroborated by further experiments carried out on Ni-11at.Cr [97]. Using these parameters, Inverse Monte Carlo (IMC) models predicted that, below 400 $^\circ$C, Ni$_2$Cr is metastable and should revert to ordered Ni$_3$Cr and Ni$_2$Cr$_2$. Experimentally, no ordered Ni$_3$Cr precipitates have yet been observed, whilst Ni$_2$Cr$_2$ has been seen to decompose into a mixture of fcc and bcc phases. This may be due to a compositional dependence of the interaction parameters used in the IMC calculations. Similarly, Caudron [98] noted that the IMC method calculated a transition temperature close to 350K (compared to the experimentally observed transition near 900K) unless the $J_9$ energetic term was made negative (as determined experimentally [97]). Successful X-ray experiments [99], using the $3\lambda$ technique [30], have also been undertaken, that were in agreement with the results obtained from neutron experiments.

An examination of the system Ni-19.9at.\%Cr was undertaken by Schönfeld [100]. Using Warren-Cowley parameters and modelling the system, the data were broken down to suggest possible Clapp configurations and hence LRO structures that may contribute to the SRO observed. A number of the (1 1 2 0) structures were considered, even those not physically observed in the phase diagram of the system. The presence of the C8 configuration suggested that the D1$_a$ structure may be important as well as the hypothetical A$_2$B$_2$ structure. Recent studies [101] from ab initio electronic calculations have accurately reproduced the experimental ordering observed in the system by Schonfeld [10].
5.2.1 Experimental details

Due to the interest in this alloy from both the superalloy and thermocouple communities, it provides a good case example for demonstrating how total scattering may provide insight into local order, and how this may be linked to important physical phenomena. Total scattering data on a single alloy sample of Ni-25at.%Cr (referred to as Ni-Cr) was collected at the ISIS Neutron Source on the POLARIS diffractometer. The alloy was the end member of a set of alloys Ni$_x$Co$_{(0.75-x)}$Cr$_{0.25}$. Initially, solid alloy fingers were made by arc melting. These were sent to TLS Technik, where they were gas atomised to produce a fine powder (<100 µm). The powder was loaded into quartz tubes and sealed under argon. The powder was heat treated at 600°C for 100hrs. The cooled sample was broken using a percussion mill and loaded into a vanadium can. Total scattering quality data for the sample was collected over a period of 6hrs.

The Mantid software was used to reduce the data and generate a file suitable for Rietveld fitting. A Rietveld fit was carried out using the GSAS software, and the total scattering data processed and reduced using the GudrunN software. The data were Fourier transformed using the StoG programme with a $Q_{\text{max}} = 36$ Å$^{-1}$, chosen to minimise truncation ripples and noise in the $G(r)$. The total scattering functions were subsequently fit using RMCPProfile. The composition of the sample was confirmed by XRF measurements, and the homogeneity by EDX.

5.2.2 Results and discussion

Rietveld fits of the data demonstrated that the material could be well described by a single phase stoichiometric random fcc structure. From the fit, the lattice parameter of the material was determined as 3.55337 ± 0.00014 Å. Initial RMC fits were carried out using smaller configurations (10 × 10 × 10, containing 4,000 atoms), and then progressed to using large configurations (20 × 20 × 20, containing 32,000 atoms). Fits were carried out fitting the $F(Q)$, $T(r)$ and Bragg data simultaneously.

However, although these refinements produced high quality fits to the data, an analysis of the resultant configurations demonstrated that there was a significant data processing error in the system. One of the example output configurations is shown in Fig. 5.6a. From the figure it is apparent that there is a definite preference for atoms of the same type to cluster together. Although the literature suggested that clustering might be observed, forming chromium rich microdomains, the composition of the domains produced by these RMC runs are well beyond the bounds predicted by the literature. Fig. 5.7 shows an example of the $T(r)$ fit from RMC after a period of translations only. There is a pronounced difference in the quality of the fit at high-$r$ compared with low-$r$. A similar effect is observed in the $F(Q)$ data. By the nature of the fitting algorithm, it is normally observed that the fit is improved in the low-$r$ region first, so this may at first seem unsurprising, and could suggest that the refinement has not been run for long enough. However, closer inspection of the data and the fit (see insert on Fig. 5.7), and a comparison with the starting configuration, revealed a distinct offset in the data.

This indicated that the peak position in the total scattering functions was not consistent with the lattice parameter calculated from GSAS. Comparing this plot with the plots of simulated data artefacts discussed in Chapter 4, Fig. 4.4, it can be seen that this difference plot is similar to that predicted for the scaled and linear offsets. It was, therefore, necessary to apply an offset
5.2. Nickel-Chromium alloys

Figure 5.6: Example output configurations from RMC refinements of the Ni-25at.%Cr data. (a) Original fits without corrections (b) After applying offset correction. Grey spheres are Nickel atoms, green spheres are chromium atoms.

Figure 5.7: $T(r)$ fit for the Ni-25at.%Cr data. Refinement halted after 60 mins of allowing only translational moves. Black crosses show data, red line the fit and the offset blue line the difference. Insert on the graph shows a magnified version of the fit at c. 27 Å, from which the offset is apparent.
to the data to correct for this effect. By applying a correction to the $F(Q)$ and then applying the
Fourier transformation using StoG, the Gudrun data can be brought in line with that calculated
using the lattice parameter from GSAS.

A simple linear correction may be proposed as:

$$Q_{\text{offset}} = mQ + c \quad (5.1)$$

To calculate the required offset the experimentally measure $F(Q)$ needs to be compared with
that predicted. A random configuration is set up using the GSAS lattice parameters and a small
Gaussian displacement of a similar magnitude to that observed from thermal displacements is
applied to all of the atoms in the system. The theoretical $F(Q)$ and the $\chi^2$ compared with the
experimentally measured data is calculated. The scale and offset ($m$ and $c$) are then varied to
rescale the $Q$-values of the observed data. The data is rebinned and the new $\chi^2$ calculated. A
plot of the variation in $\chi^2$ with $m$ and $c$ is shown in Fig. 5.8.

From this plot it was found that the optimum offset was $m = 1.00228$ and $c = -0.00398$.
The application of this scale offset is shown in Fig. 5.9, demonstrating how the fit and data
may be brought into line. Note that the difference in intensities of these peaks is due to the
fact that the configuration has not been completely refined. Running with these offsets now
produces boxes like that shown in Fig. 5.6b, showing that the clustering is indeed the result of
data processing errors in the system. This raises the question of the origin and cause of the
offsets in the system.

There are believed to be two main sources of error in neutron experiments that result in this
observed variation and offset; the first is due to the method by which the system is calibrated and
the second the result of conversion of data sets between the programmes used for the analysis.
5.2. Nickel-Chromium alloys

Figure 5.9: Theoretical and observed $F(Q)$ for the Ni-25at.%Cr (a) without and (b) with applied $Q$-scale and offset. Red line - theoretical dataset, calculated from a box using the GSAS lattice parameter. Black line - data processed in GudrunN and StoG.

The first problem arose due to the combination of the data sets from the Polaris diffractometer itself. The Mantid software serves to merge the data sets from the 3008 individual detectors on the diffractometer into their respective banks. In order to do this successfully, and calculate corrections for the individual banks and any instrumental offsets that are required, a silicon standard is used. The software takes the spectra from each detector and converts it to $d$-spacing; a reference peak is then taken in each spectra and the offsets for each detector calculated to bring the peaks in line with one another. It was found that the Mantid software was not then comparing the reference peak value to that from the silicon calibrant, so it was chance as to whether the combined peak, with the applied offsets, was in the correct position. This has now been corrected; after the offsets have been applied to bring the peaks in line with one another, they are all then shifted to equal the known standard $d$-spacing value of the calibrant. This removes the majority of the offset, however there is still a smaller effect from the output of the data.

The second problem was concerned with the data transfer and conversion between the programmes used for analysis. It is worth recalling the relationship between time-of-flight (TOF) and $d$-spacing. The energy of a neutron can be given as:

$$ E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = \frac{mL^2}{2\ell^2} $$

(5.2)

where $h$ is Planck’s constant, $m$ the mass of a neutron, $\lambda$ the wavelength, $t$ the time of flight, $p$ the momentum, $v$ the particle velocity and $L$ the detector path length. Therefore:

$$ t = \frac{m}{\hbar}L\lambda $$

(5.3)
Chapter 5. Ordering in Ni-based superalloys - \(\gamma\) phase

Braggs law can be recast from

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

(5.4)

to

\[
t = \frac{2m}{h} L \sin \theta d
\]  

(5.5)

where \(d\) is the interplanar spacing and \(\theta\) the scattering angle. The GSAS software applies an offset correction to the data of the form:

\[
t = \text{DIFC}d + \text{DIFA}d^2 + \text{ZERO}
\]  

(5.6)

where \(\text{DIFC}\), \(\text{DIFA}\) and \(\text{ZERO}\) are GSAS diffractometer constants. Therefore, by neglecting the \(d^2\) and \(\text{ZERO}\) term:

\[
\text{DIFC} = \frac{2m}{h} L \sin \theta
\]  

(5.7)

The parameter \(\text{DIFC}\) is determined by the geometry of the instrument. The Mantid software contains values for \(L \sin \theta\) for all of the detectors, and so implicitly, values for \(\text{DIFC}\). During calibration, Mantid refines these values so that the peaks are in alignment when converted from TOF to \(d\)-space. Mantid then uses these values when combining the detector banks in processing the data. However, when Mantid outputs the data, for use by GSAS in a Rietveld refinement, it converts the \(d\)-space data back into TOF using the engineering drawings and values of \(L \sin \theta\) for the diffractometer, rather than the refined values it previously calculated. Subsequent GSAS fitting then allows a refinement of the instrument parameters, including \(\text{DIFC}\) (expected for the highest scattering angle back).

The Gudrun software operates independently from Mantid and performs a similar calibration for the individual detector banks. However, unlike Mantid, it subsequently uses these \(L \sin \theta\) values in all transforms performed in the calculations. Consequently, there will be a slight discrepancy in the scale on which the data from GudrunN and Mantid are plotted. Problems arise when attempting to combine a GSAS-derived lattice parameter with the \(Q\)-space data from Gudrun. The difference in these values is only small, but, as has been shown by the apparent clustering that develops in the model, this can have a large impact on the refined configurations and the subsequent conclusions that are drawn from it.

To correct for this second problem a new version of the StoG programme was written by Dr. Helen Playford, and released in RMCProfile. The programme takes the calculated \(\text{DIFC}\) values from GudrunN and the measured instrument parameter values from GSAS and uses these values to rescale the \(Q\)-values of the data, making it compatible with the lattice parameter value obtained from GSAS. The data subsequently presented has used this new version of StoG, to account for these offsets.

A preliminary examination of the fits produced with the offset-corrected data revealed a further issue: when the Bragg is more heavily weighted, the programme struggles to fit the \(G(r)\) and \(F(Q)\) data. This is most likely due to the fact that whilst GSAS, and subsequently the
Bragg calculation in RMCProfile, takes account of instrumental parameters, Gudrun and hence the $F(Q)$ and $G(r)$ do not. The effect of low $Q$-space resolution is a pronounced damping of the $G(r)$ at higher $r$, as discussed for Cu$_3$Au in Chapter 4. However, for time-of-flight neutron diffractometers, the resolution is both $Q$- and angle-dependent and so cannot be corrected for using the same function as used in Chapter 4. In addition, as the neutron $F(Q)$ data will be formed by the merging of the banks, the resolution function will be a composite of the different resolution functions of the individual banks. Consequently, this composite instrumental resolution function can be incredibly complex. If a suitable instrumental function is generated, every point in $Q$ can be convolved with said function, before the application of the Fourier transform. This is extremely computationally expensive and complex and requires an accurate determination of the complex composite instrumental function. An easier practical solution is to fit only a restricted $r$-range, as the low-$r$ data will be unaffected by the damping. This is discussed in greater detail with reference to the L1$_2$ samples in section 6.1.5.

For the Ni-Cr data, RMC refinements were carried out as follows:

1. 20×20×20 supercells of the fcc structure were generated. Nickel and chromium atoms in a ratio of 3:1 were distributed randomly across the structure. A small Gaussian displacement of atoms away from their idealised locations was applied.

2. The total scattering functions $G(r)$ and $F(Q)$ were prepared using StoG (accounting for the offsets), varying the scale factor from 0.76 - 1.10 in steps of 0.01 and using a $Q_{\text{max}} = 36 \, \AA^{-1}$ (chosen to minimise Fourier ripples).

3. RMC refinements carried out, fitting to the $T(r)$, allowing only translations to occur in the system. Two data sets are input into the system: a) $T(r)$ up to 9.5 Å and b) 1st peak in the $T(r)$. This limited $r$-range should help to correct for the instrumental $Q$-resolution effects.

4. Boxes refined further allowing only swaps to occur.

5. Boxes refined further allowing both swaps and translations.

6. From a consideration of the resultant $\chi^2$ values of these refinements a suitable scale factor is chosen for each of the materials.

These steps allow a choice of the best scale factor for the system. The resultant calculated $\chi^2$ values from the scaling runs may be found in Fig. 5.10. From these fits a scale value of 1.04 was chosen, such that the $\chi^2$ was minimised for the broader $r$-range fit.

Having determined this scale factor, the following refinements are performed:

7. Fourteen 20×20×20 supercells of the fcc structure were generated. Nickel and chromium atoms in a ratio of 3:1 were distributed randomly across the structure. A small Gaussian displacement of atoms away from their idealised locations was applied.

8. The total scattering functions $G(r)$ and $F(Q)$ were prepared using StoG (accounting for the offsets), with the chosen scale factor and $Q_{\text{max}} = 36 \, \AA^{-1}$.
9. The RMC refinement process carried out in steps 3-5 is carried out using the fourteen supercells.

The results of the fits using this scale are shown in Fig. 5.11. Fig. 5.11(c) shows the high level of fit to these data that is obtained. Fig. 5.11(a,b) show the partials calculated from these fits and the corresponding partials if the system is randomised. As can be seen from (a) there is a notable difference in the distributions of the partials for the fitted and random case. At first glance it may appear that there is greater occupation of the NiNi (red) partial across the range due to the increased height of the peaks. However, closer observation nearer the baseline shows that there is also a difference in width, between the partials. Therefore, the exact occupation of the partials is difficult to tell from visual inspection alone.

However, the calculated Warren-Cowley parameters, Table 5.1, show that there is some degree of local ordering occurring within the system, as these values are non-zero. This agrees with what was visually apparent in Fig. 5.6b, where the Cr atoms do not appear to be distributed entirely randomly in the configuration. The negative first nearest neighbour interactions agrees with observations made in the literature. The table also shows the values for the LRO structure Pt$_2$Mo. Comparing the observed values with the theoretical values, the signs of the $\alpha$-parameters for the shells are found to be broadly in agreement. However, there are some important differences. Most importantly, the fitted data show a preference to form unlike 2nd nearest neighbours, that is not observed in the theoretical LRO structure. This is particularly significant given that the alloy is off stoichiometry from the Pt$_2$Mo structure. As such the material contains more nickel atoms, and so the shells that have $\alpha = 0$ are expected to become slightly positive, rather than the negative values observed. Therefore, although overall the pattern is broadly similar, there may be some distinct differences in the structures that are observed to form.

This may be confirmed by considering the enhancement factors in Fig. 5.10(d), where it is apparent that certain configurations are enhanced above the statistical random. Importantly, there is no observed enhancement in the C1 configuration, as discussed in Chapter 4, suggesting that the rescaling and offset correction has been correctly applied. In addition there is
5.2. Nickel-Chromium alloys

Figure 5.11: Results from fit of the Ni-25at.%Cr sample. (a,b) Calculated partials from fit and random configurations. Red - NiNi, Blue - NiCr, Black - CrCr, (c) Fit of the $T(r)$ from RMCPProfile. Black crosses show data, red line the fit and the blue line the calculated difference (offset for visualisation); (d) Calculated enhancement factors for the Clapp configurations from the refined configurations. Error bars calculated from the different enhancement factors calculated for the 14 different configurations run. Black dotted lines indicate the region in which an enhancement may be considered as statistically random.

Table 5.1: Measured Warren-Cowley parameters, $\alpha$, for the first 10 coordination shells, and their associated errors.

<table>
<thead>
<tr>
<th>Shell</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>-0.0433</td>
<td>-0.0375</td>
<td>0.0537</td>
<td>-0.0431</td>
<td>-0.0023</td>
<td>0.0296</td>
<td>-0.0022</td>
<td>0.0094</td>
<td>0.0097</td>
<td>0.0008</td>
</tr>
<tr>
<td>Error</td>
<td>0.0005</td>
<td>0.0027</td>
<td>0.0020</td>
<td>0.0014</td>
<td>0.0016</td>
<td>0.0022</td>
<td>0.0004</td>
<td>0.0024</td>
<td>0.0012</td>
<td>0.0015</td>
</tr>
<tr>
<td>$\alpha_{Pt_2Mo}$</td>
<td>-0.25</td>
<td>0</td>
<td>0.25</td>
<td>-0.25</td>
<td>0</td>
<td>0.25</td>
<td>-0.25</td>
<td>0</td>
<td>0.5</td>
<td>-0.25</td>
</tr>
</tbody>
</table>

a significant enhancement of the $C_8$, which agrees well with theoretical predictions from the literature [100]. Considering only the most enhanced configurations, those with an enhancement factor $\geq 10$, the type of structural motifs that are enhanced in the local ordering can be considered. These configurations, and the degradation pathways that connect them, are shown in Fig. 5.12. Structures that are aligned vertically have the same number of like first nearest neighbour atoms, i.e. the same local concentration.

As discussed in section 5.2, it has been suggested that at low temperatures that it may be possible for Ni-Cr alloys to order to the Pt$_2$Mo structure. If this is the case, enhancements in the
Figure 5.12: Enhanced configurations and degradation pathways for fitted Ni-25at.%Cr data. Numbers are the observed enhancement factors, taken from Fig. 5.11(b). Solid arrows indicate the dominant degradation pathway, dotted arrows the minor pathways. Grey circles represent Ni atoms and green circles Cr atoms.

$C\text{-}4$ and $C\text{38}$ structures are expected, as was discussed in Chapter 3. These data do suggest a pathway that is linked to the $C\text{38}$; however, the dominant structure with that local concentration is the $C\text{37}$ structure. For the negative configurations (which will be predominately occupied by the Cr atoms) it is the $C\text{-}5$ configuration that dominates over the $C\text{-}4$, both of which have the same local concentration. In fact the $C\text{-}4$ configuration is not observed to be enhanced in the structure. It therefore appears that for this heat-treated sample, the local structures, although similar to those necessary to form the Pt$_2$Mo structure, are not the same. This contrasts with the Cu$_3$Au sample, where the local order seemed to be tending towards the observed long-range ordered structure. This discrepancy appears to be due to the change in the second shell occupation that was noted in the $\alpha$-parameters. For the system to fully order and form the Pt$_2$Mo structure, the magnitude of this second shell effect would have to be reduced.
5.3 Conclusions

In this chapter, the ordering occurring in binary alloys Ni-Cr, Ni-Mo and Ni-W has been considered, due to the extensive use and importance of Cr, Mo and W as substitutional elements in the gamma matrix of nickel superalloys.

To investigate ordering in Ni-Mo and Ni-W, an \textit{in situ} heating X-ray total scattering experiment was designed. However, owing to a combination of experimental difficulties, total scattering data of sufficient quality for the analysis of ordering in Ni-Mo and Ni-W could not be obtained using the \textit{in situ} heating experimental setup. This experiment highlighted many of the issues raised in the previous theoretical work and development of the methodology; in particular the necessity for a crystallographic powder average, the importance of sample preparation methods, and a high-signal to noise ratio in recorded data.

The conclusions that can be drawn from the Ni-25at.%Cr sample are limited, as only a single composition at a single temperature has been considered. That being said, this sample has proven invaluable in the consideration of the correct data processing of neutron total scattering data. Fitting of the data initially resulted in very obvious clustering in the output RMC configurations, which was identified as the result of incorrect data processing. The apparent offset in the data demonstrated two key issues in the processing of data. First, an issue in the calibration sub-routine in Mantid, that has subsequently been corrected. Secondly, a calibration error in the time of flight conversion caused by the processing of the same dataset via different routes - namely Mantid/GSAS and GudrunN. A linear offset method was initially proposed and used, and is still useful in the processing of old neutron data or data from other beamlines. For the Polaris instrument, the correct mathematical correction has also been calculated and applied in a new version of the StoG programme.

Having applied these corrections, it was then possible to fit the data and obtain an insight into any ordering that might be occurring in the alloy. Owing to the additional complications of the \(Q\)-variable composite instrument resolution function, it was necessary to fit the data using only a limited \(r\) range. Using the quality of the fit to the data as a guide, the ‘correct’ scale value of the sample was chosen. The output configurations suggested that there was some level of local order occurring within the system. The order favours the \(C-5\) and \(C37\) Clapp configurations and their related pathways. This does not reflect the predicted LRO structure that the material is thought to tend towards, as it shows a distinct preference to form unlike 2nd nearest neighbour correlations, that is not observed in the Pt\(_2\)Mo structure.

Overall the sample has demonstrated the use of neutron total scattering data for such analyses, has led to the adaptation of robust processing routines, and has shown that the Ni-Cr system may be a viable area for future study. Unfortunately, literature suggests that the ordering observed in samples of Ni-Cr can take place over a significant time scale (>1,000hrs), rendering an \textit{in-situ} study of this material impossible. To allow an accurate determination of the state of order in such alloys both long-term \textit{ex situ} heat treatments and an improved understanding of the effect of quenching are required.
Chapter 6

Ordering in Ni-based superalloys - $\gamma'$ phase

6.1 L1$_2$ alloys

As discussed in chapters 1 and 5, the majority of the high temperature strength of nickel-based superalloys is derived from the presence of fine dispersions of $\gamma'$ precipitates, which are based on Ni$_3$Al, within the random gamma matrix. As dislocations pass across the coherent interface, between matrix and precipitate, energetically unfavourable planar defects are generated in the $\gamma'$ phase including: complex stacking faults (CSF), superlattice extrinsic stacking faults (SESF), superlattice intrinsic stacking faults (SISF) and antiphase boundaries (APB) $^{[102]}$. As a result, dislocations travel together and may undergo a variety of dissociation reactions to minimise the energies of the planar defects created between them. Theoretical treatments of dislocation behaviour in superalloys identify two key regimes. First, weak dislocation coupling, in which the $\gamma'$ precipitates are sufficiently small to allow matrix dislocations to pass through separately, leaving planar defects across the full width of the precipitate. Second, strong coupling, in which it is energetically favourable for matrix dislocations to pass through larger $\gamma'$ precipitates in pairs. It has been shown that the increase in the critical resolved shear stress is dependent upon the APB energy, $\gamma_{\text{APB}}$, varying with $\gamma_{\text{APB}}^{\frac{1}{2}}$, and $\gamma_{\text{APB}}^{\frac{1}{2}}$ for weak and strong coupling respectively $^{[103]}$. Consequently, the APB energies can be used to predict the strength of a material and therefore correct calculation of these values is very important for future superalloy development.

However, the direct determination of APB energies by electron microscopy is notoriously difficult with considerable discrepancy between the values reported in the literature. As such, theoretical prediction of APB energies are attractive and approaches have been proposed by which APB energies may be predicted as a function of alloy composition from thermodynamic data, such as that proposed by Miodownik and Saunders $^{[104]}$. However, in these models no allowance is given to the possibility of short-range order effecting APB energies, but rely instead on nearest neighbour interactions calculated using the Bragg-Williams method $^{[105]}$. This assumes a statistically disordered distribution of atoms within the sub-lattices.

In addition to the importance for the superalloys community, this work is highly significant for the analysis of short range order. Owing to the mathematical complexity of the previous
single crystal analyses, there are only a handful of ternary system studies [26, 106, 107]. For example, an extension of the 3A technique would require a sample to be measured using six different wavelengths. Through analysis of total scattering data it may be possible, however, to access local information in these more complex systems for the first time.

By applying total scattering techniques to a family of gamma prime alloys, it is hoped that any preferential ordering on the sub-lattices in the structure may be identified. This ultimately may allow the adaptation of existing theory to account for SRO in such systems, and explain the existing discrepancies between experimentally and theoretically determined APB energies.

6.1.1 Phase diagrams and structure consideration

It is important to consider the type of structures that might be expected to occur, due to substitution of X for Al in the L1\textsubscript{2} lattice. Taken from the literature, Fig. 6.1 shows a number of experimentally determined binary phase diagrams for the Ni-Al-X systems. The phase diagrams are shown for a constant Nickel concentration, with the Al-X ratio changing.

![Figure 6.1: Binary phase diagrams for Ni\textsubscript{3}(Al,X) for a) Ta [108], b) Ti [109] and c) Nb [110].](image)

For all the substitutions there is an appreciable solid solution of the X atom onto the Al site in the L1\textsubscript{2} in the structure. However, for the pure Ni\textsubscript{3}X the different elements form different structures. Some substitution of Ta leads to the the Ni\textsubscript{3}Ta\textsubscript{0.5}Al\textsubscript{0.5} structure, the D0\textsubscript{24} structure; whilst complete substitution yields the D0\textsubscript{8} structure. Titanium substitution likewise results in
6.1. \( \text{L}_{12} \) alloys

the \( \text{D}_{024} \) structure, whilst Nb substitution results in \( \text{D}_{022} \) ordering.

These structures, as well as the \( \text{L}_{12} \) structure, are shown in Fig. 6.2. The \( \text{L}_{12} \) is cubic with space group \text{Pm}-3m; the \( \text{D}_{022} \) is tetragonal (I4/mmm); \( \text{D}_{024} \) is hexagonal (P6\text{3}/mmc); and, the \( \text{D}_{0a} \) structure orthorhombic (Pmmn). Although at first glance, it may appear that these structures are not similar, they can all be considered as being composed of close packed layers. Two of these structures, \( \text{L}_{12} \) and \( \text{D}_{022} \), demonstrate a cubic close packing stacking sequence of the layers \( \text{ccp} \), whilst the others are hexagonally close packed, \( \text{hcp} \). These terms are used independently of the ordering within the layers and refer to the sequential positional layering of the structures. The formation of such layers suggests that the first shell potential is similar for all of the structures. Further insight into the nature of the structure can be found by considering the partial pair distribution functions of these LRO structures. For each of the structures, the theoretical partial pair distribution functions were calculated and are shown in Fig. 6.3.

![Figure 6.2: Common structures of Ni\textsubscript{3}X alloys. a) \( \text{L}_{12} \) - structure of Ni\textsubscript{3}Al, b) \( \text{D}_{022} \) - structure of Ni\textsubscript{3}Ta and Ni\textsubscript{3}Nb, c) \( \text{D}_{024} \) - structure of Ni\textsubscript{3}Ti and d) \( \text{D}_{0a} \) - structure of Ni\textsubscript{3}Ta and Ni\textsubscript{3}Nb. Nickel atoms shown in silver and X atoms shown in blue.](image)

The first note to make is that for all structures, the 1st shell is entirely equivalent, with the X-X partial being absent, and an increase in the Ni-X partial. Comparing the first nearest neighbour correlations in these structures, it is important to note that all four structures are identical, if only first nearest neighbour correlations are considered. This is perhaps surprising as it suggests that the local first shell potential for all of these structures is similar. All four structures form Ni-Ni and Ni-X correlations, at the expense of X-X correlations. Whether this is due to favourable Ni-Ni and Ni-X correlations or unfavourable X-X correlations cannot be ascertained from the first peak alone - however, the relative stability can be. Importantly this
implies that, as the first coordination shells are identical and these are all ordered systems (and hence the entropy is constant = 0), the difference between them must be caused by a second (or higher) shell effect.

If the second coordination shells of the structures are considered, then the structures do become non-equivalent. This was discussed with reference to the Cu₃Au, Chapter 4, where it was noted that it is likely that a second shell potential was required to distinguish the D₀₂₂ and L₁₂ structures. What is perhaps surprising, is that whilst the two ccp structures are now distinguishable, and the two structures based on hcp are distinguishable, a pair of one of each type of structures are still indistinguishable i.e. L₁₂ and D₀₂₄ are the same; similarly D₀₂₂ and D₀₄. It is the next potential that is required to split these structures. Beyond the second shell, the shells in the hcp and ccp structures are no longer equivalent. The hcp structures now form a new third correlation shell between the 2nd and 3rd correlation shells of the ccp. Which structure forms will be dependent on the energetic potential experienced by atoms at this distance - a favourable interaction is likely to result in the formation of the hcp structure, whilst an unfavourable interaction will result in the ccp structure.

Considering the energetic potential at the distance required to produce an hcp structure, allows the rationalisation of the observed ordering transitions on substitution, and may suggest the type of ordering that could occur in the system. For the Ta system, there is a sequential change from L₁₂ → D₀₂₄ → D₀₄ upon Ta substitution. This suggests that Ta must have a large potential at the distance corresponding to the formation of hcp layers forming X-X correlations; this drives the formation of the D₀₂₄ hexagonal structure and then a further transformation to the D₀₄. Similarly, but to a lesser extent, the same series of structural transformations may ...
occur in Titanium; however, the potential is not of a sufficient magnitude to result in D0\textsubscript{a} formation. This suggests that the Ta-Ta interaction potential at this distance is comparatively larger in magnitude than the corresponding Ti-Ti potential. For the Nb ordering to D0\textsubscript{22}, the change will be driven by the second and third ccp shell potentials, as was suggested for the Cu-Au system.

Unlike the other elements considered thus far, which substitute onto the Al-sublattice, Co is known to substitute onto the Ni lattice in the gamma prime phase. Initially, the Co forms a solid solution upon substitution for Ni. However, increased Co concentrations result in a 2-phase mixture of the L1\textsubscript{2} and the CsCl (B2) structures, or a 3-phase mixture of L1\textsubscript{2}, A1 and B2. Therefore, commenting on the change that may occur is difficult, as the new structures formed are based on a body centred cubic, bcc, lattice and so cannot be considered coherently with the fcc structure, as has been done for the previous structures. The type of ordering that might be anticipated is unknown.

\subsection*{6.1.2 Numerical descriptors}

One of the obvious questions that arises when considering the use of total scattering for the analysis of ternary or higher systems is the extension of the numerical descriptors previously discussed in Chapter 3 to higher orders. For the Warren-Cowley parameters there is the extension to higher systems described by Ceguerra et al. [53], generalised multicomponent short-range order (GM-SRO) parameters. Alternatively a configurational analysis akin to the Clapp configurations may be carried out. Taking account of all the components leads to a vast number of possible configurations. However, these can be reduced by considering certain simplifications to the system.

In this case, our interest in ordering is limited to a site specific ordering. For the Ta/Ti/Nb samples the interest is in the structure of the Al sublattice. This lattice is a primitive lattice, where each atom has six neighbours arranged in an octahedral formation. If the composition of the alloy was precise then the occupation of the sublattice should consist of only Al and X atoms. Therefore, we can formulate the partitioning of atoms across the local configurational sites, in the same manner as Clapp. This was calculated for the Aluminium sublattice and the results are shown in Fig. 6.4.

Fig. 6.4a shows the naming of atoms in the structure, akin to the Clapp numbering methods. Fig. 6.4b shows the six possible configurations that result and the new label that has been assigned to them. These arrangements are familiar in the field of coordination chemistry and could equally be labelled with the terms used by that community: Al3='cis', Al4='trans', Al5='fac' and Al6='mer'. The same labelling convention is used for the negative configurations as was used by Clapp, a demonstrative example of which is shown in Fig. 6.5. Fig. 6.4c shows the comparatively simple degradation tree for these configurations.
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Figure 6.4: Possible configurations of two atom types for the Al-sublattice in the L1$_2$. a) numbering system for the sublattice points, b) the possible configurations and the labels that can be used to refer to them, c) Degradation pathways for these configurations. For more information on the numbering system see the note in Appendix B.

Figure 6.5: Demonstration of the labelling convention, using the same method as Clapp. If all the atom types are inverted, the same configuration label is used. However, only the nearest neighbour atom types are inverted, but the central atom remains unchanged, then the sign of the configuration label changes.

A similar question can be posed for the Nickel sublattice in L1$_2$ for the case of Co substitution. Again, the different arrangements of the structure may be calculated and reduced by symmetry, yielding 22 configurations. These configurations are shown in Fig. 6.6. The configurations have been grouped to reflect the same local concentration (i.e. the same number of nearest neighbours), with the levels in the degradation tree corresponding to these groupings. Fig. 6.7 shows the degradation pathways that relate these configurations.

Using these sublattice configurations, it is possible to perform similar analyses to those carried out in the binary alloy system, through the calculation of enhancement factors. It should be noted that this has assumed a perfect occupation of the sublattices by only two components. If there are more than two components on the sublattice, it may be necessary to combine different element types to simplify the calculation.

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6.1. L1₂ alloys

Figure 6.6: Possible configurations of two atom types for the Ni-sublattice in the L1₂. Figure shows the sublattice structure and numbering, and the 22 possible configurations and the labels that can be used to refer to them.

Figure 6.7: The degradation pathways of the 22 Ni-sublattice configurations of the L1₂, shown in 6.6.
6.1.3 Experimental details

An experiment was proposed and carried out on the Polaris diffractometer at the ISIS neutron source. The experiment was designed to investigate the distribution across the sites in the ordered gamma prime structure and determine if such systems are truly disordered on the sub-lattices, or if there is any indication of ordering above and beyond the sub-lattice site preference. The following substitutional elements were chosen for study: Ta, Ti, Nb and Co. The samples prepared are shown in Table 6.1.

The samples were prepared as described in previous sections - gas atomising, sealing in quartz under argon and heat treating. A small sample of each of the alloys was cut from the sintered bar, and used for melting point determination via DSC. From the data it was decided that the alloys should be homogenised at 1280°C, with the exception of Ni-Al-10Co, which would be homogenised at 1000°C. The samples were homogenised at given temperatures for 100hrs. The resulting fused powders were broken up using a percussion mill and placed in a Vanadium can at room temperature. The heat-treated powders were placed in the neutron beam and a powder diffraction pattern taken, counting for 25 µA hours initially for every sample. Additional measurements of the ‘as-sprayed’ powders were also taken, in order to allow comparison between the pre- and post- heat-treated conditions. These data were observed, and the samples that produced single-phase diffraction patterns were then re-run in order to gain a total counting time of 900 µAhrs. The data was processed using the Mantid software, Rietveld refinements in GSAS, processed in GudrunN and Fourier transformed using StoG. Subsequent fitting was carried out in PDFgui and RMCProfile.

6.1.4 EDX and Bragg data

Rietveld fits of the Bragg data suggested that all of the heat-treated samples were well described by a stoichiometric single phase L1₂ structure. To confirm the composition of the samples, EDX (energy dispersive X-ray spectroscopy) data from the alloys were collected using an SEM (scanning electron microscope). Samples were prepared by mounting a small quantity of powder in bakelite, grinding and polishing the mounted samples. The measurements were made with Dr. Katerina Christofidou. The measured concentrations and their associated errors are shown in Table 6.1. These concentrations were measured for a series of random points in the material, and the average calculated. EDX maps of the Ni-20Al-5X alloys are shown in Fig. 6.8 and similarly for the Ni-25Al-xCo alloys are shown in Fig. 6.9.

From Table 6.1 it is apparent that the alloys considered are close to their nominal stoichiometry. These measured compositions are the values that are subsequently used in the GSAS refinements, absorption corrections, processing of the data and in the configurational boxes used in RMC profile (these values can be found in Table 6.2). It should be noted that for all atoms the nickel concentration is slightly greater than expected. Therefore a small number of Ni atoms are expected to occupy Al-sites.

From the maps in Fig. 6.8, the Ni-25at.%Al (referred to as Ni-Al), Ni-20Al-5at.%Ta (referred to as Ni-Al-Ta) and Ni-20Al-5at.%Ti (referred to as Ni-Al-Ti) alloys appear to be largely homogenous. In the Nb alloy, however, a number of particles were found to have a much lower Nb concentration. From the map shown in the figure it can be seen that this was due to unincor-
### Table 6.1: EDX recorded compositions and associated errors for L1$_2$ alloys.

| Sample       | Nominal comp. (in at.%)
|--------------|------------------------|
|              | Ni | Al | X   | Measured comp. (in at.%)
|              | Ni | Al | X   | Ni | Al | X   |
| Ni-Al        | 75 | 25 | -   | 75.7 | 24.3 | -   |
| Ni-Al-Ta     | 75 | 20 | 5   | 76.5 | 18.5 | 5.0  |
| Ni-Al-Ti     | 75 | 20 | 5   | 75.1 | 19.2 | 5.6  |
| Ni-Al-Nb     | 75 | 20 | 5   | 76.2 | 18.9 | 4.9  |
| Ni-Al-5Co    | 70 | 25 | 5   | 73.3 | 21.8 | 4.9  |
| Ni-Al-10Co   | 65 | 25 | 10  | 66.8 | 23.2 | 10.0 |

<table>
<thead>
<tr>
<th>Sample</th>
<th>error (in at.%)</th>
</tr>
</thead>
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<tr>
<td>Ni-Al</td>
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</tr>
<tr>
<td>Ni-Al-Ta</td>
<td>0.5 0.6 0.1</td>
</tr>
<tr>
<td>Ni-Al-Ti</td>
<td>0.7 0.6 0.1</td>
</tr>
<tr>
<td>Ni-Al-Nb</td>
<td>0.8 0.9 0.3</td>
</tr>
<tr>
<td>Ni-Al-5Co</td>
<td>0.4 0.4 0.1</td>
</tr>
<tr>
<td>Ni-Al-10Co</td>
<td>0.6 0.5 0.4</td>
</tr>
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</table>

Figure 6.8: EDX maps of the Ni-20Al-5X alloys. a-b) Ni-25Al, c-e) Ni-20Al-5Ta, f-h) Ni-20Al-5Ti, i-k) Ni-20Al-5Nb. Scale bar indicated in the bottom right of each image.
Figure 6.9: EDX maps of the Ni-25Al-xCo alloys. a-f) Ni-25Al-5Co, x=5, g-l) Ni-25Al-10Co, x=10. Scale bar indicated in the bottom right of each image.
porated pure Nb remaining in the sample. Due to this additional complication the Nb sample has been temporarily discounted from consideration.

Fig. 6.9 shows the maps for the Ni-25Al-Co samples. For the Ni-25Al-5at.%Co (referred to as Ni-Al-5Co) sample there are distinct regions that are Al rich and poor. Therefore, this sample has also been removed from consideration. The Ni-25Al-10at.%Co (referred to as Ni-Al-10Co), however, is homogenous. This map also shows the spherical nature of the powder particles formed by the gas atomisation process. From these images, there is an apparent variation between the different samples in the amount of sintering that has occurred. The Ni-Al-10Co showed almost no sintering between powder particles, whilst the Al,Ti,Ta showed some sintering and the Ni-Al-5Co showed nearly complete sintering, with almost no indication of the the initial spherical powder particle structure.

6.1.5 Fitting the PDF

Based on the quality of the Rietveld fits and the EDX observations, the structures are initially assumed to be single phase L1$_2$. Atomic configurations were set up to reflect this, using $20 \times 20 \times 20$ supercells of the L1$_2$ structure. Within each sublattice the atoms are distributed randomly. Initially these large box models were run, fitting the $F(Q)$ and $T(r)$ data simultaneously, across the entire $r$ range. The system was run for a variety of scale values, initially allowing only translations, and subsequently translations and swaps across all sites.

Condensing the resultant configurations back onto a unit cell demonstrated that there was a large distortion to the atomic clouds, suggesting a data processing error in the system. To determine the potential source of the error, the PDFs were fitted using PDFgui. The lattice parameters, scale factors, damping factor, broadening factor and $\delta_1$ narrowing parameter were allowed to refine. The results of these values are shown in Table 6.2. The quality of the fits was high, demonstrating that overall the structure is well described by the L1$_2$ LRO structure. It should be noted, that as PDFgui is unable to account for the local ordering occurring, these values will necessarily be slightly incorrect. They will, however, suggest if these factors are an effect that needs to be considered.

As can be seen, all samples show similar values for magnitude of $Q_{\text{damp}}$ and $Q_{\text{broad}}$. The $Q_{\text{damp}}$ parameter is the same effect and correction that was discussed and corrected for in Chapter 4. The $Q_{\text{broad}}$ parameter, however, has not been considered previously. This function included in PDFgui is to account for a broadening of PDF peaks in real space, due to the

<table>
<thead>
<tr>
<th>Sample</th>
<th>PDF Gui refined values</th>
<th>Values used in RMCP</th>
<th>Profile</th>
</tr>
</thead>
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<td></td>
<td>$a$ / Å</td>
<td>Scale</td>
<td>$Q_{\text{damp}}$ / Å$^{-1}$</td>
</tr>
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<td>Ni-Al</td>
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</tr>
<tr>
<td>Ni-Al-10Co</td>
<td>3.5746</td>
<td>0.8153</td>
<td>0.0226</td>
</tr>
</tbody>
</table>

Table 6.2: Refined parameters from PDFgui fits, assuming a completely L1$_2$ structure and the values used in the RMC refinements. The $a$ values for the RMC refinements are taken from the GSAS Rietveld fits. The scale factors are chosen using the refinement method outlined.
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\( Q \)-resolution of the diffractometer. The value is incorporated in the equation:

\[
\sigma_{ij} = \sigma'_{ij} \sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q^2_{\text{broad}} r_{ij}^2}
\]  

(6.1)

where \( \sigma_{ij} \) is the width of the peak convoluted with the delta function, \( \sigma'_{ij} \) the width calculated from the thermal displacement parameters, \( \delta_1 \) and \( \delta_2 \) are parameters to correct for correlated motion, and \( r_{ij} \) the interatomic distance between \( i \) and \( j \).

The \( Q_{\text{broad}} \) factor should not have a large effect on the refinement of ordering in a system, as it will change the breadth of the peak, but will not affect the area. However, if this value is removed from the refinement there are dramatic changes in the refined value of the \( Q_{\text{damp}} \) term. As has been discussed and demonstrated in Chapter 5, this \( Q_{\text{damp}} \) term does have a large effect on the resultant fit and the observed order when using a large box model. To accurately determine the effect of \( Q_{\text{damp}} \), knowledge is required of the \( Q_{\text{broad}} \) parameter. As discussed in Chapter 5, in relation to the Ni-Cr sample, these effects could be removed from the system by calculation and convolution of the complex composite instrument resolution function. However, this is computationally laborious due to the nature of the convolution at every stage of the calculation.

An alternative method is to reduce the \( r \) region over which the fit is carried out. The function in Eq. 6.1 will have the greatest effect on the data at high-\( r \) values. This can be seen in Fig. 6.10, which shows a plot of the change in width of the peaks, and the instrument resolution function with \( r \), using the values calculated from the Ni-Al sample (shown in Table 6.2). The function from Eq. 6.1 is plotted both with and without the \( \delta_1 \) component. This is done to distinguish the sample components, which are real and will be accounted for in the large box refinement, from the instrumental components, which will result in artefacts.

![Figure 6.10: Plot of the variation in width with \( r \) and the instrument resolution function for the Ni-Al fit carried out in PDFgui. Green line shows the instrument resolution function, related to the \( Q_{\text{damp}} \) term. Red line - how the peak width function varies with \( r \) including the \( \delta_1 \) value. Blue line - how the peak width function varies with \( r \) excluding the \( \delta_1 \) value. Black dotted line indicates maximum \( r \) value used in RMC fits.](image-url)
From this plot it is apparent that the greatest effect of these factors on the data will occur at high $r$. By restricting the refinement to the low $r$ region, these effects will be minimal and will not result in large errors and artefacts in the resultant simulations. An $r$-range, over which the system is allowed to refine, should be chosen such that these functions are as close to 1 as possible, whilst still fitting a reasonable number of peaks (from the graph $r_{\text{max}} \sim 10\text{Å}$). For these alloys a cut-off at $r = 9.5\text{ Å}$ was chosen, which occurs at a minimum in the observed PDF.

The large box fits carried out previously, fitting the entire $r$ range, also demonstrated an additional problem with the refinement process in the case of Ni-Al-Ti. Owing to the negative scattering length of Titanium, the algorithm will often move the titanium atoms to positions to correct for variations in observed intensity anywhere in the pattern, resulting in physically unrealistic peak shapes in the partial PDFs. One such example is shown in Fig. 6.11. As can be seen, the refinement has dramatically shifted the titanium atoms to correct for the intensity at various locations, resulting in broad peaks and split maxima distributions, both of which are highly unlikely in a crystalline alloy. It is, therefore, necessary to use a refinement methodology that restricts such unphysical motions.

Taking these factors into account, the following refinement process was carried out:

1. $20 \times 20 \times 20$ supercells of the L1$_2$ structure were generated. A small Gaussian displacement of atoms away from their idealised locations was applied.

2. Based on the results of the EDX scans, the proportion of atoms of each type across each sublattice was calculated. From this, a grey atom scattering length for the two atom types, A and B - reflecting the two sublattices, were calculated.

3. The total scattering functions $G(r)$ and $F(Q)$ were processed, varying the scale factor from 0.76 - 1.10 in steps of 0.01 and using a $Q_{\text{max}} = 36\text{ Å}^{-1}$ (chosen to minimise Fourier ripples).

4. RMC refinements were carried out, fitting to the $T(r)$ allowing only translations to occur in the system. Two data sets were input into the system: a) $T(r)$ up to 9.5 Å and b)
1st peak in the $T(r)$. The $F(Q)$ data were removed from these refinements, as the $Q$-space resolution will still be an issue in these data and so would still affect the resultant refinement.

5. Using these positions, the real atom types were placed in the configuration, distributing the atoms randomly across the sublattices.

6. Refinements were carried out allowing only swaps (and no translational moves) on the individual sublattices.

7. Further refinements were carried out allowing swaps across all sites in the structure. No additional translations were allowed, due to the unphysical motion of the Ti atoms that results.

8. From a consideration of the resultant $\chi^2$ values of these refinements, a suitable scale factor was chosen for each of the materials.

The $\chi^2$ results from the scale determination run are shown in Figure. 6.12. From these runs the scale factors were chosen from the minima in the $\chi^2$ values (Table 6.2). For most of the samples, the minima in the $\chi^2$ for the 1st peak fit was slightly lower than the corresponding minima in the fits of the $T(r)$. The exception for this was the Ni-Al-10Co sample, where the values were coincident. In general, the scale value selected for use was taken from the minima in the $T(r)$ fit values. The chosen scale values are shown in Table 6.2.

Having chosen the scaling values that should be used in the processing of the data the following refinements were carried out:

9. Steps 1-7 were repeated with two changes: a) For each alloy, fourteen supercells were generated and refined, b) A single scale factor was used in Step 3 (that calculated from the previous refinements, shown in Table 6.2).

It should be noted that there is very little change in the quality of the fit between the swapping on-site and then allowing the swapping to occur across all sites. This suggests that the atomic distributions are well restricted to their denoted sublattices. Consequently, in the subsequent runs and analyses, the refinements for which swapping was allowed only within the sublattice were considered.

The resultant fits of the $T(r)$s are shown in Fig. 6.13. The plots demonstrate that an excellent level of fit to the data was achieved using this refinement process. There are slight discrepancies in all the plots just after the first peak caused by small Fourier ripples in the data. The partials related to these fits are shown in Fig. 6.14. To allow a consideration of how the occupation of the partials has changed on ordering, the output configurations were taken and randomised, allowing unrestricted swapping within the sublattices, and the partials for the resultant randomised structures calculated. These are also shown in Fig. 6.14. The partials were calculated as an average of the 14 configurations that were run for each sample.

Fig. 6.14(a) and (b) show the Ni-Al sample. From the EDX composition it is suggested that the Ni-sublattice is fully occupied by nickel atoms, whilst the Al-sublattice contains a mixture of Ni and Al atoms in a ratio of 0.9715 : 0.0285. For this run, three atom types were defined: Ni

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Figure 6.12: Plot of $\chi^2$ values from RMC profile fits of the $T(r)$ calculated for different scales values. Fits carried out initially allowing translations in a two grey atom model, then allowing swaps within the sublattice and then swaps across all atomic site. a) Ni-Al b) Ni-Al-Ta c) Ni-Al-Ti d) Ni-Al-10Co. The red line is the total $\chi^2$ value, the blue line the $\chi^2$ fitting the $T(r)$ up to $r=9.5\,\text{Å}$ and the black line the fit of the first peak in the $T(r)$.

on Ni-sublattice, Ni on Al-sublattice and Al on Al-sublattice. Owing to the very small number of Ni-atoms on the Al-sublattice, the interaction between these atoms is comparatively small, and hence the corresponding partial (shown in red) is very noisy. Owing to this it is difficult to see whether there is a change in the occupation of the site and, hence, the area under the partial. However, the much larger contributions on the sublattice (the blue and black partials) show little change between the random and fitted states, suggesting that there is no preferential separation of Nickel on the aluminium site. This is important, as it allows us to consider the Ni and Al as distributing randomly across this sublattice in the other samples.

For the Ni-Al-Ta sample, the ratio of atoms on the Al site is $0.059625 : 0.740625 : 0.19975$ for Ni:Al:Ta. Assuming that the Ni/Al are indistinguishable on the Al-sublattice, this reduces the Al-sublattice to possessing only two atom types, i.e. considered as a three atom system $\text{Ni}_3((\text{Ni},\text{Al}),\text{Ta})$. The same process is done with the Ni-Al-Ti where for the Al-sublattice $0.00575 : 0.768375 : 0.225875$ for Ni:Al:Ti, i.e. $\text{Ni}_3((\text{Ni},\text{Al}),\text{Ti})$. For the Ni-Al-10Co only the two atoms occupy the Ni-sublattice, whilst the distribution of atoms on the Al-sublattice is considered random. Consequently, for all of these alloys, the system can be reduced to three atom types and six partials - three of which will vary under sublattice ordering and three of which will...
remain constant. These are shown in Fig. 6.14(c-h), where the solid lines are variant and dotted lines invariant.

From the figures it is apparent that there is a change in occupation of the partials for the three systems and, hence, a sublattice ordering. For the Ni-Al-Ta, (c) and (d), there is an increase in the occupation of the Ta-Ta partial (black) for the 1st and 2nd coordination shells of the sublattice (the 2nd and 4th coordination shells of the alloy i.e. 2nd and 4th peaks). In contrast, for the Ni-Al-Ti, there is a slight decrease in the Ti-Ti partial for the 1st and 2nd shells of the sublattice. For the Co, there appears to be a periodic oscillation in the occupation of the different shells, shown by the variation in peak area of the partials. The three alloys, therefore, appear to be exhibiting very different orderings on their sublattices.

To describe the nature of the local ordering, the new sublattice configurations can be used, calculating enhancement factors using the same mathematics presented in Chapter 3. As with the partials, it is necessary to reduce our consideration to a binary occupation on the sublattice. The configuration enhancement factors are calculated using the following simplifications: Ni-Al-Ta - Al-sublattice contains two atoms of type Ta and (Al,Ni); Ni-Al-Ti - Al-sublattice contains two atoms of type Ti and (Al,Ni). The resultant configurations are shown in Fig. 6.15.

Figure 6.13: Plot of the fits to the $T(r)$ obtained using the fitting method and chosen scale described. Black crosses indicate the data, the red line the RMC fit and the offset blue line the difference.
6.1. L12 alloys

Figure 6.14: Plot of the partial pair distribution functions for the fitted and random structures of the L12 structures considered. Each system has been reduced to a 3 component system, with two atom types on the sublattice of interest and a singular grey atom on the other site. Dotted lines indicate partials that should remain invariant upon ordering. (a,b) Ni-Al - fitted and random, red - NiNi, blue - NiAl, black - AlAl (c,d) Ni-Al-Ta - fitted and random, red - AlAl, blue - AlTa, black - TaTa (e,f) Ni-Al-Ti - fitted and random, red - AlAl, blue - AlTi, black - TiTi (g,h) Ni-Al-10Co - fitted and random, red - NiNi, blue - NiCo, black - CoCo.
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Figure 6.15: Calculated sublattice enhancement factors for the fitted structures. Red bars indicate the Al-sublattice and blue bars the Ni-sublattice (a) Ni-Al (b) Ni-Al-Ta (c) Ni-Al-Ti (d) Ni-Al-10Co. Dotted lines indicate the bounds between which an enhancement may be considered statistically random.

For the Ni-Al sample, Fig. 6.15(a), all the configurations and errors lie well within the statistically random bounds, shown by the lines on the graph. This suggests that for this concentration of nickel on the Al-sublattice, the sublattice may be considered random. This validates the assumption made for the Ni-Al-Ti sample, that the Al and Ni atoms are randomly distributed on the Al-sublattice and therefore may be combined into a single atom type in the calculation of the enhancement factors. For the Ni-Al-Ta, as the occupation of the nickel on the sublattice is higher, it may be that this assumption is not valid. However, in the absence of additional data to the contrary, this will be accepted as valid.

Considering the Ni-Al-Ta, Fig. 6.15(b), only the $Al^1$ configuration demonstrates a significant enhancement. This configuration, shown in 6.16(a), is an atom surrounded by atoms of the same type and suggests the Ta does not want to distribute itself randomly across the sublattice, but will cluster together in specific regions.

In contrast, the Ni-Al-Ti sample, Fig. 6.15(c), shows an enhancement in the $Al^4$, $Al^4$ and $Al^6$ configurations. These configurations and their related degradation pathways are shown in Fig. 6.16(b). It is apparent that the greatest enhancement is in the $trans$ configuration of the octahedra, $Al^4$. Therefore, it appears that there is a preference for the Ti atoms not to occupy adjacent sites on the sublattice. Moving to the coordinations with higher local concentrations

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Figure 6.16: Enhanced configurations and degradation pathways for fitted L1₂ structures. Numbers are the observed enhancement factors. (a) Ni-Al-Ta (b) Ni-Al-Ti (c) Ni-Al-10Co. Solid arrows indicate the dominant degradation pathway, dotted arrows the minor pathways. These are the general configuration degradation pathways (not sample specific) and, therefore, red and blue circles represent A and B atoms. In (b) A & B are Al and Ti, in (c) A & B and Ni and Co.

of unlike atoms, the meridional ‘mer’, Al₆, arrangement is preferred, suggesting that a planar arrangement of Ti-atoms is more common.

Comparing the two samples it appears that the Ti and Ta have opposite sublattice ordering effects. For the tantalum to cluster, as observed, it must have a favourable Ta-Ta interaction for the 1st coordination on the sublattice, whereas the titanium is demonstrating a reduction in the Ti-Ti coordinations at the same distance. This would likely have different effects on the strength of the material and the APB energies. Further work would be required to assess the consequence of these contrasting effects on the physical properties of a material.

For the Ni-Al-10Co sample, Fig. 6.15(d), the occupation of the Ni-sublattice is considered. There are now more enhanced configurations, owing mainly to the larger number of different available arrangements of atoms across the sublattice. In particular, there is a very large enhancement in the Ni₂₁ configuration. The enhanced configurations and dominant degradation pathways are shown in Fig. 6.16(c). It can be seen from this figure that this configuration shows the Co atoms preferentially form a square arrangement in the structure, along with the related degraded structures.

Recall that as this alloy is L1₂ in nature, every atom on the Ni-sublattice occupies the C16 configuration. By defining the nickel sublattice configurations, the system is restricted to a consideration of ordering across the like-atom sites within the C16 configuration. The C16
structure also demonstrated the unlike atoms forming a square arrangement around the central atom. It therefore appears that the cobalt atoms are ordering in such a way as to create a square arrangement in a plane perpendicular to that of the aluminium atoms, see Fig. 6.17. The driving force behind such an ordering could, therefore, be similar to that causing the initial L1\textsubscript{2} ordering - i.e. the removal of like nearest neighbour interactions in favour of unlike interactions. However, energetic simulations would be required to determine the cause of this effect.

### 6.2 Conclusions

Variations in $\gamma'$ sublattice order could have pronounced effects on the APB energies of nickel based superalloys. Understanding this order is therefore important to the prediction of a material’s strength. Historically, analysis of short-range order has been limited to the study of binary alloys, owing to the complexity of the mathematical techniques used, when extended to ternary or higher order systems.

This chapter has presented work from an investigation carried out to determine the presence and nature of sublattice ordering occurring within a set of L1\textsubscript{2} alloys. Taking the Ni\textsubscript{3}Al alloy as a reference, the structures that result from different atomic substitutions on the different lattice sites have been considered. Of particular interest are the substitutions of Ta, Ti and Nb on the Al-sublattice and Co on the Ni-sublattice. The possible configurations that may occur across the sublattices have been determined and described. These configurations have been labelled and the relationship between the configurations shown.

Samples were prepared by standard preparation methods and neutron total scattering data collected at the ISIS neutron source. Rietveld fits demonstrated that the heat treated samples were single phase and well described by a single L1\textsubscript{2} structure. To determine composition and chemical homogeneity the samples were assessed using EDX in an SEM. EDX mapping demonstrated that the Nb and 5at.%Co samples were two phase and inhomogenous, and so cannot be modelled by a single large box model. The composition of the remaining samples was determined and used in a Rietveld fit to calculate the correct lattice parameters.

The PDFs and total scattering functions were fit using PDFgui and RMCPProfile. The PDFgui fits demonstrated issues caused by the instrument resolution, whilst the RMC fits showed the need to adopt a refinement methodology to prevent physically unrealistic moves (specifically for the Ti-atoms). Based on these observations a refinement methodology was established and presented.
The fitted PDFs demonstrated a high level of fit for all of the samples. A consideration of the partials demonstrated some level of order occurring in all of the substitutional alloys. This was confirmed by the increase in enhancement factors of the new sublattice configurations. For tantalum substitution, there is an apparent clustering of like atoms on the Al-sublattice. For titanium, in contrast, the atoms order in trans and mer configurations, so as not to be occupy adjacent positions on the sublattice. Finally, the Co atoms form square arrangements on the Ni-sublattice, perpendicular to the square atomic arrangement of Al-atoms, inherent in the L12 ordering.

Overall, this work has shown how the total scattering technique and analytical methods used may be extended and applied to ternary systems. Further, it has provided valuable insight into the nature of sublattice ordering occurring within these alloys, of great importance to the prediction of APB energies and alloy strength, used in the design of industrially relevant materials.
Chapter 7

Determination of local lattice strains using pair distribution functions

7.1 Introduction

Thus far, the primary focus of the work described in this thesis has been the assessment of local chemical order within a system. However, diffuse scattering contains information on a variety of different important local effects. Indeed, the first observations of diffuse scattering in alloys were attributed to size effects [19,20] causing static displacements in the lattice. Understanding these distortions is important due to the solid solution strengthening they provide the material.

The substitution of some atoms with others of different atomic radii leads to a local distortion field around the substituent atom. This field interacts with a moving dislocation, retarding the motion and results in an increased strengthening of the material. Additional strengthening may also arise from the introduction of interstitial atoms into a lattice structure, which can produce a similar retardation of dislocations. An understanding of these distortions and their effects is therefore key to the structure-property relationship of the material. As a probe of the local-environment, total scattering analyses may allow the direct observation of such effects, thus providing new understanding and insight into a host of complex metallurgical systems.

7.2 Types of strain

The term strain is used often in metallurgy in a wide variety of circumstances, and so should be clarified for use here. It is necessary to distinguish between the different types of strain that can be exhibited in a lattice and their effect on the observed scattering. Broadly speaking there are three types of strain that are of concern when analysing scattering data, Fig. 7.1. When a material is placed under an applied stress, the material is observed to undergo a bulk deformation, where the strain is defined as the change in the dimension divided by the original dimension. This is sometimes referred to as engineering strain. This type of macrostrain results in a deformation of the whole lattice, resulting in the observed shift in the Bragg peaks, corresponding to the resultant change in the lattice parameter. Likewise, there will be a corresponding shift in the peak positions in the pair distribution function as the average interatomic distances in the material increase.
Chapter 7. Determination of local lattice strains using pair distribution functions

Figure 7.1: Types of strain exhibited by a lattice: a) Macrostrain: deformation of the lattice resulting in a change in the lattice spacings, b) Microstrain: local changes in the distribution of the lattice planes caused by effects such as dislocations, c) Local lattice strains: strain distortions in the lattice caused by size differences of substituting atoms.

In reference to a ‘strained lattice’, crystallographers are often referring to changes in the inter-planar distances caused by effects such as dislocations. This type of strain, which will be referred to as microstrain, leads to broadening of the Bragg peaks in the system, the magnitude of which has a $\tan \theta$ dependence on the scattering angle $\theta$. The effect of this on the observed diffuse scattering will be discussed in a later section.

For the High Entropy Alloy (HEA) community, references to a ‘highly-strained lattice’ refer instead to local distortions and strains caused by the size difference between the component atoms. This type of strain, which will be referred to as local lattice strain, has been used as the basis of solid solution strengthening models for lower order systems (binaries and ternaries) and has been inferred to result in additional strengthening in HEAs. The local lattice strains, such as those show in Fig. 7.1c, will affect the local environment, but are unlikely to affect the long-range average structure of the crystal.

7.2.1 Effect of local strains on scattering data

Importantly, there will be two key contributions to the offsite displacement of an atom in the structure: static and dynamic displacements. The static component will depend on the dislocation density of the material, surface effects and any local lattice strains corresponding to the displacements of atoms away from their ideal locations. The dynamic component is solely related to the thermal vibrations of the atoms about their lattice points.

For an idealised non-magnetic pure element sample at absolute zero, all atoms would occupy the ideal lattice sites of the material. When placed in a beam of neutrons, the system would act as a series of point scatterers and would produce a Bragg pattern with a constant scattering power that is independent of $Q$. As the temperature increases the atoms will vibrate and move off their ideal sites, with dynamic displacements. Although the atoms are still point scatterers, the scattering occurring from planes of atoms (Bragg scattering) will, on average, see a spherical cloud of atoms. Mathematically, this can be modelled as a point scatterer convoluted with a spherical distribution. Fourier transforming this results in a decaying form-factor and a damping of the Bragg peaks at high-$Q$. Treatment of this thermal motion in materials is typically handled with the use of a Debye-Waller factor [111,112], which defines a temperature dependant form.
factor as:

\[ f = f_0 \exp \left( -\frac{B \sin^2 \theta}{\lambda^2} \right) \]  

(7.1)

where \( B \) is the Debye-Waller factor, \( \theta \) the scattering angle, \( f_0 \) the atomic scattering factor and \( \lambda \) the wavelength. It is often useful to relate the Debye-Waller factor \( B \) to the isotropic displacement parameter \( U_{\text{iso}} \):

\[ B = 8\pi^2 U_{\text{iso}} \]  

(7.2)

It should be noted that the scattering intensity is not lost, but rather redistributed into diffuse scattering features that appear at the base of the Bragg peaks.

The effect of static distortions on a powder diffraction pattern is likely to be analogous to a thermal Debye-Waller effect; a decrease in the intensity of the Bragg peaks, with an accompanying increase in the observed diffuse scattering. Unlike the standard micro-strains discussed in crystallographic literature, these local strains produced by the atomic substitution would not, therefore, be expected to produce broadening of the Bragg peaks, but rather a damping in the intensity of peaks at high-\( Q \). Practically, the combined effects of static and dynamic displacements will therefore be subsumed in the \( U_{\text{iso}} \) term of a Rietveld refinement.

It should be noted that in the case of extreme local lattice distortion, broadening of the Bragg peaks could be observed if the effect is sufficient to change the distribution of the lattice planes. This would depend on the level of local order exhibited in the system, the magnitude of the strains (hence, in turn, the relative atomic size) and the correlation length over which the strain is observed to act. If these effects were all large, it could theoretically result in a series of rippled planes, the inefficient packing of which would result in a variation in the inter-planar spacing, causing the observed broadening of the Bragg peaks. A schematic illustration of this is shown in Fig. 7.2

![Schematic illustration of severely distorted lattice planes caused by high levels of local lattice strain, correlation of atom type and large correlation length over which the strain is observed to act. The resulting distorted planes do not pack equally or efficiently resulting in a change in the lattice plane spacings. The result is a broadening of the Bragg peak.](image)

Figure 7.2: Schematic illustration of severely distorted lattice planes caused by high levels of local lattice strain, correlation of atom type and large correlation length over which the strain is observed to act. The resulting distorted planes do not pack equally or efficiently resulting in a change in the lattice plane spacings. The result is a broadening of the Bragg peak.

The effect of substitutions that result in a variation in atomic size on the diffuse scattering was noted in a powder sample of \( \text{Ni}_3\text{Au}_2 \) and described mathematically by Warren [20], who noted the asymmetric nature of diffuse scattering peaks corresponding to this effect (in contrast to the symmetric peaks produce by thermal diffuse scattering). To consider the consequence on a PDF, the expected variation in bond lengths needs to be considered. The local lattice strains could have two possible effects on the distribution of bond lengths in the lattice. First, the average bond distance, i.e. the maximum of a PDF peak, could remain constant, but with the
distribution of bond lengths changing. Alternatively, the distribution in bond lengths could be the same, but with different average bond lengths dependent on the radii of the co-ordinating atoms. It is expected that either of these effects should lead to an increase in the observed width of the PDF peaks.

7.3 Measuring the peak width

Before considering the models for the type of broadening that might be expected, it is worth considering the numerical methods with which the peak width could be quantified to determine the degree of peak broadening.

Full width at half-maximum

A standard method of quoting peak widths is the full width at half maximum (FWHM). The peak maximum is located and the $y_{\text{max}}$ value, relative to the known baseline, recorded. Points $(x_1, y_{\text{max}}/2)$ and $(x_2, y_{\text{max}}/2)$ are located and the value of the FWHM $= |x_1 - x_2|$ is quoted. Owing to the histogrammed nature of recorded data, all of these values are unlikely to lie at bin edges, and therefore a method of extrapolation is required.

The peak maxima may be located by determining the point at which the slope of the line between two points becomes negative, simply when $y_{n+1} < y_n$. The top of the curve is then described by the four points $(x_i, y_i)$ such that: if $y_{n+1} < y_{n-1}$ then $n - 2 < i < n + 1$, whereas if $y_{n+1} > y_{n-1}$ then $n - 1 < i < n + 2$. These four points are fitted with a quadratic function, and the maximum of the quadratic calculated as $(x_{\text{max}}, y_{\text{max}})$. This construction is shown in Fig. 7.3. From this value the half maximum may be calculated and the $x_1$ and $x_2$ values corresponding to this located, linearly interpolating between $x$-values, and hence the FWHM calculated. Importantly, this makes no assumption about the peak shape and so is applicable to any peak.

Figure 7.3: Method of locating the top of a peak for quadratic fitting. Points $y_n$ and $y_{n+1}$ located using the green line. The slope of the red line connecting $y_{n+1}$ and $y_{n-1}$ can be used to determine the set of values $y_i$ which should be fitted with a quadratic.
7.4 Models for the variation in structure with substitution

Gaussian fitting

The Debye-Waller factor assumes that the thermal distribution of atoms is Gaussian in nature, and consequently the expected form of the PDF peaks would also be Gaussian. Therefore, each peak can be fitted with a standard Gaussian of the form:

\[ f(x) = A \exp\left(-\frac{(x - b)^2}{2c^2}\right) \]  \hspace{1cm} (7.3)

where \( A \), \( b \) and \( c \) are fitting parameters. \( b \) determines the position of the peak maxima, \( c \) the peak width and \( A \) is a scaling factor. Sometimes, an equivalent expression is used with a width parameter \( w \) such that \( 2c^2 = w^2 \). The measured full width at half-maximum (FWHM) can be calculated from the fitted \( c \)-parameters using the expression, \( \text{FWHM} = 2\sqrt{2\ln 2}c \). The FWHM is a measure that can be applied to any peak shape not only Gaussians and, as such, allows a comparison between peaks with different shapes. Therefore, the FWHM will generally be quoted in this work, rather than the Gaussian \( c \)-parameter, owing to its more general applicability.

One advantage of the Gaussian fitting method is that the algorithm used provides an error associated with the calculation. Unless explicitly stated, the Gaussian fitting method has generally been used in this work as there was found to be little difference between it and the quadratic model.

Peak asymmetry

Whilst the expected form of PDF peaks is approximately Gaussian, it is likely that there may be an asymmetry caused by instrumental effects or indeed due to chemical in-homogenity in the sample. Depending on the magnitude of the asymmetry it may be possible to observe it visually. However, in cases where it is more slight, a numerical measure for determining the asymmetry can be used. Peak asymmetry is often noted from a differential line shape in the difference curve when a PDF peak is fitted with a symmetric function. Likewise, calculated \( \chi^2 \) and the error on the fit will both increase. Mathematically, the asymmetry can also be measured by comparing the magnitude of the half widths at half maximum, taken in the positive and negative directions, or the turning points of the derivative of the PDF. Depending on the symmetry of the peak, the width can either be determined by the measurement of the FWHM or by fitting with a Gaussian function.

7.4 Models for the variation in structure with substitution

If the magnitude of lattice strains are to be determined from PDFs and total scattering data, an understanding of the expected variation upon atomic substitution is required. As with the determination of short-range order from PDFs, demonstrative models can provide insight into the type and magnitude of strains that might be observable from consideration of the PDF.
7.4.1 Variation in lattice parameter with substitution

A common observation in binary alloys is a change in lattice parameter, as determined from the Bragg data, upon atomic substitution in a system. Broadly speaking, for many binary systems there is a roughly linear relationship. The linear relationship is known as Vegard’s law [113] and is mathematically denoted as:

\[ a_{A_{1-x}B_x} = (1-x)a_A + xa_B \]  

where \( a_{A_{1-x}B_x} \) is the lattice parameter of the alloy \( A_{1-x}B_x \), \( a_A \) and \( a_B \) the lattice parameters of the two species A and B respectively.

For example, data from the nickel chromium system may be plotted as shown in Fig. 7.4 (data from Pearson [114]). A change in the lattice parameter with substitution with atoms of different radii is expected, and would be observable as a shift of both the Bragg pattern and the PDF peaks. From this model the theoretical atomic radii of nickel \( = 2.485 \) Å and chromium \( = 2.577 \) Å can be calculated. Whilst Vegard’s law holds for many binary systems, it is found to break down for ternary and higher order systems. Often more complex models are required to completely describe the observed lattice parameters in such cases.

![Figure 7.4: Variation in lattice parameter of Ni\(_{(1-x)}\)Cr\(_x\) with variation in Cr concentration.](image)

7.4.2 Modelling the first peak in a PDF - Simple Gaussian Model

One way to model the variation in PDF peak width with substitution is to consider the effect of the substitution on the individual partial pair correlation functions, and their contribution to the corresponding summed result.

Employing a hard sphere model, the average bond length of each partial can be calculated as the sum of the two touching atomic radii. The atomic radii can either be found from tabulated values, or by an application of Vegard’s law, fitting plots of lattice parameter vs. concentration of substituting species, or from a hard sphere close packing model applied to the PDFs of raw elements. Peaks in the partial PDFs are assumed to be roughly Gaussian in shape, with the peak maximum occurring at the average bond length.
For the peak width, the assumption is made that the width of one of the partial peaks will be the same for this system as for one of the pure elements. Assuming there is no strain caused by particle size or micro-strain in the system, it follows that the partial peaks will be affected only by thermal fluctuations in the system and instrumental broadening effects. Therefore, the width may be estimated simply by comparison to a sample of pure element.

Using these assumptions, theoretical partials can be calculated and combined using the following equation to yield a mock-PDF peak:

\[
G(r) = \sum_{i,j} c_i c_j \bar{b}_i \bar{b}_j [g(r) - 1] \tag{7.5}
\]

where \(c_i\) is the concentration of species \(i\), \(\bar{b}_i\) the scattering length of species \(i\). A precise mathematical explanation for the calculation of these partial peaks, accounting for the change in area with change in interatomic distance, is provided in Appendix A.

To determine the variation in peak width from this hard sphere type model, the above calculation was carried out on the Ni\(_{1-x}\)Cr\(_x\) system. A sample of pure nickel was measured on the POLARIS diffractometer and the peak width of the first peak in the PDF calculated as \(c = 0.0767\) Å. The Vegard’s law data shown in Fig. 7.4 were used to provide effective atomic radii of Ni and Cr. An example of the calculated partials PDFs for the alloy Ni-25at.%Cr is shown in Fig. 7.5. Fig. 7.5a shows the calculated partials, and Fig. 7.5b the partials weighted by the Faber-Ziman coefficients and the resultant summation. Fig. 7.6 shows the variation in the calculated peak, with chromium concentration for the binary system Ni\(_{1-x}\)Cr\(_x\).

As the concentration of chromium increases, so the peak maximum shifts to a higher \(r\)-value, due to the increase in the average atomic radius. The sum of the Faber-Ziman coefficients and, hence, the level of the base line, also decreases with the increased concentration of chromium, as a result of chromium having a shorter atomic scattering length than nickel. Whilst the

![Figure 7.5](image)

Figure 7.5: Plot of the calculated partial pair distribution functions and \(G(r)\) for a theoretical Ni-25at.%Cr sample using the sum of Gaussians model. a) as calculated partials b) partials accounting for the Faber-Ziman weightings, and then summed to give a \(G(r)\) peak. Blue - NiNi, Red - NiCr, Green - CrCr, Black - \(G(r)\).
experimental peak is, therefore, the sum of three Gaussians, as the maxima of these Gaussians are very close, it is almost impossible to distinguish the shape of the summed peak from that of a single Gaussian. The resultant peak can therefore be fitted with a Gaussian to estimate its width.

Plots of the peak widths and maxima, as calculated from the Gaussian fits, are shown in Fig. 7.7. Owing to the assumptions made in the model, the pure nickel and chromium samples necessarily have the same width. As the concentration of chromium in the alloy increases there is an initial increase in the peak width, up to a value of around 75% chromium, followed by a

![Figure 7.6: Calculated 1st peak in $G(r)$ using the sum of Gaussians model for samples of Ni$_{1-x}$Cr$_x$, a$_B$ alloys. Colour range is indicative of Cr concentration, with blue being pure nickel and green pure chromium. a) $G(r)$ and b) $G_{\text{norm}}(r)$.](image1)

![Figure 7.7: Output from Gaussian fits of $G(r)$ peak created using a simple sum of Gaussians model. a) Variation in $c$ parameter with concentration, b) Variation in $b$ parameter with concentration.](image2)
subsequent decrease. The maximum peak width is dependent on the interatomic distances of the smallest and largest partials, in this case the difference in the Ni-Ni and Cr-Cr distances. The skew of the distribution is controlled by the relative magnitudes of the atomic scattering lengths. In the nickel-chromium system the smaller scattering length of the chromium leads to a skew towards the higher chromium concentration. The maximum value of the peak width will occur when the magnitudes of the two outer partials are equal. In the Ni-Cr system this is calculated as $x = 0.739$, which agrees with the value calculated from the models. If the scattering lengths of the species were the same, then there would be no observable skew in the system i.e. the skew is controlled by the ratio in the scattering lengths.

For the change in the position of the peak maximum with concentration, shown in Fig. 7.7b, the dotted line indicates the peak maximum position that might be expected if it directly correlated with the lattice parameter. There is a notable difference between the predicted peak maxima, and the values expected from the lattice parameters, with the peak maximum being lower than the lattice parameter value for all concentrations. If the radii of all the atoms in the system were the same, then the partials would all be coincident, and there would be no variation in the peak maxima with increased Cr substitution. It follows that the magnitude of the difference between the peak maxima and lattice parameter value must be a function of the difference in the atomic radii. The greater the difference in the atomic radii, the greater the difference in the bond length determined from the lattice parameter and that determined from the position peak maximum. Considering the magnitude of the difference between these two values, there is an observed variation with concentration, with the largest discrepancy at c. 75at.%Cr. It is likely, therefore, that this discrepancy is also a function of the ratio of scattering lengths.

This model, whilst useful, is obviously limited to a calculation of the first coordination shell in the material. To account for higher order correlations, the spatial relationship and radii of the correlating atom types, and the atoms located at intermediate positions in the lattice would need be considered. For example, the 2nd nearest neighbour atoms in an FCC lattice do not touch. However, they both touch a set of four intermediate atoms that could be either Ni or Cr, Fig. 7.8. Therefore, there are 18 possible arrangements of atoms on the octahedron that will determine the second nearest neighbour interaction. It can be seen that this calculation will rapidly become very complex. Further, as it has been assumed that the distributions have a constant width, it implies that the atoms are non-interacting and non-bonding.
7.4.3 Modelling PDF peak widths - Simple spring model

To provide a more accurate model for the variation in peak widths that can account for bonding interactions and is able to determine the changes to higher order coordination shells, a spring model can be used. Rather than touching hard spheres, the system is modelled as a series of points attached with springs. This is similar to the previous model, as assumptions about the average bond length and lattice parameter of the material are still made, but allows a variation in the distribution of the bonds around the average length (rather than fixing the width of the distribution).

RMCPProfile contains a bond energy calculation as one of the available constraints. Running the algorithm on a box with no data allows the programme to be used as a Monte Carlo simulator. For each of the bonds in the box the potential is assumed to take the form of a Morse potential \[115\] i.e.

\[
D = D_e[1 - \exp (-\alpha(r - r_e))]^2
\]  \hspace{1cm} (7.6)

where \(D_e\) determines the depth of the potential well, \(\alpha\) determines the width of the potential well, \(r_e\) is the equilibrium bond distance and \(r\) is the interatomic distance.

For the potential employed in RMCPProfile it is assumed that \(\alpha = 2.55 \text{ Å}^{-1}\) for all bonds. This is taken from the MM3 molecular mechanics force field - as this function of RMCPProfile is geared towards calculations in molecular systems. The width of the distribution may then be controlled solely by the \(D_e\) parameter and the temperature at which the system oscillates. The Morse Oscillator is defined as an asymmetric function and, therefore, the partial PDF peaks created using this model are asymmetric reflecting this profile.

Large RMC boxes \((20 \times 20 \times 20\) unit cells\) were created, each containing 32,000 atoms. Lattice parameters were calculated as previously, assuming a simple linear combination of hard sphere interatomic distances, i.e. Vegard’s law. The interatomic \(r_e\) distances were calculated in the same manner, by summing the radii of the two interacting atoms. An initial set of boxes containing only Nickel atoms, were set up and run at a series of different energies \(D_e\) at 293 K. From the comparison of these calculated PDFs with the nickel sample measured on Polaris, it was possible to estimate an appropriate value for \(D_e\). A value for \(D_e = 0.16\) eV was chosen accordingly.

A series of Ni\(_{(1-x)}\)Cr\(_x\) boxes was generated, to predict the changes that might be observed to occur to a PDF under increased atomic substitution of atoms with a larger atomic radius. Boxes containing a random distribution of atoms were allowed to undergo translations for 120 minutes to allow for a large number of moves to be accomplished (>1,000,000 moves). Seven different boxes were run of each of the compositions of interest. The PDFs of these boxes were calculated and the widths of the first six peaks measured corresponding to the neighbour correlations within the unit cell of the material.

Fig. 7.9 shows the calculated partials for the box containing Ni-25at.%Cr. Comparing Fig. 7.9a with Fig. 7.6a, the differences between the two models can be seen. Whilst in the Gaussian model there is a distinct change in the peak maxima, for the spring model, the bond distributions have become spread out. This is more realistic as it is expected that the bonding interaction between atoms will cause the distribution of the individual bond lengths to change away from

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that of the idealised nickel. As there has been no additional chemical ordering in the system, the occupation of the partials and, hence, the area under the peak, should remain constant. The change in the breadth of the individual distributions therefore results in a decrease in the peaks height (or more precisely the Gaussian scaling parameter $A$) to compensate. In spite of this change in breadth of the distributions, a difference in the average bond length of the different bond types is still apparent. The resultant change in peak width for the $G(r)$ with concentration for the first nearest neighbour shell is shown in Fig. 7.10. It is apparent that the shape of the distribution is the same as that produced by the simple Gaussian model, seen in 7.7a.

![Graphs showing the variation in FWHM of first PDF peak with % Cr concentration from a family of Ni$_{1-x}$Cr$_x$ structures, simulated using a simple spring model. The error is calculated from the peak widths measured from different simulation runs.](image)

Figure 7.9: Partials for Ni-25at.%Cr calculated from the spring model taken from one of the simulated boxes. (a) the first $G(r)$ peak and (b) the 2nd $G(r)$ peak. Blue - NiNi, Red - NiCr, Green - CrCr. Visible noise in (b) due to the smaller number of second nearest neighbour correlations compared with the first nearest neighbour and due to the random nature of the simulation.

![Graph showing the variation in FWHM of first PDF peak with % Cr concentration from a family of Ni$_{1-x}$Cr$_x$ structures, simulated using a simple spring model. The error is calculated from the peak widths measured from different simulation runs.](image)

Figure 7.10: Variation in FWHM of first PDF peak with % Cr concentration from a family of Ni$_{1-x}$Cr$_x$ structures, simulated using a simple spring model. The error is calculated from the peak widths measured from different simulation runs.
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Considering the effect on the second nearest neighbour interaction, Fig. 7.9b, there is no obvious change in the relative interatomic distances in this shell. This is unsurprising given that this peak arises from an averaging of the number of different permutations of nearest neighbour atoms. However, there may still be a broadening of these peaks, owing to the variation in atomic size. Fig. 7.11 shows the variation measured in the peak widths of the first five peaks in the PDF. For the different coordination shells, there is still a difference in the observed peak widths with the change in concentration. However, the form of this distribution varies between the different shells. Therefore, although in the 2nd and higher coordination shells, there is no apparent split in the maximum of the partials, there is still a strain induced variation in the peak width.

![Graph](image)

Figure 7.11: Variation in FWHM of first PDF peak with at.% Cr concentration from a family of Ni$_{1-x}$Cr$_x$ structures, simulated using a simple spring model. The error is calculated from the peak widths measured from different simulation runs. Red - 1st peak, Orange - 2nd peak, Yellow - 3rd peak, Green - 4th peak, Blue - 5th peak.

From this figure it is also apparent that the first coordination shell peak has a much narrower peak width, compared with the latter shells. This can be seen more clearly in Fig. 7.12, where the variation in FWHM with $r$ for the simulated nickel pattern is shown. As can be seen, there is a large difference in the first few coordination shells, with the width subsequently plateauing.

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Figure 7.12: Variation in FWHM of PDF peak with $r$ in simulated nickel. Line indicates fit of the data using the function from Eq. 7.7.

at higher-$r$. The line plotted is the result of fitting with the following function:

$$\sigma = \sigma_0 \sqrt{1 - \frac{\delta_1}{r}}$$

(7.7)

where $\sigma_0$ is the width of the peak determined by the thermal oscillations in the system, $\delta_1$ a parameter to account for correlated motion and $r$ the interatomic distance. This function was originally implemented in the PDFgui code to model the variation in the PDF peak width as a function of $r$ due to correlated motion.

Correlated motion arises from the bonding nature of atoms. If there were no bonds in a structure all the atoms would be free to move in any direction and the peak width across $r$ would be constant (akin to the Gaussian model). If the atoms were bonded together with rigid bars, the movement of one atom would shift all other atoms, and so a series of delta functions would result. In real materials, bonds between atoms act more like springs. The movement of an atom will cause a neighbouring atom to also be dragged away from the idealised lattice point; although some of the slack will be taken up by the bond or ‘spring’. The second nearest neighbour will experience much less of a pull, as there are multiple springs that now take up the slack, and so is more free to move independently. Hence, the nearest neighbour peaks should be narrower than the subsequent peaks. The number of shells this will affect will be dependent on the structure of the material and the bond energy profile, i.e. the stiffness of the spring.

Variation in bond length

The examples given thus far are concerned only with a variation in concentration, substituting an atom with a fixed atomic radius. Hume-Rothery [2] suggested that for a binary alloy, the substitution of an atom in a binary alloy could only occur if the size difference was < 15%. This
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has been extended to multicomponent systems through the use of the delta parameter:

$$\delta = \sqrt{\sum c_i(1 - \frac{r_i}{r_{av}})^2}$$  \hspace{1cm} (7.8)

where:

$$r_{av} = \sum c_i r_i$$  \hspace{1cm} (7.9)

where $r_i$ is the radius of an individual atomic species $i$ and $c_i$ the concentration. Taking the Hume-Rothery rule as an upper bound for our models, it is possible to predict the peak broadening that could be observed due to a variation in the atomic radius at a fixed concentration.

Two possible models will be considered (shown in Fig. 7.13):

1. **Fixed Atom (FA)** - The radius of one atomic species is fixed and that of the second varies, resulting in an overall variation in the average radius and the observed lattice parameter of the material. This is based on the Hume-Rothery description, where one atom acts as a solvent, dissolving a second atom with a different atomic radius. In this case, $r_B = r_A + x$ and hence $x = \frac{2\delta}{1 - \delta}$.

2. **Fixed lattice parameter (FLP)** - As discussed in section 7.4.1, substituting atoms of a different atomic radii into a system will result in a change in lattice parameter. This change in lattice parameter will have an effect on the lattice strains. Therefore, it is necessary to try and decouple this effect from the system. A series of boxes is considered which have a constant lattice parameter, where the radii of the atoms are given as $r_A = r_{av} - \Delta$ and $r_B = r_{av} + \Delta$ and hence $\Delta = \delta$. This model reflects the calculation of the $\delta$-parameter, which considers the change away from the average atomic radius ($r_{av}$).

![Figure 7.13: Schematic illustration showing how the variation in atomic radii that could be modelled for a higher order system. The black bars indicate the atomic radii of individual atoms (labelled A and B) positioned on a horizontal axis of increasing $r$. The dotted blue line indicates the average lattice parameter of the system. The dotted red line indicates the value that is fixed in the model and from which the radii of the atoms are measured - for (a) the radius of the smallest atom, for (c) the average lattice parameter.](image)

A series of boxes was generated containing A:B atoms in a ratio of 1:1. Potentials were created that reflected the radii of the atoms described in the two models above for values of $\delta = 0, 1 \ldots 7$ (this was done, to enable future comparison to higher order systems). For the fixed atom model a value of $r_A = r_{Ni}$ was used, and for the fixed lattice parameter $r_{av} = r_{Ni}$. These values were chosen such that the two models were coincident for the case of $\delta = 0$. From the resultant boxes PDFs were calculated using the scattering lengths of Ni (for atom A) and Cr.
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(for atom B). A plot of the resultant peak widths under the different modelling conditions is shown in Fig. 7.14. The corresponding calculation using the sum of Gaussians method was also carried out and the results shown in the figure.

Figure 7.14: Variation in FWHM of the first PDF peak width with changing atomic radius of substituting atoms predicted by the different models. Red - Spring model with FLP, Blue - Spring model with FA, Orange - Gaussian model with FLP, Green - Gaussian model with FA. FLP - Fixed lattice parameter, FA - Fixed atom. Error bars given as the error in the parameter from the peak fitting algorithm.

The Gaussian model is only shown for values up \( \delta \leq 4\% \) as for values greater than this the calculated peaks are no longer well described by a single fitted peak. This highlights the slightly unrealistic nature of the Gaussian model, which essentially allows for no additional interactions between the different atom types by assuming that the widths of the individual distributions are invariant. The spring model, however, does still maintain a well defined peak shape as it allows the distributions to be stretched due to the interactions between them.

For all the models, the variation is well described by a quadratic function. As expected, the Gaussian model shows a much larger variation in FWHM as there is no relaxation in the model. Although it appears that the Gaussian model drops below the spring model for the low % differences, this is due to the lower starting width on the distributions in the Gaussian model (which uses the width calculated from experiment as opposed to the spring model which uses a refined energy value that yields a value close to the experimental value). In both cases, the FA model is higher that the FLP model. This is due to the fact that whilst the two cases have the same % difference in atomic radius they have different lattice parameters, and hence the relaxation observed will be different and so too the recorded width. Importantly, this figure demonstrates that there should be a large variation in the observed peak width that is strongly dependent on the difference in the atomic radii of the atoms.

These models were run considering an A:B ratio of 1:1, as this should show the maximum strain difference. It is also interesting to consider whether such large differences would be observed if the system were one of the less strained alloys. To test this, a series of spring models
were also run for boxes of $A_2B$, $A_3B$ and $A_4B$, again calculating PDFs using scattering lengths $b_A = b_{Ni}$ and $b_B = b_{Cr}$. The resultant plots are shown in Fig. 7.15.

\[ \text{Figure 7.15: Variation in FWHM of the first peak in the PDF with changing B concentration, calculated from the spring model, using a fixed A-atomic radius. Blue - AB, Purple - A}_2B, \text{ Red - A}_3B, \text{ Green - A}_4B. \text{ Error bars calculated from the different widths measured in the different simulations.} \]

As expected, for all compositions there is an observed increase in the strain for the alloys as the size difference between the alloying elements increases. Similarly, as the alloy becomes closer to the equiatomic composition there is an increase in the observed peak broadening for all values of $\delta$. Again, these data suggest that for alloys of these types of compositions, the magnitude of the variation in the peak width should be large enough to determine experimentally.

### 7.4.4 Brief note on the Gaussian and spring models

It is worth briefly commenting that both the spring and sum of Gaussian models are oversimplifications of the nature of a real system. For the Gaussian model, the assumption is made that the dominant effect in the peak broadening will be the change in length of the nearest neighbour interactions. The atoms are, therefore, non-interacting hard spheres and the widths of the individual partials remains fixed as though it were pure elements. For the spring model, a similar assumption is made initially; however, the relaxation of the system in accordance with the applied potential allows the widths of the distributions to change. Further, the Gaussian model is limited in the number of coordinations shells that it is able to model and can only reach $r \sim 3\text{\AA}$, whereas the spring model allows access to higher $r$ data.

Neither of the models, however, account for any variation in the observed dynamic displacements in a system. The magnitude of the thermal displacements should be a function of the elastic constant of the material, which in turn will be dependent on the melting temperature. Consequently the dynamic displacements of atoms in the lattice may change when atomic composition changes, leading to greater variation in peak widths than that caused by atomic size effects alone.
7.5 Effect of Bragg peak broadening on the PDF

Importantly, however, both models demonstrate a variation in PDF peak width on substitution with variable concentration and difference in atomic radius. This shows that there should be a sufficient observable change in the FWHM of peaks in experimental PDFs for the magnitude of local lattice strains to be determined and compared between alloys.

7.5 Effect of Bragg peak broadening on the PDF

As discussed previously, local lattice strains should not produce a broadening of the observed Bragg peaks. However, the static displacements in a structure will be affected by the microstrain and the crystallite size. Both have a well-known broadening effect on the Bragg data and it is, therefore, important to consider the effect that these may have on the observed PDF.

If the Bragg diffraction pattern is considered to be a sum of Voigt functions, i.e.

\[
f(a_n, b_n, c_n, \Gamma_n, Q) = \sum_n a_n \exp \left( -\frac{(Q - b_n)^2}{2c_n^2} \right) \otimes \frac{1}{\pi} \frac{\frac{1}{2} \Gamma_n}{Q^2 + \left( \frac{1}{2} \Gamma_n \right)^2}
\]

(7.10)

where \(a_n, b_n, c_n\) are constants associated with the Gaussian component of the Voigt function, and \(\Gamma_n\) a constant associated with the Lorentzian component, for each of the \(n\) Bragg peaks. The Fourier transform of this will be given as (see Appendix A):

\[
\mathcal{F}[f(a_n, b_n, c_n, \Gamma_n, Q)] = \sum_n a_n \sqrt{2\pi c_n^2} \exp \left( -2\pi r^2 c_n^2 - \Gamma_n \pi |r| \right) \exp(-2\pi ib_n r)
\]

(7.11)

A plot of this Fourier transform for a single peak is shown in Figure 7.16. The first exponential term in the expression determines the decay envelope of the system, whilst the second defines the periodicity of the real and imaginary oscillating functions. Varying the breadth of the observed peaks in the Bragg pattern (\(c_n\) or \(\Gamma_n\)) will change only the first exponential term in this equation, i.e. the bounding envelope of the function.

![Figure 7.16: Calculated Fourier transform of a Voigt function with \(a = 5\), \(b = 1\), \(c = 0.04\) and \(\Gamma = 0.04\). Black line indicates the decay envelope term, the red line the real part of the function and the blue line the imaginary part of the function.](image)
It follows that a change in the width of the Bragg peaks will lead to a change in the damping of the system (the envelope function) and not a change in the position of the peaks in the PDF (as these will be dependent on the oscillatory term not the envelope function).

Two common causes of peak broadening are crystallite size and microstrain broadening. The former effect can be approximately quantified by the Scherrer equation [116, 117]:

\[
\beta_L = \frac{K\lambda}{L \cos \theta}
\]

where \( L \) is the mean crystallite size, \( K \) a shape factor that is empirically found to have a value close to 0.9, \( \beta_L \) the full width half-maximum of a peak at the scattering angle, \( \theta \), and \( \lambda \) the wavelength. Likewise there is the well-known micro-strain dependence on peak width with scattering angle [118, 119]:

\[
\beta_\epsilon = C\epsilon \tan \theta
\]

where \( C \) is a factor dependent on the inhomogeneity of the strain but is typically around 4 or 5 and \( \epsilon \) the homogeneous strain. These dependencies may be converted into \( Q \)-space as follows:

\[
\beta_L = \frac{4\pi K\lambda}{L \sqrt{16\pi^2 - Q^2\lambda^2}}
\]  

\[
\beta_\epsilon = C\epsilon \sqrt{\frac{Q^2\lambda^2}{16\pi^2 - Q^2\lambda^2}}
\]

Bragg peaks at highest theta, i.e. lowest \( d \)-spacing and, therefore, highest \( Q \)-value, show the most broadening under these effects. Low-\( Q \) peaks will be the narrowest - the transform of which will have a large period oscillation with a slowly decaying envelope function. High-\( Q \) peaks will be broadened - the transform of which will have a very short period with a much faster decay function. Consequently the high frequency (short period oscillations) will be damped much faster than the lower frequency oscillations. This is demonstrated in Fig. 7.17 where the Fourier transforms of several Voigt functions with increasing \( b \) and broadening (\( c \) and \( \Gamma \)) are shown. This should lead to an observed broadening in the high-\( r \) peaks as the inclusion of high frequency oscillations will determine the resolution of the peaks. Therefore, the effect due to the Fourier transform of the Bragg data with peak broadening is two fold:

- Increased damping in the system.
- Decreased resolution of the high \( r \)-space peaks.

It is important to note that this argument considers only the effect of the change on the Bragg peaks on the PDF. There may also be a change in the diffuse scattering that could lead to an observed change in the PDF. It is simpler, however, to consider the variation in bond length distributions under these conditions. In the case of a change in the crystallite size, this may lead to a slight broadening in the peak owing to local strains in the lattice, particularly close to the surface of the nanoparticle. This effect is likely to be very small and will only be obvious if the volume of the strained surface accounts for a large proportion of the overall volume.
7.5. Effect of Bragg peak broadening on the PDF

Figure 7.17: Calculated Fourier transform of a series of Voigt functions with increase peak broadening. Green - Low frequency oscillation, with low broadening \((b = 0.5, c = \Gamma = 0.001)\), Red - Medium frequency oscillation, with medium broadening \((b = 1, c = \Gamma = 0.005)\), Blue - High frequency oscillation, with high broadening \((b = 2, c = \Gamma = 0.01)\).

- i.e. a high surface area to volume ratio and a very small particle size. The typical particle size used in our experiments is on the order of 50 microns and, as such, the volume of the strained surface (assuming a thickness of around 10 Å) accounts for only 0.006% and therefore can be easily neglected.

For microstrain the introduction of a large number of dislocations is likely to lead to a large number of local lattice distortions, and hence a change in the local peak breadth at low-\(r\). This broadening is likely to only be exhibited in the low-\(r\) region and will decrease as \(r\) increases. Again however this effect is likely to be small in an annealed bar. Typically the dislocation density of nickel is on the order of around \(10^{10}\) to \(10^{12}\) m\(^{-2}\). Assuming again that the strained region around the dislocation is of the order of 10 Å, the total strained volume of the material will only be on the order of 0.0001% and, as such, can be ignored.

The effects of crystallite size and micro-strain broadening can be summarised as follows:

**Crystallite size**

- Bragg peak broadening with \(\sec \theta\) dependence.

- Faster decay envelope in the PDF, caused by the broadening of the Bragg peaks. In the extreme case of very small particles, the PDF will become featureless above \(r_s\), where \(r_s\) is close to the diameter of the particle.

- Loss of peak high frequency components in Fourier transform and hence peak broadening in high \(r\) due to broadening of Bragg peaks.

- Broadening of low \(r\) peaks in the extreme case where the volume of the strained surface is a significant volume of overall crystallite size.
Microstrain

- Bragg peak broadening with \( \tan \theta \) dependence.

- Faster decay envelope in the PDF, caused by the broadening of the Bragg peaks. Decay is much greater than that observed due to crystal size. With lots of dislocation planes this results in damping of the PDF at high \( r \) to zero (effectively because the long-range interactions are interrupted).

- Loss of resolution and, hence, peak broadening in high \( r \) due to broadening of Bragg peaks

- Broadening of low \( r \) peaks if the dislocation density in the system is very high.

These mathematical descriptions provide theoretical predictions of the effects that might be expected from the presence of microstrain and crystallite broadening. It is hoped in the future to carry out experiments to demonstrate these principles. For the scope of the work in this thesis, however, it was necessary to remove their consideration by means of careful sample preparation.

### 7.6 Conclusions

Understanding strains in a lattice is incredibly important to developing links between physical properties and underlying structure. The metallurgical community often discusses three key types of strain: macrostrain, microstrain and local lattice strains. Local lattice strains, caused by atomic size mismatch in the lattice, are believed to affect the motion of dislocations in a material and cause the observed increased strengthening. It has been discussed how such strains are known to cause a decay in the observed \( U_{\text{iso}} \) of a material (calculated from the decay of the Bragg data) and increase the diffuse scattering.

Using two models, the first a sum of Gaussians and the second an array of atoms connected by springs, it has been shown that there is a variation in the observed peak widths in the PDF, caused by the substitution of atoms with different atomic radii. Both models show an increased broadening caused by the change in composition of the system, or the radii of the substituting atoms. The effect caused by correlated motion is also correctly reproduced from the spring model of the system. Importantly, this variation is sufficiently large to be calculable from the PDF. The mathematical methods by which the peak width can practically be measured have also been discussed.

Finally, it is noted that there are several other effects that may cause a variation in the local lattice strains and, hence, the PDF peak width. Crystallite size and dislocation density may both contribute to the strains in a lattice and could lead to variations in the Bragg peak width. By considering both the affect on the Bragg data and a physical consideration of real space, the resultant effect on the PDF is considered. Both show an effect on the damping of the system and localised variations in low-\( r \). These effects will, therefore, need to be controlled practically, if the local lattice strains of a material are to be measured from a PDF. The PDF peak width will also be a function of the instrument, which must therefore be kept constant.

In the next chapter, the various insights from this chapter are applied to the study of a high-entropy alloys, a new class of materials believed to contain high levels of local lattice strain.
Chapter 8

Local lattice strains in High-entropy alloys

8.1 Introduction - High-entropy alloys

High-Entropy Alloys (HEAs) differ from conventional metallic materials in that they are based upon multiple atomic species in near equiatomic ratios, rather than a single principal element. It might be expected that the microstructures of these alloys would contain several intermetallic phases, but much of the literature associated with these materials has reported only solid solutions with simple crystal structures, such as \( \text{fcc} \) and \( \text{bcc} \) and their related superlattice structures \([120,121]\). These observations have given rise to the concept of entropic stabilisation, which suggests that the configurational entropy of these multi-component solid solutions can overcome the enthalpy of formation of competing intermetallic phases \([120]\).

For a binary alloy it can be shown that the entropy of mixing:

\[
\Delta S_{\text{mix}} = -R(x_A \ln(x_A) + x_B \ln(x_A))
\] (8.1)

where \( x_A \) and \( x_B \) are the concentration of A and B respectively, and \( R \) is the gas constant. This is discussed in greater detail in Chapter 9. This will reach a maximum value of \( \Delta S_{\text{mix}} = 0.693R \) when the system is equiatomic. A more generalised expression may be written for any alloy with \( n \) constituent components:

\[
\Delta S_{\text{mix}} = -R \sum_{i} x_i \ln(x_i)
\] (8.2)

where \( x_i \) is the concentration of component \( i \). This expression applies only to solid solutions with a completely random structure. The maximum entropy of these systems will occur when the system is equiatomic. For a five component system the entropy of the system will be maximised when \( x_i = 0.2 \) for all \( i \) giving an entropy \( \Delta S_{\text{mix}} = 1.609R \). This entropy may be large enough that it outweighs the favourable enthalpy of intermetallic formation, resulting in a solid solution, stabilised by entropy rather than enthalpy. This is the origin of the term ‘High-Entropy alloys’. Typically HEAs are defined as alloys containing 5 or more components each with a concentration of 5-35%. An alternative definition suggests that any alloy with \( \Delta S_{\text{mix}} \geq 1.5R \) can be considered
an HEA.

From the initial observation of alloys satisfying these criteria, four core principles relating to these materials have been postulated.

1. *High entropy single phase solid solution* - The high configurational entropy caused by a random solid solution dominates the Gibbs energy leading to the stabilisation of a single phase.

2. *Highly distorted lattice* - The combination of a large number of elements, with different atomic radii will result in a highly distorted lattice, which in turn leads to increased physical strength and superior mechanical properties.

3. *Sluggish diffusion* - The local variation of atomic environments in the lattice will result in the sluggish diffusion of atoms in the lattice.

4. *Cocktail effect* - The complexity of the HEA combinations will result in beneficial interactions, resulting in unusual behaviours producing a whole that is greater than the sum of the parts.

Since their initial conception and demonstration, however, the HEA literature has become divided over these concepts. Several of the initial datasets were obtained from as-fabricated material, which is likely to have been in a metastable state, as opposed to the thermodynamic equilibrium achieved by homogenisation and long duration thermal exposures [120–126]. In addition, more recent studies have also revealed the presence of nano-scale precipitates in some alloys [127,128].

Nevertheless, for those materials that are truly single phase, multi-component solid solutions, the properties of the materials and their structure, from a local perspective, are very interesting. The local environment is likely to be more complex than that of a conventional dilute alloy. For example, in a relatively simple austenitic stainless steel, such as Fe-18Cr-8Ni wt.%, almost 75% of the atoms surrounding any given lattice site would be Fe. Conversely, in a five-component equiatomic HEA that also adopts an fcc structure, only 20% of the nearest neighbours would be atoms of the same species. This complicated arrangement of multiple atom types, each with a different size and electronic structure, is directly related to two of the four proposed HEA core effects; sluggish diffusion and severely distorted lattices [120,129,130]. Limited experimental evidence exists for either of these two effects [131], but data relating to the lattice distortion is particularly sparse and, hence, forms the basis of the work described in this chapter.

**Sluggish diffusion**

As a migrating species moves through an alloy, the potential field experienced by this atom will necessarily fluctuate due to variations in the local atomic environment. It is often argued that for a conventional alloy, this fluctuation is likely to be minimal, with all environments being roughly equivalent. In an HEA, however, there may be sites where locally the bonding is more preferable creating large minima in the potential surface across which the atom is moving (see Fig. 8.1a). These minima will act as traps, temporarily pinning the motion of individual atoms.
8.1. Introduction - High-entropy alloys

(a) Sluggish diffusion
(b) Highly distorted lattice

Figure 8.1: Schematics of two of the four core HEA principles: a) The potential that might be expected for a diffusing atom in a simple dilute solid solution and a more complex HEA, b) the ‘highly’ distorted lattice.

and resulting in a retardation of the diffusion. Limited evidence and measurements have been provided for this justification, which in itself is problematic for two reasons.

First, if the energy of the localised potential is sufficiently low compared with the surrounding, this would imply that the system is trying to order, either locally or on a long-range length-scale (depending on the exact energetics). This would, necessarily, mean that the system is not statistically random and hence the entropy of the system is reduced. Given time, the system would either reach a thermodynamic SRO state or order, making it no longer a single phase HEA.

Secondly, statistically the probability of creating one of these deep traps in a random arrangement is smaller in an HEA than in a corresponding equivalent in a binary system. Consider a vacancy in a five component fcc HEA system, acting as a ‘trap’ for a diffusing species. As the system is assumed to be random, each of the twelve nearest neighbour sites could be occupied by one of the five different lattice types. There are therefore 244,140,625 possible local arrangements of atoms around this vacancy. If energy potentials for the individual atom types are given as -2, -1, 0, 1, 2, the probability distribution of the energies of these arrangements can be plotted. Similarly, the same calculation can be carried out for a two component system with atomic energies -2 and 2, and for a three component system with energies -2, 0 and 2. This is shown in Fig. 8.2. For the binary system the energies will have discrete values -24, -20, -16, . . . 24. The higher orders will have more intermediate energy values, but the maximum and minimum energies will remain the same. To allow comparison between the systems they have all been rebinned onto the same scale as the binary alloy. As can be seen, as the complexity of the system increases (Green to Blue) the distribution of energies narrows. Consequently, the probability of finding a low energy trap actually decreases with compositional complexity.

Therefore, unless there is some local ordering taking place in the system, these traps are not likely to be generated. It is perhaps unsurprising, therefore, that this concept has yielded little supporting evidence.
Chapter 8. Local lattice strains in High-entropy alloys

Highly distorted lattice

It is well established that the addition of alloying elements into a pure metal causes local distortions in the regular atomic array, moving neighbouring host atoms away from their ideal positions. The strain fields associated with these distortions impede gliding dislocations, giving rise to strengthening. These concepts have been extended to the multi-component HEAs, where it has been suggested that the cumulative effect of a significant number of different atoms within the first coordination shell would generate a highly strained structure [120], see Fig. 8.1b. Such severely distorted arrays could give rise to a significant level of solid solution hardening, as has been reported in a number of HEA systems [122,132–134]. However, strength could also have been influenced by the presence of nano-scale precipitates within the material and significant levels of strain would be expected to destabilise the lattice, resulting in precipitation or amorphisation [135–137]. Thus, there is an obvious need to obtain new data that can clarify this matter.

One reason for the lack of clear experimental data that elucidates the extent of the lattice distortions in HEAs is the difficulty in making suitable measurements. High-resolution transmission electron microscopy imaging of the atomic columns can show local distortions [138]. However, images of this type display an average of the signal along each atom column and are susceptible to distortions caused by other effects, such as damage caused during ion beam thinning. In diffraction experiments, the displacement of atoms away from their ideal positions would affect the observed peak intensities in a similar manner to thermal vibrations [19,20], as discussed in Chapter 7. Larger distortions would reduce the intensity of each diffraction peak, with that signal becoming redistributed into diffuse scattering. Several publications have presented data showing this effect [121,122,130,132,134,139,140], but the most comprehensive example is Figure 11 in reference [130], which presents a series of single phase, fcc alloys with systematically increasing chemical complexity. However, lattice distortions are not the only factor that can cause a reduction in the observed peak intensity, particularly when comparing different samples.
8.2 Experimental Methods

measured on a laboratory diffractometer. Factors such as crystallographic texture, poor powder averaging, the fluorescence of certain atomic species, and other instrumental effects would all influence the intensity of a diffraction peak. Thus, without accounting for these effects, it cannot be conclusively determined whether the atomic lattices in single-phase multi-component solid solutions are severely distorted.

Recently, it has been suggested that the use of total scattering data can provide more information on the nature of the local arrangements and positions of the atoms in HEAs [141–143]. Total scattering measurements have been made on a ZrNbHf ternary alloy and an Al$_{1.3}$CoCrCuFeNi HEA using both X-ray and neutron radiation [141–143]. These studies have identified that the shape of the PDF peaks at short interatomic distance varied from those expected from an ideal structure and these differences were attributed to the presence of local distortions in the lattice. However, in both cases, the samples were measured in the as-cast condition, which is likely to contain solidification induced micro-segregation that could affect the PDF peak shape. Similarly, the pronounced crystallographic texture displayed in the ZrNbHf sample and the complex three-phase microstructure of the Al$_{1.3}$CoCrCuFeNi HEA, would need to be accounted for, to provide an in depth understanding of the strain in these alloys [73]. Therefore, whilst these studies hint at the capability of the technique, further measurements, with careful consideration of sample complexity and condition, are required to provide a clear picture of the local environment in HEAs.

To address this issue, total scattering measurements made with neutron radiation on a five-component equiatomic powder HEA sample in a single-phase condition are considered. The sample was gas atomised to ensure that good powder diffraction data could be obtained and textural effects avoided [73]. The results are compared to data for a Ni powder, three Ni-Cr binary alloys and a Ni-Co-Cr ternary alloy.

8.2 Experimental Methods

Gas atomised powders of Ni-33Cr (at.%) and an equiatomic CrMnFeCoNi HEA were produced by Hauner Metallische Werkstoffe. A small quantity of each powder was encapsulated within an evacuated and Ar backfilled quartz tube prior to heat treatment at 1200 °C for 2 hours followed by water quenching. The heat treatment served to both chemically homogenise the material and sinter the powders into a bar. The surfaces of the sintered bars were lightly ground to remove any potential contamination from the heat treatment process.

Total scattering measurements were performed on the Polaris instrument at the ISIS Neutron and Muon Source. To ensure that data of sufficient quality were acquired, these measurements were made for a total of four hours under ambient conditions. The scattering data were focussed and normalised using the Mantid software [76]. Rietveld refinement of the Bragg data was performed using the GSAS program. The total scattering data were processed using the GudrunN software [43] and Fourier transformed to obtain pair distribution functions using the StoG program, with a $Q_{\text{max}} = 31 \text{ Å}^{-1}$. Modelling of the total scattering data was also performed using the RMCPProfile program.

The data collected were compared to data gathered previously under the same conditions on the Polaris instrument for Ni, Ni-20Cr, Ni-25Cr and Ni-37.5Co-25Cr. The Ni was investig-
ated in the as-received powder form, whilst the alloy specimens were all fabricated using the same method as described above but with different heat treatment parameters. The Ni-Cr binaries were heat treated for 100 hours at 1000 °C, whilst the Ni-37.5Co-25Cr alloy was exposed for 100 hours at 900 °C. In addition, the sintered Ni-37.5Co-25Cr alloy bar was crushed using a hand percussion mill prior to the scattering measurement. To ensure consistency between datasets measured at different times, they were all reanalysed together and identical processing parameters used.

8.3 Results and Discussion

8.3.1 Bragg data

The neutron diffraction patterns from the different alloys are shown in Figure 8.3. In Figure 8.3, the data have also been scaled by the intensity of the Ni {111} peak to facilitate comparison of the different datasets. Without this scaling the effect would be difficult to discern, due to the different scattering powers of the material reducing changing the overall intensity of the diffraction pattern. The data indicated that in the studied condition all of the samples were single phase materials with an fcc structure. The one exception to this was the Ni sample, which contained a small volume fraction (\(\sim 2.5\%\)) of nickel oxide, evidence of which can be seen by the small reflection at a d-spacing just below 1.5 Å (indicated by an arrow in the figure). Simple inspection of the Bragg diffraction patterns in Figure 8.3 shows no obvious change in the peak damping between any of the alloys.

Rietveld refinement was carried out on all of the powder diffraction patterns and an example of a fitted dataset is given in Figure 8.4. This dataset corresponds to the HEA sample and the quality of the fit is representative of all of the other refinements. As can be seen from Figure 8.4, the entire pattern is well described by the model, which indicated that the crystallites in the sintered bars represented an adequate powder average. Rietveld refinement of the solid solution phases assumes that the constituent elements are randomly distributed across the lattice sites. Likewise, the fit does not require the addition of any corrections for texture or preferred orientation, demonstrating that the samples are indeed a crystallographic powder and so no consideration of textural effects is required.

The refined lattice parameter (\(a\)) and the isotropic thermal motion parameter (\(U_{\text{iso}}\)) for each alloy, along with the melting temperatures, are given in Table 8.1. If the data corresponding to the Ni and Ni-Cr binary alloys are considered, then the expected linear expansion of the lattice parameter with increasing Cr content is observed, in line with a hard sphere model. However, neither the refined lattice parameters of the ternary alloy nor the HEA are well described by extending this simple model.

As discussed previously, both static and dynamic displacements are subsumed within the \(U_{\text{iso}}\) term. Whilst the refined HEA dataset did produce the largest \(U_{\text{iso}}\) value, no obvious correlation could be seen between compositional complexity and the refined \(U_{\text{iso}}\) values when considering all of the datasets. In particular, the refined \(U_{\text{iso}}\) value for the Ni-37.5Co-25Cr alloy was lower than any of the binary Ni-Cr alloys or pure Ni. Whilst the relationship between local lattice strain and Bragg damping is theoretically sound [145], to make any meaningful comment about
8.3. Results and Discussion

Figure 8.3: Normalised and scaled neutron diffraction spectra of the studied alloys. The arrow indicates the presence of a NiO impurity in the Ni sample.

Figure 8.4: Rietveld refined neutron powder diffraction pattern from the CrMnFeCoNi HEA, with black markers for the experimental data, the overall fit shown in red and the residuals shown by the blue line.
Table 8.1: Rietveld refined lattice parameters ($a$) and isotropic thermal motion factors ($U_{iso}$) for all of the materials studied along with their melting temperatures ($T_m$). The errors in the lattice parameter values were less than 0.0001 Å, and less than $0.06 \times 10^{-3}$ Å$^2$ for the $U_{iso}$ terms. Values for $T_m$ were obtained from ThermoCalc using the TTNi5 Database, with the exception of CrMnFeCoNi, which was taken from [144].

<table>
<thead>
<tr>
<th>Alloy (at.%)</th>
<th>$a$ (Å)</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>$T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>3.520</td>
<td>$4.59 \times 10^{-3}$</td>
<td>1728</td>
</tr>
<tr>
<td>Ni-20Cr</td>
<td>3.547</td>
<td>$4.92 \times 10^{-3}$</td>
<td>1695</td>
</tr>
<tr>
<td>Ni-25Cr</td>
<td>3.555</td>
<td>$4.83 \times 10^{-3}$</td>
<td>1686</td>
</tr>
<tr>
<td>Ni-33Cr</td>
<td>3.567</td>
<td>$5.02 \times 10^{-3}$</td>
<td>1667</td>
</tr>
<tr>
<td>Ni-37.5Co-25Cr</td>
<td>3.551</td>
<td>$4.49 \times 10^{-3}$</td>
<td>1725</td>
</tr>
<tr>
<td>CrMnFeCoNi</td>
<td>3.597</td>
<td>$5.46 \times 10^{-3}$</td>
<td>1543</td>
</tr>
</tbody>
</table>

the magnitude of this strain would require the deconvolution of the $U_{iso}$ term into static and dynamic components.

All samples were measured at room temperature and were therefore subjected to the same thermal energy. However, the magnitude of the thermal vibrations are a function of this energy and the elastic constants of the material, which themselves are related to the melting temperature [146]. Thus, the amplitude of thermal vibrations around a lattice site will be smaller in a material at a lower homologous temperature. This effect appears to show a better correlation to the refined $U_{iso}$ values than compositional complexity, especially when considering the low $U_{iso}$ value of the Ni-37.5Co-25Cr sample. This suggests that dynamic displacements may be dominating the refined $U_{iso}$ values of all the materials, meaning the local static displacements in the HEA may not be as large as hypothesised. Further evidence may be provided by a consideration of the PDF.
8.4 Calculating the PDF

When performing the Fourier transform that yields a PDF, there are a number of input parameters that are required, that will affect the form of the PDF: scale factor, $Q_{\text{min}}$ and $Q_{\text{max}}$. The potential effect each of these could have on the peak width needs to be considered and a method for optimising the input values determined.

8.4.1 Scaling factor

Scalar multiples of functions are invariant under a Fourier transform, as noted in Appendix A. Consequently, the scalar multiple applied in StoG could equally be applied as a scaling to the resultant PDF. Assuming that the PDF is effectively a sum of Gaussians, applying a scaling factor will simply change the scale factor of each Gaussian and not the width. Hence, the observed peak width should be independent of the scaling.

Whilst this is true mathematically; practically this is not the case. Fitting a PDF with a sum of Gaussians uses the expression:

$$G_{\text{calc}}(r) = y_0 + \sum_n A_n \exp\left(-\frac{(x - b_n)^2}{2c_n^2}\right)$$  \hspace{1cm} (8.3)

where $A$, $b$ and $c$ are constants defining the Gaussian function for each of the $n$ peaks, and $y_0$ a constant. For a correctly scaled PDF, $y_0 = \sum_i \sum_j b_ib_jc_ic_j$, i.e. the sum of the Faber-Ziman partials. In fitting the peak, the $y_0$ parameter can either be held at the desired value or allowed to refine. Depending on the range over which the refinement is carried out, it may be necessary to fix this parameter to the expected value. This fixing of the baseline will have a knock on effect on the calculation of the peak width. It will either change the fit of the Gaussian, or the recorded FWHM (depending on which methodology is used for determining the width).

This transpires to be a large source of error in the calculation. Fig. 8.5 shows the measured peak width of the first six peaks in the PDF of nickel, when the scale factor is varied from 0.8 to 1. The graph shows that there is a large variation in the recorded peak width with the chosen scale. The error is particularly large for the 2nd, 4th and 6th peaks. This can be explained by considering the form of the fcc PDF. The 1st, 3rd and 5th peaks have much larger areas (as there are more neighbours at those corresponding distances) compared with the 2nd, 4th and 6th peaks.

Fixing the baseline, therefore, has a much more pronounced effect on the measured height of the smaller peaks and a corresponding large change in the measurement of the peak width. The correct choice of scale is, therefore, essential if the peak widths and, hence, local strain, are to be accurately determined. As mentioned in Chapter 2, the scale is typically chosen so as to bring the low-$r$ region of a PDF to the expected value. However, in the case of these random alloys, it is possible to suggest other mathematical methods for determining the ideal choice of scale factor.
Chapter 8.  Local lattice strains in High-entropy alloys

Choosing a scale factor

If the system is correctly scaled and completely random, then fitting the PDF with a grey-atom model should yield a perfect fit. If the data are incorrectly scaled, then in some regions the PDF will be larger than expected and in other regions, smaller than expected. In this case, the fit to the data should worsen and the average level of the difference PDFs and the integral of difference PDFs will become non-zero. Similarly, if the scale is incorrect, the magnitude of the oscillations in the difference PDF around the average average value will increase. Consequently, there should be a minimum in the error of the calculated average at the ideal scale. Based on these concepts the following procedure for choosing the optimum scale was proposed.

1. A refinement box containing only one type of atom made of $10 \times 10 \times 10$ units cells was set up that reflects the lattice parameter calculated from a Rietveld refinement of the Bragg data using the GSAS software. The Gaussdist programme was used to provide offsite displacements to model thermal fluctuations.

2. RMCProfile controls files (.dat) were set up using average ‘grey atom’ coefficients for the PDFs and for the Bragg data.

3. The total scattering data was transformed using the StoG programme, using a scale factor of 1 to yield the $F(Q)$ and $G(r)$. The $Q_{\text{max}}$ was kept fixed at a value that had been determined previously to minimise Fourier ripples.

4. RMCProfile was run, allowing translations only, to fit the $F(Q)$, $T(r)$ and Bragg data.

5. Steps 3 and 4 were repeated, using the original configuration generated in Step 1, varying the scale factor (typically in steps of 0.01 down to 0.80). All other details in the StoG calculation were kept the same.

6. From each of the runs the resultant total $\chi^2$ and the individual $\chi^2$ for each of the data sets were recorded. The change in these values with scale factor is plotted, Fig. 8.6a.
7. For each data set the difference in the $T(r)_{\text{obs}}$ and $T(r)_{\text{RMC}}$ is calculated and plotted. The difference plot is fitted with a flat line, to calculate the average value around which it oscillates. A plot of the average value and the error on this average value with the varying scale factor are plotted, Fig. 8.6b and Fig. 8.6d.

8. For each data set the difference in the integrals of the $T(r)_{\text{obs}}$ and $T(r)_{\text{RMC}}$ was calculated and plotted. The difference plot was fitted with a flat line, to calculate the average value around which it oscillates. A plot of the average value and the error on this average value with the varying scale factor are plotted, Fig. 8.6c and Fig. 8.6e.

9. For every scale factor the first six peaks of $G(r)$ were fitted with Gaussians function, fixing the baseline at the negative sum of the Faber-Ziman partials. The width of the peaks was recorded and plotted.

10. For the fits in Step 9 the average coordination number for the peak was calculated, assuming that the sample was random and using the known crystallographic density of the structure.

11. Using the plots generated from Step 6, 7 and 8 (and noting the coordination numbers calculated in Step 10) a scale factor for the system was chosen (for the Nickel case scale factor = 0.90).

From this procedure a ‘correct’ scale factor was chosen for each sample. These were compared with values calculated from PDFgui and found to be in good agreement. From Fig. 8.5, it is apparent that the choice of scale factor can lead to large variations in the observed peak width. As this appears to be the largest source of error, it serves as a good way to suggest an error on any calculated peak width. For any peak width measured, the same peak widths were measured for the scale factor $S \pm 0.02$ and used to provide bounds on the recorded peak width.

It is worth reiterating that this methodology is based on the assumption that the material is statistically random and so can be well modelled by a grey atom system. The quality of the fits produced in PDFgui, which operates using the same average information and the grey-atom runs carried out in RMCProfile suggest that this approximation is valid in these samples and, therefore, this methodology can be used.

8.4.2 The effect of the choice of $Q_{\text{max}}$

The $Q_{\text{max}}$ range for any Fourier transform is incredibly important. The longest period oscillations in reciprocal space will result in the highest frequency oscillations in real space, so to obtain the highest resolution the largest $Q$-range possible is required. It is therefore important that all Fourier transforms are calculated across the same $Q$-range and also to consider any effect the choice of $Q_{\text{max}}$ may have on the recorded PDF peak width.

The PDFs were calculated for a series of varying $Q_{\text{max}}$ values and the widths of the PDF peaks measured. A plot of the change in peak width with peak number for the different $Q_{\text{max}}$ values for the HEA sample is shown in Fig. 8.7.
Figure 8.6: Graphs used for the sample of pure Nickel to choose a correct scaling value. (a) $\chi^2$ for the different datasets used in the runs. Black - total for all datasets, Red - Bragg fit, Blue - $G(r)$ fit, Green - $F(Q)$ fit (b) Average fitted value of $(T_{\text{obs}}(r) - T_{\text{RMC}}(r))$. (c) Average fitted value of $\int (T_{\text{obs}}(r) - T_{\text{RMC}}(r))$. (d) Error in average fitted value of $(T_{\text{obs}}(r) - T_{\text{RMC}}(r))$. (e) Error in average fitted value of $\int (T_{\text{obs}}(r) - T_{\text{RMC}}(r))$. 

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8.4. Calculating the PDF

As can be seen, with the exception of the very lowest values $Q_{\text{max}} \leq 27 \text{ Å}^{-1}$, there is only a small change in the observed peak width, particularly when compared to the similar figure produced by varying the scale (see Fig. 8.5). Therefore, the $Q_{\text{max}}$ should be chosen so as to minimise the observed Fourier ripples in the system, particularly in the inter-peak region where the PDF should be flat.

Comparing these calculated PDFs, there was a notable change in the asymmetry (negative skew) of the second peak in HEA sample and likewise in the Ni-33Cr with variations in $Q_{\text{max}}$. The first peak in this system, might be expected to display a slight positive skew, due to the shorter nearest neighbour partial having larger Faber-Ziman coefficients compared to the partials for the other longer bonds. This can be seen in Fig. 8.8, which shows the partials for the HEA that are being summed and the Faber-Ziman coefficients for the individual partials (ordered by expected interatomic distance). However, as discussed previously with regards to the Gaussian model, it is difficult to determine what effect this would have on subsequent shells, such as the 2nd nearest neighbours, due to the permutations of the intermediate atom types. The only other possibility is that this asymmetry is the result of chemical inhomogeneity in the samples i.e. short-range order occurring.

However, given that this effect is $Q_{\text{max}}$ dependent, it suggests that this change is an artefact caused by the nature of performing a Fourier transform over a finite range, as opposed to a real effect in the system. Practically, a $Q_{\text{max}} = 31 \text{ Å}^{-1}$ was chosen as this minimised the observed Fourier ripples and reduced the observed peak asymmetry. Irrespective of this, as can be seen from Fig. 8.7, this asymmetry appears to have little effect on the measured peak width, which remains constant with the $Q_{\text{max}}$ variation.
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8.4.3 $Q_{\text{min}}$

As discussed, the $Q$-range over which the transform is carried out is important, which is dependent on the $Q_{\text{min}}$ value. Further, the value of $Q_{\text{min}}$ will change the low-$Q$ correction performed in StoG, as described in Chapter 2. For these data, it was noted that the Gudrun software had difficulty merging the banks at low-$Q$, resulting in a stepped edge. Due to concern about the effect this may have on the observed PDFs, the same process was carried out as previously, comparing the PDFs calculated when varying the $Q_{\text{min}}$ from 1 to 2.6 Å$^{-1}$ in steps of 0.2 Å$^{-1}$. The results are shown in Fig. 8.9. As can be seen the choice of $Q_{\text{min}}$ seems to have little effect on the recorded peak width and therefore need not be considered in these samples. In general for these samples a value of $Q_{\text{min}} = 0.2$ Å$^{-1}$ was used.

![Figure 8.8: a) Partials for HEA calculated with the Faber-Ziman weightings and b) the relative Faber-Ziman partials for the different pairs.](image)

Figure 8.9: Change in the peak width of the first six peaks of the PDF of the CrMnFeCoNi HEA, with the $Q_{\text{min}}$ of the Fourier transform. Error shown is the error in the fit from the fitting algorithm.

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8.5 PDF results

Having chosen suitable values for scale, $Q_{\text{min}}$ and $Q_{\text{max}}$ by the methodology outlined, the PDFs obtained for each of the alloys studied are shown in Figure 8.10. In all cases, the form of the PDF was typical of an $fcc$ lattice, in good agreement with the Bragg data. On visual inspection, no difference could be determined between the datasets, save the systematic shift of the peak position in $r$ consistent with the variation of lattice parameters. In addition, all of the PDFs exhibited a similar level of peak definition to high-$r$, Fig. 8.11. If the local displacements are significant in the low-$r$ coordination shells, then the cumulative effect at larger values of $r$ would cause the peaks to become so broad that they lose their form, potentially leading to a featureless PDF at high $r$. This is not observed in the data.

The data were modelled using large box models created in RMC. Critically, all of the datasets were modelled using boxes containing only a single atom type, termed a grey atom, which had a compositionally weighted average scattering length of all the constituent elements. Figure 8.12 shows the PDF of the HEA sample fitted in this way. As can be seen, the quality of the fit is extremely good, demonstrating that the system was well described by a grey atom model. Consequently, the distribution of atoms on a local scale was also likely to be random, in agreement with the average structure determined from the Bragg data and the theory proposed in the HEA literature. The fits to all the other datasets were of at least comparable, if not higher, quality than that shown in Figure 8.12, leading to the conclusion that all of the studied materials were statistically random solid solutions with an $fcc$ structure. Consequently, the potential influence of chemical inhomogeneity on the data need not be considered.

Figure 8.10: Normalised pair distributions functions ($G(r)$) for all of the studied alloys, plotted for the low $r$ region. PDFs are offset for ease of visualisation..
Figure 8.11: Normalised pair distributions functions ($G(r)$) for all of the studied alloys, plotted for the high $r$ region. PDFs are offset for ease of visualisation.

Figure 8.12: Plot of the pair distribution function, $T(r)$, for CrMnFeCoNi and fit from RMC modelling. Experimental data shown by markers, fitted data from a reverse Monte Carlo refinement using a grey atom model shown in red and the difference curve shown in blue.
Considering the data presented in Figure 8.10 and Figure 8.11, no obvious difference can be seen between the different materials studied and good peak definition can be observed over the complete $r$ range. This suggests that all of the materials have well defined lattices, with no significant long range distortion. However, to study the effect of local lattice strains in more detail, analysis of the first six coordination shells was performed using the techniques discussed in Chapter 7. The corresponding region of the $G(r)$ PDF, Figure 8.10, has been expanded for clarity in Figure 8.13. Again, with the exception of the positional shift in $r$, associated with the different lattice parameters, the form of these functions appears identical.

The width of a PDF peak is a function of the static and dynamic displacements of the atoms within the crystal, the $Q_{\text{max}}$ of the Fourier transform and the inherent instrumental effects. All of data reported in this study were acquired using the same instrument and, therefore, with only small difference in lattice parameters the inherent instrumental broadening for each material should be essentially identical and can effectively be ignored. All of the alloys considered in this study were subjected to elevated temperature heat treatments prior to investigation, which should have minimised the dislocation densities and relieved any strain caused by the atomisation process. The Ni-37.5Co-25Cr alloy was crushed following heat treatment, which could have introduced dislocations that may need to be accounted for in subsequent analysis. Surface effects would only be expected to be significant if the crystals were extremely small, such that their surface to volume ratio was high. Given that all of the alloys were exposed to temperatures in excess of 900 $^\circ$C for reasonable lengths of time, nanometer sized crystals seem unlikely. Thus, it is believed that the thermal vibrations and local lattice strains dominate the observed PDF peak widths.

![Figure 8.13: Normalised pair distributions functions ($G(r)$) for all of the alloys studied, zoomed in at low-$r$ region. PDFs are offset for ease of visualisation. No obvious change in the peak width is apparent.](image)
Visual inspection of Figure 8.13 reveals no obvious variation in the breadth of the PDF peaks between the different alloys, but to assess this more accurately each peak was fitted with a Gaussian function. The fitted values of full width at half maximum (FWHM) for all six peaks from each alloy are shown in Figure 8.14. The peak widths were determined by both of the methods described in Section 7.3 and the two methods found to be in agreement. However, for computational simplicity the Gaussian fitting method was ultimately used and the FWHM determined from that method is plotted here.

Figure 8.14: Full width at half maximum (FWHM) values from Gaussian fits to the first six peaks of the pair distribution function of each alloy.

No clear trend with respect to the relationship between PDF peak width and composition can be seen across all coordination shells. The FWHM values from the first coordination shell are always the lowest, whilst those corresponding to the other coordination shells are, broadly speaking, of similar magnitudes. This effect on the first coordination shell is believed to be a result of correlated motion between different pairs of nearest neighbouring interacting atoms and is the same effect as was observed in the spring model provided in Chapter 7 (see Fig. 7.12).

It would be expected that a monatomic sample would exhibit the narrowest PDF peaks, as there are no compositionally associated lattice strains. As such, the thermal motion of the atoms should dominate the widths of the PDF peaks. Surprisingly, this was not the case in the experimental data, where Ni-20Cr was observed to have the narrowest PDF peaks in all but the fifth coordination shell. This observation could either suggest that some form of short-range ordering was present within the Ni-20Cr sample, or that the Ni sample contained some static displacements. Since the Ni powder was studied in the as-received condition, with no knowledge...
of the prior processing history, and was found to contain a small fraction of NiO, the latter seems more likely.

The three Ni-Cr alloys showed a systematic increase in PDF peak width with greater Cr concentration. In terms of static displacements this trend is expected as, in addition to the expansion of the lattice, the local positions of the solvent atoms alter to accommodate a greater concentration of the larger solute atoms. This is in agreement with the predictions made in the previous chapter. A similar effect was also observed for the Ni-37.5Co-25Cr ternary alloy, where the substitution of Co for Ni resulted in broader PDF peaks than the Ni-25Cr binary alloy. This observation suggested that there was a greater level of strain in the lattice of the ternary alloy than in the binary alloy with the same Cr concentration. In all but the sixth coordination shell, the HEA exhibited the greatest PDF peak widths, suggesting that this lattice contained the greatest level of local strain of all the alloys considered. However, in several of the coordination shells, the magnitudes of HEA PDF peak widths were comparable to those of either Ni-33Cr or Ni-37.5Co-25Cr. Thus, whilst it is clear that the HEA lattice contained some level of local strain, it did not appear to be disproportionately larger than those found in the lattices of other, compositionally simpler alloys.

Whilst the discussion above seems to provide a logical explanation of the observed PDF peak widths, it implicitly assumed that the magnitude of the dynamic displacements were constant for all alloys. As previously discussed, the variation in $U_{\text{iso}}$ terms obtained from the Bragg data showed a correlation between the magnitude of the thermal motion and the melting temperatures, meaning that the dynamic displacements cannot be considered constant at any given temperature.

From the melting temperatures provide in Table 8.1, the broadening of the PDF peaks due to thermal motion would be expected to increase in the following order: Ni, Ni-37.5Co-25Cr, Ni-20Cr, Ni-25Cr, Ni-33Cr and CrMnFeCoNi. Considering thermally driven dynamic displacements only, the trend in the breadth of the PDF peaks is well described with the exception of the Ni and the Ni-37.5Co-25Cr samples, both of which exhibited broader peaks than would be expected. Therefore, these samples must contain a significant static displacement in order to produce such broad PDF peaks. As stated above, the processing history of the Ni sample was unknown and the Ni-37.5Co-25Cr was crushed following heat treatment, both of which could lead to increased static displacements, thereby rationalising the observed PDF peak breadth. Consequently, these observations indicate that the breadth of the PDF peak observed for the HEA sample is not necessarily dominated by static displacements.

### 8.5.1 Comparison with models

In Chapter 7, two models were used for the examination of the peak widths of a PDF under the conditions of local-lattice strain. Similar modelling may be done on these alloys to provide an idea of broadening that might be expected. For the Gaussian model, a theoretical first peak of the PDF was calculated for each of the systems of interest using the method outlined in section 7.4.2. Likewise large box spring models, section 7.4.3, were set up and run to allow the calculation of the PDF to coordination shells beyond the first. PDFs were calculated from these simulations and the peak widths of the first 6 peaks measured in the same manner as carried out
for the experimental data. The results from these models with the experimentally determined peak widths are shown in Fig. 8.15

Broadly speaking, both models show a variation in the peak width of a similar order of magnitude to those observed in the experimental data. The data from the 6th peak should be considered with great care as it is a small peak that begins to overlap with neighbouring peaks and, as such, will be highly susceptible to fitting error (hence the very high nickel value). However, although broadly of the correct magnitude, the models seem to underestimate the change in peak width with increasing compositional complexity for all of the peaks. There are several possible reasons for this as follows:

• Atomic radii - the model was calculated using theoretical atomic radii generated from previous data. If any of these radii are too small, there could be a systematic underestimation of the broadening of the PDF peaks.

• Constant bonds - for the spring model it was also assumed that the potentials for all the bonds were the same. This is unlikely to be realistic and will likely change the magnitude of the observed changes.

• Homologous temperature - it has been assumed that the dynamic displacements for all the alloys is constant and can be modelled by that of the nickel. However, this is unlikely to be the case owing to the change in homologous temperatures of the different alloys.
It is most likely a combination of these effects that could lead to under-prediction of these models compared with experiment.

Interestingly, the two models show a distinctly different predicted order in the peak widths in the first shell. The simple Gaussian model predicts what is expected and cited in the HEA literature - that the HEA will have the comparatively largest peak width and strain in the lattice. From this model it is clear that the increase in compositional complexity leads to an increase in the observed strain. However, for the spring model it can be seen that the relaxation of the bonds occurring in the system actually leads to a decrease in the peak width and observed strain with compositional complexity. Considering only the relative order predicted by this model, the nickel, Ni-37.5Co-25Cr and CrMnFeCoNi appear to be broader than those predicted. However, as discussed previously, the higher nickel and Ni-37.5Co-25Cr may be the result of strain in the lattice caused by the processing. The HEA also should have a higher level of dynamic displacements, owing to its significantly lower melting point compared with the other samples, which would result in a comparative increase in dynamic displacements.

8.5.2 Problematic quantification

Unfortunately, although the HEA literature contains reference to the highly-strained lattice, no quantitative measure has been proposed to characterise what may constitute high levels of strain. It is for this reason that the results discussed in this chapter have been comparative and qualitative in nature. However, the interest in the HEA field has led to a number of propositions as to numerical predictors that may be used to suggest the stability of an HEA. One such predictor is the $\delta$ parameter that is used as a measure of the variation in atomic radii in the system.

The parameter is defined as:

$$\delta = \sqrt{\sum c_i (1 - \frac{r_i}{r_{av}})^2}$$

where:

$$r_{av} = \sum c_i r_i$$

where $r_i$ is the radius of an individual atomic species and $c_i$ is its concentration.

The $\delta$ parameter has been widely used to assess the stability of the solid solution phases in HEAs and a working limit of 0.066 (i.e. 6.6%) has been suggested, beyond which amorphisation would be expected [137]. Recall that the Hume-Rothery rules define a stability limit for a binary alloy as a 15% difference in the atomic radii (taken relative to the smallest radius). Such an alloy would have a $\delta = 0.066$ (as the atomic size difference is measured relative to the average radius), which is the same working limit used in the HEA literature.

The definition of the delta rule, results in a natural contradiction in the HEA literature. It is suggested that the observed amorphisation is the result of the destabilisation of the structure due to the size difference of the constituent atoms. Although, not explicitly stated, this would imply that the driving force of this amorphisation is the strain produced by this size difference. This in turn, would imply that the $\delta$ parameter gives an approximate measure of the strain exhibited in a system. For a binary system, a solid solution no longer forms for $\delta > 0.066$. This might suggest a definition of ‘highly-strained’ should apply to alloys with $\delta > 0.066$. Under this
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definition, a typical binary alloy would be expected to form intermetallics, whereas an HEA, stabilised by the high entropic advantage of forming a solid solution, is able to sustain this higher level of strain in the lattice.

However, the community states that for HEA stability $\delta < 0.066$. This means that the strain in an HEA lattice could be comparable to that of a binary, as suggested by the Hume-Rothery rules. Under this definition, it would therefore be possible to characterise a large number of binary alloys as ‘highly-strained’. One possible counter explanation is that the $\delta$-parameter does not provide a reasonable measure of the lattice strain. However, this raises the question as to what is the justification for its use as a metric of stability of an HEA. For future discussions on the ‘highly-strained’ nature of HEA lattices to be useful, a more precise definition of what this constitutes must be defined.

Using this expression to assess the difference in atomic radii (values from [148]) of the alloys studied in this work yields the following results: $\delta = 0.0115$ for Ni-20Cr; $\delta = 0.0124$ for Ni-25Cr; $\delta = 0.0134$ for Ni-33Cr; $\delta = 0.0122$ for Ni-37.5Co-25Cr and $\delta = 0.0106$ for CrMnFeCoNi. Interestingly, this order seems to agree with that predicted by the spring model. There are two key points that should be noted from these values. First, none of these alloys have particularly large differences in atomic radius, all having a $\delta < 1.5\%$. Second, the $\delta$ value of CrMnFeCoNi is the smallest. Consequently, and paradoxically considering the origin of the parameter, the lattice of CrMnFeCoNi would not be expected to contain large static displacements.

The PDF peak width appears to vary approximately linearly with $\delta$ as the Cr concentration of the Ni-Cr binary alloys increases; but, as with similar calculations of lattice parameter (following Vegard’s Law), the addition of ternary or higher order additions breaks this simple trend. It is likely that this limitation is due to the simplicity of a hard sphere type approach, in particular the fact that it does not consider how the bond energies may change with different species or the effect of temperature.

If the magnitudes of the thermal vibrations are assumed to be constant then the change of the PDF peak width between the different samples can be attributed to variations in static displacements. In the first coordination shell the maximum variation is $\sim 0.02\AA$, whilst the thermal contribution is $\sim 0.18\AA$. These values clearly indicate that for all of the alloys considered in this study the thermal component dominates the magnitude of PDF peak width. In addition, as the alloys are not at the same homologous temperature, an estimation of the static component made in this manner is likely to be an overestimate in the case of CrMnFeCoNi. However, it is possible to compare this value to one that might be expected from an average hard sphere structure using $r_{\text{av}}$ with static displacements of $\delta \times r_{\text{av}}$. Using this approach, the expected magnitude of the static displacement in CrMnFeCoNi would be $\sim 0.025\AA$, which is of a similar magnitude to that of the observed variation of the first PDF peak width, indicating that this alloy does not contain an anomalous level of static lattice displacement.

Using the same approach, it is possible to estimate the expected magnitude of the static displacement of a highly strained version of the lattice. At present, the magnitude of the static displacement that constitutes a highly strained lattice has not been quantitatively defined, which makes evaluation of the concept difficult.

For CrMnFeCoNi, a $\delta$ of 0.066 would lead to a static displacement of $\sim 0.17\AA$, which is
far greater than that estimated from the experimental data and is on the order of the observed dynamic displacements. However, it is important to realise that this approach is very simplistic and does not take into account any factors apart from atomic radii. To address this, detailed calculations using first principles approaches would be required to provide a more accurate assessment of the effect of static displacements on PDF peak widths.

Without being able to accurately separate the dynamic and static displacements it is impossible to determine the exact contribution of each component but, clearly, neither can be ignored. The PDF peak widths of the HEA were generally the greatest within the alloys considered, which, in terms of a static displacement, would suggest that the HEA lattice contains the most local strain. However, the widths of these PDF peaks were not disproportionately greater than those of Ni-33Cr or Ni-37.5Co-25Cr. In addition, the dynamic displacements due to thermal motion would be expected to be greatest in the HEA as it has the lowest melting temperature. Thus, the level of static displacements required to rationalise the observed peak widths would be lower. As a result, the current data indicated that, whilst substitution of different elements into a pure metal leads to a local strain, there is no clear evidence that the level of strain is anomalously large for an equiatomic CrMnFeCoNi HEA. The comparable level of peak definition at high-$r$ in all of the obtained PDFs further supports this assertion.

This conclusion is contrary to one of the four original core principles of HEAs and challenges the concept that the lattices of multiple principal element solid solutions are, by necessity, highly distorted. However, this result is perhaps unsurprising given the extremely small variations in atomic radii of the constituent elements. Further detailed measurements should be performed on alternative single phase alloys that contain elements with greater variations in atomic radii. In addition, to enable a more rigorous analysis of local strain data, a quantitative description of what constitutes a highly distorted lattice is required.

8.6 Conclusions

The core principles of the HEA field remain the subject of a great deal of debate in the literature. Many of these core-principles are currently being investigated and challenged. To date, experimental evidence for the existence of the ‘highly-strained lattice’ in the literature is relatively sparse. Based on the previous theoretical work and the nature of total scattering and pair distribution functions as a local probe of a material, it is hoped that some insight could be provided into the nature of these materials.

The level of local lattice strain in six single phase face-centred cubic materials, with varying compositional complexity, have been studied through neutron total scattering measurements to assess the level of distortion present in the CrMnFeCoNi HEA. Rietveld refinement of the Bragg data and reverse Monte Carlo modelling of the total scattering data both indicated that, in the condition studied, all of the alloys were statistically random solid solutions. None of the Bragg data exhibited pronounced damping, which would be expected for a highly distorted lattice, and the observed variations in the $U_{iso}$ parameter could be rationalised simply in terms of homologous temperatures.

A consideration of the parameters used to generate a PDF, and their effect on the observed peak widths of a system are discussed and presented. Based on these considerations, PDFs of
all the materials were calculated and compared. The definition of the peaks in each PDF was maintained to high $r$ values in all cases, suggesting that there were no significant deviations of the atoms from the space lattice sites in any of the alloys.

Detailed analysis of the PDF peak widths corresponding to the first six coordination shells was used to assess the extent of local lattice strain in the different materials. In general, the HEA was found to have the broadest peaks, which could suggest the highest level of local lattice strain within the materials studied. However, the peaks were not markedly broader than those of Ni-33Cr or Ni-37.5Co-25Cr, indicating that the level of strain was not disproportionately larger than those present in other alloys. In addition, the width of a PDF peak is also dependent upon the magnitude of the thermal oscillations of the atoms within the lattice, which would be greater at higher homologous temperatures. Since the HEA has the lowest melting temperature of the materials considered, it would exhibit the greatest level of thermal broadening, which, consequently, would reduce the extent of local lattice strain required to rationalise a given PDF peak width. As such, the data presented here finds no clear evidence that the local lattice strain in an equiatomic CrMnFeCoNi HEA is anomalously large.

The arguments presented provide a qualitative comparison and assessment of the strain in these alloys, but are hampered by considerations of the dynamic displacements occurring in the structure. A key potential component of future work would be the accurate separation of this contributing effect, see Chapter 10. In spite of this, the work presented in this chapter demonstrates the methodology needed for the assessment of local-lattice strains from a PDF, and provides insight into the controversial HEA theory of the highly strained lattice.
Chapter 9

Energetic considerations

Ultimately, to link the observed short-range order to the physical parameters of an alloy a complete understanding of the energetics of the system is required. Likewise, calculations of phase diagrams are based on the end-members of LRO and random solid solutions. Whilst this assumption provides a powerful method for basic phase-prediction, it represents a simplification of reality in which there are far more complex possibilities for ordering in a system. To accurately calculate phase diagrams and energetics, new thermodynamic theory needs to be developed and implemented. This is beyond the scope of this thesis, however, a brief examination of the current theory, its challenges and ideas for potentially challenging this theory are presented in this chapter.

9.1 Random mixing in a binary alloy

Consider mixing two elements A and B, each of which are known to have the same crystal structure, to form a random homogenous solid solution. The mole fractions of the two species are given as $X_A$ and $X_B$ such that:

$$X_A + X_B = 1$$ (9.1)

To calculate the change in the Gibbs free energy (to suggest the stability of the phases) we allow the mixing to occur in two stages:

1. Bring together the two species as pure elements. The Gibbs free energy of the unmixed state is denoted $G_1$

2. Atomic species are allowed to mix. The change is Gibbs free energy on mixing is denoted $\Delta G_{\text{mix}}$

The total Gibbs energy of the system is then calculated as $G = G_1 + \Delta G_{\text{mix}}$. The $G_1$ term can be calculated simply as the linear sum of the independent Gibbs energy terms of the two pure species A and B, i.e. :

$$G_1 = X_AG_A + X_BG_B$$ (9.2)

To calculate the free energy of mixing, $\Delta G_{\text{mix}}$, recall that:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$ (9.3)
where $T$ is the temperature, $\Delta H_{\text{mix}}$ the change in enthalpy on mixing and $\Delta S_{\text{mix}}$ the change in entropy on mixing.

**Ideal solid solution**

For an ‘ideal’ solid solution, the approximation is made that the enthalpy of mixing is zero - i.e. there is no preference to have A-A, A-B or B-B bonds. Consequently, the Eq. 9.3 simplifies to one involving only the entropy of the system. Boltzmann related the entropy of the systems to the number of accessible ways of arranging the system:

$$S = k_B \ln W \quad (9.4)$$

where $W$ is the number of microstates accessible to the system due to thermal fluctuations in the same macrostate, and $k_B$ the Boltzmann constant. A macrostate is defined by the constant macroscopic properties of the system such as temperature, pressure, volume and density. The configurational entropy of mixing of the two elements is therefore given by:

$$S_{\text{config}} = k_B \ln \left( \frac{N!}{N_A!N_B!} \right) \quad (9.5)$$

where $N$ is the number of atoms in the system, $N_A$ the number of A atoms and $N_B$ the number of B atoms. This can be reduced by Stirlings approximation to the standard expression:

$$\Delta S_{\text{mix}} = Nk_B \ln N - N_A k_B \ln N_A - N_B k_B \ln N_B \quad (9.6)$$

For one mol of material, it follows that as $N_A = N_aX_A$ and likewise $N_B = N_aX_B$ (where $N_a$ is Avogadro’s number), which simplifies equation 9.6 to:

$$\Delta S_{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B) \quad (9.7)$$

and hence:

$$\Delta G_{\text{mix}} = RT(X_A \ln X_A + X_B \ln X_B) \quad (9.8)$$

where $R$ is the gas constant A plot of this function is shown in Fig. 9.1

It is important to note that the maximum entropy of the system is achieved when the mixture is 50:50 in ratio. It is this argument that is extended to the stabilisation of a single phase by maximising the entropy in a equiatomic mixture that has lead to the development of the field of high entropy alloys (HEAs).

**Regular solid solution**

This ‘ideal’ solid solution so far has not considered any enthalpic interaction taking place in the system between atomic species. Let us consider instead a ‘random’ solid solution where the atoms are randomly mixed. The structures will contain a certain number of A-A, A-B and B-B bonds, each with a respective energy $\epsilon_{AA}$, $\epsilon_{AB}$ and $\epsilon_{BB}$. The enthalpy ($H$) of the random solution will be given by:

$$H = P_{AA}\epsilon_{AA} + P_{AB}\epsilon_{AB} + P_{BB}\epsilon_{BB} \quad (9.9)$$
9.1 Random mixing in a binary alloy

Figure 9.1: $G_{\text{mix}}$ for an ideal binary alloy at different temperatures. Black indicates low-$T$ and red higher-$T$.

where $P_{AA}$, $P_{AB}$ and $P_{BB}$ are the probabilities of finding an AA, AB and BB bond respectively.

Consider that each atom in the structure has $d$ nearest neighbours. It follows that:

$$N_A d = 2P_{AA} + P_{AB}$$

$$P_{AA} = \frac{N_A d}{2} - \frac{P_{AB}}{2}$$

and likewise:

$$N_B d = 2P_{BB} + P_{AB}$$

$$P_{BB} = \frac{N_B d}{2} - \frac{P_{AB}}{2}$$

where $N_A$ and $N_B$ are the number of A and B atoms respectively.

Therefore, we can write:

$$H = \left(\frac{N_A d}{2} - \frac{P_{AB}}{2}\right)\epsilon_{AA} + \left(\frac{N_B d}{2} - \frac{P_{AB}}{2}\right)\epsilon_{BB} + P_{AB}\epsilon_{AB}$$

$$= \frac{N_A d}{2}\epsilon_{AA} + \frac{N_B d}{2}\epsilon_{BB} + P_{AB}(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2})$$

The first two terms in this equation are the enthalpies of the unmixed A and B components respectively. Hence:

$$\Delta H_{\text{mix}} = P_{AB}\epsilon$$

where:

$$\epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$$

This equation will of course reduce to the ‘ideal’ case if there is no difference in the energy of the different bond types.
Chapter 9. Energetic considerations

Conventionally, it is assumed that the arrangement of atoms in a regular atomic solid solution is completely random. As such, the probability of an A-B type bond is given by a simple binomial probability i.e.

\[ P_{AB} = N_a dX_A X_B \]  

(9.18)

where \( N_a \) is Avogadro’s number. This equation is only true if there is no preference between the formation of a specific bond type - i.e. \( \epsilon_{AA} = \epsilon_{AB} = \epsilon_{BB} \). However, it is common to assume that this holds for small variations of \( \epsilon \).

This is often written as:

\[ \Delta H_{\text{mix}} = \Omega X_A X_B \]  

(9.19)

where:

\[ \Omega = N_a d\epsilon \]  

(9.20)

It follows that the change in Gibbs free energy on mixing a regular solid solution may be given by:

\[ \Delta G_{\text{mix}} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B) \]  

(9.21)

It is important to understand the variation of the Gibbs free energy with changes in the \( \Omega \) parameter and the temperature of the system. Figure 9.2 shows the effect on the enthalpy, entropy and resultant Gibbs free energy with \( \Omega < 0 \) and \( \Omega > 0 \), and at high and low-T.

For exothermic interactions, i.e. \( \Omega < 0 \), the situation is relatively simple, with a large Gibbs free energy in the equiatomic mixture. The free energy decrease occurs at all temperatures - i.e. it is always favourable for a completely random mix of atom types if the bond interactions are enthalpic. However, for endothermic interactions, \( \Omega > 0 \), the case is more complex - the Gibbs free energy now becoming a balance between the negative entropic term of the system and the positive enthalphic mixing parameter. At high temperature, the entropy of the system dominates over the enthalpy, creating a Gibbs free energy minima. However, as the temperature reduces, so does the entropic term, until the entropy and enthalpy are of a similar magnitude and a maxima is created in the Gibbs free energy plot. Under these conditions, it is now thermodynamically preferable to form two phases, corresponding to the minima in the Gibbs free energy. This leads to a miscibility gap in the system.

It should be noted that the differential of equation 9.21 is:

\[ \frac{\delta \Delta G_{\text{mix}}}{\delta x} = \Omega(1 - 2x) + RT \ln \left( \frac{x}{1 - x} \right) \]  

(9.22)

where \( x = X_A \) and so \( 1 - x = X_B \). As \( x \to 0 \), then this differential will tend to a negative value, implying that there is always some decrease in the Gibbs free energy on mixing. This implies that irrespective of the sign of \( \Omega \), it will always be favourable for some small amount of mixing to occur in the system.
Figure 9.2: $\Delta G^{\text{mix}}$ for a regular binary alloy under different conditions. Red line indicates the change in enthalpy in the system, green indication the energy term that is entropy dependant and the black line the change in Gibbs free energy of the system. a) $\Omega < 0$, high-$T$, b) $\Omega < 0$, low-$T$, c) $\Omega > 0$, high-$T$, d) $\Omega > 0$, low-$T$. 
Chapter 9. Energetic considerations

Real solid solutions and short-range order

The above is obviously an over simplification of the nature of real materials. The assumptions made in these descriptions are that of maximum entropy, i.e. that the system forms a random mixture such that the entropy is maximised. For a real solution, there will be a balance between the entropy of the system and the enthalpy, with the real solution existing in the state that minimises the Gibbs energy of the system. It is this balance that will allow the existence of short-range order.

If the Gibbs free energy were to comprise only of enthalpic terms, then any preference for a given type of bond would lead to an observed clustering or ordering within the system. Only through the balance of entropy may a stabilised non-long-range ordered system occur (including a truly random solid solution). In reality this must mean that, as no two bond types are entirely identical, for any multicomponent system that is observed as a solid solution, the entropy of the ‘random’ mixing must be outweighing the enthalpy of ordering that will be trying to occur in the system. For a complete understanding of the nature of ordering a successful numerical description of the change in entropy of the system upon ordering is required. In section 9.3 a simple model to account for entropy in the system will be proposed.

9.2 Enthalpic considerations

An understanding of the thermodynamics of the system is essential if the effect of short-range order in the system is to be quantified and ultimately linked to observed strengthening properties of the system. Several methods have been proposed for the determination of interaction potentials. The simplest is the Krivoglaz-Clapp-Moss \[22,149\] method based on an Ising type Hamiltonian, which defines:

\[
\alpha_{oj} = \frac{-2c_A c_B}{k_B T} \sum_j V_{oj} \alpha_{fj} 
\]  

(9.25)

where \(o\) is an arbitrary origin, \(j\) the neighbour for calculation, \(f\) the neighbours of atom \(j\) and \(V\) the pairwise energetic potential. \(T\) is the temperature, \(k_B\) the Boltzmann constant, \(c_A\) and \(c_B\) the concentrations of A and B respectively. This method is inherently an approximation, and works best for \(c_A \approx c_B\) and at temperatures much greater than an observed ordering transition.

Alternatively the inverse Monte Carlo (IMC) method \[150\] has proved very powerful for the extraction of enthalpic terms. A large box is taken that displays the required short range order and virtual swaps made in the box - i.e. a swap is made and the change in the number of AB, AA and BB bonds recorded, and then returned to the initial configuration. The probability of such a move taking place is given as:

\[
p = \frac{\exp \left( -\Delta H_v / k_B T \right)}{1 + \exp \left( -\Delta H_v / k_B T \right)} 
\]  

(9.26)

where \(\Delta H_v\) is the energy change of the virtual swap. For a large number of virtual moves the assumption is made that overall the change in the number of a given type of bond is zero, as the system is sitting in a thermodynamic minimum. This can be calculated for any coordination...
shell $j$ by the strict equality:

$$\sum_{v=1}^{M} \Delta N_j^{BB} \frac{\exp(-\Delta H_v/k_B T)}{1 + \exp(-\Delta H_v/k_B T)} = 0$$

(9.27)

where $\Delta N_j^{BB}$ is the change in the number of BB bonds in shell $j$. $M$ is the number of virtual moves made in the system and $\Delta H_v$ the energy change of the move $v$. The set of $j$ equations defined by Eq. 9.27, can then be solved simultaneously to calculate the energy parameters for the coordination shells of the system. This method allows the extraction and calculation of the energetic parameters for a large number of shells.

Such a calculation lends itself well to being combined with the RMC method. The output configurations can be used as the starting point for the simulation and energetic parameters calculated from this. However, it is important to note that such a calculation will generate the enthalpic values of the system only at absolute zero. In both the KCM and IMC methods the system has been assumed to be in an ‘enthalpic’ minima rather than a true thermodynamic equilibrium. Therefore enthalpies generated by either of these methods must be treated with caution.

### 9.2.1 Strengthening models

Aside from the more accurate calculations of phase diagrams and phase prediction, the importance of correct calculations of energetic terms is to allow the calculation of a materials strength. As discussed, the increase in observed strength of a material has often been used as an indicator of short-range order occurring in an alloy. Although the effect of SRO on dislocation motion has been noted qualitatively, few attempts to quantify the effect have been made. Recently, work done by Pettinari-Sturmel et al. [151], has approached the problem from the aspect of quantifying the SRO by considering the variation in dislocation energy. The results of such studies are currently qualitative, with little or no analysis of the type and nature of SRO occurring in a system. One notable attempt to create a strengthening model based on short-range order parameters was made by Flinn [5].

**Flinn model for strengthening**

Consider the slip plane $(111)$ in an $fcc$ metal. Fig. 9.3 shows the atoms above and below the slip plane and the bonds that pass through the plane. It can therefore be shown that the area per bond, $B$, in the slip plane is given as:

$$B = \frac{\sqrt{3}}{4} a^2$$

(9.28)

where $a$ is the cubic lattice parameter.

Consider that the vectors describing nearest neighbours on the opposite sides of the slip plane of an atom at $a[000]$ are $\frac{a}{2}[110]$, $\frac{a}{2}[101]$ and $\frac{a}{2}[011]$; then following the passage of a dislocation with Burgers vector $b = \frac{a}{2}[1\bar{1}0]$ the vectors to the new atomic positions will be $a[100]$, $\frac{a}{2}[2\bar{1}1]$ and $\frac{a}{2}[101]$. Therefore, one of these atoms will remain a nearest neighbour. Hence the bonds

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Figure 9.3: (a) View of the FCC lattice down [111]. The diagram shows atoms in the planes above (purple) and below (green) the slip plane in the system. The red lines indicate bonds between the planes that intersect the slip plane. (b) The same structure rotated around the (101) axis by approximately 80° to show a side view of the structure.

broken per unit area, $B_t$, is given by:

$$B_t = \frac{4}{\sqrt{3}a^2} \quad (9.29)$$

Recalling the definition of the Warren-Cowley parameters, $\alpha$, it can be shown that the probability of finding an A atom neighbouring a B atom, $p^{BA}$, is:

$$p^{BA} = c_A - c_A \alpha_1 \quad (9.30)$$

where $c_A$ is the concentration of atom A in the structure and $\alpha_1$ the nearest neighbour Warren-Cowley parameter. Therefore, the probability of a given bond being A-B, $p_{A-B}$, is:

$$p_{A-B} = 2c_B p^{BA} = 2c_A c_B - 2c_A c_B \alpha_1 \quad (9.31)$$

where $c_B$ is the concentration of atom B in the structure. The excess probability (i.e. over the random configuration) of A-B bonds, $p'_{AB}$, is given by:

$$p'_{AB} = -2c_A c_B \alpha_1 \quad (9.32)$$

The increase in energy per unit area over the random configuration, $\sigma$, can be modelled as:

$$\sigma = \frac{8c_A c_B \nu}{\sqrt{3}a^2} \alpha_1 \quad (9.33)$$

where $\nu$ is the interaction energy of the unlike bond. Dividing by the magnitude of the Burgers vector $\frac{a}{\sqrt{2}}$ gives the additional yield stress:

$$\tau = \frac{16c_A c_B \nu}{\sqrt{6}a^3} \alpha_1 \quad (9.34)$$
A study of the SRO strengthening effect was subsequently carried out by Cohen and Fine [152], who concluded that the first order effect of SRO should in fact lead to a decrease in strengthening. Subsequent work by Mohri et al. [153] concluded that, based on a cluster variation model, taking into account higher order interactions, an increase in strengthening of an order around three times that predicted by the Flinn should be observed. Although the Flinn model is currently believed to be unsatisfactory to fully describe the effect of SRO on dislocation motion, no further developments to the model have been made to account for the discrepancies between model and observation.

This model, whilst limited, does raise some key issues. First, the calculation of the strength is based on the change in energy upon dislocation motion. Being able to accurately determine the enthalpic interactions in a material are therefore essential to the correct calculation of a material’s strength. However, as discussed, this will, in turn, be dependant on a correct determination of the entropy of a system. Second, the Flinn model is a limited calculation based only on changes in the first nearest neighbour interactions as a dislocation passes through the material. A question remains as to the number of shells across which the calculation must take place to accurately describe the variation in energy. The model also assumes that the energy is well modelled by pairwise interactions, as opposed to cluster interactions. Whether a model using alternative descriptors based on structural motifs, e.g. Clapp configurations, would provide a more accurate calculation remains to be seen.

### 9.2.2 Monte Carlo simulations

To answer the question of how many shells need to be considered, it is useful to consider all of the data presented so far. Recall that in Chapter 4 it was discussed how Cu₃Au initially orders such that it promotes the formation of both the D0₂₂ and L₁₂ structures. In Chapter 3 it was shown that α₁ = −\(\frac{1}{3}\) for both of these alloys, i.e. when considering the first coordination shell only, these two ordered structures are identical. It is only a consideration of the 2nd nearest neighbour interactions that distinguishes between them. Energetically this means that if there is only an interaction in the first nearest neighbour shell, both the D₀₂₂ and L₁₂ structures form. It is only by introducing a second nearest neighbour potential that an ordering in the second shell would occur and so one of the two structures will form. This can be modelled through Monte Carlo simulation.

A code was written that calculated the energy of a box based on the arrangement of the atoms, from the input of a series of potentials \(\epsilon_{AA}, \epsilon_{AB}, \epsilon_{BB}\) for the AA, AB and BB interactions respectively, in each of the coordination shells (up to the 10th coordination shell). A random pair of atoms in the box is chosen and allowed to swap. The change in energy of the box is calculated. If the energy of the box is reduced by the swap, the change is accepted; otherwise the swap may be accepted with a probability dependent on the magnitude of the energy penalty that will be experienced by making the change. Using this, the algorithm will return a configuration with the lowest energy based on the input potentials.

A series of boxes of 20 × 20 × 20 fcc cells were created containing a random distribution of A and B atoms in a ratio of 3:1. The code was run, applying a favourable negative potential to the formation of the Cu-Au bonds at the first nearest neighbour distance. It is worth noting...
that for a binary alloy, only a single potential needs to be defined for each shell. Consider an A-B atom pair, where the number of A and B atoms next to the A atom are given as \( n_{AA} \) and \( n_{AB} \) respectively, and likewise \( n_{BA} \) and \( n_{BB} \) for the atoms around B. The total energy before a swap is given as:

\[
E_{\text{before}} = \epsilon_{AA}n_{AA} + \epsilon_{AB}(n_{AB} + n_{BA}) + \epsilon_{BB}n_{BB}
\]  

(9.35)

whilst the energy after is given as:

\[
E_{\text{after}} = \epsilon_{AB}n_{AA} + \epsilon_{BB}n_{AB} + \epsilon_{AA}n_{BA} + \epsilon_{AB}n_{BB}
\]  

(9.36)

The total energy change is given as:

\[
\Delta E = \epsilon_{AB}n_{AA} + \epsilon_{BB}n_{AB} + \epsilon_{AA}n_{BA} + \epsilon_{AB}n_{BB}
\]  

(9.37)

Taking the difference of these two expressions and noting that \( n_{AA} = d - n_{AB} \) (where \( d \) is the number of nearest neighbours) and likewise \( n_{BB} = d - n_{BA} \), the energy difference can be expressed in the form:

\[
\Delta E = \frac{V}{2}(d - n_{AB} - n_{BA})
\]  

(9.38)

where:

\[
V = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})
\]  

(9.39)

Unless explicitly stated, this potential will be quoted as the potential of the shell.

The resultant boxes where analysed using the Clapp configuration enhancement factors (see section 3.4.2). One of the boxes and the calculated Clapp enhancement factors is shown in Fig. 9.4.

---

**Figure 9.4:** Example results of Monte Carlo simulation performed on a box containing a 3:1 ratio of A to B atoms. 
(a) Enhancement factors calculated from the output simulation, 
(b) Output box - Blue atoms are A atoms in the C16 configuration and Green atoms are A atoms in the C17 configuration. B atoms are not shown. The region shown in red is the D0_{22} structure and the region in yellow the L1_{2} structure.
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Importantly, there are large enhancements in the \(C16\), \(C17\) and \(C-1\) configurations, suggesting either a \(D0_{22}\) structure is forming, or a mixture of the \(L1_2\) and \(D0_{22}\) structures. Taking one of the large box models, the atoms can be coloured to reflect the configurations they occupy. Fig. 9.4b shows one such example, where A atoms in the \(C16\) configuration are coloured blue, A atoms in the \(C17\) configuration are coloured green and the remaining atoms removed from the configuration. From this it can be seen that regions of distinct order have formed in the structure. The region bounded in red is \(D0_{22}\), whilst that bounded by yellow is \(L1_2\). The simulation was also run starting with ordered boxes, reflecting the two structures. In these cases, no change is seen in the box which maintains the structure it started with.

To consider the additional effect that would result from the inclusion of a second shell potential, a series of Monte Carlo simulations were carried out, systematically varying the potentials applied to the first and second co-ordination shells in a system. Random configurations of 32,000 atoms in a 3:1 A:B ratio were allowed to undergo a series of A and B swaps, for \(V_1 = -10 \ldots 10\) and \(V_2 = -10 \ldots 10\). The system was allowed to test 5,000,000 swaps, a sufficiently large number of moves to ensure the system achieved a thermodynamic minimum. The \(\alpha\) parameters and Clapp configuration enhancement factors were calculated and are shown in Fig. 9.5 and Fig. 9.6 respectively.

It should be noted that, whilst the simulations have been carried out for sample boxes across the entire range, it is physically realistic to expect that \(|V_1| > |V_2|\), as the electronic interaction will decrease with distance away from an atom. Therefore, our consideration should be limited to the two triangular regions shown in these diagrams that incorporate the horizontal line \(V_2 = 0\). For clarity, these triangular regions will be referred to by the compass points (N,E,S,W), where E and W are the physically realistic regions. Quadrants of the graph will be referred to by directionality: top (T), bottom (B), left (L) and right (R).

From Fig. 9.5a it can be seen that, as expected, the first shell energy dominates the observed

![Figure 9.5: Warren-Cowley, \(\alpha\), parameters calculated from a series of large-box model Monte Carlo simulations. Boxes were model applying potentials to both the 1st and 2nd shell of the system. a) 1st shell \(\alpha_1\), b) 1st shell \(\alpha_2\). Dotted line indicates boundaries where \(V_1 = V_2\) and \(V_1 = -V_2\). Red indicates values of \(\alpha \sim 1\), i.e. atoms surrounded by those of the same type, and purple values of \(\alpha \sim -\frac{1}{3}\), i.e. atoms surrounded by those of the opposite type. Contours and colours have been interpolated between the points.](image-url)
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Figure 9.6: Clapp configuration enhancement factors, $\beta$, parameters calculated from a series of large-box model Monte Carlo simulations. Boxes were modelled applying potentials to both the 1st and 2nd shell of the system. The enhancement factors of nine of the most enhanced configurations are plotted. Dotted lines indicate boundaries where $V_1 = V_2$ and $V_1 = -V_2$. The different configurations have different enhancement factors and maximum values, due to the different expected number in a box simulation, therefore the colours for each box do not indicate the same absolute scale. However, they have been coloured in such a way that purple regions indicate $\beta < 3$, i.e. statistically insignificant or configuration is reduced compared with random, and red is the maximum value for each configuration (in all cases $\beta_{\text{max}} > 100$).

The $\alpha_1$ parameter. A negative 1st shell energy results in a preference to form unlike nearest neighbours and yields a negative $\alpha_1$; whilst a positive 1st shell energy results in a preference to form like nearest neighbours and yields a positive $\alpha_1$. Interestingly for $V_2 < 0$, there appears to be a much smaller effect on the resultant $\alpha_1$ parameter compared with the much greater change observed when $V_2 > 0$. Observing $\alpha_1$ also demonstrates the flaw in the application of enthalpic models, as the system only really produces structures close to random when the enthalpy is close to zero.

Fig. 9.5b shows the resultant second shell $\alpha_2$ parameter. It might be expected that this
should produce a similar figure to the previous one, but rotated by 90°. Broadly speaking this is the case as for $V_2 > 0$, large positive values for $\alpha_2$ are observed and, conversely, negative values of $\alpha_2$ for $V_2 < 0$. However, there is a distinct change in distribution of the $\alpha_2$ values compared with the $\alpha_1$ values. Taking a slice through the west region at a constant $V_1$ value, there is a change in the $\alpha_2$ value as $V_2$ varies. However, $\alpha_2 \neq 0$ when $V_2 = 0$ (except at $V_1 = 0$), but at some positive value of $V_2$.

This is due to what will be called the ‘successive shell effect’. Simply, if there is a preference for A-B to form a first nearest neighbour pair, it is likely that the structure will try and form to give an A-B-A structure. Therefore, defining the first shell interaction changes the observed distribution in the 2nd shell and makes it more likely to have a preference for like neighbours at the 2nd nearest neighbour distance. Consequently, a positive enthalpy will be required in the 2nd nearest neighbour shell for the number of nearest neighbours to be equal to that expected from the nominal stoichiometry. This explains why the $\alpha_2 = 0$ does not coincide with $V_2 = 0$. Interestingly, the system is not symmetric. Considering the east region, and a constant $V_1$ slice, $\alpha_2 = 0$ only when $V_2 = -V_1$, and is positive otherwise i.e. the second shell can never exhibit more unlike neighbours than the random structure if a positive first shell potential has been applied.

Overall, comparing $\alpha_1$ and $\alpha_2$, it is worth noting that whilst for the first nearest neighbour shell the sign of $\alpha_1$ is indicative of the sign of the interaction energy $V_1$, the same is not true for the second coordination shell, $\alpha_2$ and $V_2$.

Fig. 9.6 shows nine of the most enhanced configurations observed in the matrix of simulated models. Purple indicates no enhancement above statistical noise or a decrease in the configuration, whilst red regions indicate large enhancement facts. It is obvious that distinct regions form where different Clapp configurations and structures dominate. Interestingly the bounds of the regions are straight lines that pass through the origin, demonstrating that it is the ratio of the two shell potentials that is significant for the formation of specific structures. There are a few additional points to note that have significance to the earlier work on the Cu$_3$Au and L1$_2$.

Notice that the C1 configuration (an atom surrounded by atoms of the same type - the basis of clustering), shown in Fig. 9.6c, is only enhanced if $V_1 > 0$. Therefore, unless there is reason to believe that the first shell potential is positive (e.g. clustering occurring in a system observed by TEM), then if the C1 configuration is observed to be enhanced, it is likely due to a data processing error and as such the data needs to be reconsidered.

Comparing Fig. 9.6b and Fig. 9.6f, the distribution of the C-1 and C16 structures are very similar. The C-1, however, shows a greater spread to positive values of $V_2$ than the C16. In fact the boundary of the C-1 is closer to that of the C17 structure, Fig. 9.6g. This is important to the balance of the L1$_2$ and D0$_{22}$ structures during the ordering of Cu$_3$Au. For $V_1 < 0$, $V_2 > 0$ there is a distinct shift in the formation of the two structures as the ratio of the two potentials is varied. Whilst both are favourable, the formation of D0$_{22}$ is more prevalent when $V_2$ is close to zero. As $V_2$ becomes more negative, the D0$_{22}$ becomes less favourable and the L1$_2$ increases. This is most likely what transpires in Cu$_3$Au in the region below 500°C.

Importantly, it is both structures that form under this two potential case example, and a third shell potential is required for the system to order completely and form the L1$_2$ structure,
over the D0$_{22}$. Similarly, for Ni$_3$Nb, which forms the D0$_{22}$ structure (see Chapter 5) there must be a third shell potential at play. The difference is that for the L1$_2$ structure the potential is likely to be positive, whereas for the D0$_{22}$ it is likely to be negative - though, as demonstrated from the two shell simulation, this may be an oversimplification. Returning to the two-shell example, it can be seen that the C17 maximum field is actually relatively small and the application of a non-zero second shell potential (either positive or negative) leads to a comparative decrease in formation. Making the second shell potential increasingly negative there is an observed progression of structures, with the concurrent formation of the C-2 and C19 configurations and then the C11.

Recall that such an enhancement in the C19 and C-2 configurations, along with the C37 and C-5 configurations, was observed in the NiCr sample, presented in Chapter 5, Fig. 5.12. A plot of these enhancement factors from the two-shell Monte Carlo simulation is shown in Fig. 9.7. From this, it can be noted that at least a two shell potential is required to form this order, which occurs off the $V_2 = 0$ axis. In fact, unlike the Cu$_3$Au case where $V_1 < 0$ and $V_2 > 0$, for the Ni-Cr both $V_1 < 0$ and $V_2 < 0$. It can be suggested from the relative magnitudes of enhancement observed that for the NiCr sample, $V_2 \sim 0.4V_1$.

Figure 9.7: Clapp configuration enhancement factors, $\beta$, for C37 and C-5 configuration, calculated from a series of large-box model Monte Carlo simulations. Boxes were model applying potentials to both the 1st and 2nd shell of the system. Dotted lines indicate boundaries where $V_1 = V_2$ and $V_1 = -V_2$. The different configurations have different enhancement factors and maximum values, due to the different expected number in a box simulation, therefore the colours for each box do not indicate the same absolute scale. However, they have been coloured in such a way that purple regions indicate $\beta < 3$, i.e. statistically insignificant or configuration is reduced compared with random, and red is the maximum value for each configuration (in all cases $\beta_{\text{max}} > 100$).

For $V_1 > 0$, the E-triangle in Fig. 9.6, the structure is dominated by the formation of the C1 cluster configuration. If a negative second shell potential is applied that counteracts that of the first shell, the structure forms the C15 instead. There is a final curiosity if the ‘non-physical’ S-triangle is considered. Here, it can be seen that the C82 configuration is very prevalent, when $V_0 > 0$. This is the only region of the explored energy surface where this configuration is found. As mentioned in Chapter 4, some evidence has been provided that L1$_1$ type ordering may occur close to the melting point in Cu$_3$Au. In Chapter 3 it was shown that the C82 structure is the only constituent configuration of the L1$_1$ structure. This would imply that close to melting
there is a positive first shell potential and a larger negative second shell potential. If the model is believed to be correct, this casts doubt on the validity of the observation, which may be the result of some error in the measurement or processing of the data. Alternatively, this may show the limitations of the model suggested, which is incapable of modelling the entropy of the system and so may not produce the most thermodynamically stable structure.

The partitioning of this graph into distinct regions allows it to be used to suggest the potentials that are required to form certain types of order, as has been argued for the Cu₃Au and Ni₃Cr cases. In spite of the fact that these simulations do not consider the entropy of the system, and are incapable therefore of accurately modelling short-range order, they do provide important indicative information about the nature of the potentials that are required to form certain structures in a system.

### 9.2.3 Diffuse anti-phase boundaries and dislocations

As discussed in Chapter 1, the movement of a dislocation in the L1₂ structure results in the formation of an anti-phase boundary (APB) and large energy penalties associated with such a motion. Correspondingly, for SRO systems it is sometimes the case that a diffuse anti-phase boundary (DAPB) is the result of the passage of a dislocation, i.e. a change in the local order in the structure. This energy change can then be related to the observed strength of the material.

Calculations of the magnitude of such APB energies have historically been done by considering bonds broken and bonds made in the dislocation process. The diffuse anti-phase boundary energy can be calculated in a similar manner and is the basis of the calculation carried out by Flinn. As previously noted, current calculations of enthalpic pair interactions are effectively carried out at absolute zero, and so the exact magnitude of these values is likely to be incorrect. However, they may still provide important qualitative information about the additional strength that may result from local order in a system.

Assuming that the enthalpic driving force of ordering could be correctly calculated, an assessment of the resultant effect on the diffuse anti-phase boundary energies could be calculated from our large box models by a consideration of the change in energy due to motion of planes within the structure. A programme was written to calculate the change in energy of a system caused by the passage of a dislocation through the box. The interaction potentials between the different atom types at different distances are input into the system. A large configuration is taken and a plane in the family {111} is chosen randomly in the box. Rather than actually performing the sliding in the structure, which is computationally expensive, for each atom in the plane the vectors of the bonds broken and bonds made are considered and the energy change that would occur by the motion of the plane calculated. Fig. 9.8 shows these vectors in the fcc structure. This process allows the calculation of the energy change that would occur during the translation of the desired plane. The process is then repeated multiple times for different planes throughout the box to yield a distribution of the energy changes that would take place.

Taking the same set of simulated structures used in Chapter 3 it is possible, therefore, to calculate the change in energy associated the movement of a dislocation through the structures with different types and amounts of SRO. For each of the simulated structures 1000 different planes in the structure were tested and the energy of each calculated. From this, the average
DAPB energy was calculated for each box. The input energies are given as a multiple of $kT$ and the energy of the DAPB given per atom in the dislocation plane. For these structures values of $V_1 = -1$ and $V_2 = 0.1$ were chosen based on the formation of the L1$_2$ and D0$_{22}$ structures. The calculations were carried out both: a) when applying only the 1st shell potential and b) applying potentials for both 1st and 2nd shells. The calculated values are shown in Fig. 9.9.

From Fig. 9.9a, it is apparent that for the statistically ordered boxes, and the microdomain L1$_2$ and D0$_{22}$ structures, there is an increase in the DAPB energy as the order increases. Interestingly, no such variation is observed in the L1$_0$ structure. This is because the correlations between planes in the structure does not change when this type of ordering is present. For the statistically ordered case there is a linear increase. The L1$_2$ and D0$_{22}$ structures show the same change in energy and exhibit a polynomial type increase in energy. The difference in these is due to the change in the number of nearest neighbour correlations with the different types of ordering. This can be seen in Fig. 9.9b where the values are replotted against the theoretical $\alpha_1$ parameters, and the plots become coincident. In both cases, the statistically ordered box appears to plateau. This is, however, due to the box not having been run for a sufficiently long time to achieve complete ordering in these cases. If the $\alpha_1$ parameters for these boxes are calculated they are found to similarly plateau.

Considering Fig. 9.9c, the change in applying a second shell potential can be seen. There is no obvious observed change in the L1$_0$ energies with the introduction of a second shell potential. For the other cases, however, there is an observed increase for all types of ordering. This shows why further extensions need to be made to the Flinn model to account for more shells, and why the model under predicts the observed strengthening effect. This energy also causes a split in the energies of the L1$_2$ and D0$_{22}$ structures, with the L1$_2$ being systematically higher than that observed in the D0$_{22}$. This is due to the greater number of favourable correlations in the second shell of the L1$_2$ structure being broken, compared with the second shell correlations in D0$_{22}$.

In these examples, arbitrary potentials of $V_1 = -1$ and $V_2 = 0.1$ were chosen by suggestion that the first shell should be negative, the second positive and that $|V_1| > |V_2|$. The ‘correct’ enthalpies that would yield these observed structures might be found using the KCM or IMC methods but, as previously mentioned, these will necessarily be incorrect. However, what can be tested are output ordered structures from the Monte Carlo simulations previously carried out. For each of these structures the DAPB was calculated using the same method as described above, but using the $V_1$ and $V_2$ values that were input into the MC code to yield the specific ordered structure. A plot of the resultant DAPB energies is shown in Fig. 9.10.

Importantly, the minimum of the graph is located around the origin. This means that the application of an energy potential, either positive or negative in both the first and second coordination shells results in a DAPB energy and an increase in the observed strengthening of the material. Interestingly, there is no apparent symmetry to the graph. Comparing the E and W triangles, it is obvious that the strengthening obtained by ordering (W triangle) is considerably greater than that obtained from a cluster (E triangle). Considering only the W-triangle it is apparent that, whilst the first shell potential does provide a significant increase in DAPB energy, it is only by applying a second shell potential that there is a large increase in the DAPB energy. The maximum energy, and hence strengthening, occurs when $V_1 << 0$ and $V_2 >> 0$. This
9.2. Enthalpic considerations

Figure 9.8: Vectors showing atoms affected by the sliding of \{111\} planes in a structure. The grey circles show an atom in the fixed plane below the motion. The triangular lattice shows location of atoms in the layer above the plane of motion - intersections of lines in this lattice indicate the position of atoms. a) The vectors of atoms that are 1st nearest neighbour (blue) and 2nd nearest neighbour (green) correlations in the structure prior to the plane sliding. b) The vectors of atoms that will become 1st nearest neighbour (blue) and 2nd nearest neighbour (green) correlations if the top plane moves by a\((-\frac{1}{2}, \frac{1}{2}, 0)\). a) Represents the bonds broken and b) the bonds made by the motion.

Figure 9.9: Calculated DAPB energies for SRO boxes used in Chapter 3. (a) Calculated DAPB energies considering only the 1st shell interaction, with \(V_1 = -1\), \(n\) indicates the size of the ordered region in the \(20 \times 20 \times 20\) supercell configuration, or in the statistically ordered case the set parameter \(\alpha_1 = -\frac{n}{6n}\) (b) The same conditions as a) but plotted against the expected \(\alpha_1\) parameter, (c) Calculated DAPB energies considering second nearest neighbour correlations as well, with \(V_1 = -1\) and \(V_2 = 0.1\), plotted against \(n\). For all graphs: Black - statistically ordered boxes, Red - L1_2 micro-domain, Green - L1_0 disperse model, Blue - D0_{22} micro-domain. In (c) the dotted lines show the values from the first shell only calculations.
Chapter 9. Energetic considerations

Figure 9.10: Calculated DAPB energies for ordered boxes generated via MC simulations. The applied first and second shell potentials are used to calculated the DAPB taking 1000 different planes through the structure. The DAPB energies are calculated per atom in the moving plane. Purple indicates a DAPB=0 and Red the maximum value. Dotted lines indicate boundaries where \( V_1 = V_2 \) and \( V_1 = -V_2 \).

region, as shown previously, is where L1_2 ordering is observed to form and shows why the L1_2 is, therefore, so important as a strengthening mechanism in nickel based superalloys.

Finally, it is important to note that whilst there appears to be a regions of high DAPB energy in the top left quadrant of the figure, this does not correlate well with either the Warren-Cowley distribution, 9.5, or the regions defined by the specific Clapp configurations, 9.6. This demonstrates the importance of running such calculations and simulations as they may demonstrate strength in regions where a combination of ordering actually provides a greater strengthening effect, than a single structure enhancement or \( \alpha \) parameter might suggest.

9.3 Entropic considerations

To move towards a more complete understanding of ordering transitions, a more accurate calculation of phase diagrams and of a materials strength, a better understand of the change in entropy upon ordering is required. Here a simple model is proposed that might allow the calculation of the variation of entropy on ordering in a system, through a consideration of the change in enthalpy. Recall from Eq. 9.6 that in a random binary alloy, the entropy of the system may simply be calculated as follows:

\[
S_{\text{config}} = Nk_B \ln N - N_A k_B \ln N_A - N_B k_B \ln N_B
\]  

(9.40)

This is the maximum entropy that the system can have, as all the microstates are equivalent in terms of the bulk properties of the system.

Consider all possible permutations of atoms within a system. If there is no enthalpic preference in the system to form any type of bond, it can be seen that whatever the arrangement of atoms in the system, the enthalpy of the box will be constant. However, if an enthalpic term is applied to the system, then these arrangements are no longer energetically equivalent. Consequently, the number of equivalent microstates (states with the same enthalpy) in the system...
changes, and the entropy is reduced. Taking the extreme case of a LRO system, there is only one possible arrangement, the enthalpic minimum of the system, and hence the entropy will be zero.

Therefore, it may be possible to calculate the entropy of the system, by considering the change in the number of microstates with the same overall energy. This calculation requires the calculation of the overall enthalpy of all configurational arrangements of the system. This would be necessarily computationally laborious (or impossible) as it would require the calculation of $N!$ systems. However, it is possible to reduce the calculation by a consideration of the statistical occupation of the given configuration, in a similar manner to that suggested for the Clapp configurations in Chapter 3, and the energetic spread of those configurations.

Consider, a system where only the first shell interactions are significant. For any atom in the box the probability $a$ atoms of A in a given shell, with $d$ atoms, is given as:

$$P(x = a) = \binom{d}{a} X_A^a X_B^{d-a}$$

where $X_A$ is the concentration of A atoms and $X_B$ the concentration of B atoms, such that $X_A + X_B = 1$. For this distribution, the mean is given as:

$$\mu = d X_A$$

and the variance by:

$$\sigma^2 = d X_A X_B$$

Note that this is independent of the atom type around which it is measured. By summing over the A and B atoms in the box we may write the total energy of the system as:

$$\epsilon = \frac{1}{2} \left[ \sum_A (\epsilon_{AA} N_{AA,i} + \epsilon_{AB} N_{AB,i}) + \sum_B (\epsilon_{BA} N_{BA,i} + \epsilon_{BB} N_{BB,i}) \right]$$

$$= \frac{1}{2} \left[ \sum_A (d \epsilon_{AA} + (\epsilon_{AB} - \epsilon_{AA}) N_{AB,i}) + \sum_B (d \epsilon_{BB} + (\epsilon_{AB} - \epsilon_{BB}) N_{BA,i}) \right]$$

In this expression:

$$N_{AB,i} \sim \text{Bin}(d, X_B)$$

$$N_{BA,i} \sim \text{Bin}(d, X_A)$$

where $\text{Bin} \sim (n, p)$ is a binomial distribution with parameters $n$ and $p$. This distribution in energy will therefore have a mean:

$$\mu_\epsilon = \frac{1}{2} \left[ \sum_A (d \epsilon_{AA} + (\epsilon_{AB} - \epsilon_{AA}) \mu_{AB,i}) + \sum_B (d \epsilon_{BB} + (\epsilon_{AB} - \epsilon_{BB}) \mu_{BA,i}) \right]$$

which may be simplified to:

$$\mu_\epsilon = \frac{Nd}{2} \left[ (\epsilon_{AA} X_A + \epsilon_{BB} X_B) - X_A X_B (\epsilon_{AA} - 2\epsilon_{AB} + \epsilon_{BB}) \right]$$
Likewise, it can be shown that the variance in energy will be given as:

\[ \sigma^2 = 2NdX_A^2X_B^2 \left( \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \right)^2 \]  

(9.50)

To demonstrate the validity of the model, a series of large box models with concentration \( A_{(1-x)}B_x \) were created. For each box, a positive first shell potential \( V_1 = 1 \) was applied and the energy of the configuration calculated. Atoms were randomly chosen in the box and allowed to swap. After each move the energy of the configuration was recalculated. Each box was allowed to swap 1,000,000 times, sampling the same number of configurations. From these data, plots were drawn up showing the probability, for a given alloy concentration and potential, that a configuration has a specific enthalpy. Fig. 9.11(a) shows the distribution of enthalpies of the different configurations of an \( A_{0.75}B_{0.25} \) sample. The mean and standard deviations of these distributions were calculated. Fig. 9.11(b) and (c) show these values plotted against composition, along with the theoretical values calculated from Eq. 9.49 and Eq. 9.50. The two are found to be in agreement, demonstrating the validity of the model.

Figure 9.11: Fits of energetic distributions calculated for a series of random boxes with different concentrations. (a) An example fit of the box energies for an \( A_{0.75}B_{0.25} \) configuration. Black crosses indicate energy calculated from Monte Carlo swapping and the red line the fit with the described distribution. (b,c) Mean and sigma for the distribution in energies of the configuration using equations Eq. 9.49 and Eq. 9.50.
9.4 Conclusions

Owing to the large number of atoms in the system, and hence the large number of combined distributions, this resultant distribution will be normally distributed. If a given arrangement of atoms has enthalpy $H$ then the number of ways of arranging the system is given as:

$$W_H = W_{\text{rand}} f \left( H - \frac{1}{2} \epsilon_{\text{min}} < x < H + \frac{1}{2} \epsilon_{\text{min}} \right)$$ (9.51)

where $W_{\text{rand}}$ is the total number of ways of arranging the system, and $f(x)$ is the normal distribution at value $x$ and $\epsilon_{\text{min}}$ is the smallest value of any $\epsilon_{XX}$ for any shell in the system (i.e. the minimum bin width that is calculable by the system). Therefore, the configurational enthalpy will be given as:

$$S = k_B \ln W_{\text{rand}} + k_B \ln f \left( H - \frac{1}{2} \epsilon_{\text{min}} < x < H + \frac{1}{2} \epsilon_{\text{min}} \right)$$ (9.52)

this may be simplified by a calculation of the area using a simple rectangular box in the normal distribution i.e.

$$S = S_{\text{rand}} + k_B \ln \frac{\epsilon_{\text{min}}}{\sigma_\epsilon \sqrt{2\pi}} - k_B \frac{(H - \mu_\epsilon)^2}{2\sigma_\epsilon^2}$$ (9.53)

$$= S_{\text{rand}} + k_B \ln \frac{\epsilon_{\text{min}}}{\sigma_\epsilon \sqrt{2\pi}} - k_B \frac{(H - \mu_\epsilon)^2}{2\sigma_\epsilon^2}$$ (9.54)

where $S_{\text{rand}}$ is the entropy of the random solid solution.

What perhaps is more physically realistic is to suggest that the number of occupied microstates is dependant on the states accessible by thermal fluctuations, i.e. within the bounds of $kT$. It is more realistic therefore, to consider the entropy as:

$$S = k_B \ln W_{\text{rand}} + k_B \ln f \left( H - k_B T < x < H + k_B T \right)$$ (9.55)

$$= S_{\text{rand}} + k_B \ln k_B T \left[ \frac{1}{\sigma_\epsilon \sqrt{2\pi}} \exp \left[ - \frac{(H - \mu_\epsilon)^2}{2\sigma_\epsilon^2} \right] \right]$$ (9.56)

$$= S_{\text{rand}} + k_B \ln \frac{k_B T}{\sigma_\epsilon \sqrt{2\pi}} - k_B \frac{(H - \mu_\epsilon)^2}{2\sigma_\epsilon^2}$$ (9.57)

This method is obviously an oversimplification of the problem but may allow a calculation of the entropy of the system during ordering. The largest challenge faced will be extension of the method to higher order shells, as this will require a decoupling of the successive shell effect described in the two shell Monte Carlo simulations.

9.4 Conclusions

In this chapter, some of the important energetic effects on the nature of material have been considered. The current thermodynamic models for the Gibbs free energy for ‘ideal’ and ‘real’ solid solutions have been presented and their limitations discussed. The two main methods that have been used for the calculation of enthalpic potentials in short-range ordered systems have also been described. Through the Flinn model the link between enthalpy, short-range order parameters and observed strengthening has been demonstrated. The Flinn model, whilst useful,
Chapter 9. Energetic considerations

is limited, due to the consideration of only a single shell effect.

To understand the number of shell potentials that are significant for the formation of specific structures, and hence that need to be considered in strengthening models, a series of Monte Carlo simulations were carried out. It was shown that, by applying only a first shell potential to a configuration of $A_3B$, both $L1_2$ and $D0_{22}$ type ordering occurs. Extending the simulations to consider two coordination shell potentials provided greater insight into the link between structure and potentials. It was found that whilst the first shell potential determines the sign of the $\alpha_1$ parameter, the same does not hold for the second shell potential and $\alpha_2$, due to the successive shell effect.

It was observed that the structures formed are highly dependant on the ratio of the two shell potentials. The ordering observed below 500°C in the $Cu_3Au$ sample suggests that $V_1 < 0$, $V_2 > 0$ and that $|V_2| \leq |V_1|$. In contrast, the ordering in the $Ni_3Cr$ sample suggests that $V_1 < 0$, $V_2 < 0$ and that $|V_2| \sim 0.4|V_1|$. This demonstrates how these plots can be used to suggest the potentials in a system that result in specific types of order.

From a knowledge of the potentials, it may be possible to determine the magnitude of the strengthening effect through the calculation of diffuse anti-phase boundary energies. A method for calculating these values from large box models was presented and demonstrated. For the SRO structures calculated previously, it was shown that these energies will be strongly dependent on the corresponding $\alpha$ parameters of the interactions that are disrupted by planar motion in the structure. Importantly, different types of order will result in different amounts of observed strengthening.

The DAPB energies were also calculated for the resultant two-shell Monte Carlo simulations. This demonstrated that any order in the system will result in an increased strengthening. Importantly, a much greater strengthening is observed for ordering than clustering and is maximised for the $V_1 < 0$, $V_2 > 0$ case, which is the formation of the $L1_2$ structure. In general, there is no obvious link between the observed strengthening and either the $\alpha$ parameter or Clapp configuration distributions.

Finally, a discussion of the variation of entropy upon ordering was presented. A model was proposed that predicts the distribution in enthalpy of all the possible microstates of a structure, under the application of a potential. From this, the number of microstates with the same energy and, hence, the entropy, can be calculated. Additional extensions accounting for the successive shell effect would be required before this model can usefully be applied.

Overall, this chapter has demonstrated how a consideration of energetic effects, both enthalpy and entropy, are essential for a complete understanding of structures. These underlying energetic influences result in the formation of certain types of order within a system and also the resultant change in the observed physical properties of a material.
Chapter 10

Conclusions and Further Work

In this thesis work has been presented demonstrating how, through the analysis of total scattering data, valuable insight into local effects in alloy systems can be obtained.

10.1 Conclusions

For total scattering to be of use for the study of short-range order in alloys it was first necessary to establish whether the information content of the PDF was sufficiently high to distinguish different types and degrees of SRO. This was demonstrated by the simulation of large box models, with atomic arrangements representative of these different local structures and the calculation of theoretical total scattering functions. A comparison of these functions with theoretical random structures demonstrated that, qualitatively, the different orderings could be distinguished and identified.

Having established this, it was necessary to demonstrate how, from a large box model fit to such data, the nature of the order can be quantified. This was presented in Chapter 3. To enable this, the use of the Warren-Cowley parameters and Clapp configurations was considered and it was demonstrated how these could be applied to large box modelling. Using the distribution of Warren-Cowley parameters ($\alpha$) from the atoms in the simulated supercell it is possible to suggest the type of ordering occurring in a system. Similarly, Clapp enhancement factors, $\beta$, were developed and used to identify important structural motifs that may form during the ordering process. Of key importance to this inference is the use of degradation pathways that identify how the Clapp configurations may be related to each other.

These quantitative analyses, combined with the standard method for sample preparation and data processing presented at the end of Chapter 2, represent a new analytical methodology using total scattering for the analysis of short-range order in alloys. Using this methodology it is now possible to not only identify that short-range order is occurring within a system, but provide a detailed and description of the order. This is of paramount importance if the effect of such changes is to be incorporated into models for strengthening or changes in other physical properties.

Having developed a methodology, based on simulated datasets, it was necessary to demonstrate its efficacy using real data. X-ray total scattering data from a sample of Cu$_3$Au, a characteristic system known to shown short-range order, was collected under in situ heating
and cooling conditions and analysed using the methodology previously outlined (Chapter 4). Fitting the PDFs with a random structure, allowing only translational moves, demonstrated that there was a change in local chemical ordering occurring in the alloy, prior to the transition at c. 400°C. The difference in these PDFs also suggested that the change in chemical order was a localised effect, limited to the first few coordination shells in the structure consistent with a statistical model of homogenous short-range order.

Analysis of the Clapp configuration enhancement factors, $\beta$, and the degradation pathways showed that the $C16$ and the related configurations were particularly enhanced, indicating the developing order is related to the $L1_2$ LRO formation. An enhancement of the $C17$ configuration is also observed, suggesting that the ordering may be also related to the $D0_{22}$ structure. However below c. 500°C, there is no further increase in the $C17$ structure, whilst the $C16$ continues to increase, which suggests that ‘$L1_2$’-like order becomes preferred over ‘$D0_{22}$’-like order. Further, from the partial PDFs calculated from the resultant refinements, there was an apparent difference in the position of the peak maxima of the first peak of the CuCu, CuAu and AuAu partials. As the temperature is reduced and the ordering increases, the number of AuAu nearest neighbour correlations is observed to decrease. Complimentary neutron total scattering data identified this effect as real and not merely an artefact of the fitting procedure. This suggests that the ordering occurs so as to remove localised strain in the lattice caused by the large AuAu distances. This was confirmed by a non-linear variation in the peak width with temperature. Finally, some SRO was noted in the as-sprayed atomised samples, suggesting that some ordering may occur even under these rapid quenching conditions, raising concerns about the validity of previous results collected under ex-situ conditions.

In addition to the conclusions drawn about the Cu$_3$Au sample, the analysis of these data also highlighted the importance of correct data processing and handling, and the potentiality when fitting with a large box model to cause ordering artefacts in the refinement. The possible artefacts that could arise from some common data processing errors were demonstrated. These are equally applicable to all samples, not only alloys, and such effects need to be carefully considered and avoided when processing total scattering data.

In Chapter 5 the application of the same total scattering methodology to alloys analogous to the gamma phase in nickel-based superalloys was considered. For samples of NiMo and NiW it was hoped that a new experimental setup using a portable Linkam furnace could provide access to higher temperatures than those accessible using a standard experimental setup. However, problems encountered with both the samples and the setup rendered the data of insufficient quality to analyse.

Neutron total scattering of a sample of Ni-25at.%Cr was collected on the POLARIS instrument at ISIS. Initial fitting of data showed a clustering of like atoms, that upon reconsideration was identified to be the result of an offset in the data caused by the different data processing softwares used. As a consequence of this observation, some of the routines used in the analysis software have now been altered. Using these corrected routines, the data was reprocessed and fitted using RMCProfile. A consideration of the Clapp configurations and degradation pathways showed a preference to form the $C37$ and $C-5$ configurations, and the related degraded structures. Unlike the Cu$_3$Au samples, the observed Clapp configurations do not appear to be related
to the Pt$_2$Mo type ordering that is predicted to form in this system. From a consideration of the $\alpha$-parameters, this appears to be caused by a larger preference in the 2nd nearest neighbour shell to form unlike interactions, compared with that predicted from the Pt$_2$Mo model.

One of the potential advantages of the total scattering technique is the ability to analyse higher-order systems. In Chapter 6, using a series of L1$_2$ alloys, it was shown how the techniques and methodologies could be adapted to analyse a ternary system and identify any preferred sub-lattice ordering occurring. The possible sublattice configurations were calculated and the degradation pathways that relate them shown. From analysis of these sublattice configurations, it was shown that Ta and Ti, when substituted onto the Al-sublattice in L1$_2$ exhibit different behaviours. The Tantalum prefers to form like-atom nearest neighbours on the sublattice (shown by formation of the Al1 configuration) and, therefore, exhibits a clustering behaviour. In contrast, the titanium tries to form unlike-atom neighbours, resulting in trans (Al4) and mer (Al6) configurational arrangements. For Co, substituting onto the Ni-sublattice, the atoms prefer to adopt a square planar configuration (Ni21) in a plane perpendicular to the square planar arrangement of the Al atoms in the L1$_2$ (C16) structure. These orderings are likely to effect the APB energies of the material and, consequently, its observed strength.

As first introduced in Chapter 4, it may be possible to observe local variations in bond length and, hence, local strains in a lattice that arise as the result of the substitution of atoms by elements with different atomic radii. In Chapter 7, the use of total scattering functions as a means of assessing local-lattice strains in a material is presented. Using a sum of Gaussians model and a spring model, it has been shown that there is an observable change in the width of peaks in the PDF with atomic substitution. This change is dependant on both the concentration of the substitution and the relative atomic radii, and hence the local lattice strain. The contributing effect of other sample characteristics, such as crystallite size and microstrain broadening have also been shown.

Using the relationship between peak width and lattice strain, it is possible to use the PDF to compare the relative local lattice strains exhibited in alloys. This has been applied to the study of a material from the novel metallurgical field of high entropy alloys (HEAs). A series of increasingly compositionally complex samples were considered, to see if there was a notable change in the local lattice strains that would confirm the highly-distorted lattice hypothesis. Whilst the magnitude of the peak widths in the HEA were the largest, they were not anomalously large when compared with the compositionally simpler materials. However, the variation in the peak widths appeared to be much better modelled by the relative melting points of the materials, and hence the magnitude of static strain required to justify the increased peak width in the HEA is reduced. This observation further suggested that the HEA shows no significant level of broadening when compared with the other materials. This result is highly significant as it challenges one of the four core principles of the HEA field.

If the local effects observed in this thesis are to be linked to observed physical phenomena, particularly strength, not only is a quantification required (as demonstrated in Chapters 3, 6 and 8), but also an understanding of the underlying thermodynamic driving forces of these local effects. Chapter 9 presented a brief discussion of some of the current energetic theory and strengthening models, and some possible ideas for future adaptations. Using a series of
Monte-Carlo simulations, the possible order that can develop under the application of different enthalpic potentials was considered. This demonstrated the necessity to include the potentials of shells beyond the first nearest neighbours (up to at least the third) in order to accurately calculate the variations of strength due to local order.

The simulations also showed that the energetic parameters are not linearly related to the observed ordering parameters, due to an successive shell effect. However, by comparing the type of SRO observed in a system to the structures that develop in these simulations, it is possible to suggest the energy parameters that contributed to their formation. The diffuse anti-phase boundary energies (DAPBs) were also calculated, showing that ordering is a much more potent strengthening mechanism than clustering, but that there is no simple link between strength and either the observed $\alpha$ or $\beta$ parameters. Finally, a method through which the entropy of a system might be related to the enthalpy was presented and its limitations discussed.

10.2 Further work

In this thesis, the successful application of total scattering and reverse Monte Carlo techniques to a handful of interesting metallurgical systems has been presented, but the technique could equally be applied to any system where local ordering is believed to occur. A number of such interesting systems have already been suggested.

The initial study of a sample of Ni-25at.%Cr has demonstrated the viability of this system for further studies. Of particular importance in this system are the changes in electrical resistivity with time and the radiation damage properties of the material. Ni-Cr alloys, which are used extensively in thermocouples, are known to show a drift in electrical resistivity over their operational lifetimes that may be attributable to the development of local order [154]. These alloys have also been used in nuclear shielding applications, where the constant bombardment with nuclear radiation is believed to create vacancies and localised zones of amorphisation in the structure. The stability of such defects are believed to be strongly dependant on the local environment [155], which may encourage the generation of such defects or conversely their removal. Consequently, understanding the SRO occurring is of importance in the determination of the radiation lifetimes of materials used in nuclear applications.

Titanium alloys used extensively in both airframe and aero-engine applications contain aluminium, which serves to stabilise the mechanically desirable $\alpha$-phase and increases the tensile strength of the material. With increasing aluminium concentration, the alloy is known to undergo an ordering transition, from the disordered hexagonal $\alpha$-phase to the ordered hexagonal $\alpha_2$ phase. However, Ti-Al alloys, with Al concentration between c. 5-13at.%, have been shown to exhibit anomalous hardening after ageing heat treatments despite being nominally disordered. This effect has been attributed to the formation of short range ordered (SRO) domains with structures similar to the $\alpha_2$ phase [156]. The development of such ordering is also associated with a reduction in alloy ductility and slip localisation, which is of key importance to the service life of the material, and measured changes in electrical resistivity [157]. Efforts to characterise this ordering have principally employed TEM- based methods [158]. Whilst these studies have successfully confirmed the existence of short-range order, no studies have been performed that obtained a detailed description of the statistical arrangement of atoms associated with this or-
dering, essential in linking the underlying order to the physical properties. These alloys could therefore provide another interesting system to probe using the new methodologies.

Both of these example systems would prove invaluable for our understanding of industrially relevant materials. However, as with the example of the Cu$_3$Au system provided in this thesis, a number of systems demonstrate characteristic ordering transitions that are essential for developing an understanding of how ordering transitions proceed. Within the Cu-Au system a similar ordering transition, from A1 $\rightarrow$ L1$_2$, is observed in the system for samples of Au$_3$Cu. The results presented in this thesis suggested that the transition observed in Cu$_3$Au was driven by the removal of the large Au-Au partials causing local lattice strains. The same driving force for ordering in the Au$_3$Cu system is not possible, but instead may result from an analogous reduction in strain caused by the removal of the shorter CuCu correlations in Au$_3$Cu. Experiments would be required to determine whether this is indeed the case. This work should be combined with the development of the energetic theory required to more accurately predict these transitions and improve the calculation of phase diagrams, used extensively for phase prediction in alloy development.

In addition to the application of the SRO methodology to the study of a wide variety of alloys, similar applications of the lattice strains methods should be considered for interesting alloys. The sample of CrMnFeCoNi was chosen as it is often cited as a characteristic HEA existing in a single phase. However, as noted, the difference in the atomic radii is only very small. The refractory metal HEAs developed by Senkov et al. [159,160], such as VNbMoTaW, have been reported to exist as single phase solid solutions both in the as-cast state and following a high temperature annealing heat treatment. These bcc (body-centred cubic) alloys exhibit a much larger variation in atomic radius compared with many of the fcc HEAs. As a result, these systems could provide an ideal basis on which to assess the level of strain present in equiatomic alloys containing atoms of different size.

To further extend the analysis of local lattice strains in HEA systems, the separation of the influences of static and dynamic displacements would be incredibly beneficial. As well as assessing samples of increasing relative compositional complexity, it would be interesting to assess the observed variation in width as the temperature of the sample is reduced towards absolute zero. This would reduce the convoluting affect of dynamic displacements in the lattice and provide a more direct measure of static components.

Whilst the studies presented in this thesis have provided invaluable information on the nature of ordering occurring in idealised samples, to extend the applicability of the technique to the analysis of engineering components it would be important to consider the effects of common thermo-mechanical processing techniques on total scattering data. Of particular importance will be an understanding of the influence of texture and thermal history of the samples. As demonstrated in the consideration of the Cu$_3$Au data, quenching rates and prior thermal conditions may be incredibly important for the analysis of SRO. Likewise, an understanding of preferred orientation or texture may allow the analysis of samples such as the NiMo and NiW examples discussed previously.
10.3 Concluding remarks

This thesis has presented how the total scattering technique and reverse Monte-Carlo methods may be used for the analysis of local structural effects in alloys. New analytical methodologies for the assessment and quantification of short-range order and local lattice strains have been presented. Using these techniques, it has been shown how greater insight can be provided into a host of different interesting metallurgical systems; from historically ‘well-characterised’ systems such as Cu₃Au, to systems extensively used for industrial applications such as Ni-Cr and Ni-Al-X L1₂ alloys, and to novel metallurgical systems such as the HEAs. As such, this work presents the first steps towards a greater understanding of how the macroscopic physical phenomena can be linked to the underlying local structural fluctuations in alloy systems. This understanding may not only allow us to interpret anomalous effects in existing alloys systems, but ultimately may enable the design of new alloy systems based on these effects. Taken as a whole, it is hoped that the work presented in this thesis will open a new field of investigation into the study of local effects in alloy systems.
Appendix A

Fourier Transforms and their properties

A.1 Fourier transform of a Voigt function

Delta function

\[ \mathcal{F}[\delta(x - x_0)] = \exp(-2\pi ikx_0) \] (A.1)

Gaussian - centred at the origin

\[ \mathcal{F}[\exp(-ax^2)] = \sqrt{\pi} \frac{a}{a} \exp\left(-\frac{\pi^2 k^2}{a}\right) \] (A.2)

General Gaussian

\[ \mathcal{F}\left[a \exp\left(-\frac{(x - b)^2}{2c^2}\right)\right] = a\sqrt{2\pi c^2} \exp\left(-2\pi^2 c^2 k^2\right) \exp(-2\pi ikb) \] (A.3)

General Lorentzian

\[ \mathcal{F}\left[\frac{1}{\pi} \frac{\frac{1}{2}\Gamma}{(x - x_0)^2 + \left(\frac{\Gamma}{2}\right)^2}\right] = \exp(-2\pi ikx_0 - \Gamma\pi|k|) \] (A.4)

Voigt function - convolution of a Gaussian and Lorentzian

\[ f(a, b, c, \Gamma, x) = a \exp\left(-\frac{(x - b)^2}{2c^2}\right) \otimes \frac{1}{\pi} \frac{\frac{1}{2}\Gamma}{(x - x_0)^2 + \left(\frac{\Gamma}{2}\right)^2} \] (A.5)

\[ \mathcal{F}[f(a, b, c, \Gamma, x)] = a\sqrt{2\pi c^2} \exp\left(-2\pi^2 c^2 k^2 - \Gamma\pi|k|\right) \exp(-2\pi ikb) \] (A.6)

Note that the first exponential in the function creates the envelope function of the data and the second determines the period of the oscillation.
Appendix A. Fourier Transforms and their properties

Figure A.1: Calculated Fourier transform of a Pseudo-Voigt function with $a = 5$, $b = 1$, $c = 0.04$ and $\Gamma = 0.04$. Black line indicates the decay envelope term, the red line the real part of the function and the blue line the imaginary part of the function.

A.2 Calculation of partials

The coordination number of a specific partial can be calculated as:

$$CN = \int_{r_1}^{r_2} 4\pi r^2 c_j \rho_0 g_{ij}(r) dr$$  \hspace{1cm} (A.7)

where $c$ is the concentration, $\rho_0$ the density, $g_{ij}(r)$ the partial pair distribution function, $r$ the interatomic distance, and $i$ and $j$ atomic labels. However, if the distribution of atoms is random it follows that we would expect the coordination number of a particular partial to simply be $CN = c_i n_{nn}$, where $n_{nn}$ is the number of nearest neighbours and therefore that:

$$n_{nn} = \int_{r_1}^{r_2} 4\pi r^2 \rho_0 g_{ij}(r) dr$$  \hspace{1cm} (A.8)

Assuming that a peak in the partial will be Gaussian in shape we can re-write this as:

$$n_{nn} = \int_{-\infty}^{\infty} 4\pi r^2 \rho_0 A \exp \left( -\frac{(r - b)^2}{2c^2} \right) dr$$  \hspace{1cm} (A.9)

$$= 4\pi \rho_0 A \int_{-\infty}^{\infty} r^2 \exp \left( -\frac{(r - b)^2}{2c^2} \right) dr$$  \hspace{1cm} (A.10)
A.3. Box-Muller transform

where $a$, $b$ and $c$ are constants that define the Gaussian function. Defining a change in variable $R = r - b$

$$n_{nn} = 4\pi \rho_0 A \int_{-\infty}^{\infty} (R + b)^2 \exp \left( - \frac{R^2}{2c^2} \right) dR$$  \hspace{1cm} (A.11)

$$= 4\pi \rho_0 A \int_{-\infty}^{\infty} (R^2 + 2Rb + b^2) \exp \left( - \frac{R^2}{2c^2} \right) dR$$  \hspace{1cm} (A.12)

$$= 4\pi \rho_0 A \int_{-\infty}^{\infty} \left[ R^2 \exp \left( - \frac{R^2}{2c^2} \right) + 2Rb \exp \left( - \frac{R^2}{2c^2} \right) + b^2 \exp \left( - \frac{R^2}{2c^2} \right) \right] dR$$  \hspace{1cm} (A.13)

Recalling that:

$$\int_{-\infty}^{\infty} x^{2n} \exp \left( - \alpha x^2 \right) dx = \sqrt{\frac{\pi}{\alpha}} \frac{(2n-1)!}{(2\alpha)^n}$$  \hspace{1cm} (A.14)

we can write:

$$n_{nn} = 4\pi \rho_0 A \left[ c^3 \sqrt{2\pi} + b^2 c \sqrt{2\pi} \right]$$  \hspace{1cm} (A.15)

$$= \sqrt{32\pi^3} \rho_0 A \left[ c^2 + b^2 \right]$$  \hspace{1cm} (A.16)

(note that the $2Rb$ is antisymmetry in the integral and will therefore be zero). Importantly, this function is $b$ dependent. Therefore, if the partials have different average interatomic distances, the peaks must also change in either width or area accordingly.

A.3 Box-Muller transform

Originally described by Box and Muller [38], this method transforms a set of uniformly distributed data into a Gaussian distribution. Two random seeds are chosen, $r_1$ and $r_2$, from which two variables $z_1$ and $z_2$ can be calculated as:

$$z_1 = \sqrt{-2 \ln r_1} \cos 2\pi r_2$$  \hspace{1cm} (A.17)

$$z_2 = \sqrt{-2 \ln r_1} \sin 2\pi r_2$$  \hspace{1cm} (A.18)

The two new generated variables are independent and both normally distributed. In the gaussdist code these are calculated and then added to the $x$, $y$ and $z$ coordinates to provide a random offsite gaussian displacement to mimic thermal fluctuation in the system.
Appendix B

Clapp configurations

B.1 Face centred cubic structure

The following is a table of configuration of atoms in an fcc lattice, as derived by Clapp [55]. The occupied position shows the positions occupied by unlike atoms (text in italics indicates that the position is occupied by a like atom in the -ve Clapp configurations).

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L. Owen

196
### B.1. Face centred cubic structure

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## B.2 Body centred cubic structure

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B.3 L1_2 sublattices

B.3.1 Ni-sublattice

Table B.3: Ni-sublattice configurations in an L1_2 ordered alloy. The occupied position numbers refer to the positions in Fig. 6.6, where images of each of the configurations can also be found. The numbering is chosen such that configurations are grouped by the number of unlike nearest neighbouring (nn) atoms. Within the group (e.g. Ni3-Ni7) the labels are chosen such the those configurations were the unlike atoms are closer to each other are numbered first (Ni3) and those configurations where the unlike atoms are most spread out are numbered last (Ni7).

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### B.3.2 Al-sublattice

Table B.4: Al-sublattice configurations in an \( \text{L}_1^2 \) ordered alloy. The occupied position numbers refer to the positions in Fig. 6.4, where images of each of the configurations can also be found. The numbering of the configurations is chosen as described in for the Ni-sublattice configurations above.

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Appendix C

Structures

C.1 Face centred cubic structures

Figure C.1: Examples used of the seventeen possible long-range ordered structure predicted by Hart [57] and the D1_a structure. In many cases a smaller unit cell can be drawn, but here the structures are shown as multiples of fcc unit cells to demonstrate the ordering occurring in the system. The structures indicated by * are predicted theoretically for certain system but not observed. Those indicated ** have been neither observed nor predicted in the literature. Otherwise the structures are labelled with their common Strukturbericht notation (or the characteristic system in which they are observed e.g. Pt₂Mo). The panels identify structures with the same stoichiometry: (a) AB, (b) A₂B, (c) A₄B and (d) A₃B. A atoms are shown in blue and B atoms in red.
Figure C.1: (cont): Examples used of the seventeen possible long-range ordered structure predicted by Hart [57] and the D1\textsubscript{a} structure. In many cases a smaller unit cell can be drawn, but here the structures are shown as multiples of fcc unit cells to demonstrate the ordering occurring in the system. The structures indicated by * are predicted theoretically for certain system but not observed. Those indicated ** have been neither observed nor predicted in the literature. Otherwise the structures are labelled with their common Strukturbericht notation (or the characteristic system in which they are observed e.g. Pt\textsubscript{2}Mo). The panels identify structures with the same stoichiometry: (a) AB, (b) A\textsubscript{2}B, (c) A\textsubscript{4}B and (d) A\textsubscript{3}B. A atoms are shown in blue and B atoms in red.
C.1. Face centred cubic structures

Figure C.1: (cont): Examples used of the seventeen possible long-range ordered structure predicted by Hart [57] and the D1\textsubscript{a} structure. In many cases a smaller unit cell can be drawn, but here the structures are shown as multiples of fcc unit cells to demonstrate the ordering occurring in the system. The structures indicated by * are predicted theoretically for certain system but not observed. Those indicated ** have been neither observed nor predicted in the literature. Otherwise the structures are labelled with their common Strukturbericht notation (or the characteristic system in which they are observed e.g. Pt\textsubscript{2}Mo). The panels identify structures with the same stoichiometry: (a) AB, (b) A\textsubscript{2}B, (c) A\textsubscript{4}B and (d) A\textsubscript{3}B. A atoms are shown in blue and B atoms in red.
C.2 \((1 \frac{1}{2} 0)\) structures

The family of \((1 \frac{1}{2} 0)\) - so called due to the formation of superlattice intensity at this position.

Figure C.2: Projection down [001] of some typical LRO structures observed in the metal alloys under consideration. The black circles indicate X atoms and the white Ni atoms. Large circles are at height \(z = 0\), whilst the small circles are at \(z = \frac{1}{2}\). The planes indicated show the (420) periodicity.
Bibliography


[31] X. Jiang, G. Ice, C. J. Sparks, L. Robertson, and P. Zschack, “Local atomic order and individual pair displacements of Fe$_{46.5}$Ni$_{53.5}$ and Fe$_{22.5}$Ni$_{77.5}$ from diffuse X-ray scattering studies,” *Physical Review B*, vol. 54, no. 5, pp. 3211–3226, 1996.


Bibliography


