The application of spin polarised neutron scattering to superconductors

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The Application of Spin Polarised Neutron Scattering to Superconductors

by

Timothy John Smith

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of

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ABSTRACT

The use of spin polarised neutron scattering as an experimental probe for magnetic phenomena within solid state physics has been demonstrated in two separate studies of superconductors.

With the use of three-dimensional polarisation analysis, the magnetic response within a thermal energy window -30meV<\hbar\omega<+30meV has been measured for both insulating and superconducting compositions of the high T_c material YBa_2Cu_3O_6+x. The observed magnetic scattering from the superconducting composition (x=0.95, T_c-90K) at T=300K shows conclusively that there is negligible magnetic scattering in the normal state below 30meV. What little scattering is observed corresponds to a paramagnetic cross-section of (0.048±0.008)barns or to -3.2% of the Cu atoms carrying a spin \( \frac{1}{2} \). Similar polarised neutron measurements performed on insulating YBa_2Cu_3O_6.11, above and below T_N, reveal a small but finite level of scattering corresponding to ~18% of the Cu atoms carrying a spin \( \frac{1}{2} \) in the paramagnetic state. The observed increase in paramagnetic scattering above T_N corresponds to just 20% of that expected due to the thermal disordering of the observed ordered magnetic moment at 300K. These measurements are consistent with a magnetic excitation spectrum driven by quantum rather than thermal fluctuations for which the notion of separate magnetic and charge degrees of freedom (and therefore also the concept of local moments) may not be valid. In addition, measurements conducted on single crystal YBa_2Cu_3O_7 in its normal state revealed no indication of magnetic enhancement in the vicinity of the (\( \pi, \pi \)) point up to 30meV. This is in disagreement with theoretical predictions of an enhanced magnetic scattering in this region for spin fluctuation energies of order 10 to 20meV.

The second study demonstrates the feasibility of spin polarised neutron
scattering as a novel tool for the investigation of the flux line lattice in type II superconductors. Measurements conducted in the mixed state of niobium (T=4.5K, B=0.22T) constitute the first experimental observation of lattice distortions due to the presence of flux line vortices. The experimentally determined magnitude of the lattice distortion yields a value approximately three orders of magnitude greater than that expected due to the volume anomaly between the coexisting normal and superconducting regions. An alternative mechanism is suggested on the basis of electron redistribution between the normal and superconducting regions in which electrons are trapped by the flux lines. As a result of this process, a response in the form of a lattice distortion is induced in order to maintain charge neutrality.
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1.1 A Historical Perspective of Superconductivity

Since the beginning of the century, in the wake of the revolutionary observation that pure mercury exhibits a sudden disappearance in resistivity below 5K, superconductivity has initiated a 'race' amongst scientists to discover new and higher transition temperature superconductors as well as considerable attention towards developing a theory to account for their properties. This discovery of zero resistance by H. K. Onnes in 1911 [1], made possible only by his own success in liquefying helium (thus enabling temperatures down to 4.2K to be attained), and subsequent experiments on persisting currents in the years up to 1914, lay the foundations for further discoveries such as the Meissner effect in 1933 [2]. Indeed this effect, whereby magnetic flux is excluded from the bulk superconductor as a result of the induced magnetisation generated by the presence of persistent currents, opposing and cancelling the applied magnetic field, defines a unique characteristic of superconductors besides zero resistance - that of perfect diamagnetism. The experiments of Meissner and Ochsenfeld [2] showed that this flux expulsion is independent of whether the external field is applied in the superconducting state or the normal state. In contradiction to the classical expectation, this observation provided early indications of the macroscopic quantum nature of superconductivity. An explanation of the Meissner effect was provided by the London brothers in 1935 [3] in which they assigned a characteristic length $\lambda_L$, known as the London penetration depth, which at zero temperature is given by
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\( \lambda_L(0) = \left( \frac{m^* c^2}{4\pi n_s e^2} \right)^{1/2} \)  \hspace{1cm} (1.1)

over which the external magnetic field \( B \) will exponentially decay with distance \( r \) from the surface of the superconductor according to \( B \propto \exp(-r/\lambda_L) \). Here, \( n_s \) is the density of 'superconducting electrons' and \( m^* \) is their effective mass. One finds that \( n_s \) is directly related to what is known as the 'order parameter' \( \kappa \) (described below) and as such the penetration depth has a temperature dependence. In particular, \( n_s \rightarrow 0 \) as \( T \rightarrow T_c \) and accordingly \( \lambda_L \) becomes progressively longer as the transition temperature is approached. That is to say, as \( T \rightarrow T_c, \lambda_L \rightarrow \infty \) and the external field penetrates the sample uniformly. Consequently, in contrast to the sudden disappearance in resistivity at \( T_c \), the onset of the diamagnetic susceptibility is gradual. A further implication of the Meissner effect is a critical field \( B_C \), above which superconductivity will be destroyed. Experimental results of \( B_C \) versus \( T \) for elemental (type I) superconductors can be well approximated by a quadratic temperature dependence of the form:

\[ B_C(T) = B_C(0) \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right] \]  \hspace{1cm} (1.2)

The 1950s saw important theoretical advances coupled with further experimental discoveries related to a possible mechanism for superconductivity. A major landmark came in 1950 with the development of the Ginsburg-Landau (GL) theory [4] which provided a phenomenological description of many of the thermodynamic, electromagnetic and transport properties of the superconducting state. Related to Landau's theory of second-order phase transitions, the free energy is expanded in terms of an order parameter which takes the form of a complex pseudo-wavefunction \( \Psi \), hypothesised to be related to the local density of superconducting electrons as \( n_s = |\Psi(r)|^2 \). Under this formalism, nonlinear (in a magnetic field) and
spatial variation effects of $n_s$ were able to be treated and besides a
temperature dependent penetration depth $\lambda$, a second, temperature
dependent, characteristic length scale was obtained. The latter, known as the
coherence length $\xi$, characterises the distance over which $\Psi(r)$ can vary
without a substantial energy increase and the ratio of the two length scales
yields the important GL parameter:

$$\kappa = \frac{\lambda(T)}{\xi(T)}$$ (1.3)

In particular, the solutions to the GL equations (section 1.4.2) were able to
both distinguish and describe two fundamentally different families of
superconductor - type I and type II - in the wake of the work by Abrikosov in
1957 [5]. Abrikosov showed that the behaviour of a superconductor in a
magnetic field, which differentiates the two types, is controlled by the value of
$\kappa$. Type I materials encompass the majority of elemental superconductors
(with the notable exception of niobium) for which $\kappa < 1$, and exhibit a fully
developed Meissner effect. Type II materials on the other hand, which
comprise nearly all superconducting compounds, have small associated
coherence lengths and are characterised by the exhibition of a mixed state in
which magnetic flux penetrates the bulk material in the form of discrete
vortices.

Two further discoveries which took place in the 1950s and which were integral
in future theoretical descriptions, was that of the existence of an energy gap
in the excitation spectrum of electrons in the superconducting state and the
isotope effect. The former was observed via specific heat measurements in
which the electronic term below the superconducting transition was found not
to be linear, but instead of the form $\exp(-\Delta/k_BT_C)$ - characteristic of a system
with a gap in the excitation spectrum of energy $2\Delta$. The discovery of the
isotope effect [6], in which the superconducting transition temperature
depends on the isotopic mass of the material according to $T_C \propto M^{-\frac{1}{3}}$ (in its
simplest form), provided an important clue as to the microscopic mechanism
at work in superconductors by its implication that lattice vibrations or phonons are strongly involved. Indeed leading from this, in 1957, came a complete microscopic description of the superconducting state based on the phonon mediated pairing of opposite momentum-opposite spin Fermi surface electrons (known as Cooper pairs - see section 1.4) - commonly referred to as the BCS theory [7] (after its authors Bardeen, Cooper and Schrieffer). Despite the approximate nature of this theory and the fact that it only strictly applies to weak electron-phonon coupling systems or ‘conventional’ superconductors, its undoubted success in describing the main features of superconductivity in these materials means that it serves well as a reference theory for the less well understood high $T_C$ oxides. The important results of BCS are summarised in section 1.4.

The beginning of the 1960s provided an insight into the potential technological applications of superconductors with the discovery of the Josephson effect in which both single-electron excitations and electron pairs tunnel across a thin insulating barrier separating two superconducting electrodes. This was followed in 1964 by Littles paper [8] in which a model of high $T_C$ organic polymers was described, as a result of which, many new superconductors were discovered, culminating in a record high transition temperature for the time (1973) of 23.2K in the heavy fermion system Nb$_3$Ge.

Despite the obvious progress in the search for superconducting materials with higher transition temperatures it was becoming widely regarded that superconductivity was strictly a low temperature phenomenon. Indeed the subject was becoming considered a ‘mature’ field by the late 1970s and the search for higher-temperature superconductors abandoned with the exception of a few individuals. However, in 1986 a breakthrough came with the remarkable discovery by two such individuals - J. Georg Bednorz and K. Alex Müller - of the onset of superconductivity as high as 30K in the Ba-La-Cu-O system [8]. Thus a new family of superconducting materials, termed the high $T_C$ cuprates or oxides, was born and found to consist of two classes in the explosion of activity which followed. The class 1 materials were those related
to the system first reported on by Bednorz and Müller, namely La$_{2-x}$M$_x$CuO$_4$ (M = Ba$^{+2}$, Ca$^{+2}$ or Sr$^{+2}$), with a limiting transition temperature of 40K. The second class was discovered in 1987 by Wu et al. [9] in which they reported a “stable and reproducible superconductivity transition between 80K and 93K in the multiphase Y-Ba-Cu-O compound”. The onset of superconductivity was subsequently attributed to the single phase YBa$_2$Cu$_3$O$_{6+x}$ (x~1) (later substitution of other rare earths for Y defined the class 2 formula as MBa$_2$Cu$_3$O$_{6+x}$ with M = rare earth) - a significant discovery by its implication that the perovskite type structure and in particular the constituent copper oxide sheets common to both classes, played an important role in their superconducting properties. In addition, the fact that these class 2 oxides exhibited superconductivity at temperatures in excess of that of liquid nitrogen meant that a cheaper replacement for helium as a coolant was possible. Further studies on the cuprates yielded higher transition temperatures still, in particular the TiBaCaCuO compound discovered by Herman and Sheng [10] with a transition temperature above 125K.

Despite these cuprates sharing many of the characteristics of the so called ‘conventional’ superconductors, such as the existence of paired electrons and an energy gap (all be it anisotropic and in the range $3.5k_B T_C$ to $8k_B T_C$ as opposed to the isotropic BCS value of $3.54k_B T_C$) in the superconducting state and familiar properties including Josephson tunnelling and vortex structure, their high values of $T_C$ cast immediate doubts over the applicability of the BCS theory. Other unusual properties include:

- linear dc resistance in the normal state
- unusual behaviour of the nuclear relaxation rate below $T_C$
- close proximity of antiferromagnetic phases
- extremely small coherence lengths

Consequently since their discovery, considerable work has been focussed upon developing a superconducting mechanism for the high $T_C$ oxides. Receiving particular attention has been the possible role of antiferromagnetic
fluctuations, exhibited by all cuprates in their insulating phase, in the attainment of high transition temperatures.

1.2 Thesis Objective

The aim of this thesis has been to demonstrate the application of spin polarised neutron scattering as a probe for magnetic phenomena in two superconductors. The first of these addresses the existence of magnetic fluctuations in copper-oxide superconductors, so crucial to a magnetic mechanism being responsible for their transition temperatures. For this investigation, the question of the formation of local magnetic moments in the superconducting compound YBa$_2$Cu$_3$O$_{6+x}$ is studied for oxygen compositions in the insulating and superconducting parts of the phase diagram (see figure 1.1).

The second line of investigation focuses upon one of the more fundamental magnetic phenomena associated with superconductivity - that of the flux line lattice and its interaction with the nuclear lattice. Using, in a unique way, spin polarised neutrons in conjunction with a small-angle scattering set-up, the response of the nuclear lattice to the periodic magnetic field modulation which accompanies the formation of flux lines is studied for the type II elemental superconductor niobium. This response, by virtue of its coupling to the superconducting order parameter, enables its consequences upon the redistribution of electrons to be studied.

The theoretical aspects of spin polarisation analysis, in particular a detailed discussion of the XYZ technique, are provided in chapter 3, following a chapter on the fundamental aspects of neutron scattering. The experimental means by which both investigations were carried out, together with the data reduction, is detailed in chapter 4 and this is followed by a discussion of the Monte Carlo simulation of the prevalent problem of multiple scattering effects in neutron scattering experiments. Chapter 6 provides a description of the
sample preparation and characterisation of both the YBa$_2$Cu$_3$O$_{6+x}$ and Nb specimens and is followed by the two results chapters for each investigation. The remainder of this chapter is concerned with providing an insight into fundamental aspects of both studies.

1.3 Magnetic Properties of YBa$_2$Cu$_3$O$_{6+x}$

The concept of a magnetic mediated pairing mechanism in the high $T_C$ oxides followed discoveries in the $(La_{2-x}Sr_x)CuO_4$ and $MBa_2Cu_3O_{6+x}$ systems that the Cu atoms carry an unpaired spin with the consequent possibility that the magnetic fluctuations may be responsible for the superconductivity. For small x, these unpaired spins order antiferromagnetically with Néel temperatures ($T_N$) as high as 500K. Above the 3d ordering temperature, strong, two-dimensional spin correlations (within the CuO$_2$ planes), with large correlation lengths (hundreds of angstrom above $T_N$), have been observed in both the cuprate parent compound La$_2$CuO$_4$ [11] and YBa$_2$Cu$_3$O$_6$ [12]. The antiferromagnetic ordering displayed in the insulating phases of these materials has been found to be well described by a two-dimensional (2D) quantum Heisenberg antiferromagnet (QHAF) model. It is the large energy scale of the observed spin fluctuations which has fuelled speculation about the magnetic origin of the coupling mechanism in these compounds.

1.3.1 The Phase Diagram for YBa$_2$Cu$_3$O$_{6+x}$

As with all the cuprates, YBa$_2$Cu$_3$O$_{6+x}$ exhibits a rich variety of phenomena besides superconductivity, including metal-insulator transitions, structural transitions and antiferromagnetism. Figure 1.1 shows the experimentally determined phase diagram as deduced from NMR [13] and neutron scattering [14] studies, from which the oxygen dependence of all the physical properties is evident. For oxygen concentrations greater than a critical content x~0.4 (dependent on sample treatment), YBa$_2$Cu$_3$O$_{6+x}$ is orthorhombic while for
small $x$ it adopts tetragonal symmetry. Accompanying this structural, orthorhombic to tetragonal transition is a metal to insulator transition which also divides the antiferromagnetic region from superconductivity. Thus for $x \leq 0.4$ the system is a tetragonal antiferromagnet and for $x \geq 0.4$ it is an orthorhombic superconductor.

The chemical unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, as with all the cuprates, contains simultaneous one-dimensional and two-dimensional features in the Cu-O structure. Comprising of three copper-oxygen layers stacked along the c-axis, two of these layers have oxygen ions between the Cu ions in both the a and b crystallographic directions to form a square planar arrangement (the CuO$_2$ planes). The chemical binding within these planes is such that each Cu ion gives up two electrons - one each from the 4s and 3d shells - where the hole on the copper is strongly hybridised with the oxygen 2p and 2s orbitals as illustrated in figure 1.2. However, in the case of local spin insulators a simplified picture can be used in which the hole responsible for the magnetic moment is considered as localised on the 3d orbital. The third layer constitutes the one-dimensional structure feature in the form of a Cu-O ‘chain’ All oxygen vacancies are confined to the chain site O ions and it is the filling

---

**Fig. 1.1** Phase diagram for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [13], [14].
and ordering of these sites which control the filling of valence band states and therefore also the electronic and magnetic properties of YBa$_2$Cu$_3$O$_{6+x}$. For intermediate occupancies ($x < 1.0$) empty chain segments containing 2-fold co-ordinate Cu ions arise. These Cu ions nominally have a +1 valence (i.e. a full 3d shell) and hence carry no magnetic moment. A detailed discussion of the crystallographic dependence upon oxygen content is given in chapter 6.

1.3.2 The Magnetic Structure of YBa$_2$Cu$_3$O$_{6+x}$

Three-dimensional long range antiferromagnetic order in non-superconducting, tetragonal samples of YBa$_2$Cu$_3$O$_{6+x}$, has been confirmed by neutron scattering experiments [15, 16] indicating Néel temperatures as high as 500K. ($x = 0.0$). The derived spin arrangement of this phase shows that the magnetic structure comprises of antiferromagnetically ordered nearest neighbour spins both within (via nearest neighbour superexchange interactions) and between the CuO$_2$ planes with the spin direction fixed in the

![Fig. 1.2 Configuration of the Cu 3d and O 2p orbitals in a CuO$_2$ plane.](image)
Chapter 1

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plane (in the (100) direction). No ordered moment is observed in the oxygen deficient layers. Figure 1.3 shows the magnetic spin structure for YBa$_2$Cu$_3$O$_{6+x}$ indicating the + - + - + - sequence of Cu spins along the c-axis. Because there are two plane layers per chemical unit cell, the chemical and magnetic periodicities are the same along the c-axis and hence in a neutron scattering experiment, the magnetic Bragg index / will take an integer value.

In the a-b plane however, the magnetic unit cell is twice the chemical unit cell in both directions and corresponds to an antiferromagnetic structure with wavevector \( \mathbf{k} = (\pi/a, \pi/b, 0) \). Consequently, the magnetic phase is characterised by magnetic Bragg reflections indexed according to Miller indices \( \left( \frac{a}{2}, \frac{b}{2}, l \right) \).

The magnetic Bragg peak intensity is proportional to the square of the staggered magnetisation which in turn is proportional to the average spin \( \langle S \rangle \). Figure 1.4 shows the square of the staggered magnetisation as a function of temperature, as deduced from the intensity of the \( (1/2,1/2,1) \) Bragg peak in YBa$_2$Cu$_3$O$_{6+x}$ for various oxygen contents [14]. At zero temperature, the intensity of the Bragg peaks gives the saturated moment \( m_0 = (0.64 \pm 0.05) \mu_B \) which is somewhat smaller than the moment of \( m_0 = g\mu_B \langle S \rangle = 1\mu_B \) expected.

![Fig. 1.3 The magnetic spin structure for YBa$_2$Cu$_3$O$_{6+x}$. The large circles represent the planar Cu$^{1+}$ ions and the small circles represent the chain layer Cu ions.](image)
for spin $\frac{1}{2}$ Cu$^{2+}$ in the 3d state assuming a typical g-value of 2. The observed moment corresponds to $\langle S \rangle \approx 0.30$. This reduced spin can be ascribed to the two-dimensional nature of the antiferromagnetic ordering within the insulating phase, as will be discussed below, in which the magnetic interactions within the CuO$_2$ planes are much stronger than those between the planes. As such, the spin dynamics can be described in terms of a 2D Heisenberg system where, because of the very small size of the spin, quantum corrections become important and a large zero-point spin fluctuation is expected. Spin wave analysis applied to the spin $\frac{1}{2}$, 2D Heisenberg model yields $\langle S \rangle \approx 0.30$ [18] in good agreement with the observed ordered moment. Thus the neutron diffraction results are consistent with localised magnetic moments of approximately $1\mu_B$ and large fluctuations in spin orientation even at low
temperatures.

1.3.3 The 2D Quantum Antiferromagnet

A classical antiferromagnet would have perfect Néel order at zero temperature. At a finite temperature the spins will fluctuate around their zero temperature orientations and these fluctuations can be analysed in terms of harmonic spin waves. In a quantum mechanical antiferromagnet, spin waves are present even at \( T = 0 \) and correspond to the zero-point fluctuations of the spins. In a nearest neighbour Heisenberg model, the Hamiltonian for spin-spin interactions has the form [19]

\[
H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j
\]  

(1.4)

where the sum is over the nearest neighbour pairs and \( J \) is the exchange energy. Diagonalisation of the Hamiltonian leads to a dispersion relation for the spin wave energy \( \hbar \omega \) as a function of wave vector \( \kappa \), measured relative to a magnetic Bragg point. For small wave vectors this dispersion is linear with a velocity \( c = \omega / \kappa \) proportional to the exchange energy \( J \). Neutron inelastic experiments can directly determine the dispersion relations by the way in which the scattering function (or dynamic structure factor) \( S(\kappa, \omega) \) can be extracted from the measured cross-section which in turn is directly related to the imaginary part of the dynamic susceptibility \( \chi''(\kappa, \omega) \) by the fluctuation dissipation theorem [20]:

\[
S(\kappa, \omega) = \frac{1}{1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)} \chi''(\kappa, \omega)
\]  

(1.5)

The magnon modes in an ordered antiferromagnet have well defined dispersion relations \( \omega_{\kappa} = \omega(\kbar) \) which correspond to singularities in the response function.
where $\kappa = K + \vec{K}$ and $K$ is a reciprocal lattice vector for the magnetic crystal. The magnons are therefore detected in a scan with fixed $\vec{K}$, as satellite structures for $\omega = \pm \omega(\vec{K})$ of the elastic magnetic diffraction peaks and, if the modes are not damped, have a width which is resolution limited.

Prior to confirmatory experiments, Anderson [21] pointed out that the superexchange interaction between nearest neighbour Cu atoms within a CuO$_2$ plane should be unusually strong such that the magnetism has essentially a two-dimensional character. Neutron scattering experiments performed on the La$_2$CuO$_4$ [11] and YBa$_2$Cu$_3$O$_6$ [12] ordered antiferromagnets later revealed that the exchange interactions within the CuO$_2$ planes are indeed much larger than between the layers and give rise to two-dimensional magnetic behaviour with an overall energy scale which is much larger than the ordering temperatures would suggest. However, absent from the spin wave interpretation of the results was the notion that a quasi-elastic peak should be present, corresponding to the relaxation of short range ordered regions.

In the quasi 2D-Heisenberg model [22] with strong intraplanar coupling $J$ and very weak coupling $J_\perp$ perpendicular to the CuO$_2$ planes, there exists a temperature region $k_B T_N < k_B T < J$ with pronounced short range order effects. Unlike 3D systems where long range order ensues below a temperature of order $J$ the exchange energy, the 2D system does not order at all above $T = 0$. However the correlation length $\xi_{2D}$ increases exponentially fast as $T \to 0$ according to

$$\xi_{2D} = \exp\left(\frac{\alpha J}{k_B T}\right)$$  \hspace{1cm} (1.7)\]

where $\alpha$ is a factor of order unity. In crude terms, 3D order sets in at $T_N$ for
\[ k_B T_N = \xi_{2D}^2 \left( T_N \right) \cdot J_\perp \]  

which for a ratio \( J_{\perp}/J \sim 10^{-5} \), as predicted by Chakravarty et al. [22], can lead to high transition temperatures by virtue of the exponential rise. The exponential form of \( \xi_{2D} \) for \( T > T_N \) also has consequences for the intensity distribution of the magnetic correlation function (spoken about in the next chapter) such that a strong quasi-elastic peak corresponding to the relaxation of the short range ordered regions, should be observed [23]. This quasi-elastic peak was absent from both the spin wave experiment and spin wave interpretation of results. The definition of \( \xi \) can then be obtained in terms of the properties of this quasi elastic peak with its width in \( \kappa \) yielding \( \xi^{-1} \) and its width in \( \omega \) yielding the inverse relaxation time \( \tau \), which should also scale with \( \xi \). An accurate derivation of the width, \( \Gamma_c \), by Grempel [23], based upon mode-mode coupling theory yields

\[ \hbar \Gamma_c = \frac{1.36}{\xi} \left( \frac{0.86}{a} \frac{\hbar c}{k_B T} \right)^{1/2} \]  

where \( a \) is the lattice constant. In order to obtain a precise numerical estimate of the quasi-elastic width, the prefactor to (1.7) as determined from renormalised calculations [22] must be known:

\[ \xi = 0.5 \alpha \exp \left( \frac{2\pi \rho_s}{k_B T} \right) \]  

where \( \rho_s \) is the spin wave stiffness constant. By fitting to static properties, \( 2\pi \rho_s = 1175K \), the following relation for the 2D Heisenberg antiferromagnet with spin \( \frac{1}{2} \) was obtained

\[ 2\pi \rho_s = 0.576 \frac{\hbar c}{a} \]
from which a theoretical prediction for the quasi-elastic width of $\hbar\Gamma_c \sim 3\text{meV}$ was obtained for $T = 300\text{K}$. Confirmation of the existence of a quasi-elastic peak came from the neutron scattering study, carried out by Schärpf et al. [24], of magnetic excitations in pure $\text{La}_2\text{CuO}_4$ in the low energy region up to $12\text{meV}$. The measurements, carried out at room temperature (near $T_N$), concentrated on the low energy region where spin wave behaviour should go over into a strong quasi-elastic peak. Figure 1.5 shows the observed intensity integrated over $\kappa$ as a function of $\omega$. Also indicated are two fits in the form of a Lorentzian (solid line) and a curve $\sim \omega^{-1}$ (dashed line). The latter interprets the observed fluctuations as belonging to propagating spin waves - oscillations within short range order regions - for which a far stronger quasi-elastic peak than observed would be required. The Lorentzian $\sim (\omega^2 + \Gamma^2)^{-1}$ however, which identifies the observed fluctuations as the signature for the short range ordered regions themselves, (and which relax on the time scale $\Gamma^{-1}$) provides a good fit to the data with a width of $\hbar\Gamma = 4.0 \pm 0.3\text{meV}$. This is in accord with the theoretical prediction of $3\text{meV}$ if one acknowledges that the temperature range being considered is outside the asymptotic region for which the theories were developed. Thus the observed fluctuations represent the quasi-

---

**Fig. 1.5** Experimentally observed scattered intensity as a function of $\omega$ for $\text{La}_2\text{CuO}_4$ in the low energy region between 0 and $12\text{meV}$ [24]. The solid line represents a Lorentzian fit (quasi-elastic peak) and the dashed line a $\omega^{-1}$ fit (spin waves).
elastic peak and do not constitute propagating spin waves. In the paper by Capellmann et al. [25], the spin dynamics of the 2D spin $1/2$ Heisenberg model is studied in the frequency region $\omega < T < J$, with the main conclusion that the spin fluctuations have relaxational character and that no spin waves propagate for $\omega < T$. In doing so, they consider the impacts of 'propagating spin wave behaviour' and 'relaxational behaviour' on the imaginary part of the dynamic susceptibility $\chi''(k,\omega)$ and impose a sum rule on the related spin-spin correlation function (see 2.4.3). For propagating spin waves at $T = 0$, $\chi''(k,\omega)$ has $\delta$-function peaks which become of finite width at finite $T$ due to damping. Spin wave behaviour is then defined by a) $\chi''(k,\omega)$ having a small width in $\omega$ compared to the frequency on which the peak is centred, for fixed $k$, and b) the integral over $\omega$ of $\chi''(k,\omega)$ should be of the order of the spin wave form factor. Relaxational behaviour on the other hand is characterised by $\chi''(k,\omega)$ being peaked at $\omega = 0$, for constant $k$, decreasing for increasing $\omega$ with a characteristic width $\Gamma_c$. In the work by Tyc and Halperin [26] the temperature variation of the cutoff wavevector $k_c$, which separates the quasi-elastic and propagating spin wave regions, is assumed to be $k_c \sim \xi^{-1}$ for which the damping rate for spin waves is found to be finite but small enough for spin waves to be still well defined for energies small compared to thermal energies $k_B T$. However, such an assumption for $k_c$ is found to be inconsistent with the fulfilment of the sum rule. Instead, for low temperature, the temperature variation $k_c$ is shown to be [25]:

$$k_c = 0.481 \cdot \frac{2T}{c}$$

(1.12)

So the crossover from relaxational to spin propagating behaviour occurs at energies of order $T$ in accord with the absence of spin waves at low energies as observed in [24].

Of the various models proposed for high $T_c$ superconductivity, the 'Nearly Antiferromagnetic Fermi Liquid' theory of Millis et al. [27] discusses the
dynamic susceptibility. Their phenomenological model interpreted the spin system of the high T_c CuO_2 superconductors as consisting of disordered but antiferromagnetically correlated Cu spins in an attempt to explain NMR, NQR and Knight shift measurements revealing differing temperature dependencies of the Cu and O relaxation rates (oxygen having a Korringa T dependence). The model assumes that low frequency spin dynamics in the CuO_2 planes can be described in terms of one S = \frac{1}{2} electronic spin degree of freedom per plane and that it is this which is responsible for spin lattice relaxation and Knight shifts for the planar ^{63}\text{Cu} and ^{17}\text{O} nuclei and for the ^{89}\text{Y} nuclei. Assuming that spins are centred on the Cu sites and are antiferromagnetically correlated (with correlations that increase with decreasing temperature), the spin dynamics are described in terms of the dynamic susceptibility, for \omega \to 0, as

\chi''(\kappa, \omega \to 0) = \frac{\pi \chi_0(\omega)}{\Gamma} \left(1 + \beta \frac{(\frac{\xi}{\alpha})^4}{(1 + \frac{\xi}{\alpha} \kappa)^2}\right)

where \chi_0 is the uniform susceptibility, \xi is the spin correlation length, \Gamma is a characteristic energy of spin fluctuations, \alpha is the lattice parameter and \beta is a parameter. The conclusion reached is that the Cu spin density of states must be enhanced most strongly at some particular point of the Brillouin zone, namely near the zone corner \left(\frac{\pi}{2}, \frac{\pi}{2}\right). The characteristic energy for a zone corner spin fluctuation in their mean-field formalism is then given by:

\hbar \omega_{SF} = \hbar \Gamma \frac{\xi^2}{\alpha^2}

The theory predicts that the enhancement of the dynamic susceptibility about the zone corner should be observable via neutron scattering techniques, with an estimated spin fluctuation energy scale at T = 100K of \hbar \omega_{SF} \sim 20\text{meV}. An inherent difficulty in performing neutron scattering experiments on the cuprates is the attainment of sufficiently large crystals coupled with doubts
concerning sample homogeneity. Many of the neutron investigations which require large crystals and which have reported the coexistence of spin fluctuations with superconductivity have focussed on compositions close to the magnetic phase boundary at \( x \sim 0.5 \) [28, 29, 30, 31]. A spin polarised neutron investigation on optimally doped \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) (\( T_c \sim 90\text{K} \)) in its normal state detected no magnetic scattering up to an energy range of 25meV [32]. In summary therefore, while the existence of dynamic magnetic correlations in low-\( x \) samples of \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) is undisputed, the persistence of this behaviour in superconducting samples is not yet clarified. The spin polarised neutron study detailed in this thesis seeks to experimentally determine the nature of the magnetic excitations in both insulating and superconducting [33] compositions of \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \).

### 1.4 Lattice Distortions due to a Flux Line Lattice in Niobium

The first clue as to the involvement of nuclear lattice distortions (and in particular phonons) in the superconducting mechanism came from the discovery of the isotope effect [6] in which the superconducting transition temperature was found to depend on the isotopic mass of the material in the same way as the Debye frequency \( \omega_D \). Already in 1950, Fröhlich and others had shown that an electron-phonon interaction leads to an attractive interaction between those electrons with energies within a characteristic phonon energy \( \hbar \omega_D \) of the Fermi surface. The confirmation of nuclear lattice distortions provided the means by which such an interaction could be mediated. Based on the ideas of Fröhlich et al., Cooper, in 1956 [34], considered a non-interacting Fermi gas at 0K, so all the states are filled for \( k \leq k_F \) (\( k_F \) = wave vector on surface of Fermi sphere). If two electrons are added, which occupy states with \( k \geq k_F \) due to the Pauli exclusion principle, he showed that for electron energies near the Fermi energy \( E_F \), the net interaction potential between them is attractive and a bound pair of electrons can form.
Cooper pairing:

The bare interaction between two electrons can be described in terms of Coulomb's law in which the repulsive potential strength $V_k$ for scattering a pair of electrons with momentum transfer $k$ is given by

$$V_k = \frac{4\pi e^2}{k^2} \quad (1.15)$$

where $e$ is the electron charge. In order to extend this to the case of a solid, the effect of screening by the rest of the electrons/ions can be approximated according to the Thomas Fermi model to yield an interaction potential of the form

$$V_k = \frac{4\pi e^2}{k^2 + \kappa_T^2} \quad (1.16)$$

where $\kappa_T$ is the reciprocal of the characteristic screening length. In addition to this repulsive interaction potential, an attractive part, necessary in order for a bound state to be produced, arises when one takes into account the dynamics of the system. The lattice distortion which occurs due to the presence of an electron, takes a finite time to relax and can therefore influence a second electron passing at a later time. Consideration of this effect yields the following approximate form for the electron-electron interaction potential [35]

$$V(k, \omega) = \frac{4\pi e^2}{k^2 + \kappa_T^2} \left[ 1 + \frac{\omega_k^2}{\omega^2 - \omega_k^2} \right] \quad (1.17)$$

where $\omega_k$ is the phonon frequency at the wave vector $k$. The attractive part manifests itself in the phonon mediated second term which for low frequencies dominates the interaction potential. In a three-dimensional, two
electron system, (1.17) is typically too weak to yield a bound state however, Cooper's formalism involved the consideration of an N electron system in which he showed that, regardless of the net attractive potential strength, the ground state of an electron gas is unstable to the formation of bound pairs. The following formalism is taken from ref. [35].

For two electrons, in states just above the Fermi level, between which the interaction is attractive, the bound state is expected to have even spatial symmetry. Therefore the spin state must be an antisymmetric singlet with $S^2 = 0$ in order to satisfy the Pauli exclusion principle. The spatial part of the wavefunction may be written as

$$\Psi(r_1, r_2) = \frac{1}{V} \sum_{k_1, k_2} a_{k_1 k_2} \exp i(k_1 \cdot r_1 + k_2 \cdot r_2)$$

$$= \frac{1}{V} \sum_{k, k'} a_k \exp i(k \cdot r + K \cdot R)$$

(1.18)

where $r_1, r_2, k_1$ and $k_2$ are the positions and wave vectors respectively of the two electrons, $V$ is the normalisation volume and $K$ and $R$ are the centre of mass co-ordinates. The last two variables are not involved in the interaction potential and are therefore dropped for the remainder of the discussion. The Schrödinger equation for the wavefunction (1.18) is then

$$\left( -\frac{\hbar^2 \nabla^2}{\mu} + V(r) - E \right) \frac{1}{V} \sum_k a_k \exp i(k \cdot r) = 0$$

(1.19)

where for the moment, no conditions are placed on the interaction potential. Multiplying by $\exp(-i k' \cdot r)$ and integrating yields

$$(2E_k - E) a_k + \frac{1}{V} \sum_k a_k \int \exp i[(k - k') \cdot r] V(r) dr = 0$$

(1.20)

or
where the energies have been written in terms of the original one-electron energies $E_k$. In order to solve this analytically Cooper assumed that the electron-electron interaction potential, $V_{kk'}$, takes a $k$ independent value for $k$ states within a cut-off energy $\hbar\omega_D$ of $E_F$ and is zero for electron energies outside the range $E_F \pm \hbar\omega_D$, i.e.

$$V_{kk'} = \frac{-F}{V} \text{ for } E_F < E < E_F + \hbar\omega_D$$
$$= 0 \quad \text{for } E > E_F + \hbar\omega_D$$  \hspace{1cm} (1.22)

from which can be obtained

$$a_{k'} = F \frac{\sum_k a_k}{(2E_k - E)}$$  \hspace{1cm} (1.23)

Summing over $k'$, the coefficients $a_k$ cancel and the following eigenvalue equation is obtained

$$1 = \sum_k \frac{F}{(2E_k - E)}$$
$$= FN_F \int_{E_F}^{E_F + \hbar\omega_D} \frac{dE_k}{(2E_k - E)}$$  \hspace{1cm} (1.24)

where it has been assumed that the density of states $N_F$ at the Fermi level (for one spin state) is constant over the range of phonon energies $\hbar\omega_D$. Integrating yields
where $E_k$ is the centre of mass kinetic energy. In the weak coupling limit where $FNF \ll 1$ (implying a weak interaction potential), one obtains

\[ E = 2E_F + E_k - \Delta \] (1.26)

where the energy gap $\Delta$ is given by

\[ \Delta = 2\hbar \omega_0 \exp\left[\frac{-1}{FN_F}\right] \] (1.27)

Thus for two electrons interacting with a weak attraction in the presence of a Fermi sea, there exists a bound state lying below $2E_F$ even if both electrons are restricted to having momenta outside the Fermi sphere. The lowest energy state corresponds to a bound state of opposite spin - opposite momenta electrons which is known as the Cooper pair.

The solution as to how a bound pair of electrons can move through a lattice without scatter (i.e. superconductivity) was provided by Bardeen, Cooper and Schrieffer in 1957 [7]. The direction for their microscopic theory owed much to the existence of the Cooper pair and indeed incorporated the assumption of a weak net attractive interaction via the electron-phonon interaction, as given in (1.22). The BCS theory in essence is a many-body generalisation of the Cooper pair in which the ground state wavefunction is an antisymmetrised product of pair wavefunctions, where each pair wavefunction has a total crystal momentum of zero and a total spin of zero. Since the electrons are highly correlated, the scattering of a Cooper pair involves disturbing many more electrons than just the two which form the pair and it turns out that making a transition from one N-electron state to another is extremely unlikely.
Hence the Cooper pair can move through the system without resistance. Despite the approximations involved in the BCS theory it can, based on the net attractive interaction between electrons close to the Fermi energy, account for a large number of experimental details of the so called 'conventional' superconductors. Some of the important results of the theory are:

- there is a second order phase transition to a new electron state at a critical temperature $T_C$ expressed as

$$k_B T_C = 1.13 \hbar \omega_d \exp\left(-\frac{1}{\sqrt{F_N}}\right)$$  \hspace{1cm} (1.28)

which is in agreement with the observed isotope effect since the Debye frequency is inversely proportional to the square root of the mass (for a simple metal).

- there is an energy gap in the one electron spectrum, which at zero temperature is given by (1.27) and decreases with increasing temperature, approaching zero as $T \rightarrow T_C$. Near the transition temperature the theory yields

$$\Delta(T) = 1.74 \Delta(0) \left[1 - \frac{T}{T_C}\right]^{\frac{1}{2}}$$  \hspace{1cm} (1.29)

- the critical magnetic field, above which superconductivity is quenched, approaches zero continuously as the transition temperature is approached from below in a way described by (1.2).

- at low temperatures, the electronic term of the specific heat in the superconducting state $C_S$ is not linear but is instead described by
which is characteristic of a system which possesses an energy gap in the excitation spectrum. As a result of this, there is a discontinuity in the specific heat at the transition temperature between the normal and superconducting states given by:

\[
\frac{C_s - C_N}{C_N} = 1.43
\]

In addition to being responsible for the pairing of electrons into Cooper pairs, the lattice itself is able to react to the changes within the electronic subsystem. By virtue of the fact that only those electrons which are close to the Fermi energy, and within an energy window determined by \( \hbar \omega_D \), are involved in superconductivity, changes in the electronic system and therefore also the response of the nuclear lattice is expected to be small. Accompanying the normal to superconducting transition is a small volume change between the respective states which arises because of the contribution of the electrons near the Fermi level to the sample cohesion. This volume difference is small, amounting to \((V_N - V_S)/V_S = 10^{-5}\) to \(10^{-7}\) and it is therefore an experimental challenge to determine the existence and magnitude of such lattice distortions. Thermal expansion measurements enable the volumes of homogeneous samples in the completely superconducting (zero applied field) and normal states to be compared, however such a volume discrepancy should also be present in the mixed state of a type II superconductor for which superconducting and normal parts coexist in the form of a flux line lattice. In order to experimentally verify the existence and magnitude of lattice distortions in the Shubnikov phase of a type II superconductor, a neutron scattering experiment employing spin-polarised neutrons in conjunction with a small angle scattering set-up has been performed in the mixed state of the elemental type II material niobium. The experimental means by which the investigation was carried out is
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described in 4.4 and the corresponding results are presented and discussed in chapter 8.

1.4.1 Two Types of Superconductor

As early as 1935 [3], an understanding of the expulsion of magnetic flux (the Meissner effect) from superconducting elements had been provided in terms of a characteristic length scale $\lambda_L$ (1.1) over which the magnetic field exponentially decays from the superconductor surface. Measurements conducted by Pippard in 1953 showed that this penetration depth in alloys was very sensitive to the amount of alloying and therefore, he deduced, also to the electron mean free path $\ell$. Pippard argued that besides the penetration depth, there is a second length scale associated with the superconducting state which characterises the size of the Cooper pair. Assuming that only electrons within $k_B T_C$ of $E_F$ (i.e. in the momentum range $\Delta p \sim k_B T_C / v_F$) are important in superconductivity, this intrinsic ‘coherence’ length $\xi_0$, from the uncertainty principle $\Delta x \sim \hbar / \Delta p$, can be expressed as

$$\xi_0 = \alpha \frac{\hbar v_F}{k_B T_C}$$  \hspace{1cm} (1.32)

where $v_F$ is the Fermi velocity and $\alpha$ is a coefficient taking a BCS value of 0.18. However in the presence of impurity scattering, the electron mean free path becomes important leading to an effective coherence length $\xi$ related by

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{\ell}$$  \hspace{1cm} (1.33)

The relative sizes of the two characteristic length scales distinguishes two types of superconductor, reflected in the way in which they behave under an applied magnetic field. If one considers going from a normal-superconductor interface into the superconductor, then the system will gain condensation
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Fig. 1.6a) Magnetisation versus applied field for a bulk superconductor exhibiting the full Meissner effect (type I). b) Magnetisation curve for a type II superconductor indicating the partial penetration of flux in a field region $H_{C1} < H < H_{C2}$.

energy on a length scale $\xi$ while at the same time losing magnetic energy on a length scale $\lambda_L$. Type I or 'pure' superconductors are characterised by $\xi \gg \lambda_L$, for which there is an energy maximum at the interface. These materials favour a homogeneous phase and exhibit a full Meissner effect for $B < B_C$. For $\xi \ll \lambda_L$, there is an energy minimum at the interface characteristic of the type II or 'dirty' superconductors. Under an applied field, these materials behave in a qualitatively different manner to type I superconductors, exhibiting a mixed or Shubnikov phase above a lower critical field $B_{C1}$, in which magnetic flux is only partially expelled while the material remains superconducting. Below $B_{C1}$, a full Meissner effect is exhibited while above an upper critical field $B_{C2}$, the superconducting state is destroyed. Figures 1.6a) and b) show schematic magnetisation curves for type I and type II materials respectively. In both cases a cylindrical specimen in a longitudinal applied field is assumed.

1.4.2 The Ginsburg-Landau Equations

The Ginsburg-Landau (GL) theory of superconductivity preceded the BCS
theory by seven years, providing a phenomenological description of many experimental facts at that time. Near $T_c$, the GL theory can be considered as a limiting form of the BCS theory and indeed the complex order parameter, $\Psi$, which it introduces, can be considered as the wavefunction of the centre of mass of a Cooper pair. The starting point of the theory comes from the following postulates [36]:

- The superconductor is characterised by a complex order parameter of the form $\Psi(r) = \eta(r) \exp(i\phi(r))$ and a vector potential $A(r)$ where the magnetic induction $B = \nabla \times A$.

- Gauge invariance in the sense of quantum mechanics is postulated. The coupling charge is $q$.

- The free energy density $f(r)$ is assumed to be a regular function of $\Psi$, the gauge invariant gradient and $B$. The equilibrium value of $\Psi$ is the one which minimises $F = \int dr f(r)$.

- Maxwell's theory of electrodynamics is assumed to hold.

Under these assumptions, the free energy density in the presence of magnetic fields and spatial gradients can be expanded as follows

$$f(r) - f_N(r) = \alpha |\Psi(r)|^2 + \frac{b}{2} |\Psi(r)|^4 + \frac{\hbar^2}{2m} \left| \nabla - \frac{iq}{\hbar c} A(r) \right| \Psi(r) \right|^2 + \frac{1}{8\pi} B^2(r)$$

(1.34)

where $a = \alpha(T - T_c)$, $f_N$ is the normal state free energy density and $T_c$, $\alpha$, $b$, $m$ and $q$ are the parameters of the theory. The GL equations can be obtained by taking the derivatives of the free energy difference (1.34) with respect to $\Psi$, $\Psi^*$ and $A$, yielding:
\[-\frac{\hbar^2}{2m} \left[ \nabla - \frac{iq}{\hbar c} \mathbf{A}(r) \right]^2 \Psi(r) + a|\Psi(r)|^2 \Psi(r) + b|\Psi(r)|^2 \Psi(r) = 0 \]  
(1.35)

\[ \nabla^2 \times \mathbf{B}(r) = \frac{4\pi}{c} j(r) \]  
(1.36a)

\[ j(r) = -i \frac{\hbar q}{2m} \left[ \Psi \cdot \nabla \Psi - \Psi \nabla \Psi^* \right] - \frac{q^2}{mc} |\Psi|^2 \mathbf{A} \]  
(1.36b)

\[ j(r) = \frac{\hbar q}{m} |\Psi|^2 \left[ \nabla \phi - \frac{q}{\hbar c} \mathbf{A} \right] \]  
(1.36c)

where \( j \) is the current density.

**The Ginsburg-Landau parameter:**

Using the GL formalism, the two, temperature dependent, characteristic length scales of the superconducting state could be derived. For a homogeneous superconductor without a magnetic field, the solution of (1.35) is \( |\Psi|^2 = -(a / b)(T - T_c) \) and in a weak magnetic field it can be shown from (1.36), that the following is true:

\[ \left[ \nabla^2 - \frac{4\pi q^2}{mc^2} |\Psi|^2 \right] \mathbf{B}(r) = 0 \]  
(1.37)

Using the zero field expression for \( \Psi \), one obtains the temperature dependent penetration depth \( \lambda(T) \) in accordance with the Meissner effect

\[ \lambda(T) = \left( \frac{mc^2 b}{4\pi q^3 \alpha} \right)^{\frac{1}{2}} (T_c - T)^{-\frac{1}{2}} \]  
(1.38)

In order to express the temperature dependence of the coherence length, one must look at fluctuations of \( \Psi \) in zero field. If \( \Psi \) is written as \( \Psi(r) = \eta + \delta \eta(r) \) and (1.35) is linearised in the small quantity \( \delta \eta \) then one obtains
where for $T < T_c$

$$\xi(T) = \frac{h}{(4\pi\alpha)^{\frac{3}{2}}}(T_c - T)^{-\frac{1}{2}}$$ (1.40)

The temperature independent GL parameter $\kappa$ is then defined as the ratio of these two length scales:

$$\kappa = \frac{\lambda(T)}{\xi(T)} = \frac{q\sqrt{2}}{hc} \lambda^2(T) B_c(T)$$ (1.41)

the value of which directly determines the thermodynamic state of a system. For a normal-superconducting interface, the crossover from a positive (type I) to a negative (type II) surface energy occurs for $\kappa = 1/\sqrt{2}$. It can be shown that for $\kappa > 1/\sqrt{2}$, in the type II regime, the lower and upper critical fields are respectively given by

$$B_{c1} = \frac{B_c}{\sqrt{2}\kappa} \text{ and } B_{c2} = \sqrt{2}\kappa B_c$$ (1.42a, b)

where $B_c$ is the thermodynamic critical field defined by the magnetic energy being equal to the free energy difference between the normal and superconducting states.

**Flux quantisation:**

The idea that magnetic flux penetrates a superconductor in quantised units was recognised early on by London. The condition can be obtained using the GL theory if one integrates the current density as given in (1.36c) over a closed path $\Gamma$ such that

$$[\nabla^2 - \xi^{-2}(T)]\delta\eta(r) = 0$$ (1.39)
where the condition that the wavefunction must be single valued has been used. Applying Stokes' law and using $\nabla \times \mathbf{A} = \mathbf{B}$ one obtains

$$\Phi' = \Phi + \frac{4\pi}{c} \oint d\mathbf{l} \cdot \mathbf{B} = n\Phi_0$$

(1.44)

where $\Phi$ is the flux through the surface surrounded by $l$, $\lambda$ is the penetration depth and $\Phi_0 = \frac{hc}{q}$ is called the flux quantum. For a closed loop deep inside a superconductor, $\mathbf{B} = 0$ such that $\Phi = \Phi'$, and flux quantisation holds. The charge $q$ has been shown experimentally to be $2e$ in accordance with Cooper pairs.

1.4.3 The Flux Line Lattice

The full implications of the $\kappa > 1/\sqrt{2}$ regime were only realised with the work of Abrikosov in 1957 [5], in which he predicted the existence of a mixed state consisting of normal and superconducting regions in the form of vortices. For this regime, the surface energy between normal and superconducting phases becomes negative, causing the normal state, flux bearing regions to subdivide until a mixed state of basic unit, the flux vortex, is reached. The vortex substructure can be visualised as consisting of a cylindrical core region where the superconducting order parameter rises from zero to unity over the coherence length $\xi$. Surrounding this core is a larger region, again cylindrical, in which the supercurrent circulates. It can be shown, for $\log \kappa \gg 1$ [36], that the vortex energy per unit length is given by
from which one can see that a vortex containing $n$ flux quanta has a higher energy than $n$ vortices containing one flux quantum only. It is therefore expected that each vortex contains just one quantum of flux only.

Using this idea of flux tubes, the mixed state in an applied field $B$ may be visualised. For low magnetic fields, the self-energy of an isolated vortex is greater than the reduction in field energy which would occur if a flux quantum entered the superconductor and the full Meissner effect is exhibited. Above a critical field $B_{C1}$, this self energy criterion is just satisfied and flux begins to penetrate the superconductor parallel to the applied field. The density of vortices for fields $> B_{C1}$ is determined by the interaction forces which arise between them and for an increase in applied field, the vortices approach each other - in a sense 'compressed' by the external field against their interaction forces. At a higher critical field $B_{C2}$, the vortex cores actually touch and overlap causing the superconducting order parameter to be zero everywhere with consequent destruction of superconductivity.

**The flux line lattice in niobium:**

Pure, defect free niobium constitutes the elemental superconductor with the highest transition temperature ($T_C=9.2$K) and has a GL parameter $\kappa = 0.77$, just slightly greater than the minimum value for type II behaviour. Correspondingly, it has upper and lower critical fields of $405$mT and $173$mT respectively. The first experimental observation of the flux line lattice in type II superconductors was carried out using decoration techniques [37] which confirmed the triangular arrangement of the FLL. Neutron diffraction, as a means of investigating the periodic magnetisation density which the FLL constitutes, was first suggested by de Gennes and Matricon [38] with the immediate advantage over other techniques of probing the bulk as opposed to just the surface of the superconductor. Subsequently, Cribier et al. [39] in
1964, provided the first neutron scattering observation of the FLL in niobium, again confirming the triangular arrangement of the vortex lattice. This led to more detailed work on niobium using neutron techniques, concerning in particular the motion of flux lines [40]. In the study by Christen et al. [41], a small angle neutron scattering experiment was performed on a niobium single crystal, in its mixed state, with its <111> axis parallel to the applied field. The expected hexagonal symmetry of the (10)-type Bragg reflections was confirmed and the internal magnetic field $B$ related to the real space lattice constant $a$ for a triangular lattice by

$$
\Phi_0 = \frac{\sqrt{3}Ba^2}{2}
$$

(1.46)

where $\Phi_0$, the flux quantum, equals $2.068 \times 10^{15}$Tm$^2$. In reciprocal space, the corresponding lattice is also triangular, with a lattice parameter $a^*$ given by

$$
a^* = \frac{4\pi}{\sqrt{3}a}
$$

(1.47)

hence the position in reciprocal space of the (10) reflection, which occurs at a momentum transfer $\kappa_{10} = a^*$, is

$$
\kappa_{10} = 2\pi \frac{\sqrt{2B}}{\sqrt{3}\Phi_0}
$$

(1.48)

In addition to extensive investigations of the FLL lattice in niobium, studies have been extended to the anisotropic FLL in high $T_c$ materials [42, 43] with particular focus on the possible melting of the FLL due to thermal fluctuations. The observation of the melting transition in the high $T_c$ superconductors is, however, made difficult using neutrons by their inherently large penetration depth which has a detrimental affect on the scattered intensity. It should be noted that all of these investigations have used unpolarised neutrons. A progress review in the study of the flux line lattice can be found in ref. [44].
1.4.4 Volume Changes at the Superconducting Phase Transition

The volume anomaly which exists between the normal and superconducting states is related via thermodynamic identities to other measurable entities. In order to know about a system thermodynamically, a function encompassing the independent variables of the system must be determined - the Gibbs function - knowledge of which enables the question of the stability of a phase to be addressed. For a system in which both temperature and pressure are variables, the Gibbs function $G$ is given by

$$G = U - TS + pV$$  \hspace{1cm} (1.49)

where $U$ is the internal energy, $T$ the temperature, $S$ the entropy, $p$ the pressure and $V$ the volume. For the case of a type I superconductor, the presence of an external field $> B_c$ will destroy the superconducting state. Consequently, in describing its thermodynamic state, the effect of a magnetic field must be accounted for by the inclusion of $\bar{B}$ as an independent variable in the Gibbs function

$$G = U - TS + pV - \bar{m} \cdot \bar{B}$$  \hspace{1cm} (1.50)

where $\bar{m}$ is the magnetic moment. The Gibbs function of the superconducting state relative to the normal state as a function of temperature can then be shown to be

$$G_N(T) - G_S(T) = - \int_0^{\bar{a}_c(T)} \bar{m} \cdot d\bar{B}$$  \hspace{1cm} (1.51)

where for a superconductor in equilibrium, the magnetic moment is antiparallel to the field. For a homogeneous magnetic field and a long thin wire parallel to $\bar{B}$, the moment $\bar{m}$ is related to the homogeneous
magnetisation \( \tilde{M} \) by \( \tilde{m} = \tilde{M}V \) where \( V \) is the sample volume and \( \tilde{M} = \chi \tilde{B} / \mu_0 \). Therefore in the superconducting state where the susceptibility \( \chi = -1 \) (perfect diamagnet), \( m = -V_S B / \mu_0 \) and one obtains

\[
G_N(T) - G_S(T) = V_S \frac{B_c^2}{2\mu_0} \tag{1.52}
\]

where \( V_S \) is the volume of the superconducting state. Evaluating the pressure derivative of (1.52) at constant temperature and constant field, and using \( \left( \frac{\partial \phi}{\partial \rho} \right)_{T, B} = \rho \), one obtains the volume difference at the normal to superconducting transition:

\[
(V_N - V_S)_{B = B_c} = V_S(B_c) \frac{B_c}{\mu_0} \frac{\partial B_c}{\partial \rho} \tag{1.53}
\]

If the variable \( \zeta \) is defined as \( (V_N - V_S)/V_S \) then the change in volume at the superconducting phase transition is determined by the pressure derivative of the critical field according to

\[
\zeta|_{B = B_c} = \frac{\partial}{\partial \rho} \left( \frac{B_c^2}{2\mu_0} \right) = \frac{B_c}{\mu_0} \frac{\partial B_c}{\partial \rho} \tag{1.54}
\]

where the temperature dependence of the critical field is given by (1.2). The above formulation can be extended to the case of type II superconductors if one substitutes in the thermodynamic critical field, defined by the magnetic energy being equal to the free energy difference between the normal and superconducting states. Despite the volume changes which inevitably occur at the critical fields \( B_{c1} \) and \( B_{c2} \), the overall volume anomaly obtained is of similar magnitude to type I materials. For niobium, the experimentally observed length change [45] indicates that the volume of the normal state is smaller than that of the superconducting state. The corresponding volume anomaly at the superconductor phase transition amounts to \( \zeta = -3 \times 10^{-7} \) [46].
The neutron investigation presented in this thesis addresses the question as to how the volume change for a type II material in its mixed state, for which normal and superconducting regions coexist, affects the superconductor. To do so, the lattice distortion associated with the formation of the FLL in the type II material niobium has been studied with the use of spin-polarised neutrons in conjunction with a traditional small angle scattering set-up [47]. The experimental technique employed is described in chapter 4 and the results and discussion can be found in chapter 8. The sample preparation and crystal orientation verification are described in chapter 6.

REFERENCES


CHAPTER 2

FUNDAMENTAL NEUTRON SCATTERING

2.1 Introduction

The discovery of the neutron in 1932 [1], along with the subsequent advances in nuclear physics which saw the advent of nuclear reactors, has provided one of the most important and versatile probes for the study of solids and liquids. Development of the nuclear reactor has meant that neutrons over a wide velocity distribution (as determined by the source moderator) can be produced with a large enough flux such that beams can be collimated and a separation into narrow energy bands can be made. Of particular use, are those neutrons produced in equilibrium with a moderator near room temperature and which are commonly referred to as 'thermal' neutrons.

2.2 Fundamental Properties of the Neutron

The neutron is a chargeless, elementary particle of mass, \( m_n = 1.675 \times 10^{-27} \) kg, spin \( \frac{1}{2} \) and possesses an intrinsic magnetic dipole moment, \( \mu_n \), of \( 1.042 \times 10^{-3} \mu_B \). On account of these properties, the neutron is subject to scattering of magnetic as well as nuclear origin and therefore permits the experimental investigation of both nuclear and magnetic solid state phenomena on an atomic scale.

The velocity spectrum of neutrons produced in thermal equilibrium with the moderator or source block is close to Maxwellian in nature meaning that the flux distribution can be described thus.
where $\varphi(v)dv$ is the number of neutrons emerging per unit area per second with velocities in the range $v$ to $v+dv$, $m_n$ is the neutron mass, $k_B$ is the Boltzmann constant and $T$ is the temperature of the moderator. The Maxwellian spectrum as described in (2.1) peaks at a velocity

$$v = \left( \frac{3k_BT}{m_n} \right)^{\frac{1}{2}}$$

which, for neutrons emerging at $T=293K$, corresponds to a de Broglie wavelength, $\lambda$, of 1.789Å and an energy, $E$, of 25.3meV. Figure 2.1 shows curves of the velocity distribution for cold ($T=25K$), thermal ($T=300K$) and hot ($T=2000K$) neutrons, normalised to the same area and Table 2.1, which provides a summary of some numerical values associated with the neutron, gives approximate ranges of energy, temperature and wavelength for thermal neutrons.

The fact that the wavelength of thermal neutrons is of the same order of magnitude as typical interatomic distances found in condensed matter means that, for a periodic lattice, an interference effect in compliance with Bragg's law (2.3) can occur, yielding structural information on the scattering system:

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

Here $m$ is a positive integer, $d_{hkl}$ is the spacing between successive planes identified by the Miller indices $(hkl)$ and $\theta$ is the angle of reflection measured from the plane.

Furthermore, the energy of neutrons in the thermal regime typically lies in the range of thermally accessible fluctuations (for both nuclear and magnetic excitations) found in solids and liquids. Consequently, via inelastic processes,
dynamic characteristics of a scattering system (e.g. phonons, spin waves) can be probed.

On account of the neutron carrying zero charge, in penetrating its target, no Coulomb barrier is encountered and the interaction with matter is weak. Consequently the neutron comes close to its target nuclei thus confining information on the nuclear degrees of freedom to the strong nuclear interaction. This is unlike the case of X-rays where the scattering is restricted to an electromagnetic interaction with the electrons of the target nuclei. As a result, while the X-ray atomic scattering factors are proportional to the atomic number, $Z$, of the target nuclei, the neutron scattering amplitude, although different for individual isotopes, does not vary as a systematic function of $Z$. An important case where this differing dependence is highlighted is that of light hydrogen of which, although an appreciable scatterer of neutrons, is

![Fig. 2.1 Velocity flux distribution for neutrons as described by (2.1) at $T=25K, 300K$ and $2000K$.][2]
virtually invisible to X-rays. The weak nature of the interaction between the neutron and matter provides a further advantage over X-rays in that the comparative absorption is small. As a result, the bulk of the target sample as opposed to merely the surface is probed and corrections to the observed intensities are minimised.

The second scattering source of the neutron arises on account of its intrinsic magnetic dipole moment. In the case of a magnetic scattering system an electromagnetic interaction between the magnetic moment of the neutron and that of the target nuclei (mediated by the presence of unpaired electrons) occurs, giving rise to scattering additional to that of nuclear origin. This latter effect renders neutron scattering an indispensable tool in its unique ability to study both the static and dynamic characteristics of the magnetic sub-system.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol and Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$m_n = 939.565 \text{ MeV}$</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td>$= 1.675 \times 10^{-27} \text{ Kg}$</td>
<td></td>
</tr>
<tr>
<td>Electric charge</td>
<td>$Q_n = (4.3 \pm 7.1) \times 10^{-20} \text{ e}$</td>
<td>[4]</td>
</tr>
<tr>
<td>Spin</td>
<td>$s = \frac{1}{2}$</td>
<td>[5]</td>
</tr>
<tr>
<td>Magnetic dipole moment</td>
<td>$\mu_n = -1.913 \mu_N$ ; $\mu_N = 5.05 \times 10^{-27} \text{ J/T}$</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>$= -1.042 \times 10^{-3} \mu_B$ ; $\mu_B = 9.27 \times 10^{-26} \text{ J/T}$</td>
<td></td>
</tr>
<tr>
<td>Electric dipole moment</td>
<td>$d_n = -(3 \pm 5) \times 10^{-26} \text{ e cm}$</td>
<td>[7]</td>
</tr>
<tr>
<td>Polarisability</td>
<td>$\alpha_n = (1.2 \pm 1.0) \times 10^{-3} \text{ fm}^3$</td>
<td>[8]</td>
</tr>
<tr>
<td>Half-life</td>
<td>$T_{1/2} = 10.254 \pm 0.035 \text{ mins}$</td>
<td>[9]</td>
</tr>
<tr>
<td>Temperature</td>
<td>$60K \leq T \leq 1000K$</td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>$5 \text{meV} \leq E \leq 100 \text{meV}$</td>
<td></td>
</tr>
<tr>
<td>Wavelength</td>
<td>$4\text{Å} \geq \lambda \geq 1\text{Å}$</td>
<td></td>
</tr>
</tbody>
</table>

*Table 2.1* Some typical quantities associated with the neutron. The references indicated concern the direct measurement of the values quoted.
nuclear and magnetic sub-systems can be used in order to distinguish between the nuclear and magnetic scattering contributions to the total neutron scattering cross-section. Experimentally this involves studying the manner in which the spin orientation of the incident neutron is changed by the scattering process and is achieved by the technique of spin polarisation analysis. In particular, the ability of the technique to separate paramagnetic and other forms of incoherent scattering means that it lends itself well for the purposes of this present work. A full discussion of the underlying principles of spin polarisation analysis is given in the following chapter.

### 2.3 The Interaction Between Neutrons and Atoms

A neutron impinging upon its target will be characterised by an energy, \( E \), and wave vector, \( k \), related by the following

\[
E = \frac{\hbar^2 k^2}{2m_n} \tag{2.4}
\]

where \( k = |k| \).

During a scattering process, both variables are subject to a change such that the detected neutron has energy, \( E' \), and wave vector \( k' \). The implied transfer of energy and momentum between the incident neutron and the target sample is then

\[
E - E' = \hbar \omega = \frac{\hbar^2}{2m_n} (k^2 - k'^2) \tag{2.5a}
\]

and

\[
\hbar \kappa = \hbar k - \hbar k' \tag{2.5b}
\]

respectively, where \( \kappa \), the **scattering vector**, is defined as

\[
\kappa = k - k' \tag{2.6}
\]

The particular case of elastic scattering, where no energy is transferred to the
target sample, is satisfied when the magnitude of the wave vector remains unchanged (i.e. \( k = k' \)) subsequent to the interaction. This scenario will form the basis for obtaining an expression for the fundamental quantity measured in a scattering experiment - the scattering cross-section - and will then be generalised to include inelastic processes. The details which follow, concerning neutron scattering theory, can be found in numerous texts. [2], [10], [11], [12].

2.3.1 The Neutron Scattering Cross-section

A scattering experiment enables a number of types of information on the target system to be extracted, however there is a basic quantity measured in each case known as the scattering cross-section which can be defined in three ways.

The total scattering cross-section \( \sigma \) is defined as the total number of neutrons scattered in all directions per second and is normalised to the flux \( \Phi \) of incident neutrons.

The geometry of the scattering process is depicted in Fig. 2.2, where the solid angle, \( d\Omega \), into which neutrons are scattered is expressed in terms of a polar angle \( \theta \) and an azimuthal angle \( \phi \). According to this configuration, the number of neutrons scattered into the solid angle, \( d\Omega \), with polar co-ordinates \( \theta, \phi \), can be obtained, yielding a corresponding cross-section known as the differential cross-section. This is denoted by

\[
\frac{d\sigma}{d\Omega}
\]

The third definition of the scattering cross-section extracts additional information concerning the energy change of the neutron subsequent to its collision. Energy analysis of the scattered neutrons yields the fraction of neutrons of incident energy \( E \) scattered into an element of solid angle \( d\Omega \) with an energy between \( E' \) and \( E' + dE' \). The corresponding cross-section, known
as the partial differential cross-section, is denoted by

$$\frac{d^2 \sigma}{d\Omega dE}$$

and has the dimension of (area/energy).

The following formulation of an expression for the partial differential cross-section, evolves from the simple scenario of nuclear elastic scattering from a single spinless nucleus to accommodate assemblies of atoms with non-zero spin. This will be extended further to account for the initial and final spin states of the neutron in the discussion of polarisation analysis.

**Scattering from a single spinless nucleus:**

Because the wavelength of the neutron (of the order of $10^{-10}$ m) is much larger than the range of the nuclear force which scatters them (of the order of $1.5 \times 10^{-15}$ m), the resulting wavefunction which describes the state of the
scattered neutron consists only of s-wave ($\ell = 0$) components. i.e. the scattering from a single nucleus is spherically symmetric. An incident neutron, characterised by a wave vector $k$ and described by a plane wavefunction $\psi_k$ of the form $\exp(ikz)$, will be scattered into a state with wavefunction $\psi_{k'} (|k| = |k'|)$ characterised by a parameter, $b$, called the \textit{bound scattering length}. At a distance $r$ from the origin at which the nucleus is assumed fixed (of infinite mass), the scattered wavefunction can be written in the form

$$\Psi_k = \frac{-b}{r} \exp(ikr) \tag{2.7}$$

The total scattering cross-section of the nucleus can then be obtained in terms of the scattering length if one considers the basic definition below [11]

$$\sigma = \frac{\text{outgoing current of scattered neutrons}}{\text{incident neutron flux}}$$

$$= 4\pi r^2 \frac{|(\frac{1}{2})\exp(ikr)|^2}{v\exp(ikz)|^2}$$

$$= 4\pi b^2 \tag{2.8}$$

where $v$ is the neutron velocity.

As previously mentioned, the neutron interacts only very weakly with matter, and does so without distorting the intrinsic properties of the target sample, meaning that the amplitude of a wave scattered from one nucleus is very small at the positions of neighbouring nuclei. This condition allows the total scattering amplitude for an array of nuclei to be treated as the sum of those for the individual nuclei.

\textit{Scattering from an assembly of nuclei:}

During a scattering process, both the neutron and the target system experience a transition in quantum states the probability of which must be
determined in order to obtain an expression for the partial differential cross-section. The state of the neutron can be defined entirely by its wave vector if one ignores the spin such that, upon scattering, the neutron changes from a state \( k \) to a state \( k' \) and the target system from a state \( \lambda \) to a state \( \lambda' \), the initial state of which is described by the wavefunction \( \chi_\lambda \). The configuration of the scattering process is defined such that the number of nuclei in the target system is \( N \) and the positions of the \( j^{th} \) nucleus and the neutron are \( R_j \) (\( j = 1, \ldots, N \)) and \( r \) respectively. The sum of all processes in which the state of the target system changes from \( \lambda \) to \( \lambda' \) and the neutron from \( k \) to \( k' \) for \( k' \) lying in the solid angle \( d\Omega \), can then be represented by the differential cross-section, as defined earlier, thus

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\lambda \rightarrow \lambda'} = \frac{1}{\Phi} \frac{1}{d\Omega} \sum_{k'} W_{k,\lambda \rightarrow k',\lambda'}. \tag{2.9}
\]

where \( W_{k,\lambda \rightarrow k',\lambda'} \) is the probability of a transition from the state \( k, \lambda \) to \( k', \lambda' \) and \( \Phi \) is the flux of incident neutrons. To evaluate \( W_{k,\lambda \rightarrow k',\lambda'} \), a quantum mechanical result based on first order perturbation theory is employed known as Fermi's Golden Rule (derived in [13]). This result, for scattering purposes, is equivalent to the first order Born approximation and is valid on the condition that the incident wavefunction is much larger than the scattered wavefunction. The probability is then given by

\[
\sum_{k'} W_{k,\lambda \rightarrow k',\lambda'} = \frac{2\pi}{\hbar} \rho_k(E) |\langle k' \lambda' | V | k \lambda \rangle|^2 \tag{2.10}
\]

where \( \rho_k(E) \) is the density of final scattering states per unit energy range and \( V \) is the interaction potential giving rise to the transition. The matrix element is given explicitly by

\[
\langle k' \lambda' | V | k \lambda \rangle = \int \psi_k^{*} \chi_{\lambda'} \cdot V \psi_k \chi_{\lambda} \, dR \, dr \tag{2.11}
\]
where \( d\mathbf{R} = d\mathbf{R}_1 \, d\mathbf{R}_2 \ldots \ldots \, d\mathbf{R}_n \), and \( d\mathbf{R}_j \) and \( dr \) are elements of volume for the \( j^{th} \) nucleus and the neutron respectively.

The expression (2.10) differs slightly from the quantum mechanical derivation of the golden rule in that it is evaluated for a particular state \( \mathbf{k}' \) as opposed to being summed over all values of \( |\mathbf{k}| \). The value of \( \mathbf{k}' \) inserted into the right hand side of (2.10) is that corresponding to the centre of the range \( |\mathbf{k}| \) for which the probability of a transition from \( \mathbf{k}, \lambda \) to \( \mathbf{k}', \lambda' \) is not negligible. It is this value which corresponds to the conservation of energy for the overall system of neutron and target nuclei.

One can obtain an expression for the density of final scattering states \( \rho_{\mathbf{k}'}(E) \) provided that the normalisation constant for the neutron wavefunctions is known. This is achieved by confining the neutron and target system to a large box of volume \( L^3 \) say, such that only those neutron states with de Broglie waves periodic to the box dimensions are allowed. Doing so, one obtains for the density of final states

\[
\rho_{\mathbf{k}'}(E) = \left( \frac{L}{2\pi} \right)^3 \frac{m_n k'}{h^2} d\Omega
\]

(2.12)

where \( \left( \frac{2\pi}{L} \right)^3 \) is the unit cell volume of the lattice in phase space.

The incident flux of neutrons impinging upon the overall system can now be expressed as follows

\[
\Phi = \frac{\text{velocity of incident neutrons}}{L^3} = \frac{h k}{m_n L^3}
\]

(2.13)

Combining (2.10), (2.11), (2.12) and (2.13) now enables (2.9) to be evaluated, yielding the differential cross-section as

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\lambda \rightarrow \lambda'} = \frac{k'}{k} \left( \frac{m_n}{2\pi h^2} \right)^2 |\langle \mathbf{k}'\lambda' | \mathbf{V} | \mathbf{k}\lambda \rangle|^2
\]

(2.14)
Chapter 2 Fundamental Neutron Scattering

The interaction potential $V$ at a position $r$ is selected on the basis that, when inserted, it gives the required result of isotropic scattering for a single nucleus. It turns out that in using the Born approximation, the only form of $V(r)$ to do so is a delta function and is defined, for a nucleus at position $R$, by

$$V(r) = \frac{2\pi \hbar^2}{m_n} b \delta (r - R) \quad (2.15)$$

This result is known as the Fermi pseudo-potential.

If $\lambda = \lambda'$ and $k = k'$, as is the case for an elastic process, then for a single nucleus at $R = 0$, (2.14) can be re-written in the form

$$\frac{d\sigma}{d\Omega} = \left( \frac{m_n}{2\pi \hbar^2} \right)^2 \left| \int \exp(-i\mathbf{k}' \cdot r) V(r) \exp(i\mathbf{k} \cdot r) \, dr \right|^2 \quad (2.16)$$

where the substitution of (2.11) has been made. Substituting (2.15) into (2.16) then gives

$$\frac{d\sigma}{d\Omega} = \left( \frac{m_n}{2\pi \hbar^2} \right)^2 \left| \int \frac{2\pi \hbar^2}{m_n} b \exp(-i\mathbf{k}' \cdot r) \delta (r) \exp(i\mathbf{k} \cdot r) \, dr \right|^2 = |b|^2 \quad (2.17)$$

meaning that the total cross-section is

$$\sigma = 4\pi |b|^2 \quad (2.18)$$

hence the isotropic scattering for a single nucleus of (2.8) is recovered.

The scenario can be generalised to consider scattering from a rigid array of $N$ nuclei, with individual scattering lengths where the position vector of the $j^{th}$ nucleus is denoted by $R_j$ and the corresponding scattering length by $b_j$. In this
instance, the differential cross-section is

\[ \frac{d\sigma}{d\Omega} = \left( \frac{m_n}{2\pi \hbar^2} \right)^2 \frac{2\pi h^2}{m_n} \sum_j b_j \left| \int \exp(-i\mathbf{k} \cdot \mathbf{r}) \delta(\mathbf{r} - \mathbf{R}_j) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \right|^2 \]

\[ = \left( \frac{m_n}{2\pi \hbar^2} \right)^2 \frac{2\pi h^2}{m_n} \sum_j b_j \left| \mathbf{k} \cdot \mathbf{R}_j \right|^2 \]

(2.19)

where the Fourier transform of the potential function \( V_j(\mathbf{R}_j) \) has been performed

\[ V_j(\mathbf{k}) = \int V_j(\mathbf{R}_j) \exp(i\mathbf{k} \cdot \mathbf{R}_j) d\mathbf{R}_j \]

(2.20)

Having obtained an expression for the cross-section describing those neutrons scattered into a small solid angle d\( \Omega \) with \( |\mathbf{k}| = |\mathbf{k}'| \) it is now possible to extend the scenario to include inelastic scattering events such that analysis of the energies of scattered neutrons can be performed. In this way, the corresponding partial differential cross-section, as defined earlier, can yield information on the dynamic characteristics of a scattering system.

**The partial differential cross-section for an assembly of nuclei:**

An inelastic scattering event results in the neutron energy \( E \) changing by a finite amount, \( \hbar\omega \), as defined in (2.5). The target system responds to this change with a transition in its quantum state from \( \lambda \) to \( \lambda' \). If \( E \) and \( E' \) are the initial and final energies of the neutron, and \( E_\lambda \) and \( E_{\lambda'} \) are the initial and final energies of the target system with \( k, \lambda \) and \( \lambda' \) fixed then, by the conservation of energy

\[ E + E_\lambda = E' + E_{\lambda'} \]

(2.21)

This condition can be incorporated into the already defined differential
cross-section of (2.14) with the aid of a delta function

\[ \delta (E + E_x - E' - E_{x'}) = \delta \left( \hbar \omega + E_x - E_{x'} \right) \]  

(2.22)

which vanishes unless (2.21) is satisfied. The partial differential cross-section can then be expressed as

\[ \left( \frac{d^2 \sigma}{d\Omega dE} \right)_{\lambda \rightarrow \lambda'} = \frac{k'}{k} \left( \frac{m_n}{2\pi \hbar^2} \right)^2 \left| \langle k' \lambda' \mid V \mid k\lambda \rangle \right|^2 \delta \left( \hbar \omega + E_x - E_{x'} \right) \]  

(2.23)

or, from (2.15), (2.16) and (2.20) as

\[ \left( \frac{d^2 \sigma}{d\Omega dE} \right)_{\lambda \rightarrow \lambda'} = \frac{k'}{k} \sum b_{\lambda} \left| \exp \left( i\mathbf{k} \cdot \mathbf{R}_i \right) \right| \delta \left( \hbar \omega + E_x - E_{x'} \right) \]  

(2.24)

To this point, the neutron scattering cross-section has only been considered for the case of a target system consisting of an array of spinless nuclei of the same isotope. It has therefore been assumed that the scattering length takes the same value \( b \) for all nuclei. The scattering length consists of both a complex and a real part, the latter of which may be positive or negative depending on the energy of the incident neutron and the nucleus involved in the collision. The complex part of \( b \) represents the absorption cross-section of the target nucleus for which the principle process is radiative capture. Breit and Wigner in 1936 [14] formalised the scattering length in terms of potential and resonance scattering, the latter accounting for re-emission and absorption of the neutron by the target nucleus. The potential term arises from the neutron being considered as an impenetrable sphere and always takes a positive value. Although normally small, under certain conditions the resonance term may be both negative and large enough to dominate the potential scattering thus giving a resultant scattering length which is negative (e.g. manganese and titanium).
2.3.2 Coherent and Incoherent Scattering

In practice, a scattering system will consist of isotopic nuclei of varying abundance and spin, and because the scattering length is dependant on both the individual isotope, and the relative orientation of the neutron spin and nuclear spin (if present), it will not take a single value throughout the assembly. Instead, the scattering length assigned to a scattering system corresponds to the weighted average over all the constituent scattering lengths. If the scattering length \( b \) in an elemental target system varies from one nucleus to another as a result of nuclear spin or the presence of isotopes, then each nuclei type \( \xi \) can be assigned a scattering length \( b_{\xi} \) which occurs with a fractional concentration \( c_{\xi} \). The average value of \( b \) for the system is then

\[
\bar{b} = \sum_{\xi} c_{\xi} b_{\xi}
\]

(2.25)

and the average of \( b^2 \) is

\[
\bar{b}^2 = \sum_{\xi} c_{\xi} b_{\xi}^2
\]

(2.26)

If it is assumed that no correlation exists between the scattering lengths of any two nuclei (\( j \) and \( j' \) say) and that we have a large number of scattering systems of which the positions and motions of the constituent nuclei are identical but the distribution of \( bs \) among the nuclei differs such that every possible distribution is represented once, then the measured cross-section will approximately be the cross-section averaged over all the systems provided that each system contains a large number of nuclei. This is given by

\[
\frac{d^2\sigma}{d\Omega dE} = \frac{k'}{k} \frac{1}{2\pi} \hbar \sum_{\xi} b_{\xi} b_{j} \int \langle j', j \rangle \exp(-i\omega t) dt
\]

(2.27)
where the delta function for energy of (2.22) has been expressed as an integral with respect to time and

\[
\langle j', j \rangle = \langle \exp(-i\mathbf{k}.\mathbf{R}_j(0)) \exp(i\mathbf{k}.\mathbf{R}_j(t)) \rangle \tag{2.28}
\]

The assumption that the scattering lengths of different nuclei are not correlated means that the following conditions apply

\[
\begin{align*}
\bar{b}_j \bar{b}_j &= (\bar{b})^2, & j' \neq j, \\
\bar{b}_j \bar{b}_j &= \bar{b}^2, & j' = j. 
\end{align*} \tag{2.29}
\]

so that it can be shown [2] that

\[
\left( \frac{d^2 \sigma}{d\Omega dE} \right) = \frac{k'}{k} \frac{1}{2\pi \hbar} (\bar{b})^2 \sum_j \langle j', j \rangle \exp(-i\omega t) dt \\
+ \frac{k'}{k} \frac{1}{2\pi \hbar} (\bar{b}^2 - (\bar{b})^2) \sum_j \langle j', j \rangle \exp(-i\omega t) dt \tag{2.30}
\]

It is in the above expression that the two types of scattering can be distinguished. The first term in (2.30) represents what is known as **coherent scattering** for which it can be written

\[
\left( \frac{d^2 \sigma}{d\Omega dE} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{1}{2\pi \hbar} \sum_j \langle \exp(-i\mathbf{k}.\mathbf{R}_j(0)) \exp(i\mathbf{k}.\mathbf{R}_j(t)) \rangle \tag{2.31}
\]

\[
\times \exp(-i\omega t) dt,
\]

and the second term represents **incoherent scattering** for which the double differential cross-section is given by

\[
\left( \frac{d^2 \sigma}{d\Omega dE} \right)_{\text{inc}} = \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} \frac{1}{2\pi \hbar} \sum_j \langle \exp(-i\mathbf{k}.\mathbf{R}_j(0)) \exp(i\mathbf{k}.\mathbf{R}_j(t)) \rangle \tag{2.32}
\]

\[
\times \exp(-i\omega t) dt,
\]
where \[ \sigma_{\text{coh}} = 4\pi\langle \vec{b} \rangle^2, \quad \sigma_{\text{inc}} = 4\pi\{\langle \vec{b}^2 \rangle - \langle \vec{b} \rangle^2\} \] (2.33)

From (2.31) and (2.32) it can be inferred that coherent and incoherent scattering are of vastly different nature. The coherent scattering is a result of strong interference between the waves scattered from each nucleus and arises due to its dependence on the correlation between the positions of both the same nucleus and different nuclei at different times. Indeed strict geometrical conditions must be satisfied for the interference to be strong enough to produce this type of scattering. On the other hand, the incoherent scattering is dependant only on the correlation between the positions of the same nucleus at different times and for this reason yields no interference, and has a corresponding cross-section which is isotropic.

If one considers the simple case of an array of spinless nuclei with varying isotope then the substitution of (2.25) and (2.26) into (2.33), according to the relative abundance of each isotope, adequately evaluates the coherent and incoherent contributions. A more complicated scenario ensues if one incorporates non-zero spin into the picture for which the dependence of the interaction between two nucleons on their spins must be accounted for.

**Spin incoherence:**

A target system consisting of a single isotope and an array of nuclei with spin \( I \) will interact with an incident neutron of spin \( \frac{1}{2} \) to form one of two compound nuclei having spins of \( I + \frac{1}{2} \) and \( I - \frac{1}{2} \) respectively. Associated with these two possible compound systems will be corresponding scattering lengths denoted by \( b^+ \) and \( b^- \) respectively. Recalling that only s-wave (\( \ell = 0 \)) components are present in the scattered wavefunction, the total angular momentum is equal to the spin of the compound system. There are therefore \( 2(I+\frac{1}{2})+1 \) states of spin \( I + \frac{1}{2} \) and \( 2(I-\frac{1}{2})+1 \) states of spin \( I - \frac{1}{2} \) and for an unpolarised beam, the probability of interaction in the \( I + \frac{1}{2} \) state is given by
while in the \( l - \frac{1}{2} \) state it is

\[
\frac{2l}{(2l + 2) + 2l} = \frac{l}{2l + 1}
\]

The average scattering length is then given by

\[
\bar{b} = \left( \frac{l + 1}{2l + 1} \right) b^+ + \left( \frac{l}{2l + 1} \right) b^-
\]  
(2.34)

and

\[
\bar{b}^2 = \left( \frac{l + 1}{2l + 1} \right) |b^+|^2 + \left( \frac{l}{2l + 1} \right) |b^-|^2
\]  
(2.35)

The general case where more than one isotope is present and for which some have non-zero spins, can now be expressed by combining (2.25), (2.26), (2.34) and (2.35) as the following

\[
\bar{b} = \sum_\xi c_\xi \frac{1}{2l_\xi + 1} \{ (l_\xi + 1) b^+_\xi + l_\xi b^-_\xi \}
\]  
(2.36)

and

\[
\bar{b}^2 = \sum_\xi c_\xi \frac{1}{2l_\xi + 1} \{ (l_\xi + 1) |b^+_\xi|^2 + l_\xi |b^-_\xi|^2 \}
\]  
(2.37)

where \( c_\xi \) is the relative abundance of the \( \xi^{th} \) isotope, \( l_\xi \) its nuclear spin and \( b^+_\xi \) and \( b^-_\xi \) its scattering lengths.

### 2.4 The Magnetic Scattering of Neutrons

It has already been mentioned that in addition to scattering of nuclear origin a second source may arise by virtue of an interaction between the intrinsic magnetic moment of the neutron and that of the target nucleus (if the latter
exists). The dipole-dipole interaction which ensues between the neutron and the unpaired electrons of the nucleus can be described in terms of operators, with the magnetic moment operator for a neutron given by

$$\hat{\mu}_n = \gamma \mu_N \hat{\sigma} \tag{2.38}$$

where the nuclear magneton is $$\mu_N = \frac{e\hbar}{2m_p}$$, \(\gamma\) is a constant called the gyromagnetic ratio and takes the value -1.91, \(\hat{\sigma}\) is the Pauli spin operator for the neutron and takes eigenvalues \(\pm 1\), \(m_p\) is the mass of a proton and \(e\) is its charge.

The corresponding operator for the magnetic dipole moment of an electron is given by

$$\hat{\mu}_e = -2\mu_B \hat{s} \tag{2.39}$$

where the Bohr magneton is $$\mu_B = \frac{e\hbar}{2m_e}$$, \(m_e\) is the electron mass and \(\hat{s}\) is the spin angular momentum operator for the electron with eigenvalues \(\pm \frac{1}{2}\).

### 2.4.1 The Partial Differential Cross-section

The partial cross-section for a purely nuclear process and an unpolarised incident beam is given in (2.23), where only the wavevector \(\mathbf{k}\) of the neutron is accounted for. In describing the magnetic scattering process the spin state \(\sigma\) too must be specified such that for a process in which the system changes from a state \(\lambda\) to a state \(\lambda'\) and the neutron changes from a state \(\mathbf{k}, \sigma\) to \(\mathbf{k}', \sigma'\) the partial cross-section is given by
where \( V_m \) is the magnetic interaction potential between the neutron and the constituent electrons of the system. If one considers the interaction between the neutron and the magnetic field \( B \) due to a single moving electron then it may be shown [15] that the corresponding interaction potential can be expressed as the sum of two terms arising from the spin and the orbital motion of the electron respectively

\[
V_m = -\gamma \mu_N \vec{\sigma} \cdot \vec{B} = \gamma \mu_N \left\{ 2\mu_0 \vec{\sigma} \cdot \text{curl} \left( \frac{\vec{S} \times \vec{R}}{|\vec{R}|^3} \right) - \frac{e}{2m_e c} \left( \hat{\vec{p}}_e \cdot \frac{\vec{S} \times \vec{R}}{|\vec{R}|^3} + \vec{\sigma} \times \frac{\vec{R}}{|\vec{R}|^3} \cdot \hat{\vec{p}}_e \right) \right\}
\]

(2.41)

where \( \hat{\vec{p}}_e \) is the momentum operator of the electron given by \( \hat{\vec{p}}_e = -i\hbar \nabla \) and \( \vec{R} \) is the distance from the electron to the point at which the field is measured.

Substituting (2.41) into (2.40) and using the following identities

\[
\frac{\vec{R}}{|\vec{R}|^3} = -\nabla \left( \frac{1}{|\vec{R}|} \right)
\]

(2.42a)

and

\[
\frac{1}{|\vec{R}|} = \frac{1}{2\pi^2} \int d\vec{q} \frac{1}{q^2} \exp(i\vec{q} \cdot \vec{R})
\]

(2.42b)

where \( \vec{q} \) is a wave vector, it can be shown that, the partial differential cross-section representing a magnetic interaction for unpolarised neutrons is given by

\[
\frac{d^2\sigma}{d\Omega dE'} = \left( \gamma \mu_0 \right)^2 \frac{1}{k} \sum_{\lambda' \lambda} p_{\lambda'} \langle \lambda | \hat{Q}_{\lambda'} | \lambda' \rangle \cdot \langle \lambda' | \hat{Q}_{\lambda} | \lambda \rangle \delta (\hbar \omega + E_{\lambda} - E_{\lambda'})
\]

(2.43)
where \( \mathbf{\hat{r}} \) represents the unit vector in the direction of the scattering vector \( \mathbf{\kappa} \) (from (2.6)), \( r_0 \), known as the classical radius of the electron, is equal to \( \frac{e^2}{m_e c^2} \) and the operator \( \mathbf{\hat{Q}_\perp} \), related to the magnetisation of the target system, is defined in terms of a spin and orbital contribution as

\[
\mathbf{\hat{Q}_\perp} = \sum_i \exp(i\mathbf{\kappa} \cdot \mathbf{r}_i) \left\{ \mathbf{\hat{r}} \times (\mathbf{\hat{S}}_i \times \mathbf{\hat{r}}) - \frac{i}{\hbar |\mathbf{\kappa}|} \mathbf{\hat{r}} \times \mathbf{\hat{P}}_i \right\}
\] (2.44)

For unpolarised neutrons the Kronecker delta function is

\[
\sum_\sigma \rho_\sigma \langle \sigma | \mathbf{\hat{\sigma}_\alpha} \mathbf{\hat{\sigma}_\beta} | \sigma \rangle = \delta_{\alpha\beta}
\] (2.45)

which can be incorporated into the following identity

\[
\mathbf{\hat{Q}_\perp} \cdot \mathbf{\hat{Q}_\perp} = \sum_{\alpha\beta} \left( \delta_{\alpha\beta} - \mathbf{\hat{r}}_\alpha \mathbf{\hat{r}}_\beta \right) \mathbf{\hat{Q}_\alpha} \mathbf{\hat{Q}_\beta}
\] (2.46)

to yield an alternative expression for (2.43)

\[
\frac{d^2\sigma}{d\Omega dE} = (\gamma r_0)^2 \frac{k'}{k} \sum_{\alpha\beta} \left( \delta_{\alpha\beta} - \mathbf{\hat{r}}_\alpha \mathbf{\hat{r}}_\beta \right)
\times \sum_\lambda \rho_\lambda \langle \lambda | \mathbf{\hat{Q}_\alpha} | \lambda \rangle \langle \lambda | \mathbf{\hat{Q}_\beta} | \lambda \rangle \delta \left( \hbar \omega + E_\lambda - E_\lambda \right)
\] (2.47)

where the operator \( \mathbf{\hat{Q}} \) is related by \( \mathbf{\hat{Q}_\perp} = \mathbf{\hat{r}} \times (\mathbf{\hat{Q}} \times \mathbf{\hat{r}}) \). In terms of the magnetisation, the operator \( \mathbf{\hat{Q}}(\mathbf{\kappa}) \) is effectively the Fourier transform of the magnetisation operator \( \mathbf{\hat{M}}(r) \). That is
\[
\hat{Q}(\kappa) = \hat{Q}_s(\kappa) + \hat{Q}_l(\kappa)
\]
\[
= -\frac{1}{2\mu_B} \int \hat{M}(r) \exp(i\kappa \cdot r)
\]
\[
= -\frac{1}{2\mu_B} \hat{M}(\kappa)
\]

(2.48)

where subscripts \(S\) and \(L\) denote spin and orbital contributions respectively.

### 2.4.2 Spin and Orbital Coupling

An atom or ion possessing both spin and orbital angular momentum, denoted by quantum numbers \(S\) and \(L\) respectively, will have a resultant total angular momentum, denoted by \(J\), arising from the coupling of \(L\) and \(S\). The magnetic moment corresponding to the spin and orbital contributions are given by

\[
\mu_s = \mu_B g_s S \quad \text{and} \quad \mu_L = \mu_B g_L S
\]

(2.49)

and the resultant paramagnetic moment is

\[
\mu_J = \mu_B gS
\]

(2.50)

where

\[
g_s = \frac{J(J+1) - L(L+1) + S(S+1)}{J(J+1)}
\]

\[
g_L = \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)}
\]

(2.51)

and the Landé splitting factor is \(g = g_s + g_L\).

In some cases however, the orbital contribution is zero or is quenched by the internal electric field of the crystal (transition elements) for which the orbital...
part of (2.44) vanishes and the operator $\hat{Q}$ can be written

$$\hat{Q} = \sum_i \exp(i\kappa \cdot r_i) \hat{s}_i$$  \hspace{1cm} (2.52)

If one considers the case of a crystal scattering system in which the unpaired electrons have wavefunctions localised about the sites of the lattice described by the vectors $R_{l,d} = l+d$ then it can be shown that the partial differential cross-section for spin only scattering is

$$\frac{d^2 \sigma}{d\Omega dE} = (\gamma f_0)^2 \frac{k}{K} \sum_{\alpha \beta} \left( \delta_{\alpha \beta} - \hat{r}_\alpha \hat{r}_\beta \right) \sum_{l,d} f_d' (\kappa) f_d (\kappa) \times \sum_{l,d} S_{d}^a \left| \lambda \right> \exp(-i\kappa \cdot R_{l,d}) \hat{S}_{l,d}^a \left| \lambda \right> \times \left( \lambda \right| \exp(i\kappa \cdot R_{l,d}) \hat{S}_{l,d}^a \left| \lambda \right> \delta (\hbar \omega + E_\lambda - E_\lambda)

(2.53)

where $l$ denotes the unit cell in which the ion $d$ is located and $\hat{S}_{d}^a$ is the spin operator corresponding to the $\beta$ component of spin for the ion $l,d$. $f_d (\kappa)$ is known as the magnetic form factor and is defined as the Fourier transform of the normalised density of unpaired electrons in the ion $d$ $\tilde{\zeta}_d (r)$ such that

$$f_d (\kappa) = \int \tilde{\zeta}_d (r) \exp(i\kappa \cdot r) dr \hspace{1cm} (2.54)$$

The necessity of the form factor arises from the fact that the unpaired electrons determining the magnetic moment are distributed over a volume with linear dimensions comparable to that of the neutron wavelength, and is analogous to the electronic form factor found in X-ray scattering in that it falls off as a function of scattering angle all the way in a sharper manner. The way in which the form factor is related to the scattering vector means that the magnetic scattering decreases with increasing wave vector or incident neutron energy.

The more general case involves scattering from an ion possessing both spin
and orbital angular momentum for which a modification to the form factor of (2.54) is required. Both terms of (2.44) must now be included and the subsequent calculation of the matrix elements within \( \hat{Q} \) becomes complicated unless the case is restricted to the situation where the mean radius of the wave function of the unpaired electrons is much less than \( |\kappa|^{-1} \) (known as the dipole approximation). Doing so, it can be shown [15], that the approximate form of the operator \( \hat{Q} \) is

\[
\hat{Q} = \hat{Q}^{(D)} = \frac{1}{2} g f(\kappa) \sum_{l,d} \exp(i\kappa \cdot R_{ld}) \hat{J}_{ld}
\]

(2.55)

where \( \hat{J}_{ld} \) is the total angular momentum operator for the ion at the position \( R_{ld} \). The revised form factor \( f(\kappa) \) of the ion is given by

\[
f(\kappa) = j_0 \frac{g_s}{g} + (j_0 + j_z) \frac{g_L}{g}
\]

(2.56)

where \( j_k \) is a spherical Bessel function of order \( k \).

The partial differential cross-section for spin-orbital coupling based on the dipole approximation and for identical magnetic ions can now be written as

\[
\frac{d^2\sigma}{d\Omega dE} = (\gamma r_0)^2 \frac{k^2}{k} \left( \frac{1}{2} g f(\kappa) \right)^2 \sum_{s\beta} \left( \delta_{s\beta} - \bar{\kappa}_{s} \bar{\kappa}_{\beta} \right) \sum_{\lambda\lambda'} p_{\lambda'}
\]

\[
\times \sum_{l,d} \sum_{\lambda,\lambda'} \exp(i\kappa \cdot (R_{ld} - R_{\lambda\lambda'})) \langle \lambda | \hat{S}_{ld}^{\alpha} | \lambda \rangle \langle \lambda' | \hat{S}_{\lambda\lambda'}^{\beta} | \lambda \rangle \delta(h\omega + E_{\lambda} - E_{\lambda'})
\]

(2.57)

2.4.3 Localised Scattering Systems

The exchange interaction between two electrons depends sensitively on their states of motion which, in turn, are determined by the environment in which
each moves. When an atom combines with another to form a solid, its electrons become perturbed by the presence of neighbouring atoms. The consequences of this depends on the electron kinetic energies involved where, in the most energetic case, the electron loses its affinity to a particular nucleus and instead, moves from atom to atom throughout the lattice. These are termed itinerant electrons. However, due to the Coulomb repulsion which exists between electrons, their movements become correlated, imposing a restriction on their freedom of motion. The degree of correlation is more marked the lower the kinetic energy of an electron and in its extreme form causes the electrons to remain fixed or localised on particular nuclei. Thus a localised magnetic scattering is one in which the electrons giving rise to the moment are fixed on the atom. That is to say they do not participate in the conduction process and are located below the Fermi surface.

Local moments are only meaningful variables if the magnetic excitation spectrum $\omega_{\text{mag}}$ and charge excitation spectrum $\omega_{\text{ch}}$ are separated, namely $\omega_{\text{mag}} < \omega_{\text{ch}}$. Ionic magnets such as MnF$_2$ satisfy such criteria by virtue of the Coulomb forces giving rise to the Hund's rule moments being much stronger than the thermal energies $k_B T_N$ characterising the magnetic fluctuations. For a greater physical understanding of the expression for the magnetic cross-section, one can introduce what is known as a magnetic correlation function $\Gamma_{\text{mag}}(\kappa, \omega)$ which enables integrals of individual physical significance to be defined. To simplify the situation, a static lattice is considered for which moments reside on their equilibrium position. The partial cross-section of (2.57) can then be expressed in terms of a response function by writing the delta function as an integral with respect to time

$$\delta(h \omega + E_x - E_x') = \frac{1}{2 \pi \hbar} \int_{-\infty}^{\infty} \exp \left\{ \frac{i(E_x - E_x') t}{\hbar} \right\} \exp(-i \omega t) dt \quad (2.58)$$

so that
\[
\sum_{\lambda', \lambda} \sum_{i,d} \sum_{r, r'} \exp\{i\mathbf{k} \cdot (\mathbf{R}_{i,d} - \mathbf{R}_{r, r'})\} \langle \lambda | \hat{S}_{\alpha r}^0 | \lambda' \rangle \langle \lambda | \hat{S}_{\alpha r}^0 | \lambda' \rangle \delta(h\omega + E_{\lambda} - E_{\lambda'}) \\
= \frac{1}{2\pi \hbar} \int_{-\omega}^{\omega} dt \langle \exp[i\mathbf{k} \cdot (\mathbf{R}_{i,d}(t) - \mathbf{R}_{r, r'}(0))] \hat{S}_{\alpha r}^0 (t) \hat{S}_{\alpha r}^0 (0) \rangle \exp(-i\omega t)
\]

(2.59)

where \( \hat{S}_{\alpha r}^0 (t) = \exp(iHt/\hbar) \hat{S}_{\alpha r}^0 \exp(-iHt/\hbar) \) and \( H \) is the quantum mechanical Hamiltonian. The partial differential cross-section for a static lattice can then be written

\[
\frac{d^2 \sigma}{d\Omega dE} = \frac{(\gamma r_0)^2}{2\pi \hbar} \frac{k'}{k} \frac{N[\frac{1}{2} g f(k)]^2}{2} \sum_{\alpha, \beta} \left( \delta_{\alpha \beta} - \vec{r}_\alpha \vec{r}_\beta \right) \\
\times \sum_{i, d} \sum_{r, r'} \int dt \langle \exp[i\mathbf{k} \cdot (\mathbf{R}_{i,d}(t) - \mathbf{R}_{r, r'}(0))] \hat{S}_{\alpha r}^0 (t) \hat{S}_{\alpha r}^0 (0) \rangle \exp(-i\omega t)
\]

\[
= \frac{(\gamma r_0)^2}{2\pi \hbar} \frac{k'}{k} \frac{[\frac{1}{2} g f(k)]^2}{2} S(k, \omega)
\]

(2.60)

in which the first term is determined by the neutron and the second by the scattering sample. \( S(k, \omega) \) is referred to as the dynamical scattering function and is related by a Fourier transform in space and time, to the spin-spin correlation function

\[
\Gamma(k, \omega) = \int dt \exp(-i\omega t) \sum_{i, d} \sum_{r, r'} \exp[i\mathbf{k} \cdot (\mathbf{R}_{i,d}(t) - \mathbf{R}_{r, r'}(0))] \langle \hat{S}_{\alpha r}^0 (t) \hat{S}_{\alpha r}^0 (0) \rangle
\]

(2.61)

The partial differential cross-section is a function of both scattering vector and energy and as such can be integrated with respect to each variable over a given Brillouin zone (BZ). Removing all constants of proportionality, the scattering vector integration across the zone yields
\[ \int \frac{d^2 \sigma}{d\Omega dE'} = \sum_{l,d} \sum_{r,d'} \int dt \langle \hat{S}_{ld}(t) \hat{S}_{r'd'}(0) \rangle \exp(-i\omega t) \times \int d\kappa \exp\{i\kappa \cdot (\mathbf{R}_{ld}(t) - \mathbf{R}_{r'd'}(0))\} \]
\[ = \sum_{l,d} \sum_{r,d'} \int dt \langle \hat{S}_{ld}(t) \hat{S}_{r'd'}(0) \rangle \delta \left( \mathbf{R}_{ld}(t) - \mathbf{R}_{r'd'}(0) \right) \exp(-i\omega t) \]
\[ = \sum_{l,d} \int dt \langle \hat{S}_{ld}(t) \hat{S}_{ld}(0) \rangle \exp(-i\omega t) \]

(2.62)

and the energy-transfer integrated neutron scattering cross-section obtained is

\[ \int dE' \left( \frac{d^2 \sigma}{d\Omega dE} \right) = \sum_{l,d} \sum_{r,d'} \int dt \langle \hat{S}_{ld}(t) \hat{S}_{r'd'}(0) \rangle \exp\{i\kappa \cdot (\mathbf{R}_{ld}(t) - \mathbf{R}_{r'd'}(0))\} \times \int dE' \exp(-i\omega t) \]
\[ = \sum_{l,d} \sum_{r,d'} \int dt \langle \hat{S}_{ld}(t) \hat{S}_{r'd'}(0) \rangle \exp\{i\kappa \cdot (\mathbf{R}_{ld}(t) - \mathbf{R}_{r'd'}(0))\} \delta(t) \]
\[ = \sum_{l,d} \sum_{r,d'} \langle \hat{S}_{ld}(0) \hat{S}_{r'd'}(0) \rangle \exp\{i\kappa \cdot (\mathbf{R}_{ld}(0) - \mathbf{R}_{r'd'}(0))\} \]

(2.63)

The energy and scattering vector integrated cross-section is then

\[ \int dE' \int d\kappa \left( \frac{d^2 \sigma}{d\Omega dE} \right) = \sum_{l,d} \sum_{r,d'} \int dt \langle \hat{S}_{ld}(t) \hat{S}_{r'd'}(0) \rangle \left\{ \int d\kappa \exp\{i\kappa \cdot (\mathbf{R}_{ld}(t) - \mathbf{R}_{r'd'}(0))\} \right\} \times \left[ \int dE' \exp(-i\omega t) \right] \]
\[ = \sum_{l,d} \sum_{r,d'} \int dt \langle \hat{S}_{ld}(t) \hat{S}_{r'd'}(0) \rangle \delta \left( \mathbf{R}_{ld}(t) - \mathbf{R}_{r'd'}(0) \right) \delta(t) \]
\[ = \langle \hat{S}_{ld}(0) \hat{S}_{ld}(0) \rangle \]
\[ = S(S+1) \]

(2.64)

which yields what is known as a sum rule for the overall scattering. The
correlation function can be related to the imaginary part of the dynamic susceptibility \( \chi''(\mathbf{k},\omega) \) via the fluctuation-dissipation theorem [16]:

\[
\Gamma(\mathbf{k},\omega) = \frac{1}{1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)} \chi''(\mathbf{k},\omega)
\]  

so that, in accordance with the sum rule, conditions can be imposed upon the general properties of the dynamic susceptibility \( \chi(\mathbf{k},\omega) \). The static or real part of the susceptibility \( \chi(\mathbf{k}) \) can be obtained from the Kramers-Kronig relation:

\[
\chi(\mathbf{k}) = \frac{\pi}{\hbar} \int_{-\infty}^{\infty} \frac{\chi''(\mathbf{k},\omega)}{\omega} d\omega
\]  

and, providing that the typical fluctuation frequencies \( \omega \) are less than \( k_B T \) (in what is called the static approximation), \( \Gamma(\mathbf{k}) \) may be written:

\[
\Gamma(\mathbf{k}) = k_B T \chi(\mathbf{k})
\]  

A co-operative magnetic scattering system at zero temperature will be fully ordered and as such will give rise to elastic Bragg scattering which is well localised in \( k \)-space, in the form of a delta function in energy. An atom with quantum mechanical spin \( S \) of magnitude \( \sqrt{S(S+1)} \) will have a maximal projection onto the quantisation axis given by \( S \) such that the Bragg contribution \( l_B \) towards the sum rule is \( (b S^2) \), where \( b \) is a reduction factor \( 0 \leq b \leq 1 \). For a ferromagnet in its ground state, the magnetic moments are maximally aligned and the factor \( b \) is equal to one. However, in the ground state of an antiferromagnet the ordered spin moment takes on a reduced value as a result of quantum fluctuations which arise from i) the zero point energy in the magnon modes and, for certain configurations, ii) the partial ‘frustration’ of the constituent spins. Figure 2.3 illustrates the occurrence of frustration for the case of three Ising spins arranged on the edges of an equilateral triangle. The antiferromagnetic interaction of spin 2 with both spins
Fig. 2.3 Frustration in an equilateral triangle. In a) spins 1 and 2, and in b) spins 2 and 3 are antiferromagnetically oriented to one another. If 1 and 3 are oriented antiferromagnetically then 2 is frustrated.

1 and 3, causes the orientation of spin 2 to fluctuate between energetically degenerate states. That is to say spin 2 is frustrated. This effect is accounted for by the inclusion of $b$ which takes a value determined by the lattice type and dimension.

Upon increasing the temperature of a localised system, the spin moments of fixed magnitude, directionally disorder and the scattering becomes partly inelastic or "quasi-elastic". In addition to the ground state Bragg scattering, a second, fluctuating contribution to the sum rule arises from the non-ordered part of the magnetic moment [17]. The fluctuations of the ordered state are studied in terms of 'spin waves' which are quantised in the form of 'magnons'. The corresponding intensity $I_{sw}$ amounts to the component $S+S^z(1-b^z)$ of the sum rule such that

$$I_b + I_{sw} = N(bS^z) + N(S + S^z(1 - b^z)) = NS(S + 1)$$

(2.68)

where $N$ is the number of sites.

For a two dimensional quantum antiferromagnet, the correlation length $\xi_{2D}$ increases exponentially fast with decreasing temperature as described by (1.7). This dependence has consequences for the intensity distribution of the
magnetic correlation function such that, at a finite temperature $T > T_N$ where the thermal energy $k_B T$ is less than the exchange energy $J$ which favours magnetic alignment, the Bragg intensity is no longer a delta function in $\omega$, but is instead smeared out over a region of width $-\xi_{2d}^{-1}$ in $k$ and $-\sqrt{J} \xi_{2d}^{-1}$ in $\omega$, centred around the 2D Bragg point and $\omega = 0$ [18]. Figures 2.4 a), b) and c) show the evolving intensity spread in $k$ and $\omega$ as the temperature is increased above the ordering temperature $T_N$ relative to $J$. In addition, as the temperature is increased in the ordered state, so there is an increase in spin wave scattering such that, as the transition temperature $T_N$ is approached, the magnetic correlations between spin moments becomes negligible and long range order is lost. The temperature at which the paramagnetic state is reached corresponds to the width of the magnon dispersion in the ground state meaning that the magnetic scattering associated with the paramagnetic state will be distributed over an energy interval of order $k_B T_C$ or $k_B T_N$. However, as to whether the sum rule is fulfilled from a neutron scattering perspective, depends very much on the experimental conditions. Such experiments are constrained by the way in which $k$ and $\omega$ are related meaning that not all of $(k, \omega)$-space is accessible and only if the total scattering is integrated over can the sum rules for neutron scattering be employed.

Fig. 2.4 Distribution of scattered intensity in $k$ and $\omega$ for a) $T < T_N$ (2D Bragg point), b) $T > T_N, k_B T < J$ and c) $T > T_N, k_B T = J$ [18].
Perfect paramagnet:

For temperatures much greater than the magnetic ordering temperature \((k_B T > k_B T_C)\) or \((k_B T_N)\) there exists no spatial correlation between spins and the magnetic scattering is independent of scattering vector. This characterises the special case of a 'perfect' paramagnet in which the energy is independent of spin orientation meaning that the scattering is elastic. Because the spins are not correlated, all terms with \(l \neq l'\) vanish while for \(l = l'\)

\[
\langle \hat{S}_i^z \hat{S}_j^z \rangle = \frac{1}{2} \delta_{\alpha \beta} S(S + 1) \tag{2.69}
\]

and the cross-section can be written

\[
\frac{d\sigma}{d\Omega} = \frac{1}{2} \left( \gamma r_0 \right)^2 \left\{ \frac{1}{2} g f(\kappa) \right\}^2 N S(S + 1) \tag{2.70}
\]

The scattering as described by (2.70) is entirely incoherent with the only dependence on the scattering vector coming from the form factor.

Upon application of an external magnetic field \(B\), a paramagnet will become polarised at low temperature and if the energy changes on reversing a spin are negligibly small relative to the incident neutron energy then the scattering can again be regarded as being elastic. If the applied field is defined as being in the \(z\) direction then it can be shown that (2.70) becomes

\[
\frac{d\sigma}{d\Omega} = \left( \gamma r_0 \right)^2 \left\{ \frac{1}{2} g f(\kappa) \right\}^2 N \left[ \left( 1 - \bar{r}_z^2 \right) \left( \frac{2\pi}{V_0} \right)^3 \left\langle \hat{S}_z^2 \right\rangle^2 \sum \delta(\kappa - \tau) 
\right.

\left. + \bar{r}_z^2 \left\{ \frac{1}{2} S(S + 1) - \frac{3}{2} \left\langle \left( \hat{S}_z^2 \right) \right\rangle + \frac{3}{2} \left( \left( \hat{S}_z \right)^2 \right) + \frac{1}{2} S(S + 1) + \frac{1}{2} \left\langle \left( \hat{S}_z^2 \right) \right\rangle - \left\langle \left( \hat{S}_z \right)^2 \right\rangle \right\} \right]
\tag{2.71}
\]

The first term in the square brackets gives rise to coherent Bragg scattering and is proportional to the square of the average value of the \(z\)-component of
spin. \( V_0 \) is the volume of the unit cell and \( \tau \) is the reciprocal lattice vector. The second term is entirely contained in diffuse scattering and is proportional to the square of the fluctuations of the transverse and the z-component of the spin.

Up to now, the momentum and spin state of a neutron beam has only been specified for incident neutrons of random orientation. Polarisation of the incident beam, i.e. one consisting of neutrons whose spins have some preferred axis, and subsequent analysis of not only the spatial and energy distribution of the scattered neutrons but also their spin states yields information additional to that provided by unpolarised neutrons. The availability of higher neutron fluxes, together with the development of increasingly efficient polarisers has reduced the intensity penalty historically associated with polarised neutron experiments to such an extent that the technique is now well established as a tool for the investigation of many areas within solid state physics. The following chapter provides a discussion of the main characteristics of spin polarisation analysis.

**REFERENCES**

CHAPTER 3

SPIN POLARISATION ANALYSIS

3.1 Introduction

Since 1939, seven years after the discovery of the neutron, when Halpern and Johnson [1] first formalised the influence of the nuclear spin and magnetic moment upon the neutron spin orientation, the topic of neutron spin polarisation and realisation of its potential within condensed matter experiments has developed to such a degree that the technique is now well acknowledged as an invaluable tool for the study of many properties of solids and liquids.

The supplementary information provided by knowing the spin state functions of the neutrons before and after a scattering event, and relating them to the target system properties has now come to outweigh the historically associated intensity restraints imposed by low flux reactors and inefficient polarising monochromators. Both elastic and inelastic scattering experiments have benefited, the former from the techniques ability to distinguish unambiguously all contributions (coherent, incoherent and magnetic) to the total scattering cross-section. For the case of inelastic studies, polarisation analysis plays an important role in the separation of magnetic modes in both paramagnets and ordered magnets. In particular, polarisation analysis is vital for those experiments concerning paramagnets at high temperatures where the presence of scattering by phonons must be discriminated from all other sources. Additionally, via a range of techniques including pseudo-random flipping time of flight, neutron spectral modulation and neutron spin-echo, it is possible to study the change in neutron energy on scattering. Although
traditionally associated with the investigation of magnetic phenomena, spin polarised neutron scattering can also yield supplementary information for systems in which no conventional magnetism is involved. Polymers provide an example of such a system, where the ability of polarisation analysis to separate the coherent from the incoherent scattering enables structural information, vital for detailed modelling, to be extracted [2]. A recent review of spin polarised neutron scattering from an experimental perspective can be found in the paper by Hicks [3] providing an insight into the versatility of the technique since the pioneering work of Moon, Riste and Koehler [4].

For the purpose of this study the use of spin polarised neutrons as a probe for magnetic phenomena is demonstrated in two cases of superconductors. The first involves the use of a multidetector instrument in its energy integrated mode as a means of experimentally determining the characteristics of magnetic excitations in the high temperature superconductor YBa$_2$Cu$_3$O$_{6+x}$. Neutrons of wavelength between 3.1Å and 5.7Å are available making the instrument best suited for quasi elastic or low energy inelastic experiments.

The second line of investigation combines, in a unique way, polarised neutrons with a small angle neutron scattering (SANS) set-up, enabling the interaction between the flux line lattice and the nuclear lattice within the type II material niobium to be studied. The response of the nuclear lattice to the periodic magnetic field modulation which accompanies the formation of flux lines is coupled to the modulation of the superconducting order parameter meaning that its consequences on the redistribution of electrons can be studied. The experimental means by which both investigations were carried out are described fully in the next chapter.

3.2 The Evolution of Polarisation Analysis

Although at a time when neutron sources were too weak for the full potential of spin polarisation to be practically accessible, an early example of neutron
beam polarisation came in 1940 with the experiments of Alvarez and Bloch to determine the magnetic moment of the neutron [5]. Using a cyclotron as a source and a paraffin block as a moderator and collimator, slow neutrons (in the meV range) were transmitted through two blocks of oppositely magnetised blocks of iron acting as polariser and analyser respectively. Subsequent measurement of the difference in scattering cross-section between the two blocks enabled the modulus of the neutron moment to be determined by virtue of the scattering cross-section dependence upon the contribution of the iron magnetic moment to the scattering length. An additional element to their set-up involved a measure to prevent the neutron spins from following the variation in field direction in the transition region between the polariser and analyser. A high frequency (radio) field was applied to induce transitions between the two spin states of the neutrons - a device referred to as a radio frequency (rf) “flipper” for its ability to flip neutrons from one field direction to another.

With the advent of nuclear reactors capable of producing neutron beams of increased intensity and considerable improvements in polarising techniques, neutron scattering and in particular polarisation analysis underwent rapid development. As early as 1951, Shull [6] had managed to simultaneously monochromatise and wholly polarise a neutron beam by Bragg reflections from the (220) planes of a magnetite single crystal and in the same year Hughes and Burgy [7] developed the first polarising mirror from electroplated, magnetised cobalt. Analogous to wave optics, the basis of their operation lies in the fact that, for a magnetised medium, neutrons with spins parallel (+) or anti-parallel (-) to the field direction, impinging with a glancing angle $\theta_+^{\text{c}}$ less than a certain critical angle $\theta_\text{c}$, will undergo total reflection. It is then possible by suitable choice of material and composition to manipulate the nuclear and magnetic properties of the mirrors such that the critical angle is real for one spin state only. “Benders”, so called because the polarised beam is deflected away from the incident beam direction, with CoFe coating yield neutron polarisation in excess of 95% (compared to $-33\%$ with the transmission effect.
through magnetised iron) and transmission of the desired spin state of ~40% for cold neutrons.

Progress in the application of spin polarised neutrons accelerated during the 1960s and 1970s, triggered by the pioneering work of Moon, Riste and Koehler. Their 1969 paper [4] described a triple axis instrument adapted for polarisation analysis and demonstrated for the first time the true potential of spin polarised neutrons. Experiments conducted on mono-isotopic vanadium confirmed the then recently derived relationships for spin incoherent scattering, and the usefulness of analysing the scattered beam for polarisation for the isolation of magnetic Bragg scattering was demonstrated by studies on the antiferromagnet \( \alpha\)-Fe\(_2\)O\(_3\). Early inelastic experiments included the observation of magnon scattering in the ferromagnet Fe\(_{2.5}\)Li\(_{0.5}\)O\(_4\) and the separation of paramagnetic scattering at room temperature from MnF\(_2\).

The apparatus used by Moon et al., shown in figure 3.1 on the following page, was a triple-axis spectrometer with an Fe-8%Co crystal monochromator-polariser and analyser mounted on the first and third axis respectively. A rf-flipper located between monochromator and specimen and another positioned between specimen and analyser enabled a monochromatic beam to reach the sample with polarisation in either of the two directions perpendicular to the scattering plane. The application of guide fields in the first leg then allowed the polarisation to be rotated into the horizontal plane before being rotated back to the perpendicular by a second guide field, provided between sample and second flipper, for analysis.

The development of the cold neutron sources in the early 1970s and their use as moderators brought a 70% increase in the flux available which, together with superior polarisers, brought further advancement in the technique. In 1972, Mezei [8] introduced an improved alternative to the rf-flipper in the form of the dc-flipper which was less cumbersome and of increased stability. Based on Larmor precession of the neutron spin and consisting of a flat,
Fig. 3.1 A schematic diagram of the triple axis spectrometer adapted for polarisation analysis as used by Moon et al. [4].

rectangular coil with a well defined field region, neutron spins, upon entering the coil, experience an almost adiabatic change in the direction of the magnetic guide field.

Further strides forward in the quest for more efficient polarisers with improved angular range, were taken by Mezei and Dagleish [9] with the development of the first "supermirror". These consisted of multilayers of alternating magnetic and non-magnetic materials (bilayers of Fe and Ag in the case of [9]), chosen such that their refractive indices match for one spin state only. As a result, while one spin state "sees" just a single thick layer, the other sees all bilayers and is reflected on each interface. For an appropriate distribution of layer
thicknesses, constructive interference can occur at each interface for a range of values \( (\theta/\lambda) \) beyond the normal mirror cutoff meaning that the angular range for neutron reflection is effectively increased. Subsequent work by Schärpf [10] brought further improvements in supermirror efficiency with the use of alternate Co-Ti layers on a glass substrate. For this combination of materials, the angular range of polarised neutron reflection extends to zero grazing angle and a polarisation of 98% is achievable.

During the 1970s, a series of polarised neutron instruments were developed all of which were restricted to using a single detector and analyser due to the mechanical difficulty of incorporating polarising crystals into a multidetector set-up. The development of supermirrors at the ILL enabled a new classical polarisation instrument for long wavelengths (3.1\( \AA \) to 5.7\( \AA \)) to evolve. Adapted from the already existing diffuse scattering instrument, D7, it provided the experimental means in this work for the investigation of magnetic fluctuations in the high-\( T_c \) material YBa\(_2\)Cu\(_3\)O\(_{6+x}\). This new instrument brought two improvements over its predecessors by a) simultaneously performing polarisation analysis for 32 detectors over an angular range \( 20 = 7^\circ \) to 160\(^\circ \) and b) decoupling the monochromator and polariser by instead using a pyrolytic graphite monochromator followed by a supermirror polariser. Together these modifications achieved an intensity gain of two orders of magnitude. An overview of existing measuring techniques within classical polarisation analysis and comparisons with the D7 instrument is given by Schärpf and Anderson in [11]. Chapter 4 provides a full instrument description of D7.

More recently, development has concentrated on the use of nuclear spin polarised targets as a means of providing a wavelength independent neutron spin filter. In particular \(^3\)He gas, by virtue of the strong dependence of the neutron absorption cross-section upon the relative orientation of the neutron and nuclear spins, has become a realistic possibility as a broad band neutron filter [12], [13]. The mechanism by which the filter works is advantageous over
existing techniques due to the fact that it can be applied in the previously restricted regime of high energy/short wavelength neutrons.

3.3 The Theory of Polarisation Analysis

Prior to the advent of multidetector polarisation analysis set-ups, single detector instruments in the mould of figure 3.1 performed analysis via the $\|\perp$ difference method [14] in which the polarisation vector is rotated successively parallel and perpendicular to the scattering vector. The fact that scattering with polarisation parallel and perpendicular to the scattering vector is different only for paramagnetic and antiferromagnetic samples means that magnetic scattering can be separated from the nuclear coherent and incoherent scattering by simply taking the difference between the $\|$ and $\perp$ measurements. For the case of a multidetector however, it is not possible to satisfy the condition of polarisation $\|$ and $\perp$ to the scattering vector simultaneously for all detectors and as a result, the method of analysis must be generalised to include three dimensional analysis in which the polarisation direction is rotated into the three, mutually orthogonal, $x$, $y$ and $z$ directions. The method by which this is achieved is known as the XYZ-difference method and its derivation from the $\|\perp$ technique is given in the following section.

3.3.1 The $\|\perp$ Method

The spin state of a neutron is described relative to a reference orientation known as the polarisation direction. By convention, this common direction is defined to be along the $z$-axis in Cartesian co-ordinates. The polarisation $\mathbf{P}$ of a beam is then defined as twice the average value of the spin of the neutrons, namely

$$
\mathbf{P} = 2\langle \hat{s} \rangle = \langle \hat{c} \rangle \tag{3.1}
$$
where $\hat{\sigma}$ is the Pauli spin operator with matrices

$$
\hat{\sigma}^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}^z = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
$$

For an unpolarised beam, $P=0$ and for a completely polarised beam (i.e. all neutrons having a spin direction $(0,0,1)$ in Cartesian co-ordinates) $|P|=1$. A partially polarised beam $(0<P<1)$ is described with the aid of a spin density operator.

The spin state of the neutron with respect to the polarisation direction can be denoted by the symbols $(+)$ and $(-)$ which, by convention, correspond to the ‘spin up’ and ‘spin down’ states respectively. By suitable manipulation of the flippers in an arrangement such as figure 3.1, it is possible to measure four individual cross-sections corresponding to the spin transitions:

$$(+) \rightarrow (+), \quad (+) \rightarrow (-), \quad (-) \rightarrow (+), \quad (-) \rightarrow (-).$$

In addition, by rotating the electromagnet around the target, these spin state cross-sections can be measured for the case when the neutron spin direction in the sample is along the scattering vector $\mathbf{k}$ and also for the case when the spin is perpendicular to the scattering vector. The processes $(+) \rightarrow (+)$ and $(-) \rightarrow (-)$ involve no change in the neutron spin and are termed non-spin flip cross-sections whilst the transitions $(+) \rightarrow (-)$ and $(-) \rightarrow (+)$ involve a change in spin and are called spin flip processes. Any cross-section $k \rightarrow k'$ for unpolarised neutrons is related to the corresponding spin state cross-section by

$$
\left( \frac{d^2\sigma}{d\Omega dE'} \right)_{k \rightarrow k'} = \frac{1}{2} \ldots \text{(sum of the 4 spin state cross-sections)}
$$
Chapter 3

Spin Polarisation Analysis

Upon application of a magnetic field, any component of the neutron polarisation which is perpendicular to the field will precess around the field direction with a frequency equal to $0.265\lambda H$ [ÅG] [15] where $\lambda$ is the neutron wavelength in angstrom and $H$ is the applied field in Gauss. However, in the conventional set-up as applies here, only that part of the polarisation which is projected onto the quantisation axis (z-axis) is analysed. In order to separate the contributions to the total scattering, the $||-\perp$ difference method exploits certain ‘rules’ which govern the characteristic conditions for spin flip and non-spin flip scattering.

For the case of nuclear scattering, only those components of the nuclear interaction potential which are perpendicular to the axis of quantisation give rise to nuclear scattering with a flip of the neutron spin in the scattering process. At all reasonable temperatures ($T>5K$) nuclear spins are randomly orientated, thus coherent scattering resulting in Bragg peaks and isotope incoherent scattering are independent of polarisation and entirely non-spin flip. The spin dependence of nuclear scattering arises due to the spin dependence of the scattering length and results in spin incoherent scattering which has a spin flip as well as a non-spin flip part.

The magnetic scattering of neutrons is governed by two rules:

- Only the magnetisation component which is perpendicular to the scattering vector can give rise to magnetic scattering.

- The magnetisation component parallel to the axis of quantisation gives rise to magnetic scattering without neutron spin flip, while the magnetisation component perpendicular to the direction of the external magnetic field results in neutron spin flip scattering.

It is the differing response of magnetic scattering to parallel polarised neutrons and perpendicular polarised neutrons which enables a subtraction of
cross-sections to be made which causes all other sources to disappear and yields unambiguously the magnetic component.

The following discussion, taken largely from the paper by Schärpf and Capellmann [16], provides a derivation of cross-sections for the II-⊥ method followed by a generalisation to the XYZ-technique and its application to simultaneous measurements with a multidetector.

Referring back to (2.40), the partial differential cross-section for neutron scattering is given by

\[
\frac{d^2\sigma}{d\Omega dE} = \frac{k'}{k} \left( \frac{m_n}{2\pi\hbar^2} \right)^2 \sum_{\lambda,\lambda'} p_\lambda |(k'\sigma'\lambda' | V | k\sigma\lambda)|^2 \delta (\hbar\omega + E_{\lambda'} - E_{\lambda})
\]

where \( p_\lambda \) represents the probability of the target being in a state \( \lambda \). As before, \( k \) and \( \sigma \) are the neutron quantum numbers and \( \lambda \) the target quantum number where quantum numbers with and without primes correspond to the initial and final states respectively. \( V \) is the interaction potential between neutron and target.

The interaction potential between the magnetisation density of the electrons \( \mathbf{M}_e(r) \) and the dipole field of the neutron \( \mathbf{B}_n(r) \) which gives rise to magnetic scattering can be expressed as the following

\[
V = \frac{1}{4\pi\mu_B} \mathbf{M}_e(r) \cdot \mathbf{B}_n(r)
\]

An additional contribution to the electromagnetic potential between the neutron and scattering system arises by virtue of the interaction between the magnetic moment of the neutron and the electric field of the nuclear and electronic charges. Consequently, the expression based upon \( \mu_n \cdot \mathbf{B} \) is not
exact but is instead the first term in an expansion of powers of \( (m_0/m_n) \). The next term includes what is known as the *spin-orbit interaction* the cross-section for which is a factor of the order of \((1/1836)^2\) smaller than that associated with magnetic interactions and can in most cases be neglected. It can then be shown that the matrix element is given by

\[
\langle k'|\hat{M}_n(r)B_n(r)|k \rangle = \hat{M}_n(r) \cdot \frac{\mathbf{K}}{K} \times (\hat{\mathbf{\mu}}_n \times \mathbf{\kappa}) \exp(i\mathbf{\kappa} \cdot \mathbf{r}) = \hat{M}_n(r) \cdot \hat{\mathbf{\mu}}_n \exp(i\mathbf{\kappa} \cdot \mathbf{r})
\]

\[\text{(3.5)}\]

**XYZ geometry:**

The geometry of the scattering process is chosen such that the scattering vector \( \mathbf{\kappa} \) lies in the x-y plane. In the case of the multidetector, the individual detectors contained in the x-y plane form angles \( \alpha \) with respect to the x-axis as depicted in figure 3.2 below. This configuration can be adapted to encompass the single detector arrangement, as required by the \( \ast - \perp \) technique, simply by setting \( \alpha = 0 \). According to this configuration, the unit vector in the direction \( \mathbf{\kappa} \) is given by

\[
\frac{\mathbf{\kappa}}{K} = (\cos \alpha, \sin \alpha, 0)
\]

\[\text{(3.6)}\]

---

**Fig. 3.2** Scattering geometry for subsequent equations. The x-y plane contains the scattering vector of which makes angles \( \alpha \) for different detectors with respect to the x-axis.
so that

$$
\hat{\mu}_{nl} = \frac{\kappa}{k^2} \times (\hat{\mu}_n \times \kappa) = (\hat{\mu}_x \sin^2 \alpha - \hat{\mu}_y \sin \alpha \cos \alpha, \hat{\mu}_y \cos^2 \alpha - \hat{\mu}_x \sin \alpha \cos \alpha, \hat{\mu}_z)
$$

(3.7)

from which it may be shown that

$$
\hat{M}_0 \cdot \hat{\mu}_{nl} = \hat{\mu}_n \cdot \hat{M}_0
$$

(3.8)

$\hat{\mu}_n$ is the neutron magnetic moment operator as defined in (2.38).

For the subsequent presentation of both the II-⊥ and XYZ techniques, the following raising/lowering operators with respect to all three axes are introduced

$$
\hat{\mu}_+ = \frac{1}{2} (\hat{\mu}_y \pm i \hat{\mu}_z), \quad \hat{\mu}_- = \frac{1}{2} (\hat{\mu}_y \pm i \hat{\mu}_x), \quad \hat{\mu}_z = \frac{1}{2} (\hat{\mu}_x \pm i \hat{\mu}_y)
$$

(3.9)

Eigenstates to $\hat{\mu}_v = -\gamma\mu_n \hat{\alpha}_v (v = x, y, z)$ are indexed as $|\uparrow\rangle$ and $|\downarrow\rangle$ and in the XYZ case, flip operations are possible in all three directions $x, y, z$ corresponding to the fact that for the spin up/down at the polariser the spin at the analyser is down/up. The spin flip is described by operations as

$$
\hat{\sigma}_x |\uparrow\rangle = |\downarrow\rangle \quad \text{and} \quad \hat{\sigma}_y |\uparrow\rangle = |\downarrow\rangle \quad \text{etc. for all directions, yielding}
$$

$$
\langle \uparrow | \hat{\sigma}_x | \downarrow \rangle = 1, \quad \langle \downarrow | \hat{\sigma}_x | \uparrow \rangle = 0, \quad \langle \downarrow | \hat{\sigma}_- | \uparrow \rangle = 1
$$

(3.10)

etc. By using mixtures of eigenstates a generalisation to three dimensional polarisation analysis, as required for the XYZ technique, is permitted. This is dealt with in section 3.3.2.
3.3.1.1 Magnetic Part of the Neutron Cross-section

For the case of a single detector, the rotation of $\kappa$ parallel to the $x$-axis can be achieved by setting $\alpha=0$ in (3.7). This yields

$$\hat{M}_e \cdot \hat{\mu}_{nl} = \hat{\mu}_y \hat{M}_y + \hat{\mu}_z \hat{M}_z = -\gamma \hat{\mu}_N \left( \hat{\sigma}_y \hat{M}_y + \hat{\sigma}_z \hat{M}_z \right)$$

(3.11)

which can be rewritten in terms of operators $\hat{\sigma}_x(r), \hat{\sigma}_y(r), \hat{\sigma}_z(r)$, analogous to those in (3.9), as

$$\hat{M}_e \cdot \hat{\mu}_{nl} = \left( \hat{\sigma}_x \hat{\sigma}_x + \hat{\sigma}_y \hat{\sigma}_y + \hat{\sigma}_z \hat{\sigma}_z \right) = -\gamma \mu_N \left( \hat{\sigma}_x \hat{\sigma}_x + \hat{\sigma}_y \hat{\sigma}_y + \hat{\sigma}_z \hat{\sigma}_z \right)$$

(3.12)

The magnetic part of the correlation function $\Gamma(r, \omega)$ can then be expressed as

$$\left( \gamma \mu_N \right)^2 \Gamma_{\infty}(r, \omega) = \sum_{\lambda \lambda'} p_\lambda \left| \left\langle \lambda' \sigma \left| \hat{M}_e \cdot \hat{\mu}_{nl} \right| \lambda \sigma \right\rangle \right|^2 \delta(\hbar \omega + E_\lambda - E_{\lambda'})$$

$$= \sum_{\lambda \lambda'} p_\lambda \left| \left\langle \lambda' \sigma \left| \hat{\sigma}_x \hat{\sigma}_x + \hat{\sigma}_y \hat{\sigma}_y + \hat{\sigma}_z \hat{\sigma}_z \right| \lambda \sigma \right\rangle \right|^2 \delta(\hbar \omega + E_\lambda - E_{\lambda'})$$

$$= \left( \gamma \mu_N \right)^2 \sum_{\lambda \lambda'} p_\lambda \left| \left\langle \lambda' \sigma \left| \hat{\sigma}_x \hat{\sigma}_x \right| \lambda \sigma \right\rangle \right|^2 \delta(\hbar \omega + E_\lambda - E_{\lambda'})$$

(3.13)

**Spin flip scattering:**

In the first instance, the spin flip ($\uparrow \downarrow$) correlation function for the polarisation parallel to the scattering vector $\Gamma_{\uparrow \downarrow}^{\uparrow \downarrow}$ is derived. For this scenario, $\Pi_{\kappa \kappa' \ell \ell'} = (1,0,0)$ where $e_x$ is the $x$-component of the magnetic interaction vector. If one neglects the spin-orbit interaction, the operators $\hat{\sigma}_\pm$ can be applied separately and it follows from (3.13) that
\[
\Gamma^q_{11}(r, \omega) = \sum_{\lambda \sigma} p_\lambda \left| \langle \gamma^\prime | \hat{M}_x | \gamma \rangle \right|^2 \delta(\hbar \omega + E_\gamma - E_{\gamma^\prime}) \\
= \int \langle \left[ \hat{M}_x(r, t) \hat{M}_-(0, 0) \right] \rangle \exp(i \omega t) dt \\
= \hat{M}_{xy}(r, \omega) + \hat{M}_{xz}(r, \omega) + i(\hat{M}_{yz}(r, \omega) - \hat{M}_{yx}(r, \omega))
\] (3.14)

and similarly

\[
\Gamma^q_{i \dagger}(r, \omega) = \hat{M}_{yy}(r, \omega) + \hat{M}_{zz}(r, \omega) - i(\hat{M}_{zy}(r, \omega) - \hat{M}_{yz}(r, \omega))
\] (3.15)

The \langle \ldots \rangle brackets indicate a double - thermal and quantum mechanical - averaging and \( \hat{M}_{xx}(r, \omega) \) etc. are the time Fourier transforms of the corresponding correlation functions. The presence of the factor \( i \) signifies a \( \pi/2 \) phase shift and disappears following the Fourier transform of an odd part of the correlation function (due to the creation of a further factor \( i \)). For perpendicular polarisation in which \( \mathbf{P}_{\perp \mathbf{k} \mathbf{I} \mathbf{I} \mathbf{e}_z} = (0,0,1) \)

\[
\Gamma^q_{11}(r, \omega) = \sum_{\lambda \sigma} p_\lambda \left| \langle \gamma^\prime | \hat{M}_y | \gamma \rangle \right|^2 \delta(\hbar \omega + E_\gamma - E_{\gamma^\prime}) \\
= \hat{M}_{yy}(r, \omega) \\
= \Gamma^q_{i \dagger}(r, \omega)
\] (3.16)

and the difference between parallel and perpendicular polarisation yields

\[
\Gamma^q_{11}(r, \omega) - \Gamma^q_{i \dagger}(r, \omega) = \hat{M}_{zz}(r, \omega) + i(\hat{M}_{zy}(r, \omega) - \hat{M}_{yz}(r, \omega)) \\
\Gamma^q_{i \dagger}(r, \omega) - \Gamma^q_{11}(r, \omega) = \hat{M}_{zz}(r, \omega) - i(\hat{M}_{zy}(r, \omega) - \hat{M}_{yz}(r, \omega))
\] (3.17)

**Non-spin flip scattering:**

In an analogous way to the treatment of spin flip scattering, for \( \mathbf{P}_{\perp \mathbf{k} \mathbf{I} \mathbf{I} \mathbf{e}_x} \) one gets
\[ \Gamma^{ii}(r, \omega) = 0 \]  

(3.18)

and for \( P \cdot \xi \xi \epsilon_z \)

\[ \Gamma^{i \perp}(r, \omega) = \hat{M}_{zz}(r, \omega) \]  

(3.19)

The difference for non-spin flip scattering is therefore

\[ \Gamma^{i \perp}(r, \omega) - \Gamma^{i \perp}(r, \omega) = \hat{M}_{zz}(r, \omega) \]  

(3.20)

The expressions derived for the correlation function \( \Gamma^{i \sigma}(r, \omega)(i=\Pi, \perp) \) can then be related to the partial differential cross-section by combining (3.3) and (3.4) and including the factor \( \exp(\iota \mathbf{k} \cdot \mathbf{r}) \) from (3.5). Performing a spatial Fourier transform will yield the magnetic part of the dynamical scattering function \( S(\kappa, \omega) \) in terms of \( \kappa \) and \( \omega \), together with the form factor \( f(\kappa) \) so that one obtains the partial differential cross-section as expressed in (2.60):

\[
\frac{d^2 \sigma}{d\Omega dE} \bigg|_{\sigma\sigma'} = \left( \gamma \right)^2 \frac{k'}{k} \left( \frac{1}{2} \mathbf{g} f(\kappa) \right)^i S(\kappa, \omega)
\]

### 3.3.1.2 Nuclear Part of the Neutron Cross-section

In order to account for the nuclear part of the scattering process, the spin dependence of the nuclear scattering length must be incorporated. The spin state cross-sections are obtained by rewriting (2.24) in terms of a scattering length operator thus

\[
\left( \frac{d^2 \sigma}{d\Omega dE} \right)_{\sigma \lambda \rightarrow \sigma' \lambda'} = k^2 \sum \left\langle \sigma' \lambda' | \hat{\mathbf{B}}_j \exp(\iota \mathbf{k} \cdot \mathbf{R}_j) | \lambda \sigma \right\rangle^2 \delta(\hbar \omega + E_\lambda - E_{\lambda'})
\]  

(3.21)
where the operator \( \hat{b} \) has eigenvalues \( b^+ \) and \( b^- \) corresponding to the scattering lengths of the states \( |+\rangle \) and \( |-\rangle \) with total spin \( t=\frac{l+1}{2} \) and \( \frac{l-1}{2} \) respectively, and takes the form

\[
\hat{b} = A + B \hat{\sigma} \cdot \hat{I}
\]  
(3.22)

where \( \hat{\sigma} \) is the Pauli spin operator and \( \hat{I} \) is the spin angular momentum operator of the target nucleus. The constants \( A \) and \( B \) are selected on the basis that \( \hat{b} \) satisfies the relations

\[
\hat{b} |+\rangle = b^+ |+\rangle, \quad \hat{b} |-\rangle = b^- |-\rangle
\]  
(3.23)

Because the spin angular momentum operator of the neutron is given by \( \frac{1}{2} \hat{\sigma} \) the corresponding operator for the neutron-nucleus system is \( \hat{I} = \hat{i} + \frac{1}{2} \hat{\sigma} \). Therefore

\[
\hat{\sigma} \cdot \hat{I} = \hat{i}^2 - \hat{i}^2 - \frac{1}{2} \hat{\sigma}^2 = t(t+1) - l(l+1) - \frac{1}{2} \left( \frac{1}{2} + 1 \right)
\]  
(3.24)

which yields

\[
\hat{\sigma} \cdot \hat{I} |+\rangle = l |+\rangle \quad \text{for } t = \frac{l+1}{2}
\]

\[
\hat{\sigma} \cdot \hat{I} |-\rangle = -(l+1) |-\rangle \quad \text{for } t = \frac{l}{2}
\]  
(3.25)

It then follows from (3.22), (3.23) and (3.24) that the two scalar constants are

\[
A = \frac{1}{2l+1} \left[ (l+1)b^+ + lb^- \right]
\]  
(3.26)

and

\[
B = \frac{1}{2l+1} (b^+ - b^-).
\]  
(3.27)
Coherent scattering:

The relation $\hat{b}\uparrow\rangle$ may be written in the form

$$\hat{b}\uparrow\rangle = \{A + B(\hat{\sigma}_x \hat{i}_x + \hat{\sigma}_y \hat{i}_y + \hat{\sigma}_z \hat{i}_z)\}\uparrow\rangle$$  \hspace{1cm} (3.28)$$

so that, by applying the relations of (3.9) and (3.10), the scattering lengths for the four spin state transitions may be written:

$$\langle \uparrow | \hat{b} | \uparrow \rangle = A + B\hat{i}_z$$
$$\langle \downarrow | \hat{b} | \downarrow \rangle = A - B\hat{i}_z$$
$$\langle \downarrow | \hat{b} | \uparrow \rangle = B(\hat{i}_x + \hat{i}_y)$$
$$\langle \uparrow | \hat{b} | \downarrow \rangle = B(\hat{i}_x - \hat{i}_y)$$  \hspace{1cm} (3.29)$$

If the average over the nuclear spin states $\langle \rangle_{sp}$ is distinguished from that over the constituent isotopes of the scattering system $\langle \rangle_{iso}$, then the coherent scattering length $\overline{b}$ for the transition $\uparrow$ to $\uparrow$ is

$$\overline{b} = \langle (A + B\hat{i}_z)_{sp} \rangle_{iso}$$  \hspace{1cm} (3.30)$$

where the scalars $A$ and $B$ depend on the isotope and $\hat{i}_z$ on the nuclear spin state. However, if the nuclear spins are assumed to be randomly orientated i.e. $\langle \hat{i}_x \rangle_{sp} = \langle \hat{i}_y \rangle_{sp} = \langle \hat{i}_z \rangle_{sp} = 0$ then, from (3.29), it can be seen that coherent scattering is only present in the non-spin flip process and that the scalar $A$, averaged over all isotopes, is equal to the coherent scattering length as defined in (2.34).

$$\overline{b} = \langle A \rangle_{iso}$$  \hspace{1cm} (3.31)$$
Incoherent scattering:

From (2.33) it can be seen that incoherent scattering is proportional to $b^2 - \langle b \rangle^2$ where for the transition $\uparrow \to \uparrow$

$$b^2 = \left\langle \left\{ A + B \hat{L}_z \right\}^2 \right\rangle_{iso}$$

$$= \langle A^2 \rangle_{iso} + \langle B^2 \rangle_{iso} + 2 \langle AB \hat{L}_z \rangle_{iso}$$

(3.32)

and for random spins

$$\langle \hat{L}_z \rangle_{sp} = \langle \hat{L}_y \rangle_{sp} = \langle \hat{L}_z \rangle_{sp} = \frac{1}{2} J(J + 1)$$

(3.33)

As before $\langle \hat{L}_z \rangle_{sp} = 0$ and it may therefore be shown that for non-spin flip processes, $b^2 - \langle b \rangle^2$ is given by

$$b^2 - \langle b \rangle^2 = \langle A^2 \rangle_{iso} - \langle A \rangle_{iso}^2 + \frac{1}{2} \langle B^2 (J(J + 1)) \rangle_{iso}$$

(3.34)

while for spin flip scattering

$$b^2 - \langle b \rangle^2 = \frac{1}{3} \langle B^2 (J(J + 1)) \rangle_{iso}$$

(3.35)

An early confirmatory experiment of this result was performed by Moon et al. and reported on in their 1969 paper [4]. The specimen they measured was vanadium which, due to it being mono-isotopic i.e. $\langle A^2 \rangle_{iso} = \langle A \rangle_{iso}^2$ in (3.34), having virtually no coherent scattering length and no strong paramagnetism, provided a direct study of nuclear spin incoherent scattering. The results, shown in figure 3.3, provide clear evidence for the factor of two difference
between the non-spin flip and spin flip scattering as predicted by (3.34) and (3.35), and the independence of the total cross-section to the polarisation direction confirms the scattering to be of nuclear spin origin. The nature of the scattering from vanadium means that it is often used as a standard by which other measurements can be placed onto an absolute scale. The details of vanadium calibration measurements are discussed in section 4.3.

3.3.1.3 Partial Differential Cross-sections for Nuclear and Magnetic Parts

Combining the operator $\hat{b}_i \exp(i\mathbf{K} \cdot \mathbf{R}_i)$ with its magnetic counterpart of the form $\gamma \mathbf{r}_0 \hat{\sigma} \cdot \hat{\mathbf{Q}}_\perp$ one can express the matrix element for nuclear and magnetic scattering at a position $\mathbf{r}$ from the nucleus as

$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \frac{2\pi \hbar^2}{m_n} \left[ (A + B\mathbf{\hat{\sigma}} \cdot \mathbf{\hat{I}}) \exp(i\mathbf{K} \cdot (\mathbf{r} - \mathbf{R})) \right] + \left( \frac{r_0 \gamma}{2} \right) \mathbf{M}_e(\mathbf{r}) \cdot \mathbf{\hat{\sigma}} \cdot \exp(i\mathbf{K} \cdot \mathbf{r})$$

(3.36)

with $\mathbf{R}$ the position of the nucleus and $\mathbf{\hat{M}}_e(\mathbf{r})$ the electronic contribution measured in Bohr magnetons. In the following, it will be assumed that there
are no correlation’s between nuclear spins and electron magnetic moments, that is \( \langle \hat{l}_a \hat{M}_{\alpha \epsilon} \rangle = 0 \). It will also be assumed that there is no nuclear polarisation i.e. \( \langle \hat{l}_a \hat{b} \rangle = 0 \), no nuclear magnetic interference term i.e. \( \langle \hat{M}_{\alpha \epsilon} \hat{b} \rangle = 0 \) and only the on site correlation \( \langle \hat{l}_a \hat{l}_\beta \rangle = \delta_{\alpha \beta} \), where \( \delta_{\alpha \beta} \), the Kronecker delta function, is 1 for \( \alpha = \beta \) and 0 otherwise. Omitting these interference terms and performing the spatial Fourier transform yields the following partial differential cross-sections for spin flip and non-spin flip scattering.

**Spin flip scattering:**

With \( \text{P}_\parallel \text{k} \text{l} \text{l} \text{e}_x \)

\[
\frac{d^2 \sigma_{II}^{\parallel}}{d\Omega dE} = \frac{k'}{k} \left[ \left( \frac{r_0 \gamma}{\theta} \right)^2 \left( \frac{1}{2} g_\text{f}(\kappa) \right)^2 \hat{M}_{zz}(\kappa, \omega) + \hat{M}_{yy}(\kappa, \omega) + i\left( \hat{M}_{xy}(\kappa, \omega) - \hat{M}_{yz}(\kappa, \omega) \right) \right] + B^2 \left[ \hat{l}_\omega(\kappa, \omega) + \hat{l}_{yy}(\kappa, \omega) \right]
\]  
(3.37)

and with \( \text{P}_\perp \text{k} \text{l} \text{l} \text{e}_z \)

\[
\frac{d^2 \sigma_{II}^{\perp}}{d\Omega dE} = \frac{k'}{k} \left[ \left( \frac{r_0 \gamma}{\theta} \right)^2 \left( \frac{1}{2} g_\text{f}(\kappa) \right)^2 \hat{M}_{xx}(\kappa, \omega) + B^2 \left[ \hat{l}_{xy}(\kappa, \omega) + \hat{l}_{yx}(\kappa, \omega) \right] \right]
\]  
(3.38)

**Non-spin flip scattering:**

With \( \text{P}_\parallel \text{k} \text{l} \text{l} \text{e}_x \)

\[
\frac{d^2 \sigma_{II}^{\parallel}}{d\Omega dE} = \frac{k'}{k} \left[ B^2 \hat{l}_{xx}(\kappa, \omega) + B^2 S_{\text{cor}}(\kappa, \omega) \right]
\]  
(3.39)

and with \( \text{P}_\perp \text{k} \text{l} \text{l} \text{e}_z \)

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\[ \frac{d^2 \sigma_{\perp \perp}}{d\Omega dE} = \frac{k'}{k} \left[ \left( r_{0} \right)^{2} \left\{ \frac{1}{2} gf(k) \right\} ^{2} \hat{M}_{xx}(k,\omega) + B^{2} \hat{I}_{zz}(k,\omega) + \hat{B}^{2} S_{\text{con}}(k,\omega) \right] \]

(3.40)

For a powder sample, an average is taken over all crystallographic directions meaning that the following holds

\[ \hat{M}_{xx}(k,\omega) = \hat{M}_{yy}(k,\omega) = \hat{M}_{zz}(k,\omega) = \frac{1}{3} \hat{M}(k,\omega) \]  

(3.41)

and for nuclear spin without nuclear polarisation

\[ \hat{I}_{xx}(k,\omega) = \hat{I}_{yy}(k,\omega) = \hat{I}_{zz}(k,\omega) = \frac{1}{3} \hat{I}_{0}^2(k,\omega) = \frac{1}{3} S_{\text{incoh}}(k,\omega) \]  

(3.42)

Therefore, for the case of a powder, the following spin state cross-section are obtained:

\[ \frac{d^2 \sigma_{\perp \perp}}{d\Omega dE} = \frac{k'}{k} \left[ \left( r_{0} \right)^{2} \left\{ \frac{1}{2} gf(k) \right\} ^{2} \left[ \hat{M}(k,\omega) + i \left( \hat{M}_{zy}(k,\omega) - \hat{M}_{yz}(k,\omega) \right) \right] \right] \]  

(3.43)

\[ \frac{d^2 \sigma_{\perp \perp}}{d\Omega dE} = \frac{k'}{k} \left[ \left( r_{0} \right)^{2} \left\{ \frac{1}{2} gf(k) \right\} ^{2} \left[ \hat{M}(k,\omega) - i \left( \hat{M}_{zy}(k,\omega) - \hat{M}_{yz}(k,\omega) \right) \right] \right] \]  

(3.44)

\[ \frac{d^2 \sigma_{\perp \parallel}}{d\Omega dE} = \frac{k'}{k} \left[ \left( r_{0} \right)^{2} \left\{ \frac{1}{2} gf(k) \right\} ^{2} \hat{M}(k,\omega) + \frac{1}{3} B^{2} S_{\text{incoh}}(k,\omega) \right] \]  

(3.45)

\[ \frac{d^2 \sigma_{\parallel \perp}}{d\Omega dE} = \frac{k'}{k} \left[ \left( r_{0} \right)^{2} \left\{ \frac{1}{2} gf(k) \right\} ^{2} \hat{M}(k,\omega) + \frac{1}{3} B^{2} S_{\text{con}}(k,\omega) \right] \]  

(3.46)
where $S_{coh}(\kappa \omega)$ and $S_{incoh}(\kappa \omega)$ are the scattering functions for coherent and incoherent scattering respectively. The II-⊥ technique yields the magnetic part of the scattering exclusively from the coherent and incoherent contributions by virtue of only the magnetic part being dependent on the polarisation direction. This fact is demonstrated in another experiment by Moon et al.\cite{4} on the paramagnet MnF$_2$. Presented in figure 3.4 are the results for both polarisation directions where, for P∥κ, the scattering is entirely spin flip (the small bump in the non-spin flip signal being due to multiple Bragg scattering) while for P⊥κ the scattering cross-sections for spin and non-spin flip scattering are equal. Although the spin flip scattering includes a nuclear spin part as well as a magnetic one it can be seen from the above cross-sections that, due to the spins being randomly orientated, this contribution gives rise to equal amounts of scattering for both directions and drops out during the subtraction.

3.3.2 The XYZ Difference Technique

As mentioned already, while the condition of P⊥κ is possible to achieve simultaneously for all detectors in a multidetector instrument (providing that all
detectors are in a plane), $\Pi_N$ is not, due to the fact that each individual detector corresponds to a different scattering vector. As a result, for a multidetector, the already described II-I method must be modified to incorporate a type of three dimensional polarisation analysis in which the non-spin flip and spin flip cross-sections are measured for the three mutually orthogonal polarisation directions $x$, $y$ and $z$.

For three dimensional analysis, the polarisation of the neutrons is defined by the vector

$$P = (P_x, P_y, P_z) = P_x e_x + P_y e_y + P_z e_z$$

which, by suitable manipulation of the field in the spin turn coils surrounding the sample environment, can be rotated into the $x$, $y$ or $z$ direction.

3.3.2.1 Magnetic Spin Flip Cross-sections

**Polarisation in the $x$-direction:**

For the case of polarisation in the $x$-direction, $P_x = 1$ or $P = (1,0,0)$ or $\Pi_N e_x$. From (3.7), the potential term, $\hat{M}_e \cdot \hat{n}_l$, can be written as

$$\hat{M}_e \cdot \hat{n}_l = \hat{\mu}_x (\hat{M}_x \sin^2 \alpha - \hat{M}_y \sin \alpha \cos \alpha) + \hat{\mu}_y (\hat{M}_y \cos^2 \alpha - \hat{M}_x \sin \alpha \cos \alpha) + \hat{\mu}_z \hat{M}_z$$

however, for polarisation in the $x$-direction, this can be reduced because

$$\langle \hat{\sigma}_x \hat{\sigma}_x \rangle = 0$$

so that the magnetic correlation function can be written in the form
\[ (\gamma \mu_n)^2 \Gamma_{11}^x (r, \omega) = \sum_{\lambda\lambda'} p_\lambda \langle \lambda' \downarrow | \hat{A}_x | \lambda' \uparrow \rangle^2 (\hbar \sigma + E_\lambda - E_{\lambda'}) \delta \]

\[ + \hat{\mu}_z \hat{M}_z | \lambda' \uparrow \rangle \delta (\hbar \sigma + E_\lambda - E_{\lambda'}) \]

\[ (3.48) \]

If one defines \( \hat{A}_x = \hat{M}_y \cos^2 \alpha - \hat{M}_x \sin \alpha \cos \alpha \pm \hat{M}_y \) then this can be rewritten as

\[ \Gamma_{11}^x (r, \omega) = \sum_{\lambda\lambda'} p_\lambda \langle \lambda' \downarrow | \hat{A}_x | \lambda' \uparrow \rangle^2 (\hbar \sigma + E_\lambda - E_{\lambda'}) \delta \]

\[ = \sum_{\lambda\lambda'} p_\lambda \langle \lambda' \downarrow | \hat{A}_x | \lambda' \uparrow \rangle^2 (\hbar \sigma + E_\lambda - E_{\lambda'}) \delta \]

\[ (3.49) \]

where the factor \( (\gamma \mu_n)^2 \) cancels out with that present in the components of the neutron magnetic moment operator. As with (3.14), and according to the spin flip operations of (3.10), \( \langle \downarrow | \sigma^+ | \uparrow \rangle = 1 \). All other terms involving \( \sigma^+ \) are zero.

Neglecting the spin-orbit coupling as before, the above matrix element can be expressed in terms of the spin operators resulting in
\[ \Gamma_{\uparrow\downarrow}^{(r, \omega)}(r, \omega) = \langle \hat{A}_- \hat{A}_+ \rangle \]
\[ = \langle \langle \hat{M}_y \cos^2 \alpha - \hat{M}_z \sin \alpha \cos \alpha \rangle \hat{M}_y \cos^2 \alpha - \hat{M}_z \sin \alpha \cos \alpha \rangle \rangle + \langle \langle \hat{M}_z \hat{M}_z \rangle \rangle \]
\[ - i \langle \langle \hat{M}_z (\hat{M}_y \cos^2 \alpha - \hat{M}_z \sin \alpha \cos \alpha) \rangle \rangle + i \langle \langle \hat{M}_y \cos^2 \alpha - \hat{M}_z \sin \alpha \cos \alpha \rangle \hat{M}_z \rangle \rangle \]
\[ = \langle \langle \hat{M}_y \hat{M}_x \rangle \rangle \cos^4 \alpha + \langle \langle \hat{M}_x \hat{M}_x \rangle \rangle \sin^2 \alpha \cos^2 \alpha + \langle \langle \hat{M}_z \hat{M}_z \rangle \rangle \]
\[ - \langle \langle \hat{M}_x \hat{M}_y \rangle \rangle \langle \langle \hat{M}_x \hat{M}_x \rangle \rangle \sin \alpha \cos \alpha - i \left[ \langle \langle \hat{M}_x \hat{M}_y \rangle \rangle - \langle \langle \hat{M}_y \hat{M}_x \rangle \rangle \right] \cos 2\alpha \]
\[ + \langle \langle \hat{M}_x \hat{M}_y - \hat{M}_y \hat{M}_x \rangle \rangle \sin \alpha \cos \alpha \]
\[ (3.50) \]

The double bracketed correlation functions \( \langle \langle \hat{M}_x \hat{M}_x \rangle \rangle \) etc, for brevity, are always to be understood as being equivalent to their corresponding time Fourier transform, \( \hat{M}_{xx}(r, \omega) \) etc. For the transition \( \downarrow \) to \( \uparrow \), the above expression holds except that \(-i\) is replaced by \(+i\) in the phase shifted part.

**Polarisation in the y direction:**

Here, \( P_y = 1 \) or \( P = (0, 1, 0) \), so that the substitution
\[ \hat{A}_z = \hat{M}_z + i (\hat{M}_x \sin^2 \alpha - \hat{M}_y \sin \alpha \cos \alpha) \]
is made, to yield

\[ \Gamma_{\uparrow\downarrow}^{(r, \omega)}(r, \omega) = \langle \langle \hat{A}_- \hat{A}_+ \rangle \rangle \]
\[ = \langle \langle \hat{M}_y \hat{M}_z \rangle \rangle + \langle \langle \hat{M}_x \hat{M}_y \rangle \rangle \sin^4 \alpha + \langle \langle \hat{M}_y \hat{M}_x \rangle \rangle \sin^2 \alpha \cos^2 \alpha \]
\[ - \langle \langle \hat{M}_y \hat{M}_x \rangle \rangle + \langle \langle \hat{M}_y \hat{M}_x \rangle \rangle \sin^3 \alpha \cos \alpha - i \left[ \langle \langle \hat{M}_x \hat{M}_z \rangle \rangle \right] \]
\[ - \langle \langle \hat{M}_x \hat{M}_z \rangle \rangle \sin 2\alpha + \langle \langle \hat{M}_x \hat{M}_x \rangle \rangle - \langle \langle \hat{M}_y \hat{M}_z \rangle \rangle \sin \alpha \cos \alpha \]
\[ (3.51) \]

where as with (3.50), for the converse transition, \(-i\) is replaced by \(+i\).
**Polarisation in the z direction:**

For this configuration, $P_z = 1$ or $P = (0,0,1)$ and $\left\langle \hat{J}_z | \hat{z} | \hat{J} \right\rangle = 0$ so that, from (3.47) the correlation function is given by

$$
(\gamma \mu_N)^2 \Gamma_{\hat{z}}^2 (r, \omega) = \sum_{\lambda \lambda'} p_{\lambda} \left| \left\langle \lambda' | \hat{\mu}_x | \hat{\lambda} \right\rangle \hat{M}_x \sin^2 \alpha - \hat{M}_y \sin \alpha \cos \alpha \right|^2 + \left| \left\langle \lambda' | \hat{\mu}_y | \hat{\lambda} \right\rangle \hat{M}_y \cos^2 \alpha - \hat{M}_x \sin \alpha \cos \alpha \right|^2 \delta (\hbar \omega + E_{\lambda'} - E_{\lambda})
$$

(3.52)

which by making the appropriate substitution of

$$
\hat{A}_z = (\hat{M}_x \sin^2 \alpha - \hat{M}_y \sin \alpha \cos \alpha) \pm i (\hat{M}_y \cos^2 \alpha - \hat{M}_x \sin \alpha \cos \alpha)
$$

(3.53)

gives

$$
\Gamma_{\hat{z}}^2 (r, \omega) = \left\langle \left\langle \hat{A}_z | \hat{A}_z \right\rangle \right\rangle
= \left\langle \left\langle \hat{M}_x \hat{M}_x \right\rangle \right\rangle \sin^4 \alpha + \sin^2 \alpha \cos^3 \alpha + \left\langle \left\langle \hat{M}_y \hat{M}_y \right\rangle \right\rangle \cos^2 \alpha
- \left( \left\langle \left\langle \hat{M}_x \hat{M}_y \right\rangle \right\rangle + \left\langle \left\langle \hat{M}_y \hat{M}_x \right\rangle \right\rangle \right) \sin \alpha \cos \alpha
$$

(3.54)
3.3.2.2 Magnetic Non-Spin Flip Cross-sections

**Polarisation in the x direction:**

Because \( \langle \hat{\sigma}_x | \hat{\sigma}_x \rangle = 1 \) and \( \langle \hat{\sigma}_x | \hat{\sigma}_y \rangle = \langle \hat{\sigma}_x | \hat{\sigma}_z \rangle = 0 \), the correlation function, using (3.47) and (3.10), is given by

\[
\Gamma_{\hat{r}, \omega}^{\hat{x}}(r, \omega) = \sum_{\lambda \lambda'} \rho_\lambda \left\langle \hat{p} \hat{x} \left| \hat{\mu}_x \left( \hat{M}_x \sin^2 \alpha - \hat{M}_y \sin \alpha \cos \alpha \right) \right| \hat{p} \hat{x} \right\rangle \delta \left( \hbar \omega + E_\lambda - E_{\lambda'} \right)
\]

\[
= (\gamma \mu_n)^2 \left\{ \langle \hat{M}_x \hat{M}_x \rangle \sin^4 \alpha + \langle \hat{M}_y \hat{M}_y \rangle \sin^2 \alpha \cos^2 \alpha \right. \\
- \left. \langle \hat{M}_x \hat{M}_y \rangle + \langle \hat{M}_y \hat{M}_x \rangle \right\} \sin \alpha \cos \alpha \}
\]

(3.55)

**Polarisation in the y direction:**

In the same way as for x polarisation, the correlation function is given by

\[
\Gamma_{\hat{r}, \omega}^{\hat{y}}(r, \omega) = \langle \hat{M}_y \hat{M}_y \rangle \cos^4 \alpha + \langle \hat{M}_x \hat{M}_x \rangle \sin^2 \alpha \cos^2 \alpha \\
- \left( \langle \hat{M}_x \hat{M}_y \rangle + \langle \hat{M}_y \hat{M}_x \rangle \right) \sin \alpha \cos^3 \alpha
\]

(3.56)

**Polarisation in the z direction:**

Similarly

\[
\Gamma_{\hat{r}, \omega}^{\hat{z}}(r, \omega) = \langle \hat{M}_z \hat{M}_z \rangle
\]

(3.57)

The phase shifted and non-phase shifted parts which comprise the derived functions for the spin flip and non-spin flip correlation functions can be
distinguished using the following matrix equations. The non-phase shifted part can be expressed as

\[
\begin{pmatrix}
\Gamma_{11}^{s}(r,r) \\
\Gamma_{11}^{p}(r,r) \\
\Gamma_{12}^{s}(r,r) \\
\Gamma_{12}^{p}(r,r)
\end{pmatrix} = \begin{pmatrix}
sin^2\alpha\cos^2\alpha & \cos^4\alpha & 1 & -\sin\alpha\cos^3\alpha \\
\sin^4\alpha & \sin^2\alpha\cos^2\alpha & 1 & -\sin^3\alpha\cos\alpha \\
\sin^2\alpha & \cos^2\alpha & 0 & -\sin\alpha\cos\alpha \\
\sin^4\alpha & \sin^2\alpha\cos^2\alpha & 0 & -\sin^3\alpha\cos\alpha
\end{pmatrix} \begin{pmatrix}
\dot{M}_{xx}(r,r) \\
\dot{M}_{yy}(r,r) \\
\dot{M}_{xy}(r,r) + \dot{M}_{yx}(r,r)
\end{pmatrix}
\]

(3.58)

and the phase shifted part as

\[
\begin{pmatrix}
\Gamma_{11}^{s}(r,r) \\
\Gamma_{11}^{p}(r,r) \\
\Gamma_{12}^{s}(r,r) \\
\Gamma_{12}^{p}(r,r)
\end{pmatrix} = \begin{pmatrix}
-\sin\alpha\cos\alpha & -\cos 2\alpha \\
\sin\alpha\cos\alpha & \cos 2\alpha \\
\sin 2\alpha & -\cos\alpha\sin\alpha \\
-\sin 2\alpha & \cos\alpha\sin\alpha
\end{pmatrix} \begin{pmatrix}
\dot{M}_{xx}(r,r) - \dot{M}_{xy}(r,r) \\
\dot{M}_{yy}(r,r) - \dot{M}_{yx}(r,r)
\end{pmatrix}
\]

(3.59)

### 3.3.2.3 Elastic Magnetic Scattering in Single Crystals

For collinear magnetic structures, while the scattering functions of (3.59) will be zero, \(\langle\hat{M}_x\hat{M}_y\rangle + \langle\hat{M}_y\hat{M}_x\rangle\) in general will not, due to the fact that the components \(\hat{M}_x\) and \(\hat{M}_y\) of \(\hat{M}\) are contained in the scattering plane and are therefore strongly correlated. If the magnetisation of the lattice \(\hat{M}\) is expressed in spherical co-ordinates, with the z-axis as the pole axis such that \(\hat{M} = |\hat{M}|(\sin\tau\cos\xi, \sin\tau\sin\xi, \cos\tau)\) where \(\tau\) is the angle with the z-axis and \(\xi\) the spherical angle with the x-axis, then it can be shown that the elastic spin flip and non-spin flip cross-sections are given by:
where the magnetic structure amplitude for the (hkl) reflection from a crystal with magnetic atoms \( j \) at the positions \( (x_j, y_j, z_j) \) is defined as

\[
|F_{\text{mag}}| = \frac{\gamma}{2} \sum_j \hat{M}_j \kappa_j \exp\{2\pi i (hx_j + ky_j + lz_j)\}
\]  

(3.66)

and the lattice factor is given in terms of the reciprocal lattice vector \( \tau \) by

\[
\left|\sum \exp(i\mathbf{k} \cdot \mathbf{l})\right|^2 = N\left(\frac{(2\pi)^3}{V_0}\right)\sum \delta(\mathbf{k} - \mathbf{\tau})
\]  

(3.67)
3.3.2.4 Powder Measurements

For the case of a powder with collinear magnetisation, the magnetic cross-sections become far simpler. Because \( \langle \langle \hat{M}_z \hat{M}_z \rangle \rangle = \langle \langle \hat{M}_x \hat{M}_x \rangle \rangle = \langle \langle \hat{M}_y \hat{M}_y \rangle \rangle \) and all mixed ones are zero, the phase shifted part of (3.59) is not present while only the first three columns of the matrix (3.58) remain to describe the spin flip and non-flip cross-sections. The nuclear part remains the same as that in equations (3.36) to (3.46) and enables the following definitions to be made

\[
\frac{d^2 \sigma_{\alpha \alpha'}}{dQdE} = (\gamma r_0)^2 \frac{k'}{k} \left\{ \frac{i}{2} gf(\kappa) \right\}^2 S_{\alpha \alpha'}^\nu (\kappa, \omega) \quad (3.68)
\]

recalling that \( S_{\alpha \alpha'}^\nu (\kappa, \omega) \) is the space Fourier transform of the corresponding correlation function \( \Gamma_{\alpha \alpha'}^\nu (r, \omega) \), and

\[
\frac{d^2 \sigma_{\text{para}}}{dQdE} = (\gamma r_0)^\frac{2}{3} \frac{k'}{k} \left\{ \frac{i}{2} gf(\kappa) \right\}^2 \hat{M}(\kappa, \omega) \quad (3.69)
\]

\[
\frac{d^2 \sigma_{\text{spin}}}{dQdE} = \frac{k'}{k} B^2 S_{\text{incoh}}(\kappa, \omega) \quad (3.70)
\]

\[
\frac{d^2 \sigma_{\text{coh}}}{dQdE} = \frac{k'}{k} \vec{b}^2 S_{\text{coh}}(\kappa, \omega) \quad (3.71)
\]

Gathering all contributions to the total scattering i.e. coherent, spin incoherent, isotope incoherent and magnetic, and applying the above definitions yields six cross-sections corresponding to measurements for the three polarisation directions with and without spin flip respectively. These are:
The above expressions can then be combined in such a way that the various contributions are separated. The paramagnetic cross-section can be obtained from the following two combinations:

\[
\frac{d^2 \sigma_{\text{para}}}{d\Omega dE} = 2 \left( \frac{d^2 \sigma_{\uparrow \downarrow}}{d\Omega dE} + \frac{d^2 \sigma_{\downarrow \uparrow}}{d\Omega dE} - \frac{2}{3} d^2 \sigma_{\downarrow \uparrow} \right)
\]

(3.78)

The spin incoherent scattering can be obtained from
Spin Polarisation Analysis

and while the coherent and isotope incoherent cannot be separated (as they are both contained only in the non spin flip signal), together they can be obtained by subtracting (3.79) and (3.80) from the z-polarised non-flip cross-section thus

\[
\frac{d^2 \sigma_{\text{coh}}^{\text{spin}}}{d\Omega dE'} = \frac{3}{2} \left( \frac{d^2 \sigma_{\text{ Fol} 1}^{\text{iso}}}{d\Omega dE'} - \frac{d^2 \sigma_{\text{ Fol} 1}^{\text{incoh}}}{d\Omega dE'} - \frac{d^2 \sigma_{\text{ Fol} 1}^{\text{spin}}}{d\Omega dE'} \right)
\]

(3.80)

For the case of a non-magnetic sample, the coherent scattering can be separated from the spin incoherent scattering simply by measuring the spin flip and non-spin flip counts for z-polarised neutrons. The fact that, for unpolarised neutrons, the neutron spin interacts with the nuclear spin in such a way that the probability of the change in the spin direction of the neutron is \( \frac{1}{2} \) with flip and \( \frac{1}{2} \) without flip means that the required coherent scattering is given by the difference between the number of neutrons whose spins were not flipped and half the number of those whose spins were flipped. This is made apparent by (3.74) and (3.77) if one neglects the paramagnetic term.

\[
\frac{d^2 \sigma_{\text{coh}}}{d\Omega dE'} + \frac{d^2 \sigma_{\text{incoh}}^{\text{iso}}}{d\Omega dE'} = \frac{d^2 \sigma_{\text{ Fol} 1}^{\text{i}}}{d\Omega dE'} - \frac{1}{2} \frac{d^2 \sigma_{\text{ para}}}{d\Omega dE'} - \frac{1}{3} \frac{d^2 \sigma_{\text{ incoh}}^{\text{spin}}}{d\Omega dE'}
\]

(3.81)

The following chapter provides an instrumental description of a multidetector, namely the two-axis spectrometer D7 at the ILL, adapted to the XYZ difference technique of polarisation analysis. As previously mentioned, this set-up provided the experimental means by which the existence of magnetic fluctuations in the high-\( T_c \) material \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) was investigated. In addition, the use of spin polarised neutrons in elucidating the interference term
between nuclear and magnetic structure amplitudes is described along with
details concerning instrument calibration and data reduction. The detection
and magnitude determination of this interference term provided the
experimental means by which the lattice distortion associated with the
formation of a FLL in niobium was investigated.

REFERENCES

  1, 82, 1923 and 1929, (1986).
CHAPTER 4

INSTRUMENTATION AND DATA REDUCTION
FOR POLARISATION ANALYSIS

All data presented in this thesis were obtained via a number of neutron scattering experiments performed on instruments situated on the high flux reactor at the Institut Laue-Langevin (ILL), Grenoble. Described in this chapter are the investigative means by which polarised neutrons were utilised in the study of both the magnetic response from the high Tc series YBa$_2$Cu$_3$O$_{6+x}$, and the interaction between the flux line lattice and the nuclear lattice in the type II material niobium. Respectively, the instruments used were the diffuse scattering multidetector, D7, and the small angle diffractometer D17. In addition, unpolarised experiments were carried out on the high Tc sample using the high-resolution two-axis diffractometer, D2B, in order to clarify the crystallographic structure and oxygen content, and test for sample homogeneity. The instrumental description for this can be found in chapter 6.

4.1 The High Flux Reactor

The high flux reactor at the ILL operates at a thermal power of 58.4 MW, provided by the nuclear fission of uranium$_{235}$ within a single fuel element. Neutrons emerging in equilibrium with the D$_2$O moderator at 300K have a Maxwellian flux distribution as described in 2.2 for which the peak intensity can be modified by the inclusion of one of three additional moderators:
- The hot source, consisting of 10 dm³ of graphite at 2400K, which enhances the neutron intensity at wavelengths below 0.8Å.

- The vertical cold source consisting of 20 dm³ of liquid deuterium at 25K, with a flux of $4.5 \times 10^{14}$ n cm⁻² sec⁻¹.

- The horizontal cold source, consisting of 6 dm³ of liquid deuterium at 25K, at a position with a flux of $8 \times 10^{14}$ n cm⁻² sec⁻¹. Both cold sources enhance the neutron intensity at wavelengths greater than 3Å.

By using a number of guide tubes, many instruments can be installed which benefit from thermal or cold neutrons as well as low background. Figure 4.1 below shows a comparison between the hot, thermal and cold neutron spectra from the ILL and that from a pulsed spallation source [1]. The essential data of the high flux reactor is summarised in Table 4.1 [2].

![Fig. 4.1 Neutron flux produced by the three principle sources available at the ILL a) 2000K graphite (hot), b) 300K D₂O (thermal), c) 25K D₂ (cold), in comparison with that from the SNS spallation source [1].](image-url)
## Instrumentation and Data Reduction

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal power</td>
<td>58.4 MW</td>
</tr>
<tr>
<td>Max unperturbed thermal flux in the reflector</td>
<td>$1.5 \times 10^{15}$ cm$^2$s$^{-1}$</td>
</tr>
<tr>
<td>Max perturbed thermal flux in the beam tubes</td>
<td>$1.2 \times 10^{15}$ cm$^2$s$^{-1}$</td>
</tr>
<tr>
<td>Coolant flow in fuel element</td>
<td>2400 m$^3$/h</td>
</tr>
<tr>
<td>Coolant velocity</td>
<td>17 ms$^{-1}$</td>
</tr>
<tr>
<td>Coolant pressure (outlet)</td>
<td>4 bar</td>
</tr>
<tr>
<td>Coolant temperature (outlet)</td>
<td>50 °C</td>
</tr>
<tr>
<td>Average consumption of $^{235}$U</td>
<td>30%</td>
</tr>
</tbody>
</table>

Table 4.1 Characterising data of the high flux reactor at the ILL, Grenoble.

### 4.2 D7: A Multidetector Instrument Adapted to the XYZ Method of Polarisation Analysis

In order to exploit the rules governing a change in the neutron spin state upon scattering as described in 3.3.1, one requires a means of analysing the spin state subsequent to scattering. By incorporating analysers, which only count those scattered neutrons with the same spin direction as the polariser, and a flipper in between polariser and sample, it is possible to obtain the spin flip and non-spin flip counts. If the flipper is on, neutrons incident on the sample have spins in the opposite direction to the polarisation direction meaning that any counts recorded by the detector must be as a result of the neutron spin state being changed by the scattering process. Conversely, if the flipper is off, the non-spin flip intensity is recorded. This process is shown schematically in figure 4.2.

The original form of the D7 instrument was that of a conventional diffuse scattering machine consisting of monochromator, sample and four banks of detectors, all contained in the scattering plane. Designed to study the often weak scattering arising from disorder phenomena in solids such as point defects and short range order, various measures were incorporated so as to optimise the scattered intensity. For the case of structural investigations where the elastic and inelastic contributions to the diffuse scattering are...
Fig. 4.2 Schematic diagram, illustrating the polariser-flipper-analyser-detector set-up for measuring spin flip and non-spin flip counts.

Separated by time of flight (TOF) measurements, the resolution in both energy transfer and momentum transfer can be relaxed so as to enhance both the incident and scattered intensity. In addition, the neutron efficiency is optimised by matching the collimation of the monochromator to the size of the detectors and background intensity is minimised by an absorbing shield surrounding the instrument. The presence of these design features for the detection of weak scattering helped enable the modification of the instrument into a powerful spin analysis probe.

The instrument as it is used today is installed on the H15 cold guide tube at the ILL and utilises long wavelength neutrons in the range 3.1Å to 5.4Å. Using a highly efficient double focussing, triple graphite monochromator, equipped with three motors for rotating each of the monochromators and three for
Instrumentation and Data Reduction

<table>
<thead>
<tr>
<th>Incident wavelength $\lambda$/Å</th>
<th>Incident energy $E$/meV</th>
<th>Flux /$10^3$ cm$^{-2}$s$^{-1}$ unpolarised neutrons</th>
<th>Flux /$10^5$ cm$^{-2}$s$^{-1}$ polarised neutrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>8.5</td>
<td>2.5</td>
<td>2.0</td>
</tr>
<tr>
<td>4.8</td>
<td>3.5</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>5.4</td>
<td>2.5</td>
<td>0.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 4.2 Summary of available neutron fluxes for the spectrometer D7 [2].

Vertical focussing, one of three wavelengths 3.1Å, 4.8Å and 5.4Å may be selected with a resolution of about 3%. This process is further aided by the air cushions and marble floor upon which the instrument sits, thereby allowing easy movement of the entire machine in the required direction. Table 4.2 summarises the polarised and unpolarised fluxes associated with each wavelength.

The arrangement of D7 [3] is shown schematically in figure 4.2 and consists of four banks of sixteen $^3$He detectors, covering an angular range of $2\theta = 7^\circ$ to $160^\circ$, mounted in a horizontal plane (defined as the x-y plane) also containing the incident beam and sample. For polarisation analysis, the incident monochromatic beam is polarised using a supermirror bender type polariser [4], a device which is also used to equip alternate detectors so that the scattered beam may be analysed simultaneously for 32 different scattering vectors, incorporating a total of 6000 individual polarising mirrors throughout the angular range. Located between the polariser and sample is a dc-flipper [5], together with a correction coil which serves to compensate the vertical guide field outside the flipper. When activated, this device inverts the spin state of the incident neutrons so that the spin flip and non-spin flip scattering can be measured. Guide fields applied between the polariser and analysers ensure that the spin state of the neutron can be related to a fixed direction (defined to be the z-direction). A spin rotator, consisting of a cube of three coil pairs, enables the spin direction of the neutron to be defined at the sample position in one of the three mutually orthogonal directions $\pm P_x$, $\pm P_y$ or $\pm P_z$. After scattering, the neutron spin undergoes a further spin reorientation where the component of the spin which was rotated into the x or y direction is
brought back into the z-direction (no rotation is required for the z component) before being analysed. The measurements then yield six different data sets as described by (3.72) to (3.77), corresponding to spin flip and non-spin flip scattering for each of the three incident polarisation directions. Equations (3.78) to (3.82) demonstrate how these measured intensities can be related in order to distinguish all components of the scattering. The air cushions and Tanzboden floor upon which the D7 instrument is mounted enables diffraction scans in small steps to be carried out over the full angular range. This facility can be utilised in the separation of nuclear and magnetic Bragg peaks by performing non-spin flip and spin flip scans, where Bragg diffraction in the spin flip channel can only be magnetic in origin. The evolution of such peaks as a function of temperature can then be observed, enabling the transition point to be clarified. In addition, pneumatic elevators permit the rapid change over from a polarised instrument to an unpolarised one by lifting the analysers out of the beam path (as shown for the right hand bank in figure 4.2) which
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Instrumentation and Data Reduction

<table>
<thead>
<tr>
<th>Beam tube</th>
<th>H15 cold neutron source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Double focussing triple graphite monochromator</strong></td>
<td></td>
</tr>
<tr>
<td>Dimensions</td>
<td>7.5 x 1.7 x 0.2 cm$^3$ (15 crystals in 3 lines)</td>
</tr>
</tbody>
</table>

**$^3$He Detectors**

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Ø 5cm, length 10cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas pressure</td>
<td>$2 \times 10^5$ Pa</td>
</tr>
<tr>
<td>Distance sample-detector</td>
<td>150cm</td>
</tr>
<tr>
<td>Angular range</td>
<td>$\pm 2^\circ &lt; 2\theta &lt; \pm 165^\circ$</td>
</tr>
<tr>
<td>Background</td>
<td>1cpm/detector</td>
</tr>
</tbody>
</table>

**TOF Analysis**

<table>
<thead>
<tr>
<th>Disc chopper speed</th>
<th>10000 rpm max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>Variable from 10% to 0.67%</td>
</tr>
</tbody>
</table>

**Sample Environment**

<table>
<thead>
<tr>
<th>1.5T electromagnet with dedicated furnace and cryostat</th>
<th>1.5K &lt; T &lt; 900K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum chamber with sample changer</td>
<td>1.2K &lt; T &lt; 300K</td>
</tr>
</tbody>
</table>

Table 4.3 Characteristic values of the multidetector D7 [2].

are replaced by simple collimators. Besides the obvious intensity gain achieved, this switch is also necessary to calibrate losses by analysers.

D7, in conjunction with polarisation analysis, can also be used to separate incoherent, coherent and magnetic scattering in both low energy inelastic and quasi-elastic experiments (restricted to such by the available neutron wavelengths). This is achieved by pulsing the incident beam with a disc chopper and measuring the resultant time of flight thus performing energy analysis of the beam. The chopper rotates with a duty cycle which varies between 3% and 10% depending on the resolution requirements of the experiment with an associated reduction factor in intensity of between 33 and 10. The sensitive nature of neutron polarisation necessitates the continuous monitoring of the beam so as to check for beam depolarisation from unforeseen sources within the experimental set-up. This purpose is achieved by the installation of a monitor (monitor 2) together with an analyser placed in
the straight through beam, and enables the flipper efficiency and sample transmission to be verified. For this reason, all metallic parts of the rotating chopper must be avoided from the polarised beam in order to prevent depolarisation by eddy currents, thus the aluminium in the chopper window as well as the absorbing gadolinium layer must be removed. Table 4.3 summarises the characteristic quantities of the D7 multidetector. Sections 4.2.1 and 4.2.2 describe the two major components to the D7 set-up - the supermirror polariser and the dc-flipper respectively - and 4.2.3 details the field considerations involved in ensuring that the beam polarisation at the sample position is well defined in one of the directions P_x, P_y or P_z.

4.2.1 Polarising Supermirrors

The intrinsic spin quantum number of the neutron is \( \frac{1}{2} \) and as such, in an external field, the neutron can exist in one of two spin states (+) or (-). A neutron beam is then said to be polarised if the number of particles in each of the two spin states is not equal, for which the degree of polarisation can be defined as

\[
P = \frac{l^+ - l^-}{l^+ + l^-}
\]  

(4.1)

where \( l^+ \) and \( l^- \) are the intensities of neutrons in the respective spin states. The three principle methods by which spin polarisation may be achieved are i) Bragg reflection from a magnetised crystal, ii) transmission through a magnetised material and iii) total reflection from a magnetised mirror. Prior to the development of D7, polarisation analysis, for intensity reasons, was mainly carried out using short wavelength neutrons for which the method of Bragg reflection from the Heusler crystal Cu_2MnAl ((111) reflection) or FCC Fe_{0.06}Co_{0.92} ((200) reflection) was best suited. These crystals alone satisfied the polarising conditions of having equal nuclear and magnetic structure factors at room temperature and good reflectivity (i.e. a high magnetic
moment). Restrictions in available wavelengths of such crystals arose due to the \( d \)-spacing associated with the polarising reflection i.e \( \sin \theta = \lambda / 2d \). Thus the range in wavelength is restricted by \( 2^\circ \leq \theta < 90^\circ \) with improved resolution of Bragg peaks for small \( d \). However, the introduction of the mirror type polarisers discussed here and their subsequent advancement to supermirrors, meant that polarisation analysis became possible for cold source neutrons too.

**The principle of polarising mirrors:**

The process by which neutrons undergo total reflection is analogous to wave optics in which light entering the boundary (of refractive index \( n \)) between two media at some critical glancing angle \( \theta_c \) (which meets the condition \( n<1 \)) is no longer refracted but is instead reflected with almost no loss of intensity [6]. Consequently, by applying the de Broglie relation for wave-particle duality

\[
\lambda = \frac{h}{mv} = \frac{h}{p}
\]  

where the total energy of the particle is given by

\[
E = \frac{p^2}{2m} + V
\]  

such that

\[
\lambda = \frac{h}{\sqrt{2m(E - V)}}
\]

a refractive index for neutrons passing between two media may be defined such that the refraction and reflection is treated in essentially the same way as that for light. A neutron beam traversing the boundary between two media, 1 and 2, will experience a change in potential from \( V_1 \) to \( V_2 \) in a way which enables a layer of material to be treated as a potential well (Fig. 4.4) [7]. If the
refractive index $n$ for neutrons crossing the boundary is defined as

$$n = \frac{\lambda_1}{\lambda_2} = \sqrt{\frac{E - V_2}{E - V_1}}$$

(4.5)

where $\lambda_1$ and $\lambda_2$ are the neutron wavelengths associated with potentials $V_1$ and $V_2$ then, for $V_1 = 0$, as for a vacuum, it follows that

$$n = \sqrt{1 - \frac{V}{E}}$$

(4.6)

where $\bar{V}$ is the average depth of the potential well producing the scattering and can be related to the nuclear scattering length, from 2.3.1, thus

$$\bar{V} = N\frac{2\pi h^2 \bar{b}}{m_n}$$

(4.7)

where $N$ is the number density of neutrons with scattering length $\bar{b}$. In addition, for a ferromagnetic material, a further contribution to the potential of

**Fig. 4.4** A potential well description of a polarising mirror. The potential 'seen' by the neutron for a magnetic layer depends on the relative orientation of the neutron spin with respect to the induction $B$. 

- neutrons with spin up reflected
- spin down transmitted
- + magnetic potential $+\mu_n B$
- nuclear potential $2\pi h^2 \bar{b} / m_n$
- - magnetic potential $-\mu_n B$
\( \pm \mu_n B \) arises, the sign of which depends on the orientation of the magnetic moment of the neutron in the induction \( B \). Including this interaction, from (4.6) and (4.7), the refractive index for a magnetic layer takes two, neutron spin dependent values, given by

\[
n_z = \sqrt{1 - \frac{\lambda^2 NB}{\pi} \frac{\pm \mu_n B}{E}} \tag{4.8}
\]

which are related to the critical glancing angle \( \theta_c \) for reflection by

\[
\theta_c^+ = \sqrt{2(1 - n_z)} \tag{4.9}
\]

For neutron spins parallel to \( B \) (+), the magnetic contribution adds to the nuclear potential to create a high positive scattering potential of which, if not overcome by the total energy of the neutron, will result in reflection of that spin state. Neutrons of anti-parallel spin (-) 'see' a reduced potential by virtue of the magnetic contribution subtracting from the nuclear potential and are therefore transmitted as illustrated above. One of the first polarising mirrors to be developed was that of electroplated, magnetised cobalt [8]. However, although capable of yielding polarisation in excess of 95%, the small range in \( \theta_c \) (about 0.1 deg/Å) over which the beam was polarised meant that it had limited use.

**Supermirrors:**

The first ‘supermirror’, developed by Mezei and Dagleish [9] and stemming from the proposed use of alternating ferromagnetic and non-magnetic multilayers by Turchin [10], was a direct attempt to increase the value of \( \theta_c \) available with polarising mirrors. The materials which comprise the alternating layers are selected such that, for one spin state, the respective refractive indices match resulting in no scattering contrast. Therefore, spins parallel to the magnetic induction \( B \) in the magnetic material are reflected at the Bragg
angle corresponding to the magnetic layer thickness, and anti-parallel spins, which 'see' one broad potential well, are transmitted. By choosing a suitable range of layer thicknesses, constructive interference can be achieved for a range of values $\theta/\lambda$ beyond the mirror cut-off for one spin state while suppressing the other.

Since their conception, considerable effort has been put into improving the angular range, reflectivity and polarisation of supermirror devices. In particular Schärpf [4] has produced a range of improved supermirrors using alternate, curved Co and Ti layers on a glass substrate. In order to exclude those neutrons of the wrong spin which are reflected from the small scattering potential of the substrate, an anti-reflecting, absorbing layer must be deposited upon which the Co/Ti layers lie. This anti-reflecting layer consists of 40 alternating interlayers of Ti and Gd, deposited in such a way as to stimulate a gradual change in potential from that of Ti to that of Gd over the layer thickness of 1260Å. In this way, an effective polarising device as used on D7, can be obtained, for which the angular range of polarised reflection extends to zero grazing angle ($\theta/\lambda=0.27\text{deg Å}^{-1}$), with an average reflectivity of 75% [11]. Reflectivity curves for such a device are shown in figure 4.5 [7].

The D7 set-up incorporates 33 such polarisers, one of which serves to

![Reflectivity curves](image)

**Fig. 4.5** Measured reflectivity curves of a Co/Ti supermirror as used on D7 for the two spin states of the neutron [7].
polarise the incident beam and requires a vertical guide field of 10mT. The remaining 32 analysers are mounted directly in front of every second detector of 10cm x 5cm size, at a distance of 1.5m from the sample, in a vertical field of 40mT. The strength of the fields and the fact that, in the scattering plane, the field direction is the same everywhere (perpendicular to it), means that a sufficient guide field to maintain vertical alignment of spins is produced for the whole range of the instrument.

### 4.2.2 The dc-Flipper

The dc-flipper, based upon the Larmor precession of the neutron spin, was first proposed by Mezei in 1972 [5] and provided a replacement for the cumbersome rf-flipper. A magnetic field $H$, inclined at an angle $\theta$ to the magnetic moment of the neutron, will exert a torque and thus cause the moment of the neutron to precess about the field direction with a frequency $\omega_L$, the Larmor frequency, given by

$$\omega_L = -\gamma H \quad \text{where} \quad \frac{\gamma_{\text{neutron}}}{2\pi} = -2916.4 \text{Hz/Oe} \quad (4.10)$$

$\gamma$ is known as the 'gyromagnetic ratio'.

The $\pi$-flipper consists of a Mezei coil with a horizontal field direction $H_n$, upon which is wound a second coil with a vertical field. The latter serves as a correction coil to compensate for the vertical guide field $H_z$ outside the flipper. A neutron entering the coil with vertically aligned spins will experience an almost adiabatic change in field direction and begin to precess in a plane normal to $H_n$. For a field strength of

$$H_n = \frac{67.825}{\lambda d} \text{Oe} \quad (4.11)$$
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Fig. 4.6 Spin flip of the neutron using a dc-flipper. For a certain field \( H_f \) (4.11), the neutron will undergo half a Larmor precession during its journey through the coil.

where \( \lambda \) is the neutron wavelength in angstroms and \( d \) is the coil thickness in cm, the neutron spin undergoes half a precession on its way through the coil and a spin flip is achieved. This process is illustrated in figure 4.6.

4.2.3 The Spin Rotator

The vertical fields applied to magnetise the polariser and analyser (10mT and 40mT respectively) are strong enough to create a guide field throughout the range of the instrument. The fields of the four detector banks linearly superpose so that, at the centre of the instrument, a vertical field region of strength 1mT results. For this reason, where no spin rotation is required, no additional guide field is necessary at the sample position. However, for the case of the XYZ measurement, a ‘spin rotator’ located at the sample position and comprising of a cube of three coil pairs (x, y and z), is needed to create a field strong enough to achieve an adiabatic rotation of the neutron spins into the x, y or z direction, without changing the magnetisation of the sample. In order for the spin of the neutron to follow the field direction created by the spin rotator, the condition of adiabaticity must be fulfilled i.e. the angular frequency of the changing field direction must be less than the Larmor
Table 4.4 Spin rotator coil currents necessary for polarisation in the x, y and z directions. \( \lambda = 4.8 \text{Å} \).

<table>
<thead>
<tr>
<th></th>
<th>z-coil current (A)</th>
<th>x-coil current (A)</th>
<th>y-coil current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_z )</td>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( P_x )</td>
<td>-4.5</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>( P_y )</td>
<td>-4.5</td>
<td>0</td>
<td>7</td>
</tr>
</tbody>
</table>

frequency of the precessing neutron (\( |\omega - \omega_L| \) [12]. For polarisation in the x or y direction, the spin rotation into the scattering plane must take place on the neutron flight path from the polariser guide fields to the sample before being rotated back to the vertical on its flight path from the sample to the analysers. To do so, one must adjust the z-coil current so as to compensate for the z-field of the instrument, therefore ensuring that there is no field component in the z-direction. Knowledge of the changing field frequency, \( \omega \), in the vicinity of the rotator coils, along with the maximum deviation of the neutron spin from the field direction, enables the exact rotation of the neutron spin as a function of distance from the centre of the spin rotator to be calculated [13]. The coil currents necessary for the rotation of the neutron spin into the x, y and z directions are summarised in Table 4.4 for a neutron wavelength of \( \lambda = 4.8 \text{Å} \).

4.3 Instrument Calibration and Data Reduction

Owing to the sensitive nature of polarisation analysis and the associated intensity restrictions, a number of instrumental adjustments must be made prior to measurement, in order to both optimise the measured intensity and enable corrections to the observed scattering [14]. To do so, specific calibration measurements are performed, each with the purpose of highlighting a particular imperfection for which a correction can be made.
4.3.1 Adjustment of the Analysers

The first of the adjustments to be made is that of the analysers so as to ensure maximum transmission of the scattered neutrons to the detectors. For this purpose, a strong, non-spin flip scatterer such as quartz is measured and with the use of program controlled synchronous motors, each analyser may be swivelled by ± 2° in an automatic search for the direction of maximum count rate.

4.3.2 The Flipping Ratio Measurement

Having adjusted the analysers, it is then necessary to pinpoint any further faults within the system. For this, a value known as the flipping ratio $R$ serves as an indicator for any imperfection in the experimental set-up and is defined as the flipper-off to flipper-on counts. Due to the fact that fused quartz has no spin incoherent or magnetic cross-section, all scattering is entirely diffuse and non-spin flip in nature - characteristics of which make it well suited for the determination of the flipping ratio. To do so, the scattering from a quartz sample is measured with flipper on and off for each of the polarisation directions x, y and z. In an ideal case, the spin flip counts should be zero, however in practice a finite flipping ratio is obtained, implying a measured intensity in the spin flip channel consisting of background, those neutrons transmitted by polariser/analyser with the wrong spin direction, neutrons which are not perfectly flipped and neutrons which have become depolarised on their path through the instrument. The measured flipping ratio can be related to the polariser $P_1$, analyser $P_2$ and flipper $f$ efficiencies and the depolarisation $D$ thus

$$R = \frac{(1 + P_1 P_2 (1 - D))}{(1 + P_1 P_2 (1 - D)(1 - 2f))}$$  \( (4.12) \)
a value of which should be as high as possible (typically 20 to 50). A low value for $R$ then indicates either a problem with one of the polarisers or the flipper, or that there is a source of depolarisation in the beam path. Due to the sensitivity of maintaining a polarised beam throughout the instrument, the flipping ratio must be re-determined every time a certain aspect is changed (e.g. a change in sample environment or shift in detector banks).

The flipper efficiency is defined as the fraction of spins reversed by the activated flipper and must be optimised before the flipping ratio determination is carried out. The process by which this is achieved is an iterative one in which the flipper coil current and correction coil current are alternately adjusted in order to produce the correct resultant value for $H_n$. The flipper current is set at a value which provides a field $H_n$ as calculated from (4.11), this being the necessary current to induce half a Larmor precession of the neutron spin. A current scan for the field which compensates the guide field is then performed to which a parabola may be fitted, the minimum of which yields the best correction current. This process is then repeated for the flipper current and correction coil current until there is no change in the minimum. As with the flipping ratio, the flipper and correction coil currents must be determined for any change to the system due to their dependence on the surrounding field.

In order to correct for a finite flipping ratio, the counts arising from scattering sources other than the sample (e.g. sample can, cryostat) must be accounted for. This is achieved by taking an empty sample can measurement to yield the background counts, which is subtracted from all subsequent scattering measurements. Having made the background correction, it is then possible to obtain expressions for the flipping ratio correction in which the corrected spin flip ($i_{oo}^{cor}$) and non-spin flip ($i_{ot}^{cor}$) counts are given in terms of the respective observed counts ($i_{oo}^{ob}$ and $i_{ot}^{ob}$) and the flipping ratio $R$, as follows:

If $r$ is an imperfection of the instrument, as a result of which, in observing the
spin flip scattering, a fraction $\frac{1}{r}$ of the correct spin flip intensity is lost to the non-spin flip channel and a fraction $\frac{1}{r}$ of the correct non-spin flip intensity is gained by the spin flip channel, then

$$ I_{\uparrow \downarrow}^{ob} = I_{\uparrow \downarrow}^{corr} - \frac{1}{r} I_{\uparrow \downarrow}^{corr} + \frac{1}{r} I_{\uparrow \uparrow}^{corr} = \frac{r - 1}{r} I_{\uparrow \downarrow}^{corr} + \frac{1}{r} I_{\uparrow \uparrow}^{corr} \quad (4.13) $$

similarly for non-spin flip scattering

$$ I_{\uparrow \uparrow}^{ob} = I_{\uparrow \uparrow}^{corr} - \frac{1}{r} I_{\uparrow \uparrow}^{corr} + \frac{1}{r} I_{\uparrow \downarrow}^{corr} = \frac{r - 1}{r} I_{\uparrow \uparrow}^{corr} + \frac{1}{r} I_{\uparrow \downarrow}^{corr} \quad (4.14) $$

Combining (4.13) and (4.14) in matrix form then yields

$$ \begin{pmatrix} I_{\uparrow \downarrow}^{ob} \\ I_{\uparrow \uparrow}^{ob} \end{pmatrix} = \frac{1}{r} \begin{pmatrix} r - 1 & 1 \\ 1 & r - 1 \end{pmatrix} \begin{pmatrix} I_{\uparrow \downarrow}^{corr} \\ I_{\uparrow \uparrow}^{corr} \end{pmatrix} \quad (4.15) $$

the inverse of which is

$$ \begin{pmatrix} I_{\uparrow \downarrow}^{corr} \\ I_{\uparrow \uparrow}^{corr} \end{pmatrix} = \frac{r}{(r - 1)^2 - 1} \begin{pmatrix} r - 1 & -1 \\ -1 & r - 1 \end{pmatrix} \begin{pmatrix} I_{\uparrow \downarrow}^{ob} \\ I_{\uparrow \uparrow}^{ob} \end{pmatrix} \quad (4.16) $$

and can be written

$$ \begin{pmatrix} I_{\uparrow \downarrow}^{corr} \\ I_{\uparrow \uparrow}^{corr} \end{pmatrix} = \frac{1}{r - 2} \begin{pmatrix} (r - 1)I_{\uparrow \downarrow}^{ob} - I_{\uparrow \downarrow}^{ob} \\ (r - 1)I_{\uparrow \uparrow}^{ob} + (r - 1)I_{\uparrow \uparrow}^{ob} \end{pmatrix} \quad (4.17) $$

However, for the case of a pure coherent scatterer such as quartz, the correct spin flip intensity is zero. Therefore

$$ I_{\uparrow \downarrow}^{corr} = \frac{r - 1}{r - 2} I_{\uparrow \downarrow}^{ob} - \frac{1}{r - 2} I_{\uparrow \uparrow}^{ob} = 0 \quad (4.18) $$

or
from which the flipping ratio may now be defined as

\[
\frac{\text{flipper off counts}}{\text{flipper on counts}} = \frac{I^{ob}}{I^{on}} = (r - 1) = R
\]  

(4.20)

The inverse of (4.20) provides a direct measure of that part of the wrong spin which is transmitted by the whole assembly. From (4.17) and (4.20), the correct spin flip and non-spin flip scattering for detector \( n \) (with flipping ratio \( R_n \)), in terms of measurable quantities, is given by

\[
I^{corr}_{\uparrow \downarrow} = I^{ob}_{\uparrow \downarrow} + \frac{1}{R_n - 1}(I^{ob}_{\uparrow \downarrow} - I^{ob}_{\uparrow \uparrow})
\]  

(4.21)

and

\[
I^{corr}_{\uparrow \uparrow} = I^{ob}_{\uparrow \uparrow} - \frac{1}{R_n - 1}(I^{ob}_{\uparrow \downarrow} - I^{ob}_{\uparrow \uparrow})
\]  

(4.22)

### 4.3.3 Vanadium Calibration

In order to put a measured cross-section onto an absolute scale, one must normalise to a standard scatterer whose cross-section and scattering behaviour is well known. For this purpose vanadium is well suited, as it scatters almost purely incoherently with an incoherent cross-section of 5.187 barns and a coherent cross-section of just 0.0184 barns [15]. Consequently, for real single scattering and no absorption, the angular scattering is isotropic meaning that one can expect every detector to record the same scattered intensity. Because vanadium is essentially mono-isotopic, the incoherence results entirely from the interaction of the neutron spin with the nuclear spin of vanadium and as such yields non-spin flip and spin flip scattering in compliance with (3.34) and (3.35) i.e. for unpolarised neutrons, the probability of the change in the spin direction of the neutron upon
scattering is \frac{2}{3} with flip and \frac{1}{3} without. For this reason, in the case of a vanadium measurement corrected for background and finite flipping ratio, one would expect the inverse of the flipping ratio to be 2. However, experimentally one finds that the ratio of spin flip to non-spin flip counts is systematically less than this (of the order of 1.8 or less), indicating the need for a further correction - that for multiple scattering and absorption. One actually finds that, as a result of this experimental effect, the distribution of scattered neutrons for an incoherent scatterer is not isotropic, and necessitates the modelling of the neutron behaviour as it traverses the sample. This correction must be carried out prior to any normalisation to the vanadium.

4.3.4 Correction for Multiple Scattering and Absorption

In a neutron experiment, the quantity of interest is the flux of scattered neutrons which have undergone one scattering event only. However, in order to attain measurable levels of scattering, the inclination is to use large samples with high scattering cross-sections for which there is a high probability that neutrons will undergo second or higher order scattering processes. Consequently, the detected neutron flux contains contributions from neutrons scattered twice or more for which the corresponding fluxes must be corrected. Blech and Averbach [16] in 1965 provided a direct calculation of the differential cross-section for second order neutron scattering and showed its dependence on the ratio of the cross-sections for scattering \((\sigma_s)\) and scattering-plus-absorption \((\sigma_t)\). For a cylindrical sample of radius \(R\) and height \(h\), their expression for the multiple scattering differential cross-section was

\[
\frac{d\sigma^M}{d\Omega} = \frac{1}{4\pi} \frac{\sigma_s (\sigma_s / \sigma_t) \cdot \delta}{1 - (\sigma_s / \sigma_t) \cdot \delta}
\]

(4.23)

where \(\delta\) is a parameter dependent on sample dimensions and absorption.

The following chapter details a Monte Carlo simulation of the elastic
scattering behaviour of the neutron within the sample and describes how, for the case of the calibration specimen vanadium, polarised neutron fluxes, corresponding to scattering events up to fourth order, may be modelled to yield a correction factor accounting for multiple scattering and absorption.

Having obtained the fully corrected vanadium scattering intensity - that is the intensity of once scattered neutrons only - the fully corrected sample counts can be normalised to it and the corresponding scattering cross-section put onto an absolute scale according to

\[
\left( \frac{d\sigma}{d\Omega} \right)_\text{sam} = \frac{\sigma_{\text{van}}^{\text{incoh}}}{4\pi} \frac{N_{\text{van}}}{N_{\text{sam}}} \frac{l_{\text{sam}}}{l_{\text{van}}}
\]  

(4.24)

where \( \sigma_{\text{van}}^{\text{incoh}} \) is the incoherent scattering cross-section for vanadium in barns (=5.187 barns), \( N_{\text{sam}}, l_{\text{sam}} \) and \( N_{\text{van}}, l_{\text{van}} \) are the atomic densities and fully corrected scattering intensities for the sample and vanadium respectively.

### 4.4 D17: A Small Angle Scattering Instrument Adapted for the use of Polarised Neutrons

The flux line lattice (FLL) which arises in the mixed state of a type II superconductor constitutes a periodic arrangement in the magnetisation density of the sample and as such can interact with the magnetic moment of the neutron to yield Bragg scattering. The investigation of the FLL by neutron scattering was first suggested by de Gennes and Matricon [17] with the immediate advantage over other techniques (such as decoration techniques [18] and STM [19]) that the bulk of the superconductor, as opposed to merely the surface, is investigated. Due to the fact that the FLL has a large lattice constant (typically of the order of 1000\(\text{Å} \)), the Bragg reflections in a neutron diffraction experiment occur at small scattering angles, necessitating an appropriate instrument for their detection.
The small angle neutron scattering (SANS) diffractometer D17 is installed on the H17 cold guide tube at the ILL and has an extended range of long wavelengths from 8 to 25Å permitting studies at small scattering vectors without the need for either high spatial resolution on the detector or extremely long sample-detector distances. In its conventional configuration a beam of cold source moderated neutrons is incident upon a mechanical velocity selector, which produces a triangular wavelength distribution of neutrons with $\Delta \lambda/\lambda = 5$ or $10\%$. The neutrons pass down a 2.5m flight path through collimating slits which fix the incident neutron momentum $k_i$. Upon reaching the sample, the neutrons are scattered along a variable length flight path before reaching the two dimensional multidetector consisting of $128 \times 128$ pixels. This allows the simultaneous collection of data over some range of momentum transfer $Q = k_i - k_f$ with the plane of the detector representing a plane of reciprocal space of the scattering lattice. The detector tube can be rotated about the vertical axis by up to $90^\circ$. Figure 4.7 shows a schematic representation of the conventional SANS D17 set-up and Table 4.5 provides the numerical instrument characteristics.
### Table 4.5 Characteristic values of the SANS diffractometer D17 [2].

<table>
<thead>
<tr>
<th>Instrumentation and Data Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Beam tube</strong></td>
</tr>
<tr>
<td><strong>Monochromator</strong></td>
</tr>
<tr>
<td>Velocity selectors</td>
</tr>
<tr>
<td>Wavelength</td>
</tr>
</tbody>
</table>

### Collimation
- Guide to sample distance: $\approx 2.5\text{m}$

### Sample
- Flux at specimen at lowest resolution: $\approx 10^6\text{ncm}^{-2}\text{s}^{-1}$
- Typical size: $15 \times 25\text{mm}^2$

### Detector
- Distances $L$: 0.8; 1.4; 2.8 or 3.5m
- Rotation: 0 to $90^\circ$
- Area: $64 \times 64\text{cm}^2$
- Pixel size: $5 \times 5\text{mm}^2$
- Max. counting rate: 50kHz
- Background: 1cps for whole multidetector

#### 4.4.1 The Interference Term

Although the FLL is magnetic in origin, there exists a small nuclear scattering contribution by virtue of an accompanying distortion in the nuclear lattice. Consequently, Bragg reflections which arise due to the FLL in type II superconductors will have a nuclear contribution corresponding to this distortion in the lattice which can be observed using spin polarised neutrons [20]. This technique makes use of the fact that nuclear and magnetic scattering, from a nuclear lattice and FLL with the same spatial periodicity, will constructively interfere with a magnitude dependent on the direction of the incident neutron polarisation. Therefore by measuring the flipping ratio $R$, which is defined as the ratio of intensities observed with the neutron spin oriented parallel or antiparallel to the external field direction, the interference
term can be unambiguously determined as follows.

In an elastic spin polarised neutron scattering experiment, the magnetic $\Psi_M$ and nuclear $\Psi_N$ wavefunctions corresponding to the magnetic and nuclear contributions to a Bragg reflection, sum together to yield a total wavefunction $\Psi_{TOT} = \Psi_M + \Psi_N$. The scattered intensity $I$ is then calculated according to

$$ I = |\Psi_{TOT}|^2 = |\Psi_N|^2 + \Psi_N^* \cdot \Psi_M^* + \Psi_M^* \cdot \Psi_N + |\Psi_M|^2 $$  \hspace{1cm} (4.25)

from which the interference term $\Psi_N^* \cdot \Psi_M^* + \Psi_M^* \cdot \Psi_N$ is obtained. Now for the case of Bragg scattering, the wavefunctions are proportional to their respective magnetic and nuclear structure factors, $F_M$ and $F_N$, thus one obtains, for spin polarised neutrons with a polarisation parallel to the applied magnetic field, the intensity

$$ I_{\uparrow\uparrow} = C|F_N + F_M|^2 $$  \hspace{1cm} (4.26)

where the constant $C$ is a scaling factor, independent of neutron spin orientation. The neutron spin dependence of the cross-section is carried by the magnetic structure factor $F_M$ which changes sign upon reversing the neutron spin with respect to the applied magnetic field. In this instance therefore, the scattered Bragg intensity is given by

$$ I_{\uparrow\downarrow} = C|F_N - F_M|^2 $$  \hspace{1cm} (4.27)

If only magnetic scattering is present ($F_N = 0$) then this change in sign is irrelevant as it is the square of the structure factor which determines the scattered intensity. However, if both nuclear as well as magnetic contributions are present, then the scattered intensity will depend on the neutron spin orientation. The presence of an interference term between the scattered wavefunctions can be detected in the observed ratio of the two intensities (4.26) and (4.27). This ratio is known as the flipping ratio [21] and is defined
as

\[
R = \frac{I_{TT}}{I_{TT}'} = \frac{|F_N + F_M|^2}{|F_N - F_M|^2} = \left| \frac{1+\gamma}{1-\gamma} \right|^2 = 1 + 4\gamma
\]  

(4.28)

up to correction terms of order \(\gamma^2\) assuming that \(|F_N| \ll |F_M|\) (which is shown to be the case in 8.1) where \(\gamma = F_N/F_M\). For this ratio the scaling constant \(C\) drops out and \(R\) is a function of the ratios of the nuclear and magnetic structure factors only. If \(F_N = 0\) then the flipping ratio is 1 and a value otherwise is indicative of the presence of an interference term between magnetic and nuclear scattering. For unpolarised neutrons i.e. no interference term, the scattered intensity is given by the sum of (4.26) and (4.27) as

\[
l = C\left(|F_N|^2 + |F_M|^2\right)
\]  

(4.29)

Besides the increased sensitivity of an experiment yielding the interference term over one relying on the determination of integrated intensities, a further advantage is the absence of a scaling factor. This means that given the value for the magnetic structure factor \(F_M\), one can determine the absolute value of the nuclear structure factor \(F_N\) without further assumptions.

Figure 4.8 shows the experimental configuration as used for the FLL investigation of niobium [20] where a spin polarised neutron beam was obtained by reflection of the incident neutrons off a polarising neutron mirror

![Fig. 4.8 Schematic diagram of the experimental set-up for the flux line lattice investigation.](image)

Unpolarised neutrons  Polarising mirror  Spin flipper  Nb  Detector
of the type described in 4.2.1. A spin flipper as described in 4.2.2 allowed the neutron spin direction to be inverted with respect to the magnetic guide field direction and the spin polarisation was confirmed by temporarily placing an analyser (identical to the polarising mirror) between sample and detector.

REFERENCES


CHAPTER 5
THE MONTE CARLO CORRECTION FOR
MULTIPLE SCATTERING AND ABSORPTION

5.1 Introduction

Monte Carlo methods comprise that branch of experimental mathematics which is concerned with experiments on random numbers. According to [1], a Monte Carlo method may be defined as one that "involves deliberate use of random numbers in a calculation that has the structure of a stochastic process. A stochastic process being a sequence of states whose evolution is determined by random events." In general, problems handled by Monte Carlo methods are of two types - probabilistic or deterministic - according to whether or not they are directly concerned with behaviour and outcome of random processes [2]. The physical example of an uncharged particle traversing a medium falls into the former category and as such, a random number dependent probability distribution function can be assigned to simulate the physical random processes. In this way, the multiple scattering of a neutron in vanadium may be treated analytically where, due to the uncharged nature, all paths between collisions are straight lines with no influence on one another.

5.2 The Multiple Scattering Correction for Vanadium

Vanadium is an incoherent scatterer of neutrons and therefore, wavefunctions scattered off individual nuclei have no definite phase relations to one another.
As a result, the interference term between sites, contributing to the scattered wave intensity averages to zero and the scattering of neutrons becomes completely classical. For this reason, the assumptions about the repeated interactions of neutrons within a sample may be tested experimentally as described in section 4.3.3 where the flipping ratio determination for an almost ideal incoherent scatterer such as vanadium, provides a direct experimental measure of the effect of multiple scattering. Vanadium is therefore particularly suited for a discussion of the effect.

The physical reason for being able to experimentally observe the effect of multiple scattering using polarised neutrons, lies in the fact that for a scatterer such as vanadium, if at a reasonable temperature, the nuclear magnetic moments which determine the spin flip intensity are randomly oriented and the limiting values for the probabilities of the neutron spin flipping or not ($\frac{2}{3}$ and $\frac{1}{3}$ respectively) can be applied. However, for the case of a neutron which is re-scattered, the relative probabilities of the spin flipping or not alters, causing the flipping ratio to deviate from that expected for a single scattering process. This can be demonstrated in matrix form as follows.

In a spin polarised experiment, the spin of the neutron can adopt one of two states - spin-up or spin-down - denoted in vector form by

\[
\begin{pmatrix}
1 \\
0
\end{pmatrix} = \text{spin-up}, \quad \begin{pmatrix}
0 \\
1
\end{pmatrix} = \text{spin-down}
\] (5.1)

and the flipping/non-flipping of the neutron can be described in matrix form by

\[
\begin{pmatrix}
\frac{2}{3} & \frac{1}{3} \\
\frac{1}{3} & \frac{2}{3}
\end{pmatrix} = \begin{pmatrix}
1 & 2 \\
1 & 2
\end{pmatrix}
\] (5.2)

Therefore, if the incident neutrons are defined to be 'spin-up', the once scattered neutrons will be distributed according to
from which we get the expected ratio of 2 between the 'spin-down' and 'spin-up' neutron intensity. However, a neutron scattered for a second time will have a detected spin state subject to two interactions, meaning that the flip/non-flip process of (5.2) acts upon the incident spin state twice. i.e. for neutrons which have undergone two scattering events, the distribution of neutrons is given by

\[
\begin{pmatrix}
\frac{1}{3} \\
\frac{2}{3} \\
\frac{2}{3}
\end{pmatrix}
\begin{pmatrix}
\frac{1}{3} \\
\frac{2}{3} \\
\frac{1}{3}
\end{pmatrix}
\begin{pmatrix}
0 \\
1 \\
1
\end{pmatrix}
= \frac{1}{9}
\begin{pmatrix}
5 \\
4
\end{pmatrix}
\]

meaning that the probabilities of the neutron being flipped or not are \( \frac{4}{9} \) and \( \frac{5}{9} \) respectively giving rise to a spin flip to non-spin flip ratio of \( \frac{4}{5} \). It is by virtue of this second order ratio being less than 1 that one experimentally observes, in the presence of multiple scattering, a reduction in the spin-flip to non-spin flip ratio from that expected for single scattering only. In the same way, one can calculate the neutron spin distribution for 3\(^{rd}\) and 4\(^{th}\) fold scattering to yield

\[
\begin{pmatrix}
\frac{1}{3} \\
\frac{2}{3} \\
\frac{2}{3}
\end{pmatrix}
\begin{pmatrix}
\frac{1}{3} \\
\frac{2}{9} \\
\frac{1}{3}
\end{pmatrix}
\begin{pmatrix}
13 \\
14
\end{pmatrix}
= \frac{14}{27}
\Rightarrow \left( \frac{l_{sf}}{l_{nsf}} \right)_3 = \frac{14}{13}
\]

for neutrons undergoing three scattering events and

\[
\begin{pmatrix}
\frac{1}{3} \\
\frac{2}{3} \\
\frac{2}{3}
\end{pmatrix}
\begin{pmatrix}
\frac{13}{27} \\
\frac{14}{27}
\end{pmatrix}
\begin{pmatrix}
41 \\
40
\end{pmatrix}
= \frac{40}{81}
\Rightarrow \left( \frac{l_{sf}}{l_{nsf}} \right)_4 = \frac{40}{41}
\]

for those interacting four times.
5.3 The Probability Distribution

For the purpose of defining certain experimental entities, the situation of a neutron beam passing through a sample plate of thickness \(d\) shall be considered. The intensity of transmitted neutrons \(I_{\text{trans}}\) is reduced with respect to that of the incident beam \(I_0\), by virtue of both scattering and absorption processes, according to

\[
I_{\text{trans}} = I_0 \exp(-\mu d)
\]

(5.7)

where the attenuation coefficient, \(\mu\), is a constant, dependent on the density \(\rho\) and the total cross-section \(\sigma_t\) of the traversed material, the latter consisting of two contributions corresponding to the total scattering cross-section \(\sigma_s\), as determined by the strength of the scattering potential, and the cross-section for absorption \(\sigma_a\) such that

\[
\sigma_t = \sigma_s + \sigma_a
\]

(5.8)

The attenuation coefficient, with units of \(\text{length}^{-1}\), is then determined by

\[
\mu = \sigma_t \cdot \rho
\]

(5.9)

Despite the fact that vanadium is an incoherent scatterer and therefore \(\sigma_s\) is directionally isotropic, the intensity of detected neutrons is not independent of detector position. This is due to the fact that individual neutrons have different path lengths within the sample, dependent on the angle at which they are scattered, meaning that, in turn, the attenuation effect of multiple scattering and absorption has an angular dependence. This scenario is depicted in figure 5.1 where neutrons scattered by a small angle \(\theta\) (paths 2 and 3) have to travel through more material than one travelling along path 1 and
Fig. 5.1 Depiction of possible paths taken by a neutron through a sample. Path 3 illustrates a second order scattering event although the final direction of the neutron is the same as that along path 2 and as such is recorded by the same detector.

consequently have a greater chance of being re-scattered (path 3) or absorbed.

To model such behaviour, the scenario of a neutron beam traversing a plate of infinite thickness shall serve as a starting point for the formulation. A neutron traversing a medium will have a probability of being scattered or absorbed in the interval $x$ to $x+dx$ given by [3]

$$p(x)dx = \exp(-\mu x)\mu dx \quad (5.10)$$

The expectation value of $x$ which satisfies the discrete probability density function of (5.10), corresponds to the average distance travelled by a neutron before its first collision and is known as the mean free path $\bar{x}$.

$$\bar{x} = \int_{0}^{\infty} x \cdot p(x)dx = \int_{0}^{\infty} \exp(-\mu x)\mu xdx = \left[-x\exp(-\mu x) - \frac{\exp(-\mu x)}{\mu}\right]_{0}^{\infty} = \frac{1}{\mu} \quad (5.11)$$

The cumulative distribution function $P(x)$, yielding the probability of a neutron interacting after travelling a distance $x$, can then be defined according to
\[ P(x) = \int_0^x p(x) \, dx = \left[ -\exp(-\mu x) \right]_0^x = 1 - \exp(-\mu x) \quad (5.12) \]

with \( 0 \leq P(x) \leq 1 \).

Having defined the probability of the neutron being scattered for the first time after a distance \( x \), it is then necessary to determine the distance of the next interaction point for the same neutron. For this purpose a random number \( \xi \), uniformly distributed within the limits \( 0 \leq \xi \leq 1 \), is assigned to simulate the distribution of interaction points \( x(\xi) \) and is defined by

\[ \xi = P(x) = 1 - \exp[-\mu x] \quad (5.13) \]

If \( \xi \) is a random number between 0 and 1 so too is \( (1 - \xi) \) and for this reason the interaction point as a function of \( \xi \) can be given, for the case of an infinite plate, by

\[ x(\xi) = -\frac{1}{\mu} \ln(1 - \xi) \rightarrow -\frac{1}{\mu} \ln(\xi) \quad (5.14) \]

For a finite plate of thickness \( d \), all interactions are restricted to occur in the interval \( 0 \leq x \leq d \), for which the probability density function becomes

\[ p(x) = \frac{\mu \exp(-\mu x)}{1 - \exp(-\mu d)} \quad (5.15) \]

which can be converted into the continuous case to yield

\[ P(x) = \frac{1 - \exp(-\mu x)}{1 - \exp(-\mu d)} \quad (5.16) \]

of which, if \( \xi = P(x) \) as before, yields the interaction point as a function of \( \xi \).
\[
\chi(\xi) = -\frac{1}{\mu} \ln \left[1 - \xi (1 - \exp(-\mu d))\right]
\]  
(5.17)

5.4 The Monte Carlo Program Routine

As already stated, the general requirement of a neutron scattering experiment is the flux of single scattered neutrons which would have been observed if:

a) there was no absorption in the sample
b) having been scattered, the neutron emerged without further re-scattering.

The Monte Carlo routine described here, based largely upon the program of Johnson [4], details how the scattering of a neutron may be simulated to yield a hypothetical, once scattered spin flip (+) and non-spin flip (-) flux \( \Phi_{i\pm} \) under the assumptions of a) and b), along with calculated spin flip and non-spin flip fluxes, including absorption, for re-scattering up to 4th order (\( \Phi_{i\pm}, i = 1 \) to 4). A correction factor \( C_\pm \) of the form

\[
C_\pm = \frac{\Phi_{i\pm}}{\Phi_{1\pm} + \Phi_{2\pm} + \Phi_{3\pm} + \Phi_{4\pm}}
\]  
(5.18)

can then be obtained for each detector, by which the experimentally observed flux is multiplied, thereby performing a correction for multiple scattering and absorption at once.

By its nature, the Monte Carlo simulation follows all neutron histories, including those which do not reach a detector. For this reason, the routine can be inefficient in terms of computer time unless the neutron is restricted to follow only those trajectories required to reach a detector. In this way, only those neutrons which are finally detected are followed.

In describing the neutron history, a statistical weight is assigned, consisting of
a number of factors corresponding to various restrictions imposed upon the behaviour of the neutron. Schematic representations of single and 2nd order scattering as shown in figures 5.2 and 5.3, illustrate the origin of the contributory factors to the corresponding fluxes.

5.4.1 Once Scattered Flux

In general, the distance \( d \) a particular neutron would have to travel through the sample if it were not scattered, is not the same. To account for this, the entry point \( S_0 \) of the neutron is sampled from which the corresponding exit point, \( EX \), the neutron would take if it travelled without interaction, is obtained. The first scattering event at a point \( S_1 \) must then take place along the path length \( d \), after a distance \( x(\xi) \), determined from (5.17). In order to compensate for restricting the first event to take place within the sample, a factor \( A_1 \) of the form

\[
A_1 = \left( 1 - \exp\left(-\mu d\right) \right)
\]  

(5.19)

is incorporated into the statistical weight.

Having sampled the position \( S_1 \) of the neutron's first event according to (5.17), this is deemed to be one of scattering rather than absorption - a restraint which is corrected for with the following factor

\[
B_1 = \frac{\sigma_s}{\sigma_s + \sigma_a}
\]  

(5.20)

Upon scattering, the neutron has a probability of being scattered into a given direction of

\[
C_1 = \frac{1}{4\pi}
\]  

(5.21)
where the fact that the scattering from vanadium is isotropic has been used.

Subsequent to being scattered, the neutron must traverse a path length $d'$ through the remainder of the sample - a value which is dependent upon the counting detector position. As such, both the exit point $X2$ of the scattered neutron and the corresponding distance, $d'$, must be determined for each of the 32 detectors according to their angular positions. The neutron is then restricted to undergo no further interactions along the path length $d'$, and this is compensated for by the factor

$$D_i = \exp(-\mu d')$$  \hspace{1cm} (5.22)

In a polarised neutron experiment where one is recording the spin flip and non-flip counts, a further factor describing the probability of being flipped or not must be included. As already specified for vanadium, the probability of the spin being flipped in a scattering event is $\frac{1}{2}$ while of remaining the same it is

![Diagram](image)

Fig. 5.2 The single scattering process, indicating nomenclature for points of entry, scattering and exit.
Therefore the probability, or flux, of neutrons emerging from a sample in the direction of a detector and after being once scattered only is given by, for the case of spin flip neutrons

\[ \Phi_{1+} = \frac{2}{3} A_i \cdot B_i \cdot C_i \cdot D_i \]

and for non-spin flip neutrons

\[ \Phi_{1-} = \frac{1}{3} A_i \cdot B_i \cdot C_i \cdot D_i \]

For the calculation of the hypothetical, single scattered flux \( \Phi_{1\pm} \), one would observe if there was no absorption (\( \sigma_a = 0 \) and \( \sigma' \) effectively equal to zero), factors \( B_i \) and \( D_i \) become 1 and the attenuation coefficient in \( A_i \) becomes a function of \( \sigma_s \) only.

5.4.2 Twice Scattered Flux

The 2\(^{nd}\) order scattering flux can be constructed in a similar manner to that for single scattering. Given that the first scattering event takes place at a point \( S1 \) along the path length \( d \), the scattered direction is randomly sampled to yield a corresponding exit point \( P2 \), taken by the neutron if not re-scattered. The distance between points \( S1 \) and \( P2 \) then corresponds to a path length \( \sigma' \), along which the second scattering event, at a position \( S2 \), must occur. Sampled as before according to (5.17), the distance travelled by the scattered neutron before being scattered for a second time must be within the limits \( 0 \leq x(\xi) \leq \sigma' \), necessitating a further factor \( A_2 \) of the form of \( A_1 \) to compensate for this

\[ A_2 = \left(1 - \exp(-\mu \sigma')\right) \]
As for the first interaction, a correction factor $B_2$ must be included to compensate for the second event being one of scattering

$$B_2 = \frac{\sigma_s}{\sigma_s + \sigma_a} \quad (5.26)$$

The exit point $X3$ of the twice scattered neutron is then determined for each of the detectors along with the corresponding distance $d'$, between $S2$ and $X3$, which the neutron must travel before emerging from the sample. To compensate for no further interactions taking place along the path length $d'$, a factor $D_2$ is included

$$D_2 = \exp(-\mu d') \quad (5.27)$$

The final 2nd order fluxes for spin flip and non-flip scattering, including the respective probabilities from (5.4), consist then of the following...
\[ \Phi_{2+} = \frac{4}{9} A_1 \cdot A_2 \cdot B_1 \cdot B_2 \cdot C_1 \cdot D_2 \] (5.28)

and

\[ \Phi_{2-} = \frac{5}{9} A_1 \cdot A_2 \cdot B_1 \cdot B_2 \cdot C_1 \cdot D_2 \] (5.29)

In a similar manner, the fluxes for 3\textsuperscript{rd} and 4\textsuperscript{th} fold scattering have been constructed. The inclusion of higher order scattering provides a negligible correction at the expense of increased computing time.

**5.5 Sample Geometry**

The co-ordinate system in which the scattering is described is defined by the

[Diagram of sample geometry with labels h, k, xdet, ydet, and r.]
sample geometry which, for the case of this investigation, took the form of a cylinder. The cylindrical geometry is illustrated below in figure 5.4, in which the z-axis is defined to be the axis of the cylinder such that the surfaces of the cylindrical sample can be defined in terms of its height $h$ and radius $r$ by the equations:

$$x^2 + y^2 = r^2, \quad z_{\text{max}} = \frac{h}{2}, \quad z_{\text{min}} = -\frac{h}{2}. \quad (5.30)$$

Therefore, for an incident beam in the x-y plane and along the positive x-direction, the co-ordinates of the entry point $S_0$ can be sampled according to

$$S_{0y} = r(2\xi - 1)$$
$$S_{0x} = -\sqrt{r^2 - S_{0y}^2}$$
$$S_{0z} = h(2\xi - 1) \quad (5.31)$$

where $\xi$ is a random number equidistributed in the interval $0 \leq \xi \leq 1$.

5.5.1 Direction Cosines

Each detector $I$, lying in the x-y plane, makes an angle $w(I)$ with respect to the x-axis such that their positions may be specified by the direction cosines $x_{\text{det}}$, $y_{\text{det}}$ and $z_{\text{det}}$ as follows

$$x_{\text{det}} = \cos(w(I)), \quad y_{\text{det}} = \sin(w(I)), \quad z_{\text{det}} = 0$$

In addition, direction cosines $u$, $v$ and $w$ must be assigned to the scattered neutron which, for an isotropic source, is tantamount to choosing a point $(u, v, w)$ uniformly distributed on the unit sphere $u^2 + v^2 + w^2 = 1$. Using spherical co-ordinates $\gamma, \phi$, the element of area for this sphere as indicated in figure 5.5
Fig. 5.5 The unit sphere as used for the determination of the direction cosines \( u, v \) and \( w \).

The probability density function is therefore given by

\[
\rho(w)dw = \frac{2\pi \sin \gamma dy}{4\pi} = \frac{1}{2} dw
\]

Thus \( w \) may be determined by

\[
\xi = \int_{-\frac{1}{2}}^{\frac{1}{2}} dw = \frac{1}{2} (w + 1)
\]
Hence

\[ w = 2\xi - 1 \]  \hspace{1cm} (5.35)

The value of \( \phi \) is determined by

\[ \xi = \int \rho(\phi) d\phi = \int \frac{d\phi}{2\pi} = \frac{1}{2\pi} (\phi + \pi) \]  \hspace{1cm} (5.36)

so that

\[ \phi = (2\xi - 1)\pi \]  \hspace{1cm} (5.37)

The direction cosines \( u \) and \( v \) can then be obtained from (5.35) and (5.37) by using \( u^2 + v^2 + w^2 = 1 \):

\[ u = \rho \cos \phi = \sqrt{(1 - w^2)} \cos \phi = \sqrt{1 - \left(2\xi - 1\right)^2} \cos((2\xi - 1)\pi) \]  \hspace{1cm} (5.38)

and

\[ v = \sqrt{1 - \left(2\xi - 1\right)^2} \sin((2\xi - 1)\pi) \]  \hspace{1cm} (5.39)

5.6 Program Structure

A full listing of the program can be found in Appendix I, the structure of which is described here in terms of its constituent subroutines/functions, together with a glossary of symbols and a routine flow diagram.

SUBROUTINE DISTDET

Input parameters: X1(1), X1(2), X1(3), XDET(I), YDET(I), ZDET(I), RADIUS
Output parameters: X2(1), X2(2), X2(3), DIST

Given the scattering point X1, with co-ordinates X1(1), X1(2) and X1(3), the
point of exit from the sample \( X2 \) is determined for each detector \( I \) according to their direction cosines \( XDET(I), YDET(I) \) and \( ZDET(I) \). The distance \( DIST \) along the straight line between \( X1 \) and \( X2 \) is then calculated, corresponding to the distance the neutron must travel, if not re-scattered, before emerging from the sample to a particular detector. A check is also imposed within this subroutine, that the projection of the neutron in the x-y plane is inside the sample, for which the input parameter \( RADIUS \) is required. An error at this point loops the program back and a new neutron is sampled.

**SUBROUTINE DIRECTION**

**Output parameters:** \( XX, YY, ZZ \)

The direction cosines \( XX, YY \) and \( ZZ \) of the scattered neutron are randomly generated according to expressions (5.38), (5.39) and (5.35) respectively.

**FUNCTION DISTSCATT**

**Input parameters:** \( P1(1), P1(2), P1(3), XX, YY, ZZ, RADIUS, HEIGHT \)

**Output parameters:** \( P2(1), P2(2), P2(3) \)

Given the scattering point \( P1 \) and the direction cosines \( XX, YY \) and \( ZZ \) of the scattered neutron, the point of exit \( P2 \) is determined. As with subroutine \( DISTDET \), a check is made at this point for the projection being within the sample. However, in this case the problem is three dimensional and the possibility of the scattered neutron hitting the top or bottom of the cylindrical sample must be accounted for. To do so, information on the sample in the form of the parameters \( RADIUS \) and \( HEIGHT \) must be supplied so that the projection of the neutron can be calculated in compliance with expressions (5.30). The calculated exit point \( P2 \) is then used as an input for the next scattering event, with the distance between it and the point \( P1 \) being the path length over which the next scattering point must occur.

The following page provides a glossary of symbols in which all terminology used in the program is defined in order of their introduction. Figure 5.6 on
page 148 shows the flow diagram describing the running of the program for the first scattering event.

5.6.1 Glossary of Symbols

Input parameters to be supplied by user are denoted by the prefix *.
Relevant equations are given in brackets.

**MAIN PROGRAM:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>$3.141592654$.</td>
</tr>
<tr>
<td>FAC</td>
<td>$(\pi/180)$. (converts degrees into radians).</td>
</tr>
<tr>
<td>*RADIUS</td>
<td>Sample radius [cm].</td>
</tr>
<tr>
<td>*HEIGHT</td>
<td>Sample height [cm].</td>
</tr>
<tr>
<td>*DENSITY</td>
<td>Atomic density of sample [nuclei/Å³]</td>
</tr>
</tbody>
</table>

| FLi (i=1 to 4) | Probability of the neutron spin being flipped by the $i^{th}$ fold scattering process. |
| NFi (i=1 to 4) | Probability of the neutron spin state remaining unchanged by the $i^{th}$ fold scattering process. |

| WAV | Wavelength of incident neutrons [Å] |
| K0 | Neutron wavevector for a wavelength $\lambda=\text{WAV}$. $=\frac{2\pi}{\text{WAV}}$ [Å⁻¹]. |
| *AB | Sample absorption cross-section [barns] for neutrons with velocity $v_n=2200 \text{ms}^{-1}$ ($=\text{wavevector } K_n = 3.4942$ [Å⁻¹]). |
| SABS | Absorption cross-section [barns] for WAV=4.84Å. $=\text{AB} \times (3.4942/K0)$ [barns]. |
| *SCATT | Sample scattering cross-section [barns]. |
| SIGABS | Absorption attenuation coefficient [cm⁻¹]. |
| SIGSCATT | Scattering attenuation coefficient [cm⁻¹]. |
| SIGTOT | Total attenuation coefficient [cm⁻¹]. $=\mu$ |
| BX1 | Factor accounting for neutron being scattered rather than absorbed (5.20). |
| CX1 | Probability of neutron being scattered into a given direction. |
INEUTRON  Number of the current neutron being sampled.
*MAXRUNS  Number of neutrons to be sampled.
I  Detector number (1 to 32).
TRANS  Transmission factor = \( \exp(-\mu d) \)
J  
\( = 1 \) for spin flip scattering.
\( = 2 \) for non-spin flip scattering.

\( A_i(J, I) \) \((i=1 \text{ to } 4)\)  \(i^{th}\) fold scattering flux.

\( A_{1\text{TRUE}}(J, I) \) Hypothetical single scattered flux assuming no absorption

\( A_{1\text{TRUE}}(3, I) \) Hypothetical single scattered spin flip flux with absorption

\( A_{1\text{TRUE}}(4, I) \) Hypothetical single scattered non-flip flux with absorption

*W(I)  Angle subtended with x-axis by detector I.

XDET, YDET, ZDET  Direction cosines for each detector.

RND  Random number generated between 0 and 1 using computer timer (number of seconds elapsed since midnight) to generate the seed.

S0(1), S0(2), S0(3)  x, y, z co-ordinates of the neutron point of entry.

EX(1), EX(2), EX(3)  x, y, z co-ordinates of the exit point if the neutron traversed the sample without being scattered.

ALENGTH1  Distance travelled by neutron through sample if not scattered.

\( D_{\text{DIST}_i} \) \((i=1 \text{ to } 4)\)  = ALENGTH\( _i \times \text{SIGTOT} = \mu d \text{ in } (5.13)\).

AL1  Sampled distance travelled by neutron within specimen before the 1\textsuperscript{st} scattering event. \((5.17)\).

Si(1), Si(2), Si(3)  x, y, z co-ordinates of the \(i^{th}\) scattering point \((i=1 \text{ to } 4)\).

AXi \((i=1 \text{ to } 4)\)  Factor, including absorption, to compensate for the \(i^{th}\) scattering event taking place within the sample.

AY1  Same as AX1 except that SIGABS = 0. Used for the calculation of the hypothetical flux A1TRUE.

Er  
\( = 0 \) if projection of neutron is within sample.
\( = 1 \) if projection of neutron is outside sample. New neutron sampled.

DXi \((i=1 \text{ to } 4)\)  Factor compensating for the restriction that no further interaction takes place between the \(i^{th}\) scattering point.
and the exit point determined for each detector. The exit point and the corresponding distance to the \(i^{th}\) scattering point is calculated in subroutine **DISTDET**.

\(A_{L|n} = 1\) for zero absorption.

**ALENGTH**

Distance between the \((i-1)^{th}\) \((i=2 \text{ to } 4)\) scattering point and the exit point \(P_2\). The point \(P_2\) being determined for each scattering event using function **DISTSCATT** according to the direction cosines \(XX, YY, ZZ\) randomly generated in subroutine **DIRECTION**.

**AL** \((i=2 \text{ to } 4)\)

Distance travelled by neutron along the straight line connecting the \((i-1)\)th and the \(i\)th scattering point. (5.17).

**Q(l)**

Scattering vector corresponding to each detector [Å\(^{-1}\)]

**Z1(l), Z2(l)**

Correction factors of the form (5.18) for spin flip and non-flip scattering respectively. Calculated for each detector \(l\).

**SUBROUTINE DISTDET:**

\(X_1(1), X_1(2), X_1(3) = Si(1), Si(2), Si(3)\) respectively. \((i=1 \text{ to } 4)\).

\(X_2(1), X_2(2), X_2(3)\) \(x, y, z\) co-ordinates of the exit point taken by the neutron to reach each detector.

\(DIST\)

Distance along straight line between points \(X_1\) and \(X_2\).

\(TEST\)

Magnitude of the \(xy\)-projection of the neutron.

**SUBROUTINE DIRECTION:**

\(XX, YY, ZZ\)

Direction cosines of the scattered neutron, sampled according to (5.38), (5.39) and (5.35) respectively.

\(PHI\)

Longitude of the element of area on the unit sphere \(XX^2 + YY^2 + ZZ^2 = 1\). (5.37).

**FUNCTION DISTSCATT:**

\(P_1(1), P_1(2), P_1(3) = Si(1), Si(2), Si(3)\) respectively. \((i=1 \text{ to } 4)\).

\(P_2(1), P_2(2), P_2(3)\) \(x, y, z\) co-ordinates of the exit point of scattered neutron according to the direction cosines \(XX, YY, ZZ\).

\(DIST\)

Distance along straight line between points \(P_1\) and \(P_2\).
Chapter 5

The Monte Carlo Correction

BEGIN

Read in parameters, Zero arrays

Calculate detector direction cosines

Loop over MAXRUNS

Sample entry point S0

Calculate path length within sample

Sample first scattering point S1

Loop over number of detectors

Determine exit point for each detector and the corresponding distance to S1

DISTDET

xy-projection within sample?

NO

DIRECTION

Sample direction of scattered neutron

DISTSCATT

Determine exit point of scattered neutron

xy-projection within sample?

NO

YES

Repeat sampling for 2nd, 3rd and 4th events

Calculate distance between scattering point and exit point

Update fluxes

Loop over number of detectors

YES

END

Calculate correction factors $C_e$

Loop over number of detectors

Reached MAXRUNS?

NO

Fig. 5.6 Flow diagram of the Monte Carlo program.
5.7 Program Output

A sample output from the program is shown in Appendix II. Each data block consists of fifteen entries, the first row of which provides the detector number \( I \), the detector angle \( W(I) \), the corresponding wave-vector \( Q(I) \) and the hypothetical spin flip (\( \Phi^+_1 \)) and non-flip (\( \Phi^-_1 \)) fluxes for single scattering without absorption. The following two rows of data yield the spin-flip and non-flip fluxes for scattering up to 4\(^{th}\) order in the sequence \( \Phi^+_1, \Phi^-_1, \Phi^+_2, \Phi^-_2, \Phi^+_3, \Phi^-_3, \Phi^+_4, \Phi^-_4 \). Finally, in the third row, the correction factors \( C^+ \) and \( C^- \) for spin-flip and non-flip scattering respectively, are given. Figure 5.7 shows the values of unpolarised neutron fluxes up to 4\(^{th}\) order for isotropic scattering, as calculated for two detector positions at 6.41° and 145.24° respectively. The angular variation of the multiple scattering is shown to be weak - amounting to a deviation of less than 1% between the two detectors - with the \( i \)\(^{th}\) order scattered flux approximately a fraction \( \frac{1}{3^i} \) of the \((i-1)\(^{th}\) flux.

![Fig. 5.7 Calculated flux up to 4\(^{th}\) order scattering for two separate detectors.](image-url)
Fig. 5.8 Repeated calculations of the correction factor $C_+$ as a function of scattering vector.

The error associated with the correction factors $C_+$ and $C_-$ depends on the number of neutron histories followed i.e. upon the value of MAXRUNS. To obtain an idea of the accuracy of the simulated fluxes, the program may be run several times, using different random number sequences for the same input value of MAXRUNS. Figure 5.8 shows the scattering vector dependence of the spin flip correction factor $C_+$, for five separate runs of the program, with MAXRUNS = 5000. As one would expect, the correction factor drops off slightly as a function of scattering angle. The error in the mean in this particular case amounts to less than 0.5%.

5.7.1 The Correction to Vanadium

The effect of multiple scattering and absorption for the case of polarised neutrons and an incoherent scatterer such as vanadium, manifests itself in the observed flipping ratio as explained in 5.2. Consequently, an impact of the
correction to neutron data can be obtained by monitoring the flipping ratio before and after its application. The experimentally obtained values for the ratio of spin flip counts to non-flip counts for a vanadium sample, as determined for each detector, are shown, before and after the application of the multiple scattering correction, in figure 5.9. The observed discrepancies in the measured ratio can be accounted to experimental variations between the detectors such as different gas pressures within the detectors, differences in the settings of electronics and different analysers. Corrections for detector efficiency, background and finite flipping ratio as described in 4.3 were made in both cases prior to this analysis. The spin-flip to non-flip counts ratio for the uncorrected data i.e. neutron data containing second and higher order scattering contributions, is systematically smaller than 2 and takes an average value, over all detectors, of $1.905\pm0.013$. Including the correction for multiple scattering, results in this ratio rising to an average value of $2.001\pm0.014$, in agreement with the expected ratio of 2 for single scattering without absorption.

![Graph](image_url)

**Fig. 5.9** Ratio of spin-flip to non-flip counts as a function of scattering angle, with and without a correction for multiple scattering/absorption.
It is therefore evident that, for an incoherent scatterer, the experimental observation of the flipping ratio serves as a check for the importance of multiple scattering - a value differing markedly from 2 being indicative of a high sample density. Such an effect has a particular importance in samples exhibiting strong Bragg reflections where the probability of secondary or higher order scattering is enhanced with the result that any scattering structure is ‘washed out’. Although the program detailed here is not capable of correcting for multiple scattering in a coherent scatterer, it can correct for the isotropic absorption if the hypothetical flux for single scattering without absorption is replaced with A1TRUE(3,I) or A1TRUE(4,I). These are the hypothetical spin-flip and non-flip single scattered fluxes, allowing for absorption. Having obtained the fully corrected vanadium \( I_{\text{van}} \) and sample \( I_{\text{sam}} \) counts, the sample cross-section can be put onto an absolute scale according to (4.24).

In order to establish the importance of multiple scattering and absorption in a sample, a quick experiment yielding the transmission factor (TRANS in the program) can be performed. Using a monitor (monitor 2 on D7) to record the straight through beam, a series of measurements are made for the sample, empty can and cadmium sample. The latter, with a high neutron absorption cross-section (\( \sigma_{\text{abs}}=2520 \text{ barns} \) [5]) and dimensions identical to the sample, allows no neutrons impinging upon it to be transmitted. Therefore any counts recorded by monitor 2 can be attributed to neutrons bypassing the sample. A subsequent subtraction of the Cd counts \( (I_{\text{Cd}}) \) from the sample \( (I_{\text{sam}}) \) and empty can \( (I_{\text{empty}}) \) measurements yield respectively the number of neutrons transmitted through the sample and the number of neutrons incident upon the sample. The transmission factor is then given by

\[
\text{TRANS} = \frac{\text{Number of transmitted neutrons}}{\text{Number of incident neutrons}} = \frac{I_{\text{sam}} - I_{\text{Cd}}}{I_{\text{empty}} - I_{\text{Cd}}} \quad (5.40)
\]

where a value obtained below 80% indicates the need for a correction for multiple scattering/absorption. For the vanadium simulation as detailed
above, a transmission factor of 77.65% was obtained.

REFERENCES


CHAPTER 6

SAMPLE PREPARATION AND
CHARACTERISATION

6.1 The High-\(T_C\) Series \(\text{YBa}_2\text{Cu}_3\text{O}_{6+x}\)

In addition to the observed anisotropy of certain properties such as electrical resistivity [1], critical currents and critical fields [2], the high \(T_C\) oxides also exhibit large spatial anisotropy. A common feature of all the cuprates is a \(\text{Cu-O}\) plane to which all charge transfer is confined, and as such, plays an important role from an electrical and superconducting viewpoint as well as structurally. Figure 6.1 depicts an infinite plane of \(\text{Cu-O}\) atoms in which each \(\text{Cu}\) atom is surrounded by 4 \(\text{O}\) atoms to form a square planar configuration in the \(ab\) plane and perpendicular to the \(c\)-axis. The structural anisotropy of these materials manifests itself within a layered crystal structure in which the \(\text{Cu-O}\) planes (clustered in groups of \(n\) layers) are separated from each other by planes of other oxides and rare earths. Within the clusters of \(n\) immediately adjacent \(\text{Cu-O}\) planes exists, alternately, sparsely populated planes of \(\text{Y}\) or \(\text{Ca}\) atoms. Sets of \(\text{Cu-O}\) planes are in turn separated by a metal-\(\text{O}\) insulating layer. The system as a whole can therefore be considered

Fig. 6.1 The square-planar bonding of the \(\text{Cu-O}\) plane.
as consisting of metallic, superconducting regions and insulating regions where the creation of carriers within the two-dimensional Cu-O planes, necessary for superconductivity, are the result of charge transfer from the insulating 'charge reservoir' [3].

**The structure of perovskite:**

The crystallographic structure of all the high T_c oxides can be related to that of perovskite with general formula ABX_3. Figure 6.2 shows the structure in its idealised cubic form (space group Pm3m). Illustrated, is the unit cell with origin at the centre of atom A and atom B, from which the cubo-octahedral and octahedral co-ordination of the X atoms surrounding atoms A and B respectively, is clear. The limitations imposed by such arrangements upon the

Fig. 6.2 The idealised cubic structure of perovskite ABX_3, depicting the cubo-octahedral and octahedral co-ordination of the X atoms around atoms A and B respectively.
ion sizes can be described by a factor, \( p \), given by

\[
p = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}
\]

where \( r_A, r_B \) and \( r_X \) are the atomic radii of A, B and X respectively. In practice it is found that the cubic structure of perovskite exists for the condition \( 0.75 \leq p \leq 1.0 \) [4] however, distortions in the structure which cause deviations from the conditions \( r_A - r_X \) and \( r_B/r_X \sim 0.4 \) can give rise to other structure types with lowered symmetry. It is these which can be related to the high \( T_C \) structures for which the majority are tetragonal or nearly tetragonal with a small orthorhombic distortion.

### 6.1.1 The Structure of YBa\(_2\)Cu\(_3\)O\(_{6+x}\)

The discovery of superconductivity above 90K in multiphase samples of the Y-Ba-Cu-O system [5], subsequently attributed to the single phase YBa\(_2\)Cu\(_3\)O\(_{6+x}\) (x~1) [6], was followed by a number of structural studies by means of X-ray [7,8] and neutron [9,10,11,12] diffraction. These investigations revealed the structure to consist of a stacking of three primitive perovskite cells (3ABX\(_3\)) due to crystallographic ordering along the \( c \)-axis between the Y and Ba atoms, and indicated the simultaneous presence of both two-dimensional and one-dimensional features in the Cu-O structure. In particular the neutron scattering studies, due to their sensitivity to O presence, were able to correctly determine the space group as orthorhombic \( Pmmn \) and the location of the constituent atoms. The neutron profile analysis of YBa\(_2\)Cu\(_3\)O\(_7\) performed by Cappioni et al. [9] on room temperature data, elucidated the atomic positions Ba at 2t(\( \frac{1}{2}\frac{1}{2}z \)), \( z=0.1841 \), Y at 1h(\( \frac{1}{2}\frac{1}{2}\frac{1}{2} \)), Cu1 at 1a(000), Cu2 at 2q(00z), \( z=0.3549 \), O1 at 2q(00z), \( z=0.1581 \), O2 at 2s(\( \frac{1}{2}\frac{1}{2}z \)), \( z=0.1581 \), O3 at 2r(0\( \frac{1}{2}\frac{1}{2}z \)), \( z=0.3777 \) and O4 at 1e(0\( \frac{1}{2}0 \)). Contrary to previous X-ray studies, the O5 site at 1b(\( \frac{1}{2}00 \)), included in the model of Siegrist et al. [8], was established to be completely vacant and the O4 site

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Fig. 6.3 Structure of YBa$_2$Cu$_3$O$_7$ compared with that of tripled perovskite.

filled. Figure 6.3 shows the structure of YBa$_2$Cu$_3$O$_7$ compared with that of its tripled parent structure 3ABX$_3$. In essence, the structure of the superconductor can be derived from that of perovskite by eliminating the dotted O atoms at (00½) and (½00), ordering the cations in a Ba-Y-Ba-Ba-sequence and shifting slightly the remaining oxygen sites from their ideal perovskite positions. A consequence of the removal of certain O atoms is that the copper atoms, occupying the B-positions, are no longer at the centre of oxygen octahedra. The Cu2 site has instead a pyramidal, almost square planar co-ordination while the crystallographically independent Cu1 site, located at the origin, has square planar co-ordination in which the near square CuO$_2$ units share one corner and form 'fencelike' chains along the b-axis of the unit cell. The five co-ordinate Cu2 atoms are strongly bonded to the four nearest neighbour oxygen atoms (O2 and O3) which comprise the base of the pyramid but weakly so to the O1 site at the apex. As a result, the CuO$_2$ planes adopt a distorted geometry in which the constituent oxygen
atoms are shifted from their ideal perovskite positions to produce a puckering of the two-dimensional layers. The barium and yttrium cations are surrounded by ten and eight oxygen atoms respectively. The YBa₂Cu₃O₇ system is characterised by a mixed valency Cu²⁺ and Cu³⁺ according to the formulation YBa₂Cu²⁺³⁺₃O₇ such that an average formal Cu charge above 2+, required for superconductivity, is accomplished by the delocalisation of holes across the Cu-O framework [13].

The question of oxygen vacancies was addressed by the studies of Jorgensen et al.[12] in which they observed that the total oxygen stoichiometry decreases with increasing temperature. Associated with this decrease, is the creation of vacancies on the O4 sites only, and partial filling of the O5 site at (½00) [14]. As a result of this process, a structural transition from orthorhombic Pmmm to tetragonal P4/mmm occurs at a temperature of around 700°C and a critical oxygen content of ~O₆.₄ [12]. Studies of superconducting properties as a function of oxygen content show that, in the orthorhombic phase, Tₐ decreases as oxygen is removed and becomes zero as the structural transition is approached. Figure 6.4 shows the phase diagram of YBa₂Cu₃O₆+x [15] as deduced from NMR [16] and neutron scattering experiments [17], demonstrating the evolution of Tₐ and the onset

![Phase diagram of YBa₂Cu₃O₆+x](image_url)

**Fig. 6.4 Phase diagram of YBa₂Cu₃O₆+x.**
of long range antiferromagnetic order in the tetragonal phase as a function of oxygen content. The structural changes with regard to the location of the oxygen atoms, are followed as a function of oxygen content in figure 6.5. The left hand structure, depicting the fully oxygenated sample, shows the completely filled O4 and vacant O5 sites. Depopulation of the oxygen chain site, O4, and the simultaneous population of the previously vacant O5 site, results in the orthorhombic to tetragonal transition. The partial occupation of these sites is represented by the shaded circles in the centre structure. Further removal of oxygen in the tetragonal phase finally culminates in the right hand structure for YBa2Cu3O6.0, where both the O4 and the O5 sites are completely vacant. As the oxygen content is reduced, the Ba atoms move along the c-axis, away from the plane of the O2 and O3 atoms until, for the deoxygenated sample, the co-ordination of the Ba atom becomes eight fold [18]. The disordering of the oxygen atoms into the previously vacant O5 site, destroys the one-dimensional 'chains' present in the orthorhombic phase so that for x=0.0, the Cu1 atoms become two co-ordinated. In addition, as oxygen is removed so the distance from Cu2 to O1 increases, giving rise to a
more square planar co-ordination of the Cu2 atom. This corresponds to a mixed valency of localised univalent copper on the Cu1 site and divalent copper on the Cu2 site according to the formulation YBa$_2$Cu$_{2+2}$Cu$_{1+0}$O$_{6.0}$. The co-ordination of the Cu1 site for intermediate oxygen dopings (x>0.0) becomes complicated by the fact that random distribution of the excess oxygen over the O4 and O5 sites gives rise to an unusual three fold co-ordination of the Cu$^{1+}$ atoms. Single crystal measurements observing twinning in the orthorhombic phase support a model in which ordered microdomains with variable oxygen compositions, coexist in the same crystal [13]. In this way, the number of three co-ordinated Cu$^{1+}$ atoms is minimised and the usual co-ordination of copper (that is two fold co-ordination for Cu$^{1+}$ and four, five or six fold co-ordinations for Cu$^{2+}$ and Cu$^{3+}$) is respected according to the formula (YBa$_2$Cu$_{2+3}^{$3+}$O$_{7}$)$_{x}$(YBa$_2$Cu$_{1+2}^{$1+}$O$_{6}$)$_{1-x}$.

For the purpose of this study, polarised neutron experiments were carried out on two samples of YBa$_2$Cu$_3$O$_{5+x}$, corresponding to the superconducting orthorhombic phase and the insulating tetragonal phase. The following sections detail the sample preparation and their characterisation via neutron profile analysis.

6.1.2 Sample Preparation

Both of the samples were prepared by Ulrich Beck at the Max-Planck-Institut für Festkörperforschung (MPI), Stuttgart. The hygroscopic nature of the samples necessitated extreme handling precautions in order to avoid hydrogen contamination. Owing to the large incoherent scattering cross-section of hydrogen, its presence gives rise to a high spin flip cross-section, causing a bad signal-to-noise ratio and renders the determination of the weak magnetic signal from these materials difficult. Manipulations were therefore carried out in a dry box or with the Schlenck technique and the handled compounds allowed to dry for several hours in a high vacuum to remove possible traces of water.
All traces of water were removed from the educts by passing oxygen through a tube loaded with $P_{4}O_{10}$ coated silica gel. The starting materials $Y_2O_3$, $BaO_2$ and $CuO$ were treated prior to mixing in the following ways:

- $Y_2O_3$ was heated to 1050°C in a quartz tube under high vacuum with a final pressure of 3x$10^{-6}$mbar.
- Due to the fact that the starting $BaO_2$ emanates water when exposed to a vacuum line, it was first dried in a dynamic vacuum for two hours before being placed in an alumina boat, within a quartz tube, and dried under streaming oxygen at 600°C overnight.
- $CuO$, placed in an alumina boat within a quartz tube, was dried in a stream of oxygen for 2.5 days at 800°C.

**Oxygen rich sample:**

The starting materials $Y_2O_3$ (7.614g), $BaO_2$ (22.882g) and $CuO$ (16.094g) were mixed intensively in a mortar before being ground and pressed into pellets of diameter 20mm. The pellets, of total mass 44.67g, were placed in a alumina boat within a quartz tube and heated to 360°C under high vacuum to remove any traces of water. The quartz tube was then flooded with oxygen and the temperature raised to 950°C over a 24hour period and held at that temperature for 20hours. The temperature was then lowered at a rate of 60°C per hour to room temperature and the pellets (now of mass 42.94g) removed and ground for 1hour. From the resulting powder, seven parts of between 4g and 8g were ground further, before the powder as a whole was ground for 3mins and pressed into eight pellets of between 3g and 8g (total mass = 41.82g). The pellets were returned to the alumina boat and quartz tube and put under a vacuum ($P\sim5\times10^{-5}$mbar) at 210°C for 1hour before the tube was flooded with oxygen at 360°C and left overnight. The temperature was then raised to between 930°C and 950°C for the order of 60hours before being lowered to room temperature, at which point the pellets were removed and ground to form the final powder sample (mass=41.23g).
Oxygen deficient sample:

The procedure followed in obtaining the oxygen deficient sample involved a two step deoxygenation process in which a sample of intermediate oxygen content was obtained before being again treated to yield the oxygen deficient sample.

The original oxygen rich sample was used for the parent compound, from which 27.20g was heated in a degased quartz tube under a dynamic vacuum. The temperature was raised to 500°C over a 3hour period and held for 48hours under a pressure of 10^-4 mbar. Of this deoxgenated material, 26.43g was mixed with 12.88g of the original oxygen rich sample, before being pressed into pellets and stored in a degased quartz tube. In order to remove any traces of water, the tube was evacuated and heated slowly until the pressure began to increase, after which the mixture was annealed at 500°C for 12hours. Upon cooling, the pellets were removed and ground to form a powder sample of mass 38.35g. Subsequent X-ray diffraction analysis revealed lattice parameters of $a=3.8423\text{Å}$, $b=3.8718\text{Å}$ and $c=11.7562\text{Å}$, consistent with an oxygen content of YBa$_2$Cu$_3$O$_{6.45}$ [19].

To form the final oxygen deficient sample, 38.15g of the YBa$_2$Cu$_3$O$_{6.45}$ sample was placed in a degased quartz tube. Having evacuated the tube at room temperature and measured the total mass, the sample was heated to 600°C under a high vacuum and held at that temperature for 12hours before being cooled and removed to yield the final sample of mass 37.80g. An initial measure of the final oxygen content could be derived from the weight loss and the initial oxygen content, for which an estimated composition of YBa$_2$Cu$_3$O$_{6.09}$ was obtained.
6.1.3 High Resolution Powder Diffraction (HRPD)

Despite the role played by both X-ray and neutron scattering techniques, it is the latter which has taken prominence in elucidating the structures of the high T_c compounds. Although, compared to synchrotron sources, the neutron source is disadvantaged from an intensity (and resolution) perspective, the greater penetrating power of the neutron, the absence of a form factor in nuclear scattering and, in particular for the high T_c oxides, the high scattering power of light atoms for neutrons (enabling the location of the oxygen atoms amidst heavy atoms to be determined) goes some way to compensate for this. In addition, neutron high resolution powder diffraction (HRPD), is superior for many purposes due to its simple, well defined line shape and the reduced systematic errors associated with it.

The Rietveld method of profile analysis \cite{20} enables the crystal structure of a sample to be refined directly from a powder diffraction pattern. Due to the difficulty in preparing sufficiently large crystals for neutron scattering and the complex twinning often inherent in many of the high T_c compounds, the powder technique, in conjunction with the Rietveld method, has played a major role in determining the structures of these materials.

6.1.3.1 Instrumentation

Neutron powder intensities can be collected by one of two techniques. The more traditional, and the one employed on reactor based installations, involves fixing the incident wavelength (using a monochromator crystal) and registering the resultant diffraction pattern as a function of scattering angle, with a multidetector. The alternative, energy dispersive, technique, particularly suited to accelerator based neutron sources, consists of scattering all wavelengths into a particular angle. For both cases, in order to maximise the information available from a diffraction pattern, the resolution (\(\frac{\Delta \theta}{\theta}\)) must be
optimised in a compromise with intensity. Differentiation of the Bragg
condition for reflection ($\lambda = 2d\sin\theta$) yields

$$\frac{\Delta d}{d} = \Delta \theta \cot \theta \quad (6.2)$$

where $d$ is the spacing between planes of atoms and $2\theta$ is the scattering
angle. The intensity on the other hand depends on the waveband

$$\frac{\Delta \lambda}{\lambda} = \Delta \theta_M \cot \theta_M \quad (6.3)$$

where $\Delta \theta_M$ is the angular mosaic spread of the monochromating crystal
reflecting at an angle $2\theta_M$. Figure 6.6 provides a schematic layout of a
monochromator type HRPD where, for this wavelength focussing geometry,
the incident and detected beams are highly collimated by Soller slits $\alpha_1$ and
$\alpha_3$, to yield a peak width $\Delta 2\theta$ given by

$$\Delta 2\theta = \sqrt{\alpha_1^2 + \alpha_3^2} \quad (6.4)$$

Fig. 6.6 A schematic layout of the monochromator type HRPD.
Resolution requirements:

The resolution of any powder diffractometer is ultimately limited by the size and perfection of the individual grains of the sample and for a particle size of 10 microns or less, amounts to $\frac{\Delta d}{d} = 10^{-3}$. It stands to reason, that the best resolution should be achieved for that part of the diffraction pattern with the highest density of peaks. Taking the example of a cubic lattice, the Bragg condition for the $(hkl)$ reflection is given by

$$\frac{2a\sin\theta}{\lambda} = \sqrt{h^2 + k^2 + l^2} = \sqrt{n}$$

(6.5)

where $a$ is the lattice parameter. Since $h$, $k$ and $l$ are integers so too is $n$, meaning that successive lines occur most for $\Delta n = 1$. By differentiation, the line spacing $\Delta \theta$ is given by

$$2a\cos \theta \cdot \Delta \theta = \frac{\lambda}{2\sqrt{n}} \cdot \Delta n = \frac{\lambda}{4a\sin \theta}$$

$$\therefore \Delta \theta = \left(\frac{\lambda}{2a}\right)^2 \frac{1}{\sin 2\theta}$$

(6.6)

from which it can be seen that peaks are far apart for small and large scattering angles and closely packed for $2\theta \approx 90^\circ$. For optimum performance, the instrument line width $H_K$ given by

$$H_K^2 = U\tan^2 \theta + V\tan\theta + W$$

(6.7)

with $V \approx -2U\tan \theta_M$, should be manipulated so that its minimum (corresponding to the focussing geometry $2\theta = 2\theta_M$) corresponds with the minimum in the line separation. This can be achieved by choosing a large monochromator take-off angle.
6.1.3.2 D2B: A High Resolution Powder Diffractometer

The D2B instrument [21], installed on the H11 thermal beam tube at the ILL, is a two-axis, high resolution diffractometer, particularly suited to the Rietveld refinement of crystallographic structures. Its arrangement is shown schematically in figure 6.7 and consists of 64 He\textsuperscript{3} detectors, located 1 m from the sample position and spaced at 2.5° intervals over the complete 160° scattering range. A complete diffraction pattern can therefore be obtained with 100 detector steps, each of 0.025°. The incident beam collimation, α\textsubscript{i}, may be 35' (open) or 5', determined by a 300 mm high × 60 mm wide Soller collimator [22], consisting of 25 micrometre thick Mylar foil blades painted with neutron absorbing gadolinium oxide. The monochromator consists of 28 Ge[115] crystals, hot pressed so as to increase their mosaic spread to some Δθ\textsubscript{M} ~ 20'. In this way, sufficient intensity is obtained for the large monochromator take-off angle, θ\textsubscript{M} = 135°, which characterises the D2B instrument. Bragg scattering from various [hh\textsubscript{1}] planes enables monochromatic incident beams in the wavelength range 1.051 Å to 3.152 Å to

![Diagram](image_url)
Table 6.1 Characteristic values of the D2B high resolution diffractometer.

<table>
<thead>
<tr>
<th>Beam tube</th>
<th>H11 thermal beam</th>
</tr>
</thead>
<tbody>
<tr>
<td>MONOCHROMATOR</td>
<td></td>
</tr>
<tr>
<td>28 Ge[115] crystals of $1 \times 5 \times 1\text{cm}^3$</td>
<td></td>
</tr>
<tr>
<td>Take-off angle</td>
<td>$2\theta_{\text{m}} = 135^\circ$</td>
</tr>
<tr>
<td>Germanium [hkl]</td>
<td>Wavelength (Å)</td>
</tr>
<tr>
<td>557</td>
<td>1.051</td>
</tr>
<tr>
<td>337</td>
<td>1.277</td>
</tr>
<tr>
<td>551</td>
<td>1.464</td>
</tr>
<tr>
<td>335</td>
<td>1.594</td>
</tr>
<tr>
<td>331</td>
<td>2.398</td>
</tr>
<tr>
<td>113</td>
<td>3.152</td>
</tr>
</tbody>
</table>

SAMPLE

| Flux at sample ($\lambda = 1.594\text{Å}$) | $= 10^6$ high resolution |
| Beam size at sample | $2 \times 5 \text{cm}^2$ |
| Angular range | $5^\circ < 2\theta < 165^\circ$ |
| | $0^\circ < \omega < 360^\circ$ |

DETECTORS

64 He$^3$ counting tubes

| Background without sample | 0.1 Hz |

SAMPLE ENVIRONMENT

| Cryostat | 1.5 to 300K |
| Cryofurnace | 1.5 to 600K |
| Furnace | 200 to 1000K |
| Dilution cryostat | 50 to 4000mK |
| Pressure cell | 2 Gpa and 4 to 300K |

be produced. For the optimum wavelength of 1.594Å (achieved by reflection off the [335] plane), the measured sample flux is $7 \times 10^6 \text{ncm}^{-2}\text{sec}^{-1}$ with 35’ primary collimation and $10^6 \text{ncm}^{-2}\text{sec}^{-1}$ with 5’ primary collimation. Because a very large beam is used, intensity gains are permitted through vertical focussing by the 300mm high composite monochromator onto about 50mm at the sample position (approximately 3m from the monochromator). In order to eliminate scattering by air along the long incident path, an evacuated beam
tube is used. Along the flight path between the sample and each of the detectors, is situated a Mylar foil Soller collimator, providing a divergence $\alpha_3 = 5'$ and a beam cross-section of $20\text{mm} \times 100\text{mm}$ high for the $25\text{mm}$ diameter, $5$ atmosphere $\text{He}^3$ detectors. As a result, the divergence from sample to detector approximately matches that from monochromator to sample. Both the detectors and collimators are enclosed in $150\text{mm}$ thick $\text{B}_4\text{C}$ resin so that background originating from anything other than the sample is minimal. The detectors are calibrated for efficiency and precise angular separation by scanning them all through a single peak. Table 6.1 provides a summary of the characteristic values of the D2B instrument [23].

6.1.4 Profile Analysis

In describing the expected neutron diffraction pattern from a structure with a size and distance distribution, an analogy can be drawn with X-ray spectra in classical crystallography [24]. A crystal of finite size can be described in real space as a finite, regular arrangement of unit cells. This in turn can be idealised by an infinite lattice of points, convoluted with the function describing the finite size of the crystal. In practice, the points are atoms of finite size and must therefore be described by the convolution with a function describing their electron distribution. In this way, known as the kinematic approximation, the influence of different structural parts on a spectrum can be resolved into separate factors.

To obtain the scattering pattern of a structure in kinematic approximation, one must perform Fourier transforms of the above parts separately. The full scattering pattern then consists of the lattice factor convoluted with the Fourier transform of the shape factor and multiplied by the structure factor and the atomic form factor. The lattice factor, a sum of $\delta$ functions, is the Fourier transform of the infinite lattice (normally referred to as the reciprocal lattice). The structure factor is the Fourier transform of the unit cell and, together with the lattice factor, describes the Bragg peaks with zero width and
infinite height. The real width and height of the peaks is then given by the convolution with the Fourier transform of the shape of the crystallites. In addition, for X-ray spectra, the electron distribution is described by the atomic form factor. For neutron scattering in which the fundamental scattering body is the nucleus, this factor is absent, however, for magnetic structures with electrons of uncompensated spin, the form factor is present with particular effect at high scattering vectors.

An additional factor is necessitated to compensate for the departure from ideal order resulting from thermal vibrations of the atoms. The constituent atoms can be considered to occupy a 'cage' of certain size as a result of their movement. If the thermal vibrations are assumed to be isotropic, then a temperature factor $B_i$ can be attributed to the $i^{th}$ atom of the form [24]

$$B_i = 8\pi^2 \overline{u_{ij}^2}$$

(6.8)

where $\overline{u_{ij}^2}$ is the mean square displacement of the $i^{th}$ atom, perpendicular to the reflecting plane. The effective increase in size of the atom and the associated reduction in intensity is then accounted for by the Debye-Waller factor of the form $\exp\left(-2B_i\left[\frac{\sin \theta}{\lambda}\right]^2\right)$.

It is now possible to express the intensity $y_{O\i}$ observed in a neutron diffraction pattern at the angular position $2\theta_i$ as [25]

$$y_{O\i} = y_{Bi} + \sum K K G_{ik} + e_i$$

(6.9)

where $y_{Bi}$ is the background contribution, $I_K$ is the integrated intensity of reflection $K$, $G_{ik}$ is a function describing the peak shape and $e_i$ is a random variable drawn from a population of zero mean. The integrated intensity depends on the structure of the material and is given by
where \( A \) is a scale factor, \( j_k \) is the multiplicity of reflection \( K \), \( L_k \) is the Lorentz factor and \( F_{NK} \) and \( F_{MK} \) are the nuclear and magnetic structure factors respectively. For the case of the measurements described here, only the nuclear structure is being verified for which the structure factor is given by [26]

\[
F_{hkl} = \sum_{i=1}^{N} \left[ b_i \exp\left[2\pi i (hx_i + ky_i + lz_i)\right]\exp\left[-B_i \left( \frac{\sin \theta_i}{\lambda} \right)^2 \right] \right] \tag{6.11}
\]

where the sum extends over all \( N \) atoms contained in the unit cell, \( b_i \) is the scattering amplitude of atom \( i \) located at the position \( x_i, y_i, z_i \), \( hkl \) are the Miller indices of the reflection occurring at the angular position \( \theta \) and \( B_i \) is the isotropic thermal factor as given by (6.8).

### 6.1.4.1 The Rietveld Refinement

It can be seen from equations (6.9) to (6.11) that the observed scattered intensity can be used to refine the structural parameters of a sample. By using the program 'FULLPROF' [27], Rietveld analysis [20] may be performed on powder diffraction data collected on an instrument such as D2B. The essence of the technique is to minimise the quantity

\[
M_p = \sum_{i=1}^{N} w_i \left[ (y_{Ci} - y_{Bi}) - \sum_{k=1}^{2} I_k G_{ik} \right]^2 \tag{6.12}
\]

for which the program uses a Newton-Raphson algorithm. Here, the background subtracted intensity, \( (y_{Ci} - y_{Bi}) \), observed at the angular position \( \theta_i \), is compared with the theoretical prediction \( \sum_k I_k G_{ik} \), based on a proposed structural model and peak shape function \( G_{ik} \). The second term in (6.12) corresponds to the calculated intensity \( y_{Ci} \) at the \( i^{th} \) step. The quantity \( w_i \) is a
weighting factor necessitated by the way in which multidetector instruments, such as D2B, record neutron counts. Data is produced in which different numbers of detectors contribute to the intensity at various steps and the output data file lists the number of detectors contributing to each datum \( y(i) \), together with \( y(i) \) where \( y(i) \) is the average counts per detector. The FULLPROF program generates a variance table in which the variance at each step \( i \) is calculated as

\[
\text{Var}(i) = \frac{y(i)}{\text{(Number of detectors)}}
\]  

(6.13)

the reciprocal of which yields the weight, \( w_i \), associated with the intensity at step \( i \).

**Background:**

In order to minimise the function (6.12), the background level must be known at all points of the diffraction pattern. This can be inserted manually, point by point, by the user as a function of scattering angle however, if the background is observed to be a slowly varying function of scattering angle, then the counts \( y_{Bi} \) at the angle \( 2\theta \) may be obtained from a specified refinable function

\[
y_{Bi} = \sum_{m=0}^{\text{4}} B_m \left( \frac{2\theta_i}{\text{BKPOS}} - 1 \right)^m
\]

(6.14)

which enables the background to be estimated in regions containing Bragg peaks. \( B_m \) are the refinable coefficients of the polynomial and BKPOS is the user supplied origin of the polynomial in degrees \( 2\theta \). In this instance, the function to be minimised becomes
Chapter 6  

Sample Characterisation

Peak shape:

The peak shape for neutron diffraction has a full width at half maximum primarily dependent upon the instrumental parameters and in many cases is well approximated by a Gaussian of the form

\[ M_p = \sum_{i=1}^{N} w_i \left[ y_{o_i} - \left( y_{o_i} + \sum_{K=1}^{N} I_K G_{ik} \right)^2 \right] \]  

(6.15)

where \( M_p \) is the total intensity of a set of reflections. The peak shape can be described by the full width at half maximum (FWHM) of the Gaussian function, which is given by

\[ \text{FWHM} = \frac{4 \ln 2}{H_K} \left( \frac{1}{\sqrt{\pi}} \right) \exp \left[ -\frac{4 \ln 2}{H_K^2} \left( 2\theta - 2\theta_K \right)^2 \right] \]  

(6.16)

where \( H_K \) is the full width at half maximum of the \( K^{th} \) Bragg reflection at position \( 2\theta_K \) as given by the instrumental resolution function of (6.7).

However, in some cases the physical conditions of the sample may give rise to peak broadening, introducing a Lorentzian-like character of the form:

\[ L = 2 \left( \frac{2\theta - 2\theta_K}{H_K^2} \right) \left[ 1 + 4 \left( \frac{2\theta - 2\theta_K}{H_K^2} \right)^2 \right]^{-1} \]  

(6.17)

In order to accommodate the effect of both instrumental and specimen features upon the profile function, a refinable mixing parameter, \( \eta \), can be introduced to combine the Gaussian and Lorentzian functions and yield a pseudo-Voigt function of the form:

\[ G_{\eta} = \eta L + (1 - \eta) G \]  

(6.18)

The mixing parameter is refined as a linear function of \( 2\theta \) with variables \( \eta_0 \) and \( \eta_1 \), according to

\[ \eta = \eta_0 + \eta_1 2\theta \]  

(6.19)
Refinement strategy:

For a refinement to be performed, an input control file must be prepared within which all instrumental and crystallographic parameters are contained. The Rietveld refinement essentially means the refinement of three models:

a) The structure model
b) The diffractometer model
c) The background model

where a good result for a) necessitates a refinement of b) and a good estimate of c). Parameters to be refined are denoted by a codeword, numbered in the sequence in which they are to be refined.

The first stage of the refinement procedure involves making a visual comparison between the observed data and the simulated powder pattern based upon the initial unrefined model parameters. At this point the scale factor is set to 1.0, the half-width parameters are set to $U=V=0$ and $W=0.01$ and all isotropic temperature factors are set to zero. By comparing the calculated and observed line positions, good refinement starting values for the unit cell parameters ($a$, $b$, $c$) can be obtained and a common 2θ-zero shift checked for (the latter being vital in order for the refinement to ‘lock in’ to the observed line positions). In addition, the 2θ full width at half maximum of the strongest line can be determined so as to obtain a good starting value for the profile width parameter $W$ and the background level ascertained for its refinement.

Having established good starting parameters, the scale factors, reflection positions and background level are refined. To do so, codewords are assigned in the following sequence:

- Scale factor
- 2θ-zero
- Unit cell parameters \((a, b, c, \alpha, \beta, \gamma)\)
- Background polynomial coefficients \(B_m\) \((m=0 \text{ to } 5)\)

Following a successful refinement at this point, the pattern intensities must be refined for which the profile shape parameters (dependent on the profile shape function selected) are dealt with first. For the case of the pseudo-Voigt function, shape parameters are refined in the following order:

- Half width parameters \((U, V, W)\) - determines instrumental resolution function
- Mixing parameters \(\eta_0\) and \(\eta_1\)

The final stage of the refinement involves refining those structural parameters which influence the diffracted intensities. This is done in the following order:

- Fractional atomic co-ordinates \((x_i, y_i, z_i)\)
- Isotropic temperature factors \(B_i\)
- Anisotropic temperature factors \(\beta_{ij}\)
- Atomic site occupancies \(N_i\)

The process of refinement is an iterative one and is done over a number of cycles (as defined by the user). The level of agreement between the observed and calculated patterns is evaluated at every point of the powder pattern and expressed by means of a difference plot or by the following agreement factors:

\[
R_{Bragg} = \left[ \frac{\sum |I_o - I_c|}{\sum I_o} \right]
\]  

\[
R_p = 100 \times \left[ \frac{\sum |y_{oi} - y_{oi}|}{\sum y_{oi}} \right]
\]
\[ R_w = 100 \times \left[ \frac{\sum w_i (y_{\alpha i} - y_{c i})^2}{\sum w_i y_{\alpha i}^2} \right]^{\frac{1}{2}} \]  
(6.22)

\[ R_E = 100 \times \left[ \frac{N - P + C}{\sum w_i y_{\alpha i}^2} \right]^{\frac{1}{2}} \]  
(6.23)

These are printed at the end of each cycle, enabling the user to monitor the effect of introducing new refinement parameters and to check for any divergence during the refinement. In these expressions, \( N \) is the number of independent observations, \( P \) is the number of refined parameters, \( C \) is the number of constraints, \( y_i \) is the intensity at the angular position \( \theta_i \), \( I \) is the Bragg intensity and \( w \) is the statistical weight. \( R_{\text{Bragg}} \) is the agreement factor based upon observed and calculated integrated Bragg intensities, \( R_P \) is the profile agreement factor, \( R_W \) is the weighted profile agreement factor and the factor \( R_E \) expresses the theoretical agreement expected from counting statistics alone. The ratio \( R_W/R_E \) yields the statistical quantity 'chi', a value less than 2 for which, indicates a well refined structure.

6.1.5 Sample Characterisation

6.1.5.1 Oxygen Rich Sample

Powder neutron diffraction measurements were undertaken at room temperature with a neutron wavelength of 1.594Å on the high resolution two-axis diffractometer D2B at the ILL, Grenoble. An 11.98g specimen of the oxygen rich sample was contained, under an argon atmosphere, in a thin walled vanadium cylinder and measured for, in steps of 0.05°, over the angular range 0 to 162.45°. Figure 6.8 shows the modelled and observed scattering profiles, the bottom plot of which yields the difference between the calculated and actual intensities. The marks on the upper boundary show the
Fig. 6.8 Observed and calculated neutron powder patterns for oxygen rich YBa$_2$Cu$_3$O$_{6+x}$ at room temperature. The difference plot is shown at the bottom. The upper ticks show the synthesis of the modelled structure.

synthesis for the structure derived. The observed data was modelled with the Rietveld technique, using the orthorhombic space group $Pmmn$ and initial unit cell parameters/atomic positions taken from the paper of Cappioni et al. [9]. An estimate of the background was made using the polynomial function of (6.14) and the peak profiles were found to be well described by the pseudo-Voigt function of (6.18). The region $0^\circ \leq \theta \leq 10^\circ$ was excluded from the refinement owing to the partial attenuation of the incident beam. The initial occupancies $N$ of the O4 site (at (0%0)) and O5 site (at (½00)) were both set to 0.5 and allowed to vary simultaneously with the atomic co-ordinates $x$, $y$, $z$, temperature factors $B$, and profile parameters. Refinement of the temperature factors of the O4 and O5 sites yielded a large negative value and a large positive value respectively indicating that a model in which both sites are
Table 6.2 Refined structural parameters of oxygen rich YBa$_2$Cu$_3$O$_{6+x}$.

<table>
<thead>
<tr>
<th>Atom/Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{iso}$ [Å$^2$]</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y 1(h)</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.42(3)</td>
<td>1.00</td>
</tr>
<tr>
<td>Ba 2(t)</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$0.1845(2)$</td>
<td>0.43(3)</td>
<td>2.00</td>
</tr>
<tr>
<td>Cu 1(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.48(3)</td>
<td>1.00</td>
</tr>
<tr>
<td>Cu 2(q)</td>
<td>0</td>
<td>0</td>
<td>$0.3555(2)$</td>
<td>0.47(2)</td>
<td>2.00</td>
</tr>
<tr>
<td>O 1(cq)</td>
<td>0</td>
<td>0</td>
<td>$0.1581(2)$</td>
<td>0.95(3)</td>
<td>2.00</td>
</tr>
<tr>
<td>O 2(s)</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$0.3785(2)$</td>
<td>0.59(3)</td>
<td>2.00</td>
</tr>
<tr>
<td>O 3(r)</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>$0.3779(2)$</td>
<td>0.50(3)</td>
<td>2.00</td>
</tr>
<tr>
<td>O 4(e)</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\beta_{11}=0.046(3)$</td>
<td>0.95(1)</td>
</tr>
</tbody>
</table>

$a = 3.8201(1)\text{Å}$  
$b = 3.8834(1)\text{Å}$  
$c = 11.6785(3)\text{Å}$

$R_{Bragg} = 4.79$  
$R_p = 7.63$  
$R_w = 8.67$  
$R_E = 6.34$

\[
\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33})
\]  
(6.24)

The final positional and thermal parameters for each atom, together with the unit cell dimensions $a$, $b$ and $c$, are given in Table 6.2. In addition, the $R$-factors as defined in expressions (6.20) to (6.23) are supplied, yielding a 'goodness of fit' or chi-squared of 1.87. The atoms are numbered in the convention of figure 6.3.

From figure 6.8, it can be seen that no extra peaks are present besides those...
derived from the model, indicating that the sample is a pure one-phase compound. Refinement of the structure, using the orthorhombic space group \textit{Pmmm}, provides entirely satisfactory results with the final oxygen stoichiometry established to be YBa$_2$Cu$_3$O$_{6.95}$(1). The refined unit cell parameters and atomic positions provide good agreement with other studies on fully oxygenated YBa$_2$Cu$_3$O$_7$ [9,10,11,12].

\textit{SQUID measurements:}

Susceptibility measurements using SQUID magnetometry were performed so as to clarify the superconducting nature of the sample and its associated onset temperature \( T_c \). The term SQUID is an acronym for Superconducting Quantum Interference Device and its operation lies in the formation of the Cooper pairs synonymous with the superconducting state. The Cooper pairs of mass \( 2m_e \) and charge \( 2e \) act as single particles with de Broglie wavelength appropriate to \( 2m_e \). In the case of a bulk superconductor under zero magnetic field, the phase of the wavefunction of the Cooper pairs is the same everywhere. The result of this phase coherence throughout the sample is that, for a superconducting ring, the wavefunction must go through an integral number of oscillations around the loop. That is to say, the magnetic flux within a superconducting ring is quantised with one quantum of flux \( \hbar/2e \) per oscillation. The application of a magnetic field can change the phase relationship of the wavefunction and it is the measurement of this effect which forms the basis for SQUID magnetometry. A schematic representation of a SQUID is shown in figure 6.9 consisting of weak links X and Y in the form of thin insulating layers. The Cooper pairs tunnel through such junctions with a current described well by the Josephson current-phase relationship [29]

\[
I = I_c \sin \theta \tag{6.25}
\]

where \( I_c \) is the maximum super current that the weak link can support and \( \theta = (\theta_1 - \theta_2) \) is the phase difference of the superconducting wavefunction across the weak link. Consequently, measurement of the current through a
weak link gives a measure of the phase difference across that link. The supercurrent at \( W \) divides between paths \( X \) and \( Y \) and recombines at \( Z \). A magnetic field from the magnetised sample is applied to the route through \( Y \) only, thus introducing a 'path length difference' between the two paths and a resulting 'interference pattern' in the supercurrent measured at \( Z \). By counting the 'fringes' and analysing the current within them, an accurate measure of the field strength at \( Y \) can be obtained.

Figure 6.10 shows the mass susceptibility of \( \text{YBa}_2\text{Cu}_3\text{O}_{6.95} \) as a function of temperature for field cooled and zero field cooled data in an applied field of 1000Oe. Measurements were conducted on a 273mg sample of the oxygen rich specimen over the temperature range 5 to 120K in 1K steps at the MPI, Stuttgart. A demagnetisation correction was applied to the value of the external field. The zero field data indicates the setting up of screening supercurrents which result from a diamagnetic signal in the superconducting state. That the sample is indeed superconducting, is demonstrated by the observed Meissner effect in the field cooled data, indicating an onset temperature \( T_C \) of 91.4K. The oxygen content corresponding to this critical temperature from the phase diagram in figure 6.4, is consistent with the value...
6.1.5.2 Oxygen Deficient Sample

A neutron powder diffraction experiment was carried out on a 12.30g sample of the oxygen deficient specimen, using the D2B diffractometer as before. All experimental conditions were identical to those for the oxygen rich sample characterisation and a Rietveld refinement, using the tetragonal space group $P4/mmm$, was performed based upon the structural parameters contained in [30]. As before, an estimate for the background level was made using the polynomial function of (6.14) and the peak shapes were well described by the pseudo-Voigt mixing function of (6.18). Isotropic temperature factors were
Fig. 6.11 Observed and calculated neutron powder patterns for oxygen deficient YBa2Cu3O6+x at room temperature. The difference plot is shown at the bottom. As before, the upper ticks show the synthesis of the derived model.

applied to all atoms and again, the region 0°≤2θ≤10° was excluded from the refinement. The space group P4/mmm is a supergroup of Pmmm and the two structures are related by an order-disorder transition involving the statistical ordering of the O atoms in the basal plane as described in 6.1.1. Unlike for the orthorhombic structure, in the P4/mmm space group positions O2 (½0z) and O3 (0½z) and positions O4 (0½0) and O5 (½00) are equivalent and are thus equally occupied. Figure 6.11 shows the observed, calculated and difference plots following the refinement and Table 6.3 details the final structural and thermal parameters together with the agreement R-factors. The ratio (Rw/Rf)² yields a chi-squared value of 1.97 for the above structural parameters, indicating an entirely satisfactory model. The final refined oxygen occupancy of YBa2Cu3O6.11(2) is in agreement with the initial estimate of YBa2Cu3O6.09 based upon weight loss calculations and the absence of any extra peaks in the observed data, again provides confirmation of a single
Table 6.3 Refined structural parameters of oxygen deficient YBa$_2$Cu$_3$O$_{6-y}$.

<table>
<thead>
<tr>
<th>Atom/Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{oo}$ [Å$^2$]</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y 1(d)</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.45(2)</td>
<td>1.00</td>
</tr>
<tr>
<td>Ba 2(h)</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.1945(2)</td>
<td>0.36(3)</td>
<td>2.00</td>
</tr>
<tr>
<td>Cu1 1(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.90(3)</td>
<td>1.00</td>
</tr>
<tr>
<td>Cu2 2(g)</td>
<td>0</td>
<td>0</td>
<td>0.3609(1)</td>
<td>0.30(2)</td>
<td>2.00</td>
</tr>
<tr>
<td>O1 2(g)</td>
<td>0</td>
<td>0</td>
<td>0.1525(2)</td>
<td>1.13(3)</td>
<td>2.00</td>
</tr>
<tr>
<td>O2 4(i)</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0.3795(2)</td>
<td>0.41(3)</td>
<td>4.00</td>
</tr>
<tr>
<td>O4 2(f)</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>0.99(3)</td>
<td>0.11(2)</td>
</tr>
</tbody>
</table>

$a = 3.8581(1)$Å $b = 3.8581(1)$Å $c = 11.8221(3)$Å

$R_{Bragg} = 5.18$ $R_p = 5.22$ $R_w = 7.48$ $R_E = 5.33$

6.2 The Type II Elemental Superconductor Niobium

For the purpose of studying the interaction between the periodic lattice of flux lines and the nuclear lattice, a single crystal of the type II elemental superconductor niobium was investigated in its intermediate (Shubnikov) state. In order for a successful SANS experiment to be performed, the crystal orientation had to be determined prior to the experiment so that the chosen configuration of the crystallographic axis relative to the applied field and incident beam could be mounted.

6.2.1 Sample Preparation

The single crystal used was float-zone grown using the Czochralski technique
[31] from very high purity stock, spark machined into a disk of diameter 12mm and thickness 1mm and annealed for 60 hours at 800°C under an argon atmosphere of 18 mbar before being electropolished. The latter involved constructing a series circuit where the platinum crucible in which the crystal lay was used as a cathode. A voltage of 12 to 20 volts corresponding to a current density of between 20 and 35A/dm² was then applied before the crucible was submerged for the order of ten minutes in a small volume of solution with composition 175ml hydrofluoric acid (40%), 175ml nitric acid and 650ml water [32].

6.2.1.1 Czochralski Growth

The fundamental method by which crystal pulling is achieved can be described in six basic steps:

1. The melt from which a seed crystal is to be pulled is heated to just above its melting point. Temperature differences both radially and vertically should be small so that the bulk of the melt is within say ±20° of its mean temperature.
2. The rotating seed crystal is brought slowly into contact with the melt and allowed to reach thermal equilibrium. The optimum temperature of the melt is defined as that which causes the seed to melt slowly and at a decreasing rate so that it remains in contact with the melt.
3. Pulling is commenced at a slow rate and the new crystal should grow with a diameter slightly less than the seed diameter.
4. Growth rates are increased to their final values causing the diameter of the pulled crystal to decrease and a long, narrow neck is grown.
5. The melt temperature is lowered causing the crystal diameter to increase until a temperature, determined by the user, is reached. At this point the crystal attains its final diameter.
6. Growth is terminated and the crystal detached by either increasing the pulling rate (so that the crystal breaks contact with the melt) or increasing
the melt temperature so that the crystal diameter decreases slowly to zero.

6.2.2 Crystal Orientation

The element niobium has a body centred cubic (BCC) structure (space group \( \text{Im} \overline{3} \text{m} \)) with two atoms per unit cell, lattice point co-ordinates of 000 and \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \), and unit cell dimensions of 3.30\( \text{Å} \) [33]. The conditions for reflection can be obtained from the geometrical structure factor \( S_{hkl} \), which is the Fourier transform of the unit cell and for X-ray diffraction is shown to equal [24]

\[
S_{hkl} = \sum_{j=1}^{N} f_j \exp \left\{ 2\pi i \left( h x_j + k y_j + l z_j \right) \right\}
\]

(6.26)

where \( f_j \) is the atomic scattering factor of the \( j^{th} \) atom, \( x_j, y_j, z_j \) are the fractional co-ordinates of the \( j^{th} \) atom and \( h, k, l \) are the Miller indices denoting planes of atoms. The intensity of the diffracted beam is proportional to \( |S_{hkl}|^2 \).

6.2.2.1 The Laue Method

The Laue method enables the orientation of a crystal to be determined based upon the observed scattering distribution of an X-ray or neutron beam of continuous wavelength. In essence, the crystal selects out and diffracts the discrete values of the wavelength \( \lambda \) for which planes exist of spacing \( d_{hkl} \) and incidence angle \( \theta \) satisfying the Bragg law \( 2d_{hkl} \sin \theta = n\lambda \). To form a strong diffracted beam the following three equations, known as the Laue conditions, must be satisfied simultaneously for integer values of \( q, r \) and \( s \) [34]

\[
\mathbf{a} \cdot \Delta \mathbf{k} = 2\pi q; \quad \mathbf{b} \cdot \Delta \mathbf{k} = 2\pi r; \quad \mathbf{c} \cdot \Delta \mathbf{k} = 2\pi s
\]

(6.27)
where \(a, b, c\) are the crystal axes and \(\Delta k\) is the difference between the initial and scattered wavevectors.

**Reciprocal space:**

Just as the three vectors \(a, b, c\) define the real space lattice of a crystal structure, so can vectors \(a^*, b^*\) and \(c^*\) be defined which describe a second lattice, in Fourier space, known as the reciprocal lattice. The two sets of fundamental vectors are related by the definitions:

\[
a^* = 2\pi \frac{b \times c}{a \cdot b \times c}; \quad b^* = 2\pi \frac{c \times a}{a \cdot b \times c}; \quad c^* = 2\pi \frac{a \times b}{a \cdot b \times c}
\]  

(6.28)

and the reciprocal lattice points \(G\) in Fourier space may be defined as

\[G = ha^* + kb^* + lc^*\]  

(6.29)

It can then be shown that if \(\Delta k\) is equal to any reciprocal lattice vector \(G\), then the Laue equations of (6.27) for wave diffraction are satisfied [34].

The diffraction pattern recorded by a Laue X-ray camera is essentially a map of the reciprocal lattice of a crystal. A reciprocal lattice point is necessarily on the normal to its set of planes and the distance of the point from the origin is proportional to the wavelength. Therefore for a continuous distribution of wavelengths, there will be a continuous series of points and the reciprocal lattice becomes a set of weighted radial lines through the points corresponding to a particular wavelength. The Laue photograph of a stationary crystal then consists of a series of spots along the radial lines corresponding to reflections which simultaneously satisfy the Laue conditions of (6.27) by the correct choice of wavelength. A crystal mounted with a particular axis parallel to the X-ray beam will produce a Laue diffraction pattern showing the symmetry of that axis. In this way, the orientation of crystals relative to their morphology may be determined. Figure 6.12 shows a
schematic diagram of a Laue back scattering camera. An X-ray source is used which provides a wide range of wavelengths with a well defined minimum $\lambda_{\text{min}}$ corresponding to a collision in which the bombarding electron loses the whole of its energy in a single process. This is given by

$$\lambda_{\text{min}} = \frac{hc}{eV_0}$$  \hspace{1cm} (6.30)

where $\lambda_{\text{min}}$ is in angstrom and $V_0$ is the applied voltage in kV characterising the energy of the electrons which bombard the target (in this case W). A pinhole arrangement gives a well collimated incident beam and flat photographic film, perpendicular to the direct beam, is placed at A to receive the back scattered (high angle) diffracted beams. Where the direct beam would otherwise hit the film, a movable beam trap is fitted through which the direct beam can escape without giving rise to scattered radiation. Film B (not used in this case) receives all forward scattered (low angle) X-rays. The sample holder comprises an adjustable goniometer which enables minor rotary adjustments to be made to the specimen position.

A Laue photograph was taken with the incident beam along the cylinder axis of the disc shaped, niobium crystal. A light beam from an extended source was directed through the collimator and the crystal position adjusted to the centre.

![Fig. 6.12 A schematic diagram of the Laue X-ray camera.](image-url)
Chapter 6

Sample Characterisation

Fig. 6.13 Laue photograph with the direct beam along the cylinder axis of the niobium crystal indicating the 3-fold symmetry of the \((111)\) axis.

of the beam. A supply voltage of 20kV, supply current of 20mA and an exposure time of ten minutes yielded the Laue photograph of figure 6.13. The cylindrical crystal was grown with a \((111)\) zone seed crystal and therefore the cylinder axis may be expected to be along the \([111]\) direction. The 3-fold symmetry expected for a \([111]\) direction is not obvious from figure 6.13 although a mirror plane and two strong zones, as indicated, are evident. This would imply that the triad axis is not directly along the cylinder axis. A simulation of the Laue pattern (using the program ORIENTEX) expected for a \([111]\) direction is shown in figure 6.14 where, as expected for perfect alignment, the mirror planes intersect each other at 120°. The similarity of the
two patterns essentially confirms that the crystal is correctly orientated and further verification was obtained from a second photograph in which the crystal was rotated about the cylinder axis by 120° to yield an identical pattern to figure 6.13.

If the [111] axis is vertical, then the two orthogonal axes are [1 1 0] along the beam and [1 1 2] horizontal to [111] in the plane of the film. Turning the crystal through 90° so that the cylinder axis was vertical enabled a [1 1 0] axis along the beam direction to be identified (figure 6.15). For a cubic system, the angle between two planes $h k l$ and $h_1 k_1 l_1$ is given by [35]
Fig. 6.15 Laue photograph of the [110] axis symmetry perpendicular to the cylinder axis of the niobium disk.

\[ \cos \phi = \frac{hh_i + kk_i + ll_i}{\left[(h_i^2 + k_i^2 + l_i^2)(h_i^2 + k_i^2 + l_i^2)\right]^{1/2}} \]  \hspace{1cm} (6.31)

from which, for the [110] axis parallel to the incident beam, one expects a pattern containing planes at angles as indicated in figure 6.16.

The pattern in figure 6.15, with reflection planes indicated, implies that the [111] is not vertical meaning that the [111] axis is about 15° off from the cylinder axis. This is consistent with figure 6.13 not giving a perfect triad axis.
Fig. 6.16 Expected reflection planes and corresponding subtending angles for the [1\bar{1}0] axis along the beam.

REFERENCES


Since the discovery of superconductivity in copper oxide materials [1], intense focus has been placed on forming an understanding of both their unusual properties in the normal state and the origin of the physical mechanism involved in Cooper pair formation. A common feature of all the cuprate superconductors is the close proximity of an antiferromagnetic phase for which long range order ensues up to Néel temperatures ($T_N$) as high as 500K [2, 3, 4]. In addition, neutron scattering experiments performed on the high T$_C$ parent compound La$_2$CuO$_4$ (in its pure state) [5] and YBa$_2$Cu$_3$O$_{6+x}$ (for small x) [6], have revealed that strong, two-dimensional spin correlations persist, within the CuO$_2$ planes, above the long range order temperature with a magnetic energy scale orders of magnitude larger than that indicated by $T_N$. It is the existence of these large magnetic energies that has fuelled speculation that a magnetic mechanism provides the energy scale needed for the attainment of high superconducting transition temperatures. Crucial to the compliance of the several magnetic models proposed (e.g. [7, 8, 9]), is the presence of magnetic fluctuations (implying local moments) in the superconducting phase of these high T$_C$ compounds. It is therefore an important requirement for the characteristics of the magnetic excitations to be experimentally determined in these systems. A study is presented here for the high T$_C$ superconducting series YBa$_2$Cu$_3$O$_{6+x}$.

The magnetic structure of the oxygen deficient compound ($0 < x < 0.5$) has been determined on the basis of neutron scattering [10, 11, 12, 13] and NMR
[14] measurements and found to comprise of antiferromagnetically coupled CuO$_2$ planes along the c-axis in which the direction of the Cu$^{2+}$ spins are fixed in the plane. Characterising this magnetic structure is the propagation vector $q = (\pi, \pi)$, in the vicinity of which, for specimens with small $x$, the inelastic response is observed to be strongly localised [6]. Particular focus has been placed therefore on the evolution of this response, as a function of both oxygen content and energy transfer, as to whether a magnetic mechanism is giving rise to superconductivity. Of crucial importance to the discussion is the positive identification of the response as being magnetic where, even for antiferromagnetic compositions $x < 0.5$, the total magnetic cross-section is at most 1% of the nuclear scattering.

In order to unambiguously distinguish a magnetic response from all other scattering, an isothermal technique such as spin polarised neutrons with polarisation analysis is essential. In particular, three-dimensional polarisation analysis [15] as described in chapter 3, in which spin flip ($l_{\uparrow\downarrow}$) and non-spin flip ($l_{\uparrow\uparrow}$) scattering intensities are recorded for polarisation of the incident beam in three mutually orthogonal directions $\nu = x, y, z$, yields corresponding scattering cross-sections in terms of individual scattering contributions (equations (3.72) to (3.77)). The magnetic scattering rate can then be determined from the following combination of observed intensities

$$\frac{1}{2} I_{mag} = I_{\uparrow\downarrow} + I_{\uparrow\uparrow} - 2I_{\uparrow\downarrow}^* = 2I_{\uparrow\downarrow} - I_{\uparrow\downarrow}^* - I_{\uparrow\uparrow}^* \quad (7.1)$$

Appropriate normalisation of the observed scattering rate to a vanadium standard scatterer (as discussed in 4.3) enables the observed response to be placed on an absolute scale. Thus the technique of polarised neutrons yields uniquely the magnetic correlation function given by (2.61):

$$\Gamma(\kappa, \omega) = \int \sum_{l_d} \exp \left\{ i \kappa \cdot \left( R_{l_d}(t) - R_{l_d}(0) \right) \right\} \langle \hat{S}_{l_d}(t) \cdot \hat{S}_{l_d}(0) \rangle$$

$$\quad (7.2)$$
where $\mathbf{R}_{id}$ is the position of the ion $d$ located in unit cell $l$ and $\hat{S}_\beta^l$ is the operator corresponding to the $\beta$ component of spin for the ion $l$, $d$. This in turn is related to the dynamic susceptibility thus

$$\Gamma(k, \omega) = \frac{1}{1 - \exp(-\frac{\omega}{k_B T_N})} \chi''(k, \omega)$$  \hspace{1cm} (7.3)$$

In the case of a local moment picture, for which the charge and magnetic degrees of freedom are separated, neutron scattering from the ground state comprises coherent magnetic Bragg scattering and coherent inelastic magnetic scattering, i.e., spin waves. Since the charge and magnetic degrees of freedom are separated, the spin waves are able to disperse out to the zone boundary. The zone-boundary energy of the spin waves is then typically of the same order as the Néel temperature $k_B T_N$. Important for the implications of the experiment therefore, is the sum rule which is obtained if the magnetic fluctuations are integrated throughout the zone (as discussed in 2.4.3):

$$\sum_\kappa \int d\omega \Gamma(k, \omega) = N\langle S^z \rangle = NS(S + 1)$$  \hspace{1cm} (7.4)$$

Here, the sum over $\kappa$ is taken over a Brillouin zone and the integral over frequency is from $-\infty$ to $+\infty$. Experimentally however, the integral in $\omega$ is restricted to a finite region where, for the case of this study, the energy integration is carried out along a 'curved path' in the scattering vector - energy transfer plane. The experimental energy integration is limited on the neutron energy loss side by the kinetic energy of the neutrons employed. The investigation discussed here utilised neutrons of wavelength 4.84Å thus limiting the cross-section measured directly, to contributions from energies $\hbar \omega < 3.5 \text{meV}$. On the neutron energy gain side, a measure of the amount of energy which the sample can transfer to the neutron in the scattering process is determined by the temperature of the sample. In effect therefore, it is the sample temperature which characterises the energy interval over which the experimental integration is carried out. For the local moment system
described above, the range of integration necessary to obtain the sum rule is typically of the order of $k_B T_N$. An adequate description of these local moment systems is provided by the Heisenberg model in which the sum rule is identified as consisting of a Bragg component $(bS)^2$ and an inelastic contribution $S+S^2(1-b^2)$ where $b$ is a quantum correction which in this case takes a value of order $\frac{1}{16}$ [16]. At finite temperatures, the moments become directionally disordered but their magnitude remains fixed. Thus, the paramagnetic phase is characterised by disordered local moments and if the same range of $\kappa$ and $\omega$ integration is carried out, the sum rule should be conserved.

Presented here are the results of a spin polarised neutron investigation carried out on two powder samples of YBa$_2$Cu$_3$O$_{6+x}$ with respective oxygen compositions in the insulating and superconducting parts of the phase diagram. In order to avoid local inhomogeneities which arise in samples with intermediate oxygen compositions, the powder specimens were prepared with oxygen concentrations far from the borderline in the compositional phase diagram. Particular importance was placed during their preparation, on ensuring that the samples were free of residual traces of hydrogen as

![Contour paths](image)

**Fig. 7.1** Contour paths over which the energy integration is taken for a neutron wavelength of 4.84Å.
described in 6.1.2. The presence of hydrogen, due to its large incoherent cross-section, renders the error bars associated with the magnetic signal to be large by virtue of the way the magnetic scattering rate is obtained from the differences of large scattering cross-sections. Sample structure and homogeneity were verified from high resolution powder diffraction measurements as described in 6.1 for which a Rietveld refinement revealed oxygen occupancies of $\text{YBa}_2\text{Cu}_3\text{O}_{6.11}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ respectively. Magnetisation measurements performed on the oxygen rich sample clarified its superconducting nature with a transition temperature indicative of optimal doping ($T_c = 91.4K$). All spin polarisation measurements were performed on the D7 multidetector at the ILL, Grenoble in its energy integrated mode (see section 4.2 for an instrumental description) allowing the study of magnetic fluctuations in the energy range $-30\text{meV} < h\omega < +30\text{meV}$. The paths in the scattering vector - energy transfer plane, along which the integration is carried out, are shown in figure 7.1 for the experimental configuration used. Measurements were carried out in the antiferromagnetically ordered and paramagnetic states of the $\text{YBa}_2\text{Cu}_3\text{O}_{6.11}$ sample at room temperature and 450K respectively. For the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ sample, the search for magnetic fluctuations was conducted in its normal phase at room temperature. In addition, measurements carried out on single crystal $\text{YBa}_2\text{Cu}_3\text{O}_7$, in its normal state, have been performed with regard to the magnetic response in the vicinity of the $(\pi, \pi)$ point in reciprocal space.

### 7.1 Magnetic Fluctuations in $\text{YBa}_2\text{Cu}_3\text{O}_{6.11}$

The investigation was carried out on a 37.45g powder sample using a selected neutron wavelength of $4.84\text{Å} (3.5\text{meV})$. For both 300K and 450K measurements the specimen was contained in a thin walled, aluminium cylinder under a helium atmosphere, located in a non-inductively wound furnace. Having optimised the flipper and correction coil currents for maximum spin flipper efficiency, calibration measurements as detailed in 4.3 were performed, enabling corrections for finite flipping ratio (typically of order
for each detector) and background to be made. Normalisation to the scattering of a vanadium standard (for which a correction for multiple scattering was made, as detailed in chapter 5) permitted all subsequent sample data to be placed on an absolute scale.

7.1.1 Measurement of the Ordered Moment

In order to verify the existence of long range antiferromagnetic order within the sample, 28 diffraction scans were performed first at room temperature and then in its paramagnetic state at 450K (\(> T_N \)). This involved measuring the spin flip and non-spin flip scattered intensity as a function of scattering angle for z-polarised neutrons only. The detector banks were shifted in fifteen steps of 0.5° intervals, enabling the full range \(7^\circ < 2\theta < 160^\circ \) to be covered without gaps in the resolution. By virtue of the fact that spin flip Bragg reflections can only be magnetic in origin, comparison of the scattering pattern for the two spin states of the neutron enables peaks of magnetic and nuclear origin to be distinguished. Figures 7.2 a) and b) overleaf, show the non-spin flip and spin flip scattering patterns respectively for YBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) at room temperature. Nuclear and magnetic peaks have been indexed using the Bragg condition for reflection, \(\lambda = 2d\sin\theta \), where for a tetragonal system

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (7.5)
\]

with \(a = 3.8581\text{Å} \) and \(c = 11.8221\text{Å} \) as derived from the structural refinement described in 6.1.5.2. Details of the various peaks are provided in Table 7.1 including, for the case of the nuclear peaks, the structure factors as calculated according to (6.11) using the Cambridge Crystallography Subroutine Library. Clearly evident in the spin flip signal are the magnetic (\(1\frac{1}{2}1\frac{1}{2}1\)) and (\(1\frac{1}{2}1\frac{1}{2}2\)) Bragg peaks, although the latter is sitting on the shoulder of a strong nuclear reflection. Due to the high intensity of the nuclear peaks, the finite instrumental flipping ratio gives rise to an appreciable amount of
Fig. 7.2 a) Non-spin flip and b) spin flip scattering patterns for YBa$_2$Cu$_3$O$_{6.11}$ at room temperature. The magnetic peaks, absent in a) are clearly evident in the spin flip signal. Note the large difference in scale for the two signals.
nuclear scattering in the spin flip signal. By normalising the integrated intensity of the magnetic \((\frac{1}{2}\frac{1}{2}1)\) peak to the nuclear (001) reflection, the ordered moment could be determined based on the well determined magnetic structure [3]. The two Bragg peaks were fitted using a Gaussian shape function, as shown in figures 7.3a) and b), and the observed integrated intensities \(I_{\text{obs}}^{\text{nuc}}\) and \(I_{\text{obs}}^{\text{mag}}\) determined. Background scattering was taken into account by subtracting a horizontal line in compliance with the average level. The calculated nuclear integrated intensity, based on data in Table 7.1, was obtained using the following expression

\[
I_{\text{calc}}^{\text{nuc}} = \frac{F_{\text{calc}}^{\text{nuc}}^2 \times M \times B \times \text{absorption}}{2 \sin \theta \sin 2\theta} \tag{7.6}
\]

where \(M\) is the peak multiplicity and \(B\) is the temperature factor. The calculated magnetic integrated intensity could then be obtained by normalising according to

\[
I_{\text{calc}}^{\text{mag}} = \frac{I_{\text{obs}}^{\text{mag}}}{I_{\text{obs}}^{\text{nuc}}} \times I_{\text{calc}}^{\text{nuc}} \tag{7.7}
\]

which in turn yields the normalised magnetic structure factor. Assuming an

| hkl | \(\sin \theta / \lambda \) (Å\(^{-1}\)) | \(|F_{\text{nuc}}^{\text{calc}}|\) | \(M\) |
|-----|--------------------------------|----------------|-----|
| 001 | 0.0423 | 1.6142 | 2 |
| 003 | 0.1269 | 0.8673 | 2 |
| 100 | 0.1296 | 1.6510 | 4 |
| 101 | 0.1364 | 0.8743 | 8 |
| 004 | 0.1692 | 2.8760 | 2 |
| 103 | 0.1814 | 2.6771 | 8 |
| 111 | 0.1881 | 1.6806 | 8 |
| \(\frac{1}{2}\frac{1}{2}1\) | 0.1009 | - | 2 |
| \(\frac{3}{2}\frac{3}{2}2\) | 0.1247 | - | 2 |

Table 7.1 Peak details for the nuclear and magnetic reflections as calculated using the Cambridge Crystallographic Subroutine Library.
Fig. 7.3 Gaussian fits to a) the (001) nuclear peak and b) the ($\frac{1}{2}$$\frac{1}{2}$$\frac{1}{2}$) magnetic peak. In both cases, the background level has been subtracted in order to obtain the integrated intensities. The integrated intensity of the magnetic peak corresponds to an ordered moment of $0.62 \pm 0.03\mu_B$.

average formfactor $\bar{f}^2(\kappa) = 0.8$ [15], the ordered moment corresponding to the observed magnetic Bragg intensity amounts to $0.62 \pm 0.03\mu_B$. This value is in compliance with the fact that, for a two-dimensional quantum antiferromagnet with spin $\frac{1}{2}$, quantum corrections become important and the Bragg contribution to the scattering is modified to $(bS)^2$ (see 2.4.3). For the case treated here, the reduction factor, $b$, which is dependent on lattice type and dimension, takes a value of $\frac{1}{2}$ [16]. Thus one does not observe the full ordered moment of $1\mu_B$ for spin $\frac{1}{2}$ (the Landé g-factor being 2) as expected at $T = 0$. The spin flip scattering pattern observed at $T = 450K$ is shown in figure 7.4 for which the region of dominant magnetic scattering has been selected. As for room temperature, nuclear peaks are present due to the finite instrumental flipping ratio, however, there is no sign of any Bragg reflections corresponding to long range magnetic order, thus indicating that the sample is
Chapter 7

Magnetic Fluctuations in YBa$_2$Cu$_3$O$_{6+x}$

Fig. 7.4 Spin flip scattering pattern for YBa$_2$Cu$_3$O$_{6.11}$ at $T = 450$K. The absence of the magnetic Bragg peaks confirms the disappearance of long range antiferromagnetic order.

in its paramagnetic state.

7.1.2 The Paramagnetic Scattering Above and Below $T_N$

Within a localised moment picture, the total, energy integrated magnetic intensity is proportional to $S(S+1)$. In addition to the contribution from the ordered part of the magnetic moment (which is proportional to $S^2$) a second, scattering vector independent contribution arises due to the disordered part of the magnetic moment. This disordered contribution is proportional to $S(S+1) - S^2$ and in the absence of quantum fluctuations in the ground state, for spin $\frac{1}{2}$, should amount to half of the energy integrated scattering. Using the XYZ technique of polarisation analysis (see section 3.3.2), the paramagnetic response was determined for YBa$_2$Cu$_3$O$_{6.11}$ in both its ordered state (300K) (excluding those detectors corresponding to magnetic Bragg reflections) and
its paramagnetic phase (450K) for a thermally determined energy window of ±30meV. For the case of the room temperature measurement, two different detector bank positions (separated by 1.5°) were measured for such that the whole scattering vector range $0.18\AA^{-1} < k < 2.49\AA^{-1}$ could be covered without a gap in resolution. Typical counting times were of the order of 30 hours per data point in the ordered phase and 50 hours per data point above the ordering temperature (one position only). As a check for the presence of adsorbed hydrogen, the nuclear spin-incoherent scattering was obtained by the combination

$$I^{\text{spin}}_{\text{incon}} = \frac{3}{2}(3I^{x} \gamma_{1} - I^{x} \gamma_{1} - I^{y} \gamma_{1})$$

(7.8)

which yielded a corresponding cross-section of $1.66 \pm 0.04$ barns, comparing favourably with the theoretical value. The paramagnetic scattering as a function of scattering vector is shown for YBa$_2$Cu$_3$O$_{6.11}$ in its ordered (fig. 7.5) and paramagnetic states (fig. 7.6). For the room

![Graph](image-url)
Fig. 7.6 Magnetic scattering as a function of scattering vector for YBa$_2$Cu$_3$O$_{6.11}$ above the antiferromagnetic ordering temperature, T = 450K.

temperature data, regions containing magnetic Bragg peaks have been excluded and in both cases, points corresponding to nuclear Bragg positions (denoted by large error bars) have been dropped from the plot. The paramagnetic cross-section averaged over scattering vector, amounts to in each case:

\[
\sigma_{para}^{O_{6,11}} (300K) = 0.204 \pm 0.013 \text{ barns/formula unit} \\
\sigma_{para}^{O_{6,11}} (450K) = 0.263 \pm 0.012 \text{ barns/formula unit}
\]

7.1.3 Discussion

The small but finite level of scattering vector independent magnetic scattering observed in the ordered state, is expected on the basis of partial occupation of the O sites within the Cu-O chains (Cu1 and O4 positions) which results from the non-zero doping for this sample. As a consequence, some of the
chain site Cu atoms will have neighbours while others will not, thus creating a fraction of Cu moments within the chains which are loosely coupled to the magnetisation distribution in the CuO$_2$ planes. These Cu 'impurity' moments do not participate in the long range order of the Cu moments in the CuO$_2$ planes which manifests itself in the observed magnetic Bragg peaks. This notion is suggested by form factor measurements [18] where, for an intermediate oxygen concentration of O$_{6.5}$, it was shown that an applied field induces moments in the Cu-O chains. At low temperatures the amplitude of this moment increases like $T^{-1}$, consistent with almost free Cu moments in the chain. In addition the observation at low $T$ of magnetic Bragg peaks with half integer indices in the $c$-direction (indicating doubling of the corresponding magnetic unit cell length) [19] can be explained on the grounds of loosely coupled Cu moments in the chains. If there really are weakly coupled Cu1 moments present within the chains, then their expected scattering contribution to the magnetic cross-section is proportional to (7.4). In order to obtain an estimate for the fraction of chain site Cu atoms carrying a moment, $N_{Ch}$, the observed magnetic scattering can be compared to the total paramagnetic scattering cross-section, $\sigma_T$, given by

$$\sigma_T = 4\pi \times \left(\frac{2}{3}\gamma f_0 \left\{ \frac{1}{2} gf(\kappa) \right\}^2 S(S+1) \right)$$  \hspace{1cm} (7.9)$$

which for spin $\frac{1}{2}$ and a form factor of unity, amounts to $\sigma_T(S = \frac{1}{2}) = 1.83$ barns/formula unit. Assuming an averaged form factor of $f^2(\kappa) = 0.8$, the observed magnetic scattering amounts to

$$\sigma_{\text{param}}^{(300\text{K})} = N_{Ch} \times 0.8 \times \sigma_T(S = \frac{1}{2})$$  \hspace{1cm} (7.10)$$

which yields a corresponding concentration of chain site moments of $N_{Ch} \approx 14\%$. For an oxygen stoichiometry of YBa$_2$Cu$_3$O$_{6.11}$, a maximum of 20% of chain site Cu atoms are expected to carry a full moment of 1$\mu_B$, under the assumption that all oxygen atoms are distributed such that no two are nearest
neighbours. Thus within the finite experimental energy integration, our observed magnetic scattering is consistent with the expectation that partial O4 occupation results in loosely coupled Cu1 moments.

Similar analysis performed on the $T = 450K$ data reveals a corresponding concentration of moment carrying Cu atoms (assuming that only Cu atoms within the chains contribute to the scattering) of $N_{Ch} \approx 18\%$. The observed increase in paramagnetic scattering upon raising the temperature to 450K, can be compared with that expected due to the disordering of the ordered moment as a result of thermal fluctuations. For a spin $\frac{1}{2}$, the maximum possible contribution to Bragg scattering is one third of the total energy integrated cross-section ($S^2$ being $\frac{1}{4}$ of $S(S+1)$) - a fraction which occurs only if the full moment of $1\mu_B$ contributes to the Bragg intensity. The investigation presented here revealed a reduced aligned moment at room temperature of $0.62\mu_B$ with the result that the maximum contribution of the Bragg intensity to the overall scattering will be reduced by a factor of $(0.62)^2$. Since there are two moment carrying Cu atoms in the CuO$_2$ planes, the theoretical contribution to the paramagnetic scattering above $T_N$ from the disappearance of long range order amounts to

$$\sigma_{\text{Bragg}}^{T_N} = 4\pi \times \left( \frac{(0.62)^2}{3} \times 2 \right) \times \sigma_T(S = \frac{1}{2}) = 0.47 b/\text{formula unit} \quad (7.11)$$

So the observed ordered moment at $T = 300K$ should add an additional 0.47 barns above $T_N$ to whatever paramagnetic scattering was observed at 300K. Comparing the observed scattering at 300K and 450K yields an increase of $0.059 \pm 0.018$ barns above $T_N$, which must be multiplied by a factor $\frac{1}{2}$ to account for the ordered moment being carried by two Cu atoms. Thus there is a discrepancy of approximately a factor of 5 between the expected rise in paramagnetic scattering due to thermal fluctuations and that observed. Indeed although this weak enhancement might be due to quasi two-dimensional short range order, it could plausibly be accounted to residual
three dimensional short range order since the experimental data in the
paramagnetic state was obtained just above $T_N$. In order to understand the
magnetic properties in these compounds, itinerant antiferromagnetism may
have to be invoked in which amplitude fluctuations play an important role in
the phase transition [20]. The definition of amplitude is given by
$$\sum \int d\omega \Gamma(\kappa, \omega),$$
where for itinerant magnetism in magnetic transition metals, a
substantial fraction of the magnetic fluctuations are shifted from the broad
single particle charge excitation spectrum (typically of order eV’s) towards low
energies. If however, a separation of charge and magnetic energy scales
cannot be made then the concept of magnetic amplitude becomes invalid and
the notion of the magnetic moment as a slow variable becomes meaningless
as does any discussion for the cuprates with regard to localised moments. A
phase transition driven by amplitude fluctuations may result in a spread in
energy over a region $> k_B T_N$ as opposed to the reduced energy region
$\sim \sqrt{\hbar J \cdot \xi^{-1}}$ present in systems with giant 2D short range order of stable
moments (section 2.4.3). This wider energy region of amplitude fluctuations
may explain the low experimentally observed magnetic scattering and the
absence of a strong quasi elastic peak in the vicinity of the 2D Bragg point
above $T_N$.

To conclude therefore, the observed paramagnetic response for
$\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ both in its ordered state and above $T_N$, is consistent with the
notion of loosely coupled chain site Cu moments which arise due to the partial
occupation of the chain O4 site. However, the observed level of magnetic
scattering is much reduced from that expected from a local moment picture in
which, for a spin $\frac{1}{2}$, the disordered part of the magnetic moment yields half of
the total energy integrated scattering. It is therefore argued that the magnetic
excitation spectrum is not driven by temperature but rather by quantum
fluctuations which exist over a much wider range than the thermal spectrum.
In addition, the enhancement of the paramagnetic scattering above $T_N$ is only
$\sim 20\%$ of that expected on the basis of a thermal disordering of the observed
magnetically ordered moment at room temperature. It is therefore concluded
that the moment on the Cu atoms within the CuO$_2$ planes, which become disordered as a function of increasing temperature, also participate in the quantum fluctuations.

7.2 Magnetic Fluctuations in YBa$_2$Cu$_3$O$_{6.95}$

The investigation of magnetic fluctuations in the superconductor YBa$_2$Cu$_3$O$_{6.95}$ was carried out on a 40.01 g powder sample contained in a thin walled aluminium can under helium atmosphere and located in a helium flow cryostat. Using the D7 instrument in its energy integrated mode with the same configuration as for the oxygen deficient sample, the magnitude and 

![Graph](image)

Fig. 7.7 The magnetic cross-section integrated up to 30meV as a function of scattering vector for YBa$_2$Cu$_3$O$_{6.95}$ in its normal state at 300K. The dashed line indicates the $\kappa = 0$ scattering expected on the basis of susceptibility data provided in figure 7.9.
wavevector dependence of the magnetic response was determined in the normal state ($T = 300K$) for a thermally determined energy range up to 30meV [21]. Instrumental adjustments and calibration measurements were conducted as described in 4.3 for which a typical instrumental flipping ratio of obtained for each detector. A preliminary scan was carried out for wave vectors between $0.18 < \kappa < 2.51\text{Å}^{-1}$ in the superconducting state at 1.5K. These data, which were collected in the form of spin flip and non-spin flip with respect to the vertical z-axis, did not reveal any peaks of magnetic origin thus indicating the absence of long range order. All subsequent data was collected using three-dimensional polarisation analysis, in the normal state at 300K. In order to cover the entire range without a gap in resolution, two detector bank positions were used. The typical counting time per data point amounted to 120 hours. A check for the presence of adsorbed hydrogen was obtained from the spin incoherent scattering cross-section (7.8) which revealed a value of $1.70 \pm 0.03$ barns, in agreement with the theoretical value. Figure 7.7 shows the energy integrated magnetic response up to 30meV in the normal state of $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$. These data suggest a magnetic response both negligible in magnitude and independent of wave vector within the experimental error bars. What little scattering is observed corresponds to a paramagnetic cross-section, averaged over wave vector of:

$$\sigma_{\text{para}}^{0.95} = 0.048 \pm 0.008 \text{ barns}.$$ 

In addition to powder measurements, a spin polarised neutron experiment was carried out on a 32g single crystal of composition $\text{YBa}_2\text{Cu}_3\text{O}_7$ in its normal state. The investigation was concerned with surveying the magnetic response up to 30meV as a function of reciprocal space in the vicinity of the $(\pi, \pi)$ propagating vector which characterises any antiferromagnetic order. The spin flip signal as a function of reciprocal space is shown in figure 7.8 for which no enhancement is displayed in the region of the $(\pi, \pi)$ point. This measurement is therefore in disagreement with the 'Nearly Fermi Liquid' theory of Pines and co-workers [9] in which the magnetic response of optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is predicted to be peaked in the vicinity of the
Fig. 7.8 Energy integrated spin flip signal up to 30meV as a function of reciprocal space for single crystal YBa$_2$Cu$_3$O$_7$ in its normal state. $T = 300$K. Indicated on the figure is the location of the nuclear Bragg reflections and the $(\frac{1}{2}\frac{1}{2}l)$ plane along which any magnetic response is predicted to be localised.

($\pi, \pi$) point within an energy range 10 - 20meV.

7.2.1 Discussion

If one compares the observed paramagnetic cross-section up to 30meV of 0.048± 0.008barns with that expected for a full spin $\frac{1}{2}$ moment, the corresponding concentration of Cu atoms carrying a spin $\frac{1}{2}$ is obtained, amounting to ~3.2%. From this observation the conclusion can be drawn that in the normal state, there is essentially very little scattering intensity within an energy interval up to 30meV. This is further supported by single crystal measurements conducted over the same energy interval in which a survey of the magnetic response as a function of reciprocal space revealed no
enhancement in the vicinity of the characteristic magnetic propagating vector.

A frequent statement in the literature [22] purports that the uniform susceptibility of YBa$_2$Cu$_3$O$_{6+x}$ is characterised by strong antiferromagnetic correlations. Using susceptibility data shown in figure 7.9 from Johnston [22], the expected magnetic scattering at $\chi = 0$ can be determined by virtue of the relationship between the spin-spin correlation function and the uniform susceptibility:

$$\sum_i \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = 3k_B\chi T$$  \hspace{1cm} (7.12)

which in turn is related to the partial differential cross-section by

$$\frac{d\sigma}{d\Omega} = \frac{2}{3} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle (\Omega \gamma)^2 r^2$$  \hspace{1cm} (7.13)

From figure 7.9, the uniform susceptibility for YBa$_2$Cu$_3$O$_{6.96}$ at 300K amounts to 4.19 erg emu/g which, upon converting into the appropriate units, yields an

Fig. 7.9 Magnetic susceptibilities versus temperature for various oxygen concentrations of the YBa$_2$Cu$_3$O$_{7-x}$ system [22]. The data has been corrected for Curie type impurities/defects.
expected $\kappa = 0$ magnetic scattering cross-section, as indicated by the red dashed line in figure 7.7, of 0.0325 barns/sr. In order to be able to extrapolate the neutron data to the $\kappa = 0$ value based on susceptibility measurements, it has to be assumed that there exists a substantial amount of short range magnetic order giving rise to a large contribution at small scattering vectors. Inspection of the susceptibility data clearly indicates that in the normal state above $\sim$90K, the susceptibility of the YBa$_2$Cu$_3$O$_7$ compound is larger than the O6 sample. Indeed as the oxygen content is reduced the uniform susceptibility falls systematically. The thermal dependence of the susceptibility is very similar for all compositions, with a tendency for it to increase as the temperature is raised. Neither the variation in magnitude of the susceptibility with oxygen content nor the temperature variation is consistent with the existence of local moments. It may also be noted that the Sommerfeld coefficient for YBa$_2$Cu$_3$O$_{6+x}$, extracted from specific heat data [23], scales in the same way with oxygen content. Comparisons between the magnitudes of electronic specific heat and spin susceptibility functions for given oxygen contents conclude that the spin and charge degrees of freedom are not separated. Furthermore, the absence of an EPR (electron paramagnetic resonance) signal from Cu$^{2+}$ in superconducting and insulating YBa$_2$Cu$_3$O$_{6+x}$ up to temperatures of order 570K [24] is strong evidence that local moments do not exist. While explanations for the disappearance of EPR in the metallic state can be offered on the grounds of extremely short spin-lattice relaxation times, the same argument cannot be used for the paramagnetic regions of the antiferromagnetic insulating regimes (for which spin-lattice relaxation times are long compared to the EPR signal time scales). These observations are consistent with an almost itinerant description in which the charge gap is small compared to the band width.

To conclude therefore, the polarised neutron results presented here and in [21] demonstrate that there is neither an elastic or quasi-elastic magnetic response in the normal state of YBa$_2$Cu$_3$O$_{6.95}$. What little magnetic response is observed within the energy window $-30\text{meV} < h\omega < +30\text{meV}$ corresponds to $\sim$3.2% of the Cu atoms carrying a spin $\frac{1}{2}$. This is inconsistent with the notion
of localised moments within the CuO₂ planes, a conjecture which is supported by the magnitude and thermal variation of the uniform susceptibility. These conclusions are in accord with the polarised neutron results on \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) in which the notion emerges that the magnetic and charge degrees of freedom are not separated so that even in these materials, the concept of a local moment picture may not be valid. Comparison of some of the properties of the \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) series with the itinerant antiferromagnet Cr reveal a number of shared features however, the paramagnetic response above \( T_N \) is not one of them. In chromium, strong antiferromagnetic correlations which occur around the staggered wavevector are centred on \( \omega = 0 \) and persist beyond 2.2\( T_N \) [25].

REFERENCES


CHAPTER 8

OBSERVATION OF THE LATTICE DISTORTION IN THE SHUBNIKOV PHASE OF NIOBIUM

In order to optimise the application of certain aspects of superconductivity, a more detailed understanding of the interaction between magnetic flux lines in type II superconductors is required, as, for many applications, it is vital to minimise the motion of flux lines which give rise to dissipation in a system. In particular, an identification of the basic interaction between the flux line lattice (FLL) and the nuclear structure will permit a more detailed comprehension of the FLL structure as well as a determination of its orientation relative to the nuclear lattice.

The interaction between the periodic lattice of flux lines and the nuclear lattice in single crystal niobium, has been investigated using spin polarised neutrons in a small angle scattering experiment. This technique, sensitive to the interference term between the nuclear and magnetic structure factors (as described in 4.4.1), has enabled the nuclear distortion associated with the formation of the FLL in the Shubnikov phase, to be detected and its magnitude determined, opening up a new line of investigation into the interaction between the periodic magnetic field modulation and the nuclear structure factor.

8.1 A Simple Model for the Lattice Distortion

An external magnetic field will penetrate a type II superconductor in its
Shubnikov phase in the form of a flux line lattice [1] as described in 1.4.3. The approximation for a single flux line involves considering it as a tube with a normal core of radius $\xi$, the coherence length, around which supercurrents circulate in order to shield the magnetic field. As described in 1.4.4, associated with the normal to superconductor phase transition is a volume anomaly which in the case of a FLL, where normal regions exist in a superconducting matrix, results in a stress field. The aim here is to obtain a simple estimate of the magnitude of the volume effect and its contribution to the scattered intensity in a neutron experiment. To do so, a simplified model of the volume variation can be considered which enables an order of magnitude estimate of that nuclear scattering arising due to a lattice distortion.

The normal core of a flux line can be considered as a cylinder of radius $\xi$ cut out from a homogeneous superconductor which is then driven normal by an applied field. As a result of this phase change, there will be a volume variation given by [2]

$$\zeta = \frac{V_N - V_S}{V_S}$$

(8.1)

where $V_N$ and $V_S$ are the normal and superconducting volumes of the cylinder respectively. This is in turn related to the pressure derivative of the critical field as given in (1.54). For niobium, the observed length change [3] indicates that the volume is reduced upon becoming normal and consequently, if the normal material is re-inserted into the superconductor, both the superconducting and normal material must distort in order for their surfaces to match. However, for an order of magnitude estimate, it suffices to take into account only the core distortion, resulting in an increased density of the normal material with respect to the superconducting and the development of a gap, $\Delta R$, between the normal and superconducting materials. It should be noted however, that the gap $\Delta R$ is a manifestation of the simplified model used for an order of magnitude estimate. Rather the lattice will distort,
resulting in a continuous deformation of the lattice without any gap. However, for the purpose of estimating the nuclear scattering contribution, the model described here is appropriate. In reality the gap does not exist.

Figure 8.1 provides a schematic representation of the FLL in two-dimensions, indicating the hexagonal unit cell with lattice parameter \( d \). The core of each flux line is represented by a dashed circle of radius \( \xi \) and the boundary of the superconducting material by a solid circle. From [4], the volume variation \( \zeta \) for niobium is of the order of \(-3 \times 10^{-7}\) and the coherence length \( \xi = 350\text{Å} \), which yields an order of magnitude estimate for the normal to superconducting gap \( \Delta R \), of \( \sim 10^{-4}\text{Å} \). The nuclear scattering density is obtained from the scattering potential as defined in 2.3.1 and for the normal core is given by

\[
\rho_N = \frac{2\pi \hbar^2}{m_n} \frac{n b_{NP}}{V_N} \tag{8.2}
\]
which changes with respect to the superconducting scattering density $\rho_s$ according to

$$\Delta \rho = \rho_n - \rho_s = -\zeta \rho_s$$

Here, $m_n$ is the neutron mass, $n$ is the number of niobium atoms inside the volume $V$ and $b_{Nb}$ is the nuclear coherent scattering length of niobium, namely $0.7054 \times 10^{-12} \text{cm}$ [5]. Thus as a result of this volume effect in the core, the nuclear structure factor amplitude of a single straight flux line, and using cylindrical co-ordinates, is given by

$$F_{N}^{(\text{core})}(k) = \frac{m_n}{2\pi \hbar^2} \int_0^{2\pi} \int_0^{\frac{\xi}{r}} \int_0^{\frac{2}{3} \Delta \rho \exp(-i k \cdot r)} dr d\theta$$

where the factor of two-thirds arises by virtue of the volume change only occurring in directions perpendicular to the axis of the flux line. It is the corresponding modulation of the nuclear scattering density $\Delta \rho$ which gives rise to the nuclear contribution to the scattering. This modulation amounts to $\Delta \rho = +3 \times 10^7 \rho_s$ for niobium where evaluating (8.4), one obtains

$$F_{N}^{\text{core}} = -2\pi \frac{b_{Nb}}{V_{Nb}} \frac{\xi}{k} J_1(k \cdot \xi)$$

Here, $k$ is defined as $2\pi/\lambda_n$, where $\lambda_n$ is the neutron wavelength. For $\lambda_n = 11 \AA$ as used in the experiment, $k$ amounts to $\sim 6 \times 10^{-3} \text{Å}^{-1}$. The product $k \cdot \xi$ amounts to 2.1 for a coherence length of 350Å, yielding a value for the Bessel function $J_1(k \cdot \xi)$ of $\sim 0.5$.

In addition to that arising from the density modulation, a second contribution to the nuclear structure amplitude arises in this model due to the gap $\Delta R$ between the superconducting and normal material. The effect of this is negative compared to the core amplitude, however for an order of magnitude
estimate it can be neglected.

If one considers the two-dimensional, periodic flux line arrangement of figure 8.1, the result for a single flux line may be generalised to the case of a FLL, yielding an average nuclear structure amplitude per niobium atom $F_N$. The nuclear scattering is normalised to one niobium atom by multiplying the nuclear structure amplitude by $V_{Nb}/A_{cell}$ where $A_{cell}$ is the area of the unit cell of the FLL. For a triangular lattice as in figure 8.1, $A_{cell} = \frac{\sqrt{3}}{2} d^2$ (where $d$ is typically of the order of 1000Å), resulting in an average nuclear structure amplitude of

$$
\bar{F}_N = \frac{4\pi}{\sqrt{3}} b_{Nb} \xi \left( \frac{\xi}{d} \right)^3 \left( J_1(k \cdot \xi) \right) \tag{8.6}
$$

Thus one obtains an estimate for the average nuclear structure amplitude per niobium atom of $\bar{F}_N = 6 \times 10^{-8} b_{Nb}$.

The magnetic scattering amplitude contribution to a Bragg reflection defined by wavevector $k$, for the case of the superposition of isolated flux lines in a regular lattice, can be shown [6] to be given by

$$
F_M(k) = + \frac{m_n}{2\pi h^2} \int d\mathbf{r} \mu_n B(r) \exp(-ik \cdot r) \tag{8.7}
$$

where $\mu_n$ is the magnetic moment of the neutron defined in (2.38). For the experimental scattering geometry used, the scattering vector and the magnetic field direction are at right angles meaning that the magnetic structure amplitude can be treated as a scalar rather than a vector quantity. Evaluation of the integral [6] results in a magnetic structure amplitude proportional to
\[ F_M \sim \frac{\gamma \cdot |\sigma \cdot B|}{1 + k^2 \lambda^2} \]  \hspace{1cm} (8.8)

where \( \lambda \), the penetration depth, is of the order of 450Å for niobium [7]. Normalising to one niobium atom as before yields an average magnetic structure amplitude, in units of \( b_{Nb} \), of \( \bar{F}_m = 1.57 \times 10^2 b_{Nb} \). Thus, based on a simple model for the volume effect, one expects experimentally to obtain a gamma value, \( \gamma = F_N/F_M \), of the order of \( 10^{-6} \).

### 8.2 Experimental Observation

In order to experimentally verify the existence of lattice distortions due to a FLL, a highly sensitive method using spin polarised neutrons was employed. The existence of a nuclear as well as magnetic contribution to a Bragg reflection can be distinguished by virtue of the magnetic scattering amplitude dependence upon the relative orientation of the neutron spin (the nuclear scattering amplitude has no such dependence). Consequently, if both contributions exist, an interference term will be obtained which manifests itself in the measured value for the flipping ratio as described in 4.4.1.

For the neutron scattering experiment, a single crystal of the type II superconductor niobium \( (T_C = 9.2K) \), prepared and verified for crystal orientation as described in 6.2, was oriented inside a horizontal superconducting magnet such that the field direction, the \( \langle 111 \rangle \) axis of the crystal and the incident neutron beam were all parallel to one another. Thus in the experimental configuration, the scattering vector was perpendicular to the magnetic field. To ensure good resolution, a cadmium disk (neutron absorbing) with a hole of diameter 6.3mm was fixed in front of the sample, enabling the Bragg reflections to be well separated from the direct neutron beam. The experiment was carried out on the small angle scattering instrument D17 (see section 4.4) at the ILL, Grenoble, incorporating a
Fig. 8.2 a) Reflected (left) and transmitted (right) scattered intensity for the activated flipper, b) flipper deactivated.

polarising mirror and spin-flipper as illustrated in figure 4.8. Neutrons with a wavelength of 11Å were obtained by using a mechanical selector for which the spread in wavelength amounted to 10%. Guide fields applied along the neutron flight path ensured that the spin polarisation was preserved. As an initial check for beam polarisation, an analyser (a second polarising mirror) was placed between sample and detector and the scattered intensity measured in the mixed state with the spin flipper activated (figure 8.2a)) and deactivated (figure 8.2b)). The analyser was positioned such that the three left side FLL Bragg reflections impinged upon it where the left hand scattering in each figure corresponds to the reflected intensity. Because the dominant scattering contribution from a FLL is of magnetic origin, only for one spin direction will the mirror reflect and indeed this is evident from the figures, where in 8.2b) (flipper off) the neutrons are being reflected by the mirror and in 8.2a) (flipper on) the reflected intensity is substantially reduced. Due to the finite flipping ratio and the fact that the direct beam has an intensity several orders of magnitude greater than that of the FLL Bragg reflections, the direct beam intensity is observed for both spin orientations. However, the relative spin up and spin down intensity of the direct beam provides a measure of the instrumental flipping ratio for which a value in excess of 30 was obtained. For all subsequent measurements, the neutron spin analyser was removed from
The FLL was created by cooling the niobium sample ($T_C = 9.2$K) through the normal to superconducting transition from 20K down to 4.5K, in an applied field of 0.22T ($B_{c1} = 0.17$T, $B_{c2} = 0.40$T). The intensity of the resulting scattering was measured alternately for spin up and spin down neutrons in fifteen minute intervals. In order to measure the background scattering, the sample temperature was raised into the normal state ($T \sim 20$K) and then re-cooled to 4.5K in zero field. Upon reaching a stabilised temperature, a field of 0.03T (less than the lower critical field for niobium) was applied, acting as a guide field for the spin polarised neutrons, before the scattered intensity was measured as before. Figure 8.3 shows the resultant scattering pattern of neutrons from the FLL, directly revealing the reciprocal lattice with six-fold symmetry. For Bragg reflections with a broad rocking curve i.e. for a distorted FLL, the Bragg condition can be simultaneously fulfilled for all first order
Fig. 8.4 Background subtracted, spin-flip scattering profile for niobium in a field of 0.22T and T = 4.5K. The six-fold symmetry of the first order Bragg reflections is seen centred on the remainder of the direct beam. The scale on the x and y axes corresponds to the pixel number on the multidetector.

Bragg reflections. In this case, the possible momentum transfers for all six (10) reflections (as given by (1.48)) are approximately parallel to the plane of the detector, giving the six-fold pattern as shown. The corresponding scattering profile is shown in figure 8.4 for spin flip neutrons, to which a background subtraction has been made. The structure at the centre of the plot corresponds to the remnant direct beam intensity.

In obtaining the Bragg scattered intensity, only those data points are summed for which the measured intensity exceeds a value of 1% of the maximum count rate of the Bragg reflection. The region of the direct beam is excluded from the summation and the total intensity of all the first order Bragg reflections is determined for non-spin flip $I_{11}$ and spin flip $I_{14}$ scattering to yield the flipping ratio $R$ [8]. The ratio obtained is as $R-1 = 4\gamma$ as shown in
section 4.4.1, resulting in an experimental gamma value for niobium in a field of 0.22T and at T = 4.5K of

\[ \gamma = \frac{R - 1}{4} = -0.003740 \pm 0.000893 \]  \hspace{1cm} (8.9)

In addition to applying a background correction, the above flipping ratio has in principle to be corrected for finite beam polarisation and flipper efficiency. However the impact of such corrections, in view of the high instrumental flipping ratio obtained (~ 30) and the closeness of the FLL flipping ratio to one, is negligible and therefore has not been applied for the above gamma value. The error obtained in the experimental gamma value is large and of the order of 24% as a result of the large numbers involved in determining the flipping ratio of interest.

### 8.3 Discussion of Results

The spin polarised neutron scattering observation of a flipping ratio which deviates from a value of one, provides unequivocal confirmation of a nuclear contribution to the FLL Bragg intensity, arising due to an accompanying nuclear lattice distortion. However a comparison of the experimentally observed gamma value (~ $10^{-3}$) with that obtained on the basis of a simple model for the volume effect ($\gamma \sim 10^{-6}$), yields a disagreement amounting to approximately three orders of magnitude. Thus the size difference between the normal and superconducting materials which coexist in a FLL, commonly used for the description of FLL - nuclear lattice coupling, is insufficient in explaining the observed size of the nuclear modulation in the Shubnikov phase of niobium. This provides indication that an alternative mechanism is at work.

In order to understand the mechanism which gives rise to the relatively large flipping ratio in the Shubnikov phase, one has to take into account the fact
that the mixed state of a type II superconductor does not constitute a homogeneous system. As a result of the coexistence of normal and superconducting material a shift of chemical potential $\mu$ of the material within the non-superconducting core of the flux line must arise. According to band structure estimates, the derivative of the chemical potential with respect to the lattice parameter $a$ takes a value $\frac{\partial \mu}{\partial a} = -89 \text{eV} \AA^{-1}$ and an upper limit for the shift of $\mu$ can be obtained from the size of the gap of the superconductor. With $\Delta \mu = 10\text{K}$, this process yields an order of magnitude value for the change in lattice parameter of $\Delta a/a \approx 10^{-5}$. This distortion of the lattice is one to two orders of magnitude larger than that due solely to the volume effect, and it is therefore argued that the shift in chemical potential, necessitated by the inhomogeneous nature of the Shubnikov phase, is the dominant process in determining the size of the lattice distortion due to the presence of a FLL in type II superconductors. Thus the experimental observation reported here and in [9], provides evidence for the existence of an electronic mechanism within the bulk of a superconductor which traps electrons within the core of a magnetic flux line [10]. This redistribution of electrons is accompanied by a redistribution of charge which in turn, via a lattice distortion, must be compensated by an adjustment in the positive background charge [11].

8.3.1 An Electronic Mechanism for Lattice Distortions

An explanation for the observed magnitude of the lattice distortion in the mixed state of niobium is given by Kusmartsev et al. [11] in terms of the self-trapping of electrons and the charging of the flux line cores [12]. The first experimental evidence for the phenomenon of electron self-trapping (initially predicted by Rashba [13]) was found in the area of semiconductors. In essence, self-trapping will occur if the total energy of a system, consisting of elastic and electronic energies, is lowered by deformations such that electrons are localised in the resulting potential well. The tendency for this type of electron localisation is strongly enhanced for a system with impurities.
and defects [10] as it is these which induce localised states. Low dimensional systems or ones with strong electron-phonon coupling also exhibit an enhanced self-trapping effect.

In an analogous way, it may be conjectured that the inhomogeneity which arises in the mixed state of a type II superconductor due to the existence of vortices, create potential wells in which the electrons may be trapped. This idea of 'bound states' inside the core of a flux line was first suggested by Caroli et al. [14]. In addition, the tendency towards electron localisation will be further enhanced by the existence of local lattice deformations and it is these that will constitute the phenomenon of electron self-trapping by vortex cores.

In order to estimate the effect of electron self-trapping within vortices on the nuclear modulation, the same simple model for a single flux line will be used as before in which a cylinder of normal fluid is embedded into a superconductor. In this approximation, no account is taken for the flow of supercurrent around the vortex core and it is assumed that each electron in the normal fluid interacts with the lattice. Only if an electron is localised i.e. not having a plane wave wavefunction, will the free energy \( F \) be reduced by local deformations around the electron cloud. For a system geometry with two-dimensional character, as in the case of the flux line, a bound state electron will be created by the potential well which accompanies any deformation. If the dispersion of the electron band has a form \( \varepsilon(k) = d + \varepsilon_0(k) \) with \( \varepsilon_0(0) = 0 \), then the value \( d \), on the creation of a deformation potential well, will become a local function of the deformation \( Q(r) \) i.e. \( d(Q(r)) \). In the case of a metal, this fluctuation of the band width may be expressed through the chemical potential \( \mu \) as a function of local lattice parameter. For a system in chemical equilibrium, the real chemical potential is constant and the same for both superconducting and normal electrons. Therefore in the case of the simplified flux line as considered here, the local deformation \( Q(r) \) arising in the core creates the potential
where $\mu(0)$ is the chemical potential for no deformation and $Q(r) = \text{div}(\vec{u})$ with $\vec{u}$ a displacement vector. As a result of this deformation potential, the electrons gain the energy

$$\delta F_n = \int \delta n(r) \mu(r) dr$$

(8.11)

where $n(r)$ is the electron concentration. This total concentration can in turn, be distinguished into two parts, $n_0$ and $\delta n$, where $n_0$ is an average electron concentration and $\delta n$ is a fluctuation in the concentration associated with the local deformation. It is assumed that $\int \delta n(r) dr = 0$. The creation of a deformation causes the elastic part of the total energy, amounting to $K_0 Q^2/2$, to be lost meaning that the total contribution to the free energy from the deformed region is equal to

$$F = F_0 + \int \left[ \mu(r)n(r) + \frac{K_0 Q^2(r)}{2} \right] dV$$

(8.12)

Minimising (8.12) with respect to the deformation $Q(r)$ yields

$$Q(r) = -\frac{M}{K_0} \delta n(r)$$

(8.13)

where $K_0$ is the elastic constant and $M$ is determined as $\frac{\partial \mu}{\partial Q}(0)$.

By modelling the normal and superconducting electrons using a two-fluid approach, an estimate can be made for the concentration of self-trapped electrons. The fluctuating part $\delta n(r)$ can be considered as the difference between the total electron concentration $n(r)$ and that of the normal
component \( n_0 \). For metals, a quasi-classical approach can be taken in which the electrons occupy a Fermi sphere of radius \( k_F \) and energy \( E_F = \frac{k_F^2}{2m} \). At the superconducting phase transition, a gap \( \Delta \) opens near \( E_F \) in the superconductor which is absent for the normal material. This allows for an electron redistribution between the normal and superconducting phases such that the number of electrons associated with the normal state decreases. In effect the Fermi momentum of these electrons reduces from \( k_F = \sqrt{2mE_F} \) to \( k'_F = \sqrt{2m(E_F - \Delta)} \) so that the total electron concentration is approximately given by \( n \sim k'_F^3 = n_0 \left(1 - \frac{1}{2} \frac{\Delta}{E_F}\right) \). Consequently, the difference in concentration between the superconducting and normal phases which arises due to the redistribution of electrons, amounts to \( \delta n(r) = n_0 \frac{1}{2} \frac{\Delta}{E_F} \) where \( n_0 \) is an average concentration of electrons in the metal.

Having expressed the fluctuating part of the electron concentration as a constant, the distortion of the local lattice parameter \( a \) which arises due to the creation of the mixed state can be expressed in terms of the superconducting gap using (8.13):

\[
\frac{\Delta a}{a} \sim \frac{Q}{3} = -\frac{M}{4K_0} \frac{\Delta}{E_F} \tag{8.14}
\]

Thus the lattice distortion which occurs due to the self-trapping of electrons within a vortex core is determined by the derivative of the chemical potential \( M \) and the ratio \( \frac{\Delta}{E_F} \). For niobium, which has a moderately high transition temperature \( (T_C = 9.2K) \), the Fermi energy is of the order of electron-volts and the ratio \( \frac{\Delta}{E_F} \), of the order of \( 10^{-3} \).

Multiplying (8.14) by three to obtain the equivalent volume anomaly \( \zeta \) and substituting into (8.5) yields the following structure factor for nuclear Bragg scattering from a single flux line.
The above expression can be generalised to the case of a FLL as before by normalising to one Nb atom. For a triangular lattice therefore, one obtains for the nuclear structure factor

\[
F_N = -\frac{3\pi b_{\text{Nb}}}{2V_{\text{Nb}}} \frac{\Delta}{E_F} \frac{M}{K_0} \frac{\xi}{k} J_1(\xi \cdot k)
\]  

(8.15)

where \( d \) is the lattice constant for the FLL. Substitution of the appropriate parameters for niobium yields a gamma value of the order of \( 10^{-4} \), in good agreement with the magnitude observed experimentally.

In conclusion the observed magnitude of the lattice distortion associated with the formation of a FLL in the type II superconductor niobium, reveals that the volume anomaly observed in thermal expansion experiments, does not account for the observed size of the nuclear modulation. It is therefore argued that an electronic mechanism based on the self-trapping of electrons by vortex cores, is dominant in creating the volume difference. The observed lattice distortion, it is suggested, is a response to the redistribution of electrons between the normal and superconducting materials which coexist in the Shubnikov phase of a type II superconductor.

REFERENCES


The use of spin polarised neutron scattering as an experimental tool within solid state physics has been demonstrated for the investigation of magnetic phenomena in two instances of superconductor. The first of these studies utilised the unique ability of three dimensional polarisation analysis in unambiguously distinguishing magnetic scattering from all other sources. In this way, an experimental determination of the wavevector dependence of magnetic excitations in the high \( T\text{c} \) system \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) could be achieved over a thermally determined energy window of \( \pm 30\text{meV} \). Measurements conducted on a powder sample in the insulating regime of the compositional phase diagram (\( x=0.11 \)) confirmed the existence of long range antiferromagnetic order at \( T = 300\text{K} \) with a corresponding aligned moment on the planar Cu sites of \( 0.62\mu\text{B} \). The value obtained for the ordered moment is consistent with the existence of quantum fluctuations (arising due to the small size of the spin) for which the full Bragg contribution to the total energy integrated scattering (corresponding to an ordered moment of \( 1\mu\text{B} \) at \( T=0 \)) must be modified by the inclusion of a reduction factor \( b \). Extraction of the paramagnetic response in both the ordered (300K) and paramagnetic (450K) states revealed a small but finite scattering cross-section corresponding to a concentration of Cu atoms carrying a spin \( \frac{1}{2} \) of 14% and 18% respectively. This is consistent with the level of scattering expected on the basis of weak coupling between chain site Cu moments (arising by virtue of the partial occupation of the chain O4 site) but is much less than that expected on the grounds of a localised moment picture. In addition, the observed increase in paramagnetic scattering above \( T_N \) is only \(-20\% \) of that expected on the basis
of thermal disordering of the observed magnetically ordered moment. The conclusion is reached therefore that, while the existence of paramagnetic fluctuations in insulating YBa$_2$Cu$_3$O$_{6.11}$ is confirmed, the level of scattering is much reduced compared to that expected from a total energy integration of the magnetic signal from a localised moment system. It is therefore argued that amplitude fluctuations existing over an energy range wider than the thermal energy window accessible in the experiment, play an important role in the phase transition. For this, itinerant antiferromagnetism may have to be invoked in which the magnetic and charge degrees of freedom are not separated thus rendering the concept of a localised moment in the discussion of the cuprates invalid.

Three dimensional polarisation analysis conducted on the superconducting composition YBa$_2$Cu$_3$O$_{6.95}$ in its normal state (300K), revealed a negligible amount of magnetic scattering in the energy window ±30meV, corresponding to a cross-section of 0.048 ± 0.008barns or a concentration of ~3.2% of spin ½ Cu atoms. This is incompatible with the notion of the existence of local moments in the CuO$_2$ planes, a conjecture which is further supported by the thermal and oxygen concentration variation observed for the uniform susceptibility together with the absence of an EPR signal from Cu$^{2+}$ in both insulating and superconducting compounds. This conclusion is consistent with the spin polarised study on the insulating composition YBa$_2$Cu$_3$O$_{6.11}$. In addition, a study of the magnetic response as a function of reciprocal space for single crystal YBa$_2$Cu$_3$O$_7$, revealed no enhancement in the vicinity of the (π, π) point up to energies of 30meV. The absence of a magnetic response is in contradiction to the prediction of the ‘Nearly Fermi Liquid Theory’ in which the dynamic susceptibility is peaked at the corner of the Brillouin zone within an energy range 10 to 20meV.

The second line of investigation combined spin polarised neutrons with a small angle scattering set-up in a unique way to yield the first unambiguous experimental observation of the lattice distortion associated with the presence of a FLL in type II superconductors. In particular, the experimental technique
as described demonstrates the feasibility of the investigation of the FLL with spin polarised neutrons and as such can be regarded as a novel tool in the study of superconductors. The observation of a flipping ratio in a mechanically hard material such as niobium provides confirmation of the sufficient sensitivity attained by the technique. A comparison between the observed lattice distortion in the mixed state of niobium ($\gamma \sim 10^{-3}$) and that expected from a simple model ($\gamma \sim 10^{-5}$) in which the nuclear lattice deforms in compliance with the volume anomaly between the coexisting normal and superconducting states observed in thermal expansion measurements, yields a discrepancy of approximately three orders of magnitude. This disagreement cannot be remedied by small alterations of parameters used in the calculation and as such, it is concluded that the volume effect, commonly used in the literature to model the coupling between the FLL and the nuclear lattice, is insufficient to account for this spin polarised neutron observation.

In providing an alternative mechanism to explain the observed size of the flipping ratio, consideration has to be placed on the fact that the Shubnikov phase, for which normal and superconducting regions coexist, constitutes an inhomogeneous state. It is suggested that, due to the existence of a gap (near $E_F$) in the superconducting regions, a redistribution of electrons between the two coexisting states occurs in which electrons are trapped by the vortex cores. Because the normal and superconducting regions are spatially separated, this redistribution of electrons is accompanied by a redistribution of charge which has to be compensated by an adjustment in the positive background charge. Thus the trapping of electrons by vortices is accompanied by a response in the form of a nuclear lattice distortion (therefore distorting the nuclear charges) thereby restoring the charge neutrality of the system.

The use of spin polarised as a novel tool for the study of bulk superconducting properties has yet to be fully realised. Further exploration of the technique is expected to yield increased understanding of the FLL-nuclear...
lattice interaction in type II superconductors and enable a more detailed description of the electronic mechanism believed to be at work.

The nuclear lattice-FLL interaction is responsible for determining the pinning forces which in turn determine the critical currents in superconductors. A relevant parameter in determining the size of the lattice distortion from the point of view of an electronic mechanism, is the ratio \( \frac{\Delta}{\varepsilon_F} \) which for niobium takes a value of order \( 10^{-3} \). For the case of high \( T_C \) superconductors, this ratio is different due to their high transition temperatures, and corresponding Fermi energies are of approximately two orders of magnitude less than those of metals. Consequently a distinction can be drawn between the mechanism involving electron redistribution and that solely based on the volume anomaly, in terms of their impact on the pinning forces involved. If the observed lattice distortion is due to an electronic mechanism as described, then the pinning forces, and therefore also the critical currents, will be high in the high \( T_C \) materials due to an increase in the ratio \( \frac{\Delta}{\varepsilon_F} \) \((\sim 10^{-1})\). On the other hand, if the mechanism is merely based on the volume anomaly between normal and superconducting states then small pinning forces are expected due to the small coherence length in high \( T_C \) superconductors. The observation of high critical current densities in the oxide superconductors therefore provides an indication that an electronic mechanism based on the self trapping of electrons is dominant in determining the pinning forces. However to date, no spin polarised neutron experiment has been performed with relation to the FLL in high \( T_C \) superconductors and as such, this comprises a direction of study to be taken in the near future. In addition, with regard to the nature of the vortex core charging, work is currently in progress in ascertaining the field and temperature dependence of the magnitude of the lattice distortion.
APPENDIX I

PROGRAM LISTING FOR THE MONTE CARLO SIMULATION OF
MULTIPLE SCATTERING AND ABSORPTION IN A VANADIUM SAMPLE

DECLARE FUNCTION DISTSCATT (P1() AS DOUBLE, P2() AS DOUBLE, XX#, YY#, ZZ#, Er%)
DECLARE SUB DIRECTION (XX#, YY#, ZZ#)
DECLARE SUB DISTDET (X1() AS DOUBLE, X2() AS DOUBLE, XXX#, YYY#, ZZZ#, DIST#, Er%)

**** SET UP ARRAY DIMENSIONS ****

DIM W(32) AS DOUBLE, Q(32) AS DOUBLE
DIM XDET(32) AS DOUBLE, YDET(32) AS DOUBLE, ZDET(32) AS DOUBLE
DIM S0(3) AS DOUBLE, EX(3) AS DOUBLE
DIM S1(3) AS DOUBLE, S2(3) AS DOUBLE, S3(3) AS DOUBLE, S4(3) AS DOUBLE
DIM X1(3) AS DOUBLE, X2(3) AS DOUBLE, P1(3) AS DOUBLE, P2(3) AS DOUBLE
DIM DX1(32) AS DOUBLE, DX2(32) AS DOUBLE, DX3(32) AS DOUBLE, DX4(32) AS DOUBLE
DIM Z1(32) AS DOUBLE, Z2(32) AS DOUBLE
COMMON SHARED RADIUS#, HEIGHT#, K, ERRER%
COMMON SHARED S1() AS DOUBLE, S2() AS DOUBLE, S3() AS DOUBLE, S4() AS DOUBLE, X1() AS DOUBLE, X2() AS DOUBLE, P1() AS DOUBLE, P2() AS DOUBLE

***** INPUT PARAMETERS *****

CLS
pi = 3.141592654#
FAC = (pi / 180)
INPUT "Input sample radius (cm):"; RADIUS#
INPUT "Input sample height (cm):"; HEIGHT#
INPUT "Input sample density (atoms/Ang^3):"; DENSITY#

Probability of FL/NF for 1,2,3,4 interactions:-

FL1 = (2 / 3)
NF1 = (1 / 3)
FL2 = (4 / 9)
NF2 = (5 / 9)
FL3 = (14 / 27)
NF3 = (13 / 27)
FL4 = (40 / 81)
NF4 = (41 / 81)

INPUT "Give neutron wavelength (Ang):"; WAV#
KO# = (2 * pi) / WAV#
INPUT "Input sample absorption x-section (barns) (v = 2200m/s):"; AB#
SABS# = AB# * (3.4942 / KO#)
INPUT "Input sample scattering x-section (barns):"; SCATT#
Appendix I

Program Listing

SIGABS# = SABS# * DENSITY#
SIGSCATT# = SCATT# * DENSITY#
SIGTOT# = SIGABS# + SIGSCATT#
PRINT "SIGTOT(cm^-1)="; SIGTOT#

BX1# = SCATT# / (SABS# + SCATT#)
CX1# = 1 / (4 * pi)

***** Set initial arrays to zero *****
IRUN% = 0
ERRER% = 0
INEUTRON% = 0
INPUT "Give number of neutrons to be sampled:"; MAXRUNS%
TRANS# = 0
FOR I = 1 TO 32
    FOR J = 1 TO 2
        A1(J, I) = 0!
        A2(J, I) = 0!
        A3(J, I) = 0!
        A4(J, I) = 0!
    NEXT J
    FOR J = 1 TO 4
        AI TRUE(J, I) = 0!
    NEXT J
NEXT I

INPUT "Enter output filename:"; O$
INPUT "Enter filename containing detector angles:"; F$
OPEN O$ FOR OUTPUT AS #2

*** Read in detector angles ***
OPEN F$ FOR INPUT AS #1
FOR I = 1 TO 32
    INPUT #1, W(I), x, x, x, x, x
NEXT I

FOR I = 1 TO 32
    XDET(I) = COS(ABS(W(I)) * FAC)
    YDET(I) = SIN(ABS(W(I)) * FAC)
    ZDET(I) = 0
NEXT I
CLOSE #1

CLS
FOR K = 1 TO MAXRUNS%
    INEUTRON% = INEUTRON% + 1
    LOCATE 14, 5
    PRINT "K="; K

***********************

100

***** 1st SCATTERING EVENT *****

RAN DOMIZE TIMER

S0(2) = RADIUS# * (2 * RND - 1)
S0(1) = -SQR(RADIUS# ^ 2 - S0(2) ^ 2)
S0(3) = .5 * HEIGHT# * (2 * RND - 1)

*** Determine exit point 'EX' for no interaction ***
EX(1) = -S0(1)
EX(2) = S0(2)
EX(3) = S0(3)
Appendix I Program Listing

**** Determine distance between S0 and EX, 'ALENGTH1' ****
A11# = S0(1) - EX(1)
A21# = S0(2) - EX(2)
A31# = S0(3) - EX(3)
ALENGTH1# = SQRT(A11# * A11# + A21# * A21# + A31# * A31#)

**** Determine point of first interaction 'SI' ****
DIST1# = ALENGTH1# * SIGTOT#
AL1# = -LOG(1 - RND * (1 - EXP(-DIST1#))) / SIGTOT#
SI(1) = S0(1) + AL1# * (EX(1) - S0(1))
SI(2) = S0(2) + AL1# * (EX(2) - S0(2))
SI(3) = S0(3) + AL1# * (EX(3) - S0(3))
AX1# = 1 - EXP(2 * SIGTOT# * S0(1)): 'With absorption
AY1# = 1 - EXP(2 * SIGSCATT# * S0(1)): 'Without absorption
CTRU1# = AX1# * CX1#
CONST1# = AX1# * CX1#

********************************************************************

**** Determine exit point 'X2' to reach each detector and distance 'DIST' from scattering point SI
********************************************************************
FOR I = 1 TO 32
XXX# = XDET(I)
YYY# = YDET(I)
ZZZ# = ZDET(I)
CALL DISTDET(S1(), X2(), XXX#, YYY#, ZZZ#, DIST#, Er%)
IF Er% = 1 THEN
GOTO 100
END IF
DX1(I) = EXP(-SIGTOT# * DIST#)
NEXT I

200

********************************************************************

**** Determine exit point 'P2' of scattered neutron ****
DELME# = DISTSCATT(S1(), P2(), XX#, YY#, ZZ#, Er%)
IF Er% = 1 THEN
GOTO 200
END IF

********************************************************************

***** 2nd SCATTERING EVENT *****

300

**** Determine distance 'ALENGTH2' between S1 and exit point P2 ****
A12# = S1(1) - P2(1)
A22# = S1(2) - P2(2)
A32# = S1(3) - P2(3)
ALENGTH2# = SQRT(A12# * A12# + A22# * A22# + A32# * A32#)

**** Determine 2nd scattering point 'S2' ****
DIST2# = ALENGTH2# * SIGTOT#
AL2# = -LOG(1 - RND * (1 - EXP(-DIST2#))) / SIGTOT#
S2(1) = S1(1) + AL2# * (P2(1) - S1(1))
S2(2) = S1(2) + AL2# * (P2(2) - S1(2))
S2(3) = S1(3) + AL2# * (P2(3) - S1(3))

AX2# = 1 - EXP(-SIGTOT# * ALENGTH2#)
CONST2# = CONST1# * AX2# + BX1#

'* Determine exit point 'X2' to reach each detector and distance 'DIST' from scattering point S2 '******************************************
FOR I = 1 TO 32
XXX# = XDET(I)
YYY# = YDET(I)
ZZZ# = ZDET(I)
CALL DISTDET(S2(), X2(), XXX#, YYY#, ZZZ#, DIST#, Er%)
IF Er% = 1 THEN
GOTO 300
END IF
DX2(I) = EXP(-SIGTOT# * DIST#)
NEXT I

'* Generate direction cosines XX, YY and ZZ of scattered neutron '******************************************
CALL DIRECTION(XX#, YY#, ZZ#)

'* **** Determine exit point 'P2' of scattered neutron ****
DELME# = DISTSCATT(S2(), P2(), XX#, YY#, ZZ#, Er%)
IF Er% = 1 THEN
GOTO 400
END IF

'****** 3rd SCATTERING EVENT ******

500
'* Determine distance 'ALENGTH3' between S2 and exit point P2 '******************************************
A13# = S2(1) - P2(1)
A23# = S2(2) - P2(2)
A33# = S2(3) - P2(3)
ALENGTH3# = SQR(A13# * A13# + A23# * A23# + A33# * A33#)

'* **** Determine 3rd scattering point 'S3' ****
DIST3# = ALENGTH3# * SIGTOT#
AL3# = -LOG(1 - RND * (1 - EXP(-DIST3#))) / SIGTOT#
S3(1) = S2(1) + AL3# * (P2(1) - S2(1))
S3(2) = S2(2) + AL3# * (P2(2) - S2(2))
S3(3) = S2(3) + AL3# * (P2(3) - S2(3))

AX3# = 1 - EXP(-SIGTOT# * ALENGTH3#)
CONST3# = CONST2# * AX3# + BX1#

'* Determine exit point 'X2' to reach each detector and distance 'DIST' from scattering point S3 '******************************************

238
FOR I = 1 TO 32
XXX# = XDET(I)
YYY# = YDET(I)
ZZZ# = ZDET(I)
CALL DISTDET(S3(), X2(), XXX#, YYY#, ZZZ#, DIST#, Er%)
IF Er% = 1 THEN
GOTO 500
END IF
DX3(I) = EXP(-SIGTOT# * DIST#)
NEXT I

600
'* Generate direction cosines XX, YY and ZZ of scattered *'
'* neutron '*********************************************************
CALL DIRECTION(XX#, YY#, ZZ#)

'* Determine exit point 'P2' of scattered neutron ****
DELM# = DISTSCATT(S3(), P2(), XX#, YY#, ZZ#, Er%)
IF Er% = 1 THEN
GOTO 600
END IF

700
'* Determine distance 'ALENGTH3' between S3 and exit point P2 ****
A14# = S3(1) - P2(1)
A24# = S3(2) - P2(2)
A34# = S3(3) - P2(3)
ALENGTH4# = SQR(A14# * A14# + A24# * A24# + A34# * A34#)

'* Determine 4th scattering point 'S4' ****
DIST4# = ALENGTH4# * SIGTOT#
AL4# = -LOG(1 - RND * (1 - EXP(-DIST4#))) / SIGTOT#
S4(1) = S3(1) + AL4# * (P2(1) - S3(1))
S4(2) = S3(2) + AL4# * (P2(2) - S3(2))
S4(3) = S3(3) + AL4# * (P2(3) - S3(3))
AX4# = 1 - EXP(-SIGTOT# * ALENGTH4#)
CONST4# = CONST3# * AX4# * BX1#

'* Determine exit point 'X2' to reach each detector and distance *'
'* 'DIST' from scattering point S4 '*********************************************************
FOR I = 1 TO 32
XXX# = XDET(I)
YYY# = YDET(I)
ZZZ# = ZDET(I)
CALL DISTDET(S4(), X2(), XXX#, YYY#, ZZZ#, DIST#, Er%)
IF Er% = 1 THEN
GOTO 700
END IF
DX4(I) = EXP(-SIGTOT# * DIST#)
NEXT I
Appendix I

Program Listing

***** ONCE SCATTERED FLUX *****

Once scattered FL/NF flux assuming zero absorption and no further interactions between Sl and EX (SIGABS=0, BX1=1, DX1=1)
FOR I = 1 TO 32
A1TRUE(1, I) = A1TRUE(1, I) + CTRUE* FL1
A1TRUE(2, I) = A1TRUE(2, I) + CTRUE* NF1
NEXT I

Once scattered FL/NF flux with absorption but with no further interactions between Sl and EX (DX1=1=DX)
FOR I = 1 TO 32
A1TRUE(3, I) = A1TRUE(3, I) + (CONST1* FL1)
A1TRUE(4, I) = A1TRUE(4, I) + CONST1* NF1
*PRINT "A1TRUE(3,I)="; A1TRUE(3, I)
'SLEEP
NEXT I

Once scattered FL/NF flux with absorption and with compensating factor for further interactions between Sl and EX
FOR I = 1 TO 32
A111, I = A111, I) + CONST1* DX1(I) • FL1
A112, I) = A1(2, I) + CONST1* DX1(I) • NF1
NEXT I

***** TWICE SCATTERED FL/NF FLUX *****

FOR I = 1 TO 32
A2(1, I) = A2(1, I) + CONST2* DX2(I) • FL2
A2(2, I) = A2(2, I) + CONST2* DX2(I) • NF2
NEXT I

***** THIRD SCATTERED FL/NF FLUX *****

FOR I = 1 TO 32
A3(1, I) = A3(1, I) + CONST3* DX3(I) • FL3
A3(2, I) = A3(2, I) + CONST3* DX3(I) • NF3
NEXT I

***** FOURTH SCATTERED FL/NF FLUX *****

FOR I = 1 TO 32
A4(1, I) = A4(1, I) + CONST4* DX4(I) • FL4
A4(2, I) = A4(2, I) + CONST4* DX4(I) • NF4
NEXT I

***** TRANSMISSION FACTOR 'TRANS' *****

TRANS = TRANS + EXP(2 • SIGTOT • S0(1))

IRUN% = IRUN% + 1
P! = IRUN% / (MAXRUNS% / 5)
Appendix I

Program Listing

IF P! = INT(IRUN% I (MAXRUNS% I 511 THEN
LOCATE 12, 5
PRINT "NUMBER"; P! * (MAXRUNS% I 5 I, "OF"; MAXRUNS%
END IF
NEXT K

I = 1 TO 32
FOR J = 1 TO 2
Al(J, 11
Al (J,
A2(J, 11 = A2(J,
A3(J, I I = A3(J,
A4/J, 11
1'.4 (J,
.fOR

11
11
II
11

I
I
I
I

INEUTRON%
INEUTRON%
INEUTRON%
INEUTRON%

NEXT J

FOR J = 1 TO 4
A1TRUE(J, 11
A1TRUE(J, 11 I INEUTRON%
NEXT J
NEXT I
FOR I = 1 TO 32
Zl(II = (AI TRUE (L 11 I
'FLIP
Z2 (I)
(A1TRUE(2, I I I
NON-FLIP
NEXT I

(AI (1, 11 + 1'.2(1, 11 + A3(1,

11 + A4 (1,

I 11 I

(AI (2, 11 + A2(2,

11 + 1'.4(2,

I 11 I

FOR I = 1 TO 32
Q(II
(4 * pi * SIN(ABS(W(lll
NEXT I
TRANS = (TRANS I (INEUTRON%II
PEINT "TRANSMISSION="; TRANS

I I + A3(2,

* .5 * FACII I WAV#

* 100

FOE I = 1 TO 32
PRINT 12, USING "11 ,1".,1,.1 1.11"
'.,1,1,.1.1",.,
1 .• 11,11111".,1 1.111111111111 '.'1'111"1""
1.""111"11'1
1 .• #.111.1".11 1.1"'111""1 1.'11'1"1'1111 '.,11".111.1"
' .• ## ••• , . " . 1 ,
1.111 1.111"; I; W(II; Q(II; A1TRUE(1
, 11; Al TRUE (2, I I; Al (1, I I; Al (2, I I; A2 ( 1, I I; A2 (2, 11; 1'.3 ( 1, I I ;
1'.3 (2, I I; A4 (1, I); A4 (2, I I; Zl (I); Z2 (I I
NEXT I
PEINT 12, "Transmission factor (%1 ="; TRANS
CLOSE 11
CLOSE 12
,***************************************************** ***********~***

,***** SUBROUTINE DIRECTION *****

SUE DIRECTION (XXI, YYI, ZZ'I
pi = 3.1415926541
ZZ# = 2 * RND - 1
PHI# = pi • (2 • RND - 1 I
CONSTAt = SQR (1 - ZZ# * ZZI I
XX, = CONSTAI * COS(PHII * (pi I 18011
YY# = CONSTAI * SIN(PHI' * (pi I 18011
END SUB
,~**************************************************** ***************

,***** SUBROUTINE DISTDET *****

SUB DISTDET (Xl(1 AS DOUBLE, X2(1 AS DOUBLE, XXXI, YYYI, ZZZI,
Er%1

241

DlSTI,


CONS# = 1 / (XXX# * XXX# + YYY# * YYY#)
ACONST# = -(X1(1) * XXX# + X1(2) * YYY#) * CONS#
BCONST# = CONS# * (RADIUS# * RADIUS# - X1(1) * X1(1) - X1(2) * X1(2))
ARG# = BCONST# + ACONST# * ACONST#

IF ARG# < 0 THEN
ARG# = ABS(ARG#)
END IF
IF ARG# > 0 AND ARG# < .0000001# THEN
ARG# = 0
END IF

ALAMBDA# = ACONST# + SQR(ARG#)
X2(1) = X1(1) + ALAMBDA# * XXX#
X2(2) = X1(2) + ALAMBDA# * YYY#
X2(3) = 0

DIST# = SQR((X1(1) - X2(1)) ^ 2 + (X1(2) - X2(2)) ^ 2)

' **** Check that projection is inside cylindrical sample ****

TEST# = SQR(X2(1) * X2(1) + X2(2) * X2(2))
LOCATE 6, 5
PRINT "TEST=", TEST#, "RADIUS=", RADIUS#
'SLEEP
IF (TEST# > RADIUS# > 10 ^ -5) THEN
ERR% = 1
LOCATE 10, 5
PRINT "ERR IN DISTDET: TEST=", TEST#, "RADIUS=", RADIUS#
'SLEEP
ERROR% = ERROR% + 1
LOCATE 19, 40
PRINT "TOTAL ERRORS =", ERROR%
ELSE Error% = 0
END IF

END SUB

FUNCTION DISTSCATT (P1() AS DOUBLE, P2() AS DOUBLE, XX#, YY#, ZZ#, Er%)

CONS# = 1 / (XX# * XX# + YY# * YY#)
ACONST# = -(P1(1) * XX# + P1(2) * YY#) * CONS#
BCONST# = CONS# * (RADIUS# * RADIUS# - P1(1) * P1(1) - P1(2) * P1(2))
ARG# = BCONST# + ACONST# * ACONST#

IF ARG# < 0 THEN
ARG# = ABS(ARG#)
END IF
IF ARG# > 0 AND ARG# < .0000001# THEN
ARG# = 0
END IF

ALAMBDA# = ACONST# + SQR(ARG#)
P2(1) = P1(1) + ALAMBDA# * XX#
P2(2) = P1(2) + ALAMBDA# * YY#
P2(3) = P1(3) + ALAMBDA# * ZZ#

IF (ABS(P2(3)) < .5 * HEIGHT#) THEN
GOTO 800

242
ELSE GOTO 900
END IF

' **** If the end point lies on the cylinder wall ****

DIST# = SQR((P1(1) - P2(1))^2 + (P1(2) - P2(2))^2 + (P1(3) - P2(3))^2)

' Check that projection is inside cylindrical sample

TEST# = SQR(P2(1)*P2(1) + P2(2)*P2(2))
IF (TEST# - RADIUS# > 10^-5) THEN
Er% = 1
ERRER% = ERRER% + 1
LOCATE 19, 40
PRINT "TOTAL ERRORS ="; ERRER%
ELSE Er% = 0
END IF
GOTO 1000

900

' **** If neutron emerges via top/bottom of sample ****

IF ZZ# < 0 THEN
ALAMBDA = (HEIGHT# * .5 + P1(3)) / ABS(ZZ#)
ELSE
ALAMBDA = (HEIGHT# * .5 - P1(3)) / ZZ#
END IF

P2(1) = P1(1) + ALAMBDA*XX#
P2(2) = P1(2) + ALAMBDA*YY#
P2(3) = P1(3) + ALAMBDA*ZZ#

DIST# = SQR((P1(1) - P2(1))^2 + (P1(2) - P2(2))^2 + (P1(3) - P2(3))^2)

' Check that xy-projection is within sample

TEST# = SQR(P2(1)*P2(1) + P2(2)*P2(2))
IF TEST# > RADIUS# THEN
Er% = 1
LOCATE 9, 5
ERRER% = ERRER% + 1
LOCATE 19, 40
PRINT "TOTAL ERRORS ="; ERRER%
ELSE Er% = 0
END IF
GOTO 1000

1000

END FUNCTION

********************************************************************

********************************************************************
APPENDIX II

SAMPLE OUTPUT FROM MONTE CARLO SIMULATION

I, W(I), Q(I), ATRUE(1,I), ATRUE(2,I), A1(1,I), A1(2,I), A2(1,I), A2(2,I), A3(1,I), A3(2,I), A4(1,I), A4(2,I), Z1(I), Z2(I)

1  -93.14000 1.8855 0.00360950274158 0.00180475137079
   0.002847436431 0.0014237182153 0.0000943255753 0.0001179069739
   0.000004067259 0.0000037767404 0.0000001191765 0.0000001221559
   1.225 1.168
2  -87.48000 1.7951 0.00360950274158 0.00180475137079
   0.00284843277 0.0014224216386 0.00096768504 0.0001183460678
   0.000004092303 0.0000037999957 0.0000001201315 0.0000001231347
   1.226 1.168
3  -81.82000 1.7003 0.00360950274158 0.00180475137079
   0.002842509649 0.0014212548246 0.000950319266 0.0001187899130
   0.000004117011 0.0000038229385 0.0000001210569 0.0000001240833
   1.227 1.168
4  -76.16000 1.6013 0.00360950274158 0.00180475137079
   0.002840451977 0.0014202259886 0.000953867869 0.0001192334884
   0.000004141186 0.0000038453872 0.0000001219448 0.0000001250833
   1.228 1.168
5  -70.50000 1.4985 0.00360950274158 0.00180475137079
   0.002838654126 0.0014193276063 0.000957386265 0.0001196732618
   0.000004164592 0.0000038671209 0.0000001227892 0.0000001258589
   1.229 1.170
6  -64.84000 1.3920 0.00360950274158 0.00180475137079
   0.00283712081 0.0014185560404 0.000950835884 0.0001201044903
   0.000004186995 0.0000038879240 0.0000001235858 0.0000001266754
   1.229 1.170
7  -59.18000 1.2821 0.00360950274158 0.00180475137079
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   0.000004208312 0.0000039077186 0.0000001243308 0.0000001274391
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8  -53.52000 1.1690 0.00360950274158 0.00180475137079
   0.002834760099 0.0014173800496 0.000967310585 0.0001209138279
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Appendix II

Program Output

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## Program Output

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Transmission factor (%) = 77.6341
LIST OF PUBLICATIONS


