Exchange bias in manganese alloys with mixed magnetic behaviour

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Exchange bias has been a well known property of materials consisting of a ferromagnet interfaced with an antiferromagnet for many years, and the anisotropy resulting from the interaction has recently been nominated as a possible means for overcoming the superparamagnetic limit in high-density magnetic information storage media. However, a generalized theoretical description of the phenomenon remains elusive. More recently, analogues between the exchange bias effect and the behaviours of spin glass materials have become increasingly recognized. In this thesis, the analogues between exchange bias and spin glass systems are explored in a set of concentrated spin glass samples that exhibit a strong sensitivity to short range order of magnetic entities.

A number of models were developed to analyze and account for the measurements of magnetization made on these samples. The first was a simple, empirical model, based on an approximation of non-interacting, monodisperse, superparamagnetic clusters against a paramagnetic background to fit single branches of minor hysteresis loops. In this model, the parameter to describe the coercive field was added ad hoc. Another, more sophisticated, model was based on a modified Stoner-Wohlfarth expression for magnetic clusters and applied to the data using Monte Carlo simulations. The best fits resulted from this model when the cluster easy axis orientations were allowed to have a Gaussian distribution.

The cooling field dependence of an aged Cu$_{81.2}$Mn$_{18.8}$ alloy was explored in detail at temperatures below the glass temperature, $T_g$. Aging for 62 days had the effect of increasing the susceptibility by a factor of 2.2 and increasing $T_g$ slightly. A “step”
Abstract

magnetization, $M_{s4}$, was observed in minor hysteresis loops that increased monotonically with cooling field, $H_{FC}$, while the exchange bias field, $H_{EB}$, decayed with cooling field, which was interpreted as evidence for a magnetically disordered phase which becomes frozen at $T_g$. The shape of the step showed asymmetric reversal, which was successfully accounted for within the modified Stoner-Wohlfarth model. The resultant parameters suggested that the unidirectional anisotropy energy decreases with cooling field.

The magnetic properties of a Cu$_{83.6}$Mn$_{16.4}$ alloy that had previously been exposed to neutron irradiation were compared with those observed for the aged Cu$_{81.2}$Mn$_{18.8}$ alloy. The neutron irradiated sample, labeled “2I2”, showed a greater susceptibility in its temperature dependent magnetization, and a greater step magnetization, a greater training effect and suppressed exchange bias in minor hysteresis loops measured at low temperature. This was consistent with previous investigations that have shown that aging of concentrated CuMn enhances ferromagnetic interactions. Several models based on different assumptions were applied to the data, the most plausible of which suggested that magnetic clusters become multi-domain when the system is cooled in particularly high fields.

The structure and magnetism of a set of Ni$_{71}$Mn$_{29}$ and Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples were investigated at a range of temperatures, in order to explore their aging and cooling field dependence. The Ni$_{71}$Mn$_{29}$ samples exhibited unusual behaviour at low temperature, particularly double-stepped hysteresis loops after cooling in high field, which was attributed to the presence of a Ni-rich phase within these samples. Strong evidence exists for the interaction between the Ni-rich phase and the rest of the sample. The presence of Cu in Ni$_{68}$Mn$_{29}$Cu$_3$ samples caused a factor of 82 decrease in the temperature dependent susceptibility, while the behaviour of $M$-$H$ loops at low temperature resembled those observed for the aged Cu$_{81.2}$Mn$_{18.8}$ alloy. The presence of Cu also appeared to enhance the exchange bias field in Ni$_{68}$Mn$_{29}$Cu$_3$, but the presence of the Ni-rich phase in Ni$_{71}$Mn$_{29}$ hindered a direct comparison from being made.

In summary, a modified Stoner-Wohlfarth model was successfully able to account for magnetic hysteresis loops of two concentrated CuMn alloys using physically plausible parameters. The model suggested that for both samples unidirectional anisotropy decreases with cooling field, which is qualitatively consistent with the domain state model. The model was not able to simulate hysteresis loops of Ni$_{68}$Mn$_{29}$Cu$_3$, owing to the unusual asymmetric reversal observed.
Statement of Originality

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

Signed:

Lester Barnsley

Date:
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Chapter 1

Introduction

1.1 Overview

Research in the magnetic properties of systems with micro- and nano-size features is motivated by the potential of such materials for applications in fields such as high density information storage [1–3], spintronics [4] and biomedicine [5–7]. In particular, as the bit densities of magnetic information storage technologies increase, the size of the particles which store the bits approaches the superparamagnetic limit, a fundamental size limit below which magnetic particles are no longer stable against thermal fluctuations [8, 9]. It is the magnetic anisotropy energy of small magnetic particles that allows them to remain stable and, therefore, useful for information storage applications. It has been proposed that exchange anisotropy, arising out of a short-ranged interaction that takes place when a ferromagnet (FM) is interfaced with an antiferromagnet (AFM), may be used as a means for beating the superparamagnetic limit [2].

Unidirectional exchange anisotropy, or exchange bias, has been a well-known property of FM-AFM interfaced systems for decades [10–12]. However, a generalized theory that accounts for all aspects of observed behaviour in all systems that exhibit exchange bias remains elusive [13, 14], due to the innate complexity of real systems, which feature domain structures, short and long range order, defect structures, uncompensated spins at the interfaces and texture at the interfaces [15–19].
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The exchange anisotropy concept has also been used to account for the exotic behaviour observed in concentrated spin glass systems [20–23], where no long range magnetic order exists. More recently there has been increased recognition among researchers that numerous analogues exist between exchange bias and spin glass systems [24–29], such as the presence of shifted hysteresis loops, a complex energy landscape featuring numerous local energy minima and magnetically frustrated configurations. This analogue was shown explicitly in a recent experimental paper on a thin film system consisting of an interface between a ferromagnetic cobalt layer and a low concentration CuMn spin glass layer [30].

In this project, the analogues between exchange bias and spin glass systems were explored in materials that exhibit a strong sensitivity to short range order of magnetic entities. In particular, the magnetism of a set of concentrated spin glass systems was studied, and close attention was paid to observed phenomena that are canonically associated with exchange bias systems, such as shifted hysteresis loops, training and asymmetric reversal.

Experimental apparatus was required for this project. This thesis will introduce a vibrating sample magnetometer (VSM) system that was developed specifically for this work. Mathematical models used to account for the measurements made for this project will be discussed in a subsequent chapter.

This chapter contains the thesis structure, as well as an overview of important concepts related to magnetism that are necessary to understand the interpretations posed in the subsequent experimental accounts. These concepts include magnetic order, such as ferromagnetism and antiferromagnetism, the demagnetizing field, superparamagnetism, arising from the thermal fluctuations of small magnetic particles, exchange bias magnetism, resulting from the interactions at an FM-AFM interface and mictomagnetism, which occurs in magnetically disordered materials that have a random mixture of FM and AFM interactions.
1.2 Thesis structure

This thesis is divided into nine chapters and four appendices. Chapter 1, titled “Introduction”, outlines the motivations of the project and the structure of the thesis and briefly examines some of the important concepts necessary to understand the more complex ideas discussed in subsequent chapters.

Chapter 2 is the “Literature review”, which will give an overview of the existing literature pertinent to this project, with the aim of highlighting some of the important trends in current research.

Chapter 3, “Experimental Techniques”, will detail the experimental apparatus used in this project, particular a vibrating sample magnetometer (VSM) which was designed and assembled specifically for this work. The capabilities, as well as the limitations of this VSM will be examined closely. Sample preparations techniques and apparatus for characterizing samples will also be briefly introduced.

In Chapter 4, “Models”, the various mathematical frameworks used to model the measurements of magnetization made on samples in this project will be introduced. The general assumptions that underpin these models will be considered, and the physical plausibility of their resultant parameters will be discussed, with a particular focus on the applications and limitations of the models.

In Chapter 5, “Magnetic properties of aged high concentration CuMn alloy”, an experimental study of the magnetism of an aged Cu\textsubscript{81.2}Mn\textsubscript{18.8} alloy sample at temperatures well below the glass temperature ($T_g$) will be reported. Minor hysteresis loops at these temperatures exhibit a strong sensitivity to cooling field, which is accounted for with the aid of some of the models introduced in Chapter 4.

In Chapter 6, “Field cooling dependence of neutron irradiated CuMn alloy”, the magnetic properties of a sample of Cu\textsubscript{83.6}Mn\textsubscript{16.4} that was previously exposed to neutron irradiation will be reported. The sample exhibits a strongly enhanced magnetic susceptibility compared with samples of CuMn with the same Mn concentration, aged using thermal treatment. At temperatures well below $T_g$, a tendency towards ferromagnetic behaviour is observed, as well as a strong sensitivity to cooling field. The models from Chapter 4 are applied to interpret the results.
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Chapter 7, “Summary of findings of investigations on CuMn”, will list a summary of the important findings from the previous two chapters, with a particular focus on comparing the similarities between the magnetism of the two CuMn samples.

In Chapter 8, “Magnetic properties of NiMn and NiMnCu alloys”, the structural and magnetic properties of a set of Ni$_{71}$Mn$_{29}$ and Ni$_{68}$Mn$_{29}$Cu$_3$ alloys will be reported. Particular focus will be given to the results recorded at low temperature, and how they depended on the cooling field and the previous thermal treatment conducted on the samples.

Chapter 9 is the “Conclusions”, which will summarize the important findings of this project.

Appendix A, “Smartloop”, will detail a simple predictive control algorithm used to help ensure an even distribution of data points in hysteresis loops in regions where the magnetization changes suddenly.

Appendix B, “Electronic circuits”, will display block schematics of electronic apparatus designed specifically for this work.

In Appendix C, “Labview diagrams for VSM” and Appendix D, “Labview diagrams for Monte Carlo simulations”, block diagrams of Labview software compiled in this project will be shown.

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<thead>
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<th>Quantity</th>
<th>Symbol</th>
<th>CGS unit</th>
<th>MKS conversion</th>
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<tr>
<td>Magnetic field intensity</td>
<td>$H$</td>
<td>1 Oe</td>
<td>$\frac{1000}{4\pi}$ A/m</td>
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<tr>
<td>Magnetic flux density</td>
<td>$B$</td>
<td>1 G</td>
<td>$1 \times 10^{-4}$ T</td>
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<tr>
<td>Magnetic moment</td>
<td>$\mu$</td>
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<td>Bohr magneton</td>
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<td>$\mu_0$</td>
<td>1 G/Oe</td>
<td>$4\pi \times 10^{-7}$ H/m</td>
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1.3 Magnetic units

Despite a push from some quarters to convert scientists researching magnetism to use SI or MKSA units [31], CGS units are still commonly used as a conventional unit set of choice in much of the peer-reviewed literature. In this thesis, CGS will be used for magnetic moment (emu) and magnetic field intensity (Oe). Magnetization will be given in units of emu/g, as opposed to emu/cm$^3$, for convenience. Susceptibility will be given in emu.g$^{-1}.Oe^{-1}$. Density value be reported using g/cm$^3$. Distances will be given in SI units, except when reporting on values relating to atomic scale phenomena, in which case Å will be used due to its convenience. Anisotropy energy densities will be reported in SI units (J/m$^3$). Conversion factors between CGS and MKS are given in Table 1.1.

1.4 Ferromagnetism and antiferromagnetism

Ferromagnetism describes the magnetism of strongly magnetic materials, which occurs as a result of a spontaneous magnetization due to the internal alignment of macroscopic volumes of electronic spins within the material. It is a well known magnetic property of some elements, particularly many rare earth metals and transition metals, most characteristically in the 3d metals iron, cobalt and nickel, and many alloys. Ferromagnets exhibit complex magnetic behaviour below a transition temperature, the Curie temperature ($T_c$), such as hysteresis, domain formation and spontaneous magnetization. Well above $T_c$, the susceptibility falls approximately with $T^{-1}$.

Weiss [32] first proposed a simple model for ferromagnetism, in which a single spin experienced an isotropic effective field due to the alignment of all nearby spins parallel to each other. This field was labeled the molecular field and given as

$$H_\lambda = \lambda M$$  \hspace{1cm} (1.1)

where $\lambda$ is the molecular field constant and $M$ is the magnetization. With an applied field, $H$, and a molecular field acting on all spins, the expression for magnetization
Figure 1.1: The Bethe-Slater curve for direct exchange of 3d electrons. $J_{12}$ is the exchange integral, $r_{ab}$ is the interatomic distance and $r_{3d}$ is the effective radius of the incomplete 3d electron shell. The Bethe curve gives a phenomenological description of the relationship between the exchange integral and interatomic distance. It does not apply to cases of indirect exchange or superexchange.

At temperature, $T$, then becomes a transcendental equation given by

$$M(H) = \frac{N_v g_J \mu_B \mathfrak{B} (g_J \mu_B \mu_0 (H + \lambda M(H))}{k_B T}$$

(1.2)

where $N_v$ is the concentration of magnetic species per unit volume, $g_J$ is the Landé g-factor, $j$ is the total angular momentum quantum number, $\mu_B$ is the Bohr magneton, $k_B$ is the Boltzmann factor and $\mathfrak{B}(y)$ is the Brillouin function.

Within the local moment model, the molecular field arises from an exchange interaction that takes place between neighbouring electrons whose wavefunctions overlap. For two overlapping electron wavefunctions $\psi_a(r_1)$ and $\psi_b(r_2)$ from neighbouring atoms at positions $r_a$ and $r_b$ and nuclear charges, $qZ_a$ and $qZ_b$, the exchange integral, $J_{12}$, takes the form

$$J_{12} = \frac{q^2}{4\pi \epsilon_0} \int dr_1 \int dr_2 \psi_a^*(r_1) \psi_b^*(r_2) \left( \frac{Z_a Z_b}{|r_a - r_b|} + \frac{1}{|r_1 - r_2|} \right) \left( \frac{Z_a}{|r_a - r_2|} - \frac{Z_b}{|r_b - r_1|} \right) \psi_a(r_2) \psi_b(r_1),$$

(1.3)

in which an exchange of electrons is allowed to take place in the region where the wavefunctions overlap. The interaction potential is contained within parentheses, the
first of the four terms describing the repulsion between the two nuclei, the second describing the repulsion between the two electrons and the third and fourth describing the attraction between each electron and the alternate atom. The spin-dependent component of the interaction energy of two ions with overlapping electronic wavefunctions is given as

$$E_{12} = -2J_{12} S_1 \cdot S_2$$

(1.4)

where $S_1$ and $S_2$ are the total spins of each ion due to all their electrons.

For short range, the exchange interaction is of the order of $\sim 10^3$ times larger than the dipole interaction [31]. Positive values of exchange favour ferromagnetic alignment between interacting spins, while negative values of exchange favour antiferromagnetic alignments. The dependence of the exchange integral on interatomic distance can be calculated from the total interaction potential [33], and is expressed as the Bethe-Slater Curve (Figure 1.1). The molecular field constant can be related to the exchange integral within the Ising model for $n$ nearest neighbour interactions

$$\lambda = \frac{2J_n}{\mu_0 N_v g_S^2 \mu_B^2}$$

(1.5)

where $g_S$ is the absolute value of the electron spin $g$-factor.

Domains form in ferromagnetic systems as a way to minimize the magneto-static energy stored in the external magnetic field due to a magnetized volume. Domains consist of regions of aligned spins and are separated by transition structures called Bloch walls, in which spins coherently rotate from the direction of one domain to the direction of the neighbouring domain over a typical thickness of a few hundred lattice spacings. Below the critical domain size, the energy required by a volume of magnetized material to form a Bloch wall is greater than the energy released from the external field by splitting into two domains, which leads to the formation of a single domain particle [34]. The critical domain size in nickel is about 65 nm [35].

Antiferromagnetic order occurs in elemental 3d metals when interatomic distances are sufficiently small that $J$ becomes negative. Antiferromagnetic crystals consist of ordered magnetic structures with no net magnetization. These structures consist of
sublattices that have ferromagnetic character. Above the characteristic Néel temperature ($T_N$), the antiferromagnetic order disappears and the materials behaves as a paramagnet.

### 1.5 Demagnetization and superparamagnetism

A demagnetizing field arises in magnetized samples which depends on the sample shape and, in most cases, opposes the direction of the applied field. The demagnetizing field occurs due to sample end effects, and is accounted for within Maxwell’s equations by two boundary conditions, the first requiring the tangential component of the magnetic field intensity, $H$, to be continuous across the sample’s surface, and the second requiring the normal component of the magnetic flux density, $B = \mu_0 (H + M)$ to also be continuous across the surface ($M$ is the sample’s internal magnetization vector, and goes to zero everywhere outside the sample). The demagnetizing field requires a correction to be made to the internal field

$$H_{\text{int}} = H_a - DM$$  \hspace{1cm} (1.6)

where $H_{\text{int}}$ is the internal field, $H_a$ is the applied field and $D$ is the demagnetization factor, which is shape dependent. Where $H_a$ and $M$ are not parallel, $D$ is a tensor. The demagnetization factor can be solved exactly for a uniformly magnetized ellipsoid [36], by defining a quantity called the “magnetostatic potential”, $\phi_m$, such that

$$H = -\nabla \phi_m.$$  \hspace{1cm} (1.7)

The relevant Maxwell’s equation allows us to write

$$\nabla \cdot B = 0 = \mu_0 \nabla \cdot (H + M).$$  \hspace{1cm} (1.8)

As the magnetization inside the sample is uniform, $\nabla \cdot M = 0$ and

$$\nabla \cdot H = -\nabla \cdot \nabla \phi_m = -\nabla^2 \phi_m = 0,$$  \hspace{1cm} (1.9)
which is Laplace’s equation. Using the boundary conditions mentioned above, \( \phi_m \) can be solved both inside and outside the sample, and, provided the sample has uniform magnetization, \( \mathbf{H}_{\text{int}} = -\nabla \phi_{\text{mint}} \) takes the general form given in equation 1.6.

Unless otherwise specified and where known, reported values for field in this thesis refer to the \( z \)-axis projection of \( \mathbf{H}_{\text{int}} \). Efforts have been made to choose sample geometries that reduce the effects of demagnetization, so that, as much as possible, \( \mathbf{H}_{\text{int}} \approx \mathbf{H}_a \). Long cylinders, flat discs and prolate ellipsoids with large aspect ratios have small demagnetization factors when their long axes are aligned with the field and are therefore examples of preferred sample geometries.

When single domain particles are embedded in a non-magnetic matrix, they behave as giant magnetic moments. If these moments correlate internally, but do not interact with each other, they exhibit superparamagnetism [8]. Above a certain temperature, the magnetization of a giant magnetic moment becomes thermally unstable and will flip randomly, making it unsuitable for storing magnetic memory. The size of the particles also contribute to their magnetic stability.

Superparamagnetism may be treated within the Stoner-Wohlfarth model [37]. For simplicity, we consider an ensemble of single domain ellipsoids with the same giant moment, \( \mu_{\text{eff}} \), the same volume, \( V \) and the same uniaxial, or shape, anisotropy, \( K \), and their long axes are all orientated with the field. The energy of a single giant moment is

\[
E(\theta) = -\mu_{\text{eff}} \mu_0 H \cos \theta + KV \sin^2 \theta
\]

(1.10)

where \( \theta \) is the angle between the moment’s alignment and the field. The uniaxial anisotropy energy term, \( KV \sin^2 \theta \), originates from the surface energy of the particle, as will be shown in the following derivation. We start by considering a dipole, \( \mu \), consisting of two monopoles, \(+m\) and \(-m\) separated by a small distance \( dz \), so that \( d\mu = m \, dz \) and the magnetostatic potential difference between the monopoles is

\[
d\phi_m = \nabla \phi_m \cdot dz = -\mathbf{H} \cdot dz.
\]

(1.11)

The potential energy of the dipole is then

\[
dU = \frac{\mu_0}{2} m d\phi_m = -\frac{\mu_0}{2} m \mathbf{H} \cdot dz = -\frac{\mu_0}{2} d\mu \cdot \mathbf{H}.
\]

(1.12)
Figure 1.2: Cluster energy as a function of $\theta$, as described by equation (1.10), for positive and negative fields, with the cluster easy axis aligned with the field. The uniaxial anisotropy energy $KV$ acts as a barrier between the $\theta = 0^\circ$ and $\theta = 180^\circ$ states.

Using the magnetization, $M = d\mu/dV$, and integrating equation 1.12, we can derive the self-energy of a magnetized volume which, in the case of a single domain ellipsoid in zero applied field, is,

$$U = -\frac{\mu_0}{2} \int_V H_{\text{int}} \cdot M \, dV.$$  \hspace{1cm} (1.13)

If the demagnetization factor is a tensor, then

$$H_{\text{int}} = \begin{bmatrix} H_x \\ H_y \\ H_z \end{bmatrix} = - \begin{bmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_z \end{bmatrix} \begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix}$$  \hspace{1cm} (1.14)

and

$$U = \frac{\mu_0}{2} \int_V (D_x M_x^2 + D_y M_y^2 + D_z M_z^2) \, dV.$$  \hspace{1cm} (1.15)
As the components of the $D$ must sum to 1, for an ellipsoid with the long axis pointing in the $z$ direction,
\[ D_x = D_y = \frac{1}{2} (1 - D_z). \] (1.16)

Therefore,
\[
U = \frac{\mu_0}{2} \int_V \left( \frac{1}{2} (1 - D_z) \left( M_x^2 + M_y^2 \right) + D_z M_z^2 \right) dV
\]
\[
= \frac{\mu_0}{2} \int_V \left( \frac{1}{2} (1 - D_z) M^2 \sin^2 \theta + D_z M^2 \cos^2 \theta \right) dV
\]
\[
= \frac{\mu_0 M^2}{2} \int_V \left( D_z + \frac{1}{2} \sin^2 \theta (1 - 3D_z) \right) dV,
\] (1.17)

and, provided $D_z < \frac{1}{3}$, the $\sin^2 \theta$ component of the shape anisotropy energy can be seen explicitly in the angle dependence of equation 1.17. This uniaxial shape anisotropy both defines the shape easy axis and acts as an energy barrier between the $\theta = 0^\circ$ and $\theta = 180^\circ$ states. This is why enhanced anisotropy stabilizes the magnetization of superparamagnetic systems.

Superparamagnetism is a dynamic effect, and the observed phenomena are dependent on experimental parameters, particularly the experimental measurement time, $\tau_e$. The time dependent magnetization for the above ensemble of single domain particles with all shape easy axes aligned with the field and zero cooling field is
\[
M(t) = N_v \mu_{\text{eff}} \tanh \left( \frac{\mu_{\text{eff}} \mu_0 H}{k_B T} \right) \left( 1 - e^{-\frac{t}{\tau}} \right)
\] (1.18)

where $N_v$ is the concentration of single domain particles and $\tau$ is the relaxation time, which is the average amount of time it takes for a single domain particle to flip its magnetization randomly, due to thermal fluctuations. As the particle must thermally overcome the uniaxial anisotropy energy to flip its magnetization, the relaxation time may be approximately described by an Arrhenius equation,
\[
\tau = \tau_0 e^{\frac{KV}{T_B}}
\] (1.19)

where $\tau_0$ is called the attempt time, and is characteristic of the material. The attempt time is typically taken as $\sim 10^{-9}$ s. The blocking temperature, $T_B$ is the temperature at which the relaxation time and the experimental measurement time are equal. Well
above $T_B$, each single domain particle will flip its magnetization randomly several times during the course of a measurement, and the measured magnetization will tend towards the equilibrium magnetization (the $t \gg \tau$ case in equation 1.18), which is zero in zero field. Below $T_B$, the system is referred to as “blocked”, meaning frozen in time, and the magnetization of the ensemble will remain stable. In this regime, the measured magnetization is closer to the initial $M(t = 0)$ state, which in general, is established by the cooling field.

1.6 Exchange bias

Exchange bias was traditionally recognized as a property of materials consisting of interfaces between ferromagnetic and antiferromagnetic components. The phenomenon was discovered in surface oxidized cobalt nanoparticles by Meiklejohn and Bean in 1956 [10]. An exchange interaction at the interface results in an additional anisotropy, which manifests in hysteresis loops that are shifted along the field axis, generally in the negative direction, when the system is cooled in field below the antiferromagnetic Néel temperature. This exchange anisotropy is unidirectional in nature, while the shift in field is referred to the exchange bias field.
Figure 1.4: A simplified schematic of the exchange bias effect in a system consisting of a ferromagnet (FM) interfaced with an antiferromagnet (AFM). When the system is cooled in a cooling field, $H_{FC}$, below the AFM Néel temperature, the ordering of the AFM establishes an exchange interaction across the interface, which pins the FM to its field cooled state preferentially.

Meiklejohn and Bean [10, 11] proposed a simple model in which an ideal hard ferromagnet interacts with a rigid antiferromagnet across an interface. The energy per unit volume is then given as

$$E(\theta) = -M_s \mu_0 H \cos \theta + K \sin^2 \theta - J \cos \theta$$  \hspace{1cm} (1.20)

where $M_s$ is the saturation magnetization of the ferromagnetic component and $J$ is the exchange interaction energy per unit volume between the ferromagnetic and antiferromagnetic components. If only the $\theta = 0^\circ$ and $\theta = 180^\circ$ states are stable, then we calculate the coercive fields as the fields at which magnetization flips from positive to negative and then back again. As the system was cooled in positive field, we start from the positive magnetization state ($\theta = 0^\circ$). The magnetization flips when the system overcomes the uniaxial anisotropy barrier, which occurs when the coercive field is

$$H_{c\downarrow} = -\frac{K + J}{\mu_0 M_s}.$$  \hspace{1cm} (1.21)

The system is now in the $\theta = 180^\circ$ state. To reverse its magnetization, it must again overcome the uniaxial anisotropy barrier, which occurs when

$$H_{c\uparrow} = \frac{K - J}{\mu_0 M_s}.$$  \hspace{1cm} (1.22)
The exchange bias field, $H_{EB}$ is taken as the midpoint of the two coercive fields

$$H_{EB} = \frac{H_{c\downarrow} + H_{c\uparrow}}{2} = -\frac{J}{\mu_0 M_s}.$$  \hspace{1cm} (1.23)

The predicted values of exchange bias field from this model are significantly higher than the experimentally observed quantities, typically by an order of magnitude [12]. Theoretical considerations, particularly over the past two decades, have taken into account the influence of domains, both in the ferromagnetic and antiferromagnetic components [38, 39], the role of compensated [40, 41] and uncompensated [42, 43] spins on the antiferromagnetic side of the interface, and the influence of texture at the interface [15, 16, 41]. These models have had success in accounting for behaviour in a plethora of systems, but a generalized framework that predicts all aspects of exchange bias remains elusive [13, 14]. Recent work has been particularly concerned with FM-AFM bilayers, which reflects the experimental focus [13, 44].

The domain state model has had particular success accounting for some of the more exotic behaviours exhibited by exchange bias systems, such as the influence of non-magnetic dopants within the AFM bulk, the dependence on disorder, the training effect (in which $|H_{EB}|$ decreases upon consecutive hysteresis cycles) and the dependence on cooling field [45–48]. Within this model, domain formation within the antiferromagnetic component, and not just at the interface, is critical to exchange bias magnetism. As domain walls form preferentially in the antiferromagnetic component at defect sites, these defect sites act to pin the domain walls, stabilizing the antiferromagnet at the interface, which hinders the reversal of the ferromagnetic component. Exchange bias is therefore enhanced by the introduction of non-magnetic dopants into the antiferromagnet, or the presence of a magnetically disordered component, within the domain state model, which has been confirmed experimentally.

1.7 Spin glasses and mictomagnetism

A spin glass is a system which is magnetically disordered, consisting of a mixture of ferromagnetic and antiferromagnetic interactions and an absence of long range magnetic order [49]. The characteristic behaviour of spin glass systems is a sharp
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(c) Spin glass.

Figure 1.5: (a) A simplistic 2-D schematic of a spin glass system consisting of a noble metal doped with magnetic impurities. (b) An example of the RKKY interaction. $J_{12}$ is the exchange integral, and $r_{ab}$ represents the interspin distance. After Binder [49].

cusp in the temperature dependent susceptibility in low fields, which takes place at what is labeled the glass temperature, $T_g$ or the freezing temperature [50, 51]. The use of the latter term implies that a magnetic phase transition takes place at $T_g$, but whether one actually does or whether the observed behaviour below $T_g$ is a consequence of a system not in thermal equilibrium is still debated [49, 52], though, from an experimentalist viewpoint, the former formulation is easier to reconcile with the observations [53].

The classical spin glass consists of a noble metal (Cu, Au, Ag) doped with a small concentration of magnetic impurities (Mn, Fe). The atomic moments are localized on the dopant atoms, and interact with nearby moments through the RKKY indirect exchange interaction (Figure 1.5(b)), which oscillates strongly with interspin distance owing to a near-singularity in the wavevector-dependent conduction electron susceptibility [54, 55]. Above the glass temperature, the system exhibits a paramagnetic ($T^{-1}$) response, but as the the spin glass is cooled through the glass temperature, the spin configuration becomes frozen, resulting in behaviour which is strongly sensitive to cooling field. The spin glass becomes magnetically blocked below $T_g$, and its magnetic response indicates the presence of magnetic frustration and a disordered energy landscape with numerous local minima.
The magnetic properties of spin glasses are sensitive to thermal treatment during the preparation process \cite{23}. Aging of spin glasses such as CuMn causes the diffusion of the magnetic ions away from a homogeneous distribution and, depending on the aging conditions, short range order may arise, in which nanoscopic clusters form \cite{56–60}. If the interactions within these clusters are mostly ferromagnetic, the susceptibility of the sample rises significantly at all temperatures, while $T_g$ itself will also rise slightly \cite{59}.

Spin glasses with higher concentrations of magnetic impurities show a particularly strong sensitivity to aging, as well as a number of other exotic effects that are only weakly observed at lower concentrations, such as enhanced exchange anisotropy and asymmetric reversal. Such systems were labeled “mictomagnetic” (ie, mixed magnetic) by Beck \cite{61}, who proposed a model following Kouvel \cite{22}, in which regions of clusters with mostly ferromagnetic alignments interacted with a disordered matrix that was mostly antiferromagnetic. CuMn is considered mictomagnetic between approximately 9 and 25 at.% Mn \cite{61}. Neutron studies in mictomagnetic CuMn have shown that aging induces short range order among neighbouring Mn atoms at the second nearest neighbour position, which tends to correspond to a positive magnetic short range order parameter and weak ferromagnetic correlations \cite{56, 62, 63}.
Chapter 1 References


[34] C. Kittel, Phys. Rev. 70, 965 (1946).


Chapter 1. Introduction


Chapter 2

Literature review

2.1 Overview

Exchange bias has been a well known property of materials consisting of an interface
between a ferromagnet (FM) and antiferromagnet (AFM) for several decades [1, 2],
however a theoretical description that accounts for all observed phenomena in all
systems remains elusive [3, 4]. Spin glass systems have also been studied for decades,
and in more recent times, analogues between the two sets of phenomena have been
increasingly recognized. In this chapter, a portion of the existing literature concerned
with the magnetic properties of spin glasses and exchange bias materials is reviewed.
Particular focus is directed to studies of systems where analogues between the two
effects are acknowledged, such as mictomagnets with relatively high concentrations of
magnetic impurities, and exchange bias materials with disordered antiferromagnetic
components.

2.2 Experimental aspects of spin glasses

The magnetic properties of alloys consisting of noble metals doped with low concen-
trations of magnetic impurities have interested researchers for many decades [5], but
research in the experimental aspects of spin glasses accelerated with the discovery of a
sharp cusp in the low-field temperature dependent susceptibility of AuFe alloys [6, 7].
This cusp coincides with what is now referred to as the glass or freezing temperature, $T_g$. The question of whether $T_g$ signifies a magnetic phase transition has been debated [8–10], and is further complicated due to the absence of a magnetic structure with long-range order [11]. Claus and Kouvel [12] interpreted $T_g$ as the temperature at which local anisotropy is established within the spin glass as it is cooled. Murani [13] interpreted the results of neutron scattering experiments on AuFe at and below $T_g$ as evidence for a wide distribution of magnetic relaxation times, analogous to an ensemble of superparamagnetic particles with a distribution of energy barriers and Néel times. However, models based on superparamagnetism have been unable to sufficiently account for all important aspects of spin glass behaviour, such as the critical behaviour at $T_g$ and shifted hysteresis loops, particularly at temperatures well below $T_g$ [9].

### 2.2.1 Copper manganese

Copper manganese is a particularly interesting spin glass system because the lattice positions correspond approximately to the oscillations of the RKKY interaction [14]. Many structural studies have been performed on copper manganese systems using neutron techniques, such as neutron polarization analysis [15–20] and small-angle neutron scattering (SANS) [21, 22], much of which has been spurred by interest in a diffuse neutron diffraction peak around the $(1 \frac{1}{2} 0)$ reflection found by Meneghetti and Sidhu [23], which they attributed to magnetic short-range order (SRO). Subsequent neutron studies have found that short-range order of manganese occurs at the second nearest neighbour positions, which coincides with weak ferromagnetic interactions [14, 15, 17].

Atomic short-range order in copper manganese is highly sensitive to thermal treatment [24]. Mukhopadhyay and Beck [25] interpreted their measurements of a set of micromagnetic CuMn alloy samples between 9 at.% and 25 at.% Mn, aged at 100°C as the aging increasing the effective moment and concentration of magnetic clusters within the samples. If thermal treatment induces the precipitation and growth of clusters that consist of mostly ferromagnetic correlations, then the magnetic properties of CuMn may be enhanced by aging, which has been demonstrated by several
accounts [12, 26, 27]. Gray and Smith [28, 29] found that the susceptibility of micromagnetic \(CuMn\) alloys around \(T_g\) is most greatly enhanced by relatively low aging temperatures, of the order of 100\(^\circ\)C, despite the slower kinetics of aging at such temperatures. This was later interpreted within a model based on the diffusion of vacancies into fixed vacancy sinks, which exist in higher concentration as the temperature rises above 100\(^\circ\)C [30]. This means that the short-range ordering process, which reaches an equilibrium once the supply of vacancies is exhausted, is completed faster at higher temperatures. This, along with thermal fluctuations at higher aging temperatures, effectively limits the achievable extent of SRO.

Gray [30] demonstrated that SRO in \(CuMn\) could be driven to equilibrium using neutron irradiation. The neutron irradiation acts as a continuous vacancy supply, allowing SRO to continue to an extent unachievable using thermal treatment processes. A sample of neutron irradiated \(Cu_{83.6}Mn_{16.4}\) exhibited a 20 times increase in susceptibility at \(T_g\) compared to the as-quenched value. Subsequent neutron studies on a neutron irradiated \(Cu_{80}Mn_{20}\) alloy sample by Cussen and coworkers [31, 32] reported the onset of magnetic long-range order, induced by the irradiation process.

Magnetic studies of \(CuMn\) have focused on the exotic behaviours exhibited at temperatures well below \(T_g\). Kouvel [33] measured magnetic hysteresis loops of \(CuMn\) alloys between 5 and 29 at.% Mn. At 1.8 K within loops measured between \(\pm 10\) kOe, the samples would exhibit a paramagnetic response after cooling in zero field, but after cooling in a field, or “field cooling”, a significant non-linearity would appear in the negative field region of the loops. Kouvel developed a model (discussed in more detail in section 4.3) in which such hysteresis loops could be split into a linear and asymmetric component, the latter of which was seen as analogous to the shifted hysteresis loops observed by Mickeljohn and Bean [1, 2] in surface oxidized cobalt nanoparticles, which have a FM-core/AFM-shell structure. In a subsequent model, Kouvel [34] interpreted the magnetic properties of \(CuMn\) alloys in terms of interacting ferromagnetic and antiferromagnetic domains.

Subsequent understanding of the magnetism of micromagnetic \(CuMn\) for \(T \ll T_g\) developed around magnetic clusters [25, 35–38]. The non-linearity in \(CuMn\) hysteresis loops that appeared after field cooling was labeled the “step” magnetization by
Schwink and coworkers [39, 40], who interpreted it as the magnetism of internally ferromagnetic clusters that interact with a quasi-isotropic “spin glass” matrix of frozen, blocked spins. Schwink and coworkers [40, 41] probed the local anisotropies of clusters in CuMn alloys using magnetic measurements, and found that both the shape (modeled as uniaxial) anisotropy of clusters [42, 43], and the unidirectional anisotropy arising from their interaction with the spin glass matrix [44] are field dependent quantities.

SANS has been used to characterize clusters in CuMn. Gray et al. [21] measured SANS profiles of an aged Cu$_{83.3}$Mn$_{16.7}$ alloy between 5 and 220 K and found that the magnetic clusters appear diffuse and ramified, estimating that they each contained between 100 and 200 Mn atoms. Schönfeld et al. [22] conducted SANS experiments on two Cu$_{83}$Mn$_{17}$ alloys aged at different temperatures for different times and found comparable results.

Some theoretical attempts to understand the magnetically disordered matrix in micromagnets have developed around the idea of a percolation cluster which forms below $T_g$ [38, 45, 46]. If the correlations throughout the matrix are mostly ferromagnetic and remain unbroken, an entity that Smith [38] referred to as the “infinite cluster” forms. As the infinite cluster coincides with $Q = 0$ scattering, it cannot be easily characterized using experimental techniques such as SANS.

### 2.2.2 Nickel manganese

Alloys of NiMn consisting of about 25 at.% Mn have attracted attention from researchers due to the sensitivity of their magnetic properties to atomic disorder. Based on magnetic measurements, Kaya and Kussmann [47] determined that ordering of Ni$_3$Mn occurs between 400 and 500°C, and that it behaves as a ferromagnet when highly ordered, forming a superlattice. The disordered alloy exhibited a paramagnetic response. Carr [48] predicted that nearest neighbour Ni-Ni and Ni-Mn pairs would interact ferromagnetically, but nearest neighbour Mn-Mn pairs would interact antiferromagnetically, which was confirmed by neutron experiments [49]. When Kouvel and Graham [50] measured the low temperature magnetic properties of disordered NiMn alloys with compositions between 20 and 30 at.% Mn, they observed shifted
hysteresis loops after field cooling, which was interpreted in terms of an exchange interaction with unidirectional anisotropy.

Polarized-neutron diffuse scattering measurements were made by Cable and Child [49] to characterize the magnetic moment distribution in NiMn alloys as a function of Mn concentration. They found that, for compositions between 5 and 20 at.% Mn, a greater moment was localized on the Mn atoms than the Ni atoms, but the moments localized on both atoms decreased with Mn concentration. A cluster model was proposed by Goldfarb and Patton [52] to account for the temperature dependence of disordered Ni$_3$Mn. Abdul-Razzaq and Kouvel [51, 53] reported on the magnetic phase diagram of disordered NiMn between 20 and 30 at.% Mn (Figure 2.1). They observed a multicritical point at 23.9 at.% Mn and 102 K, which supported prior theoretical predictions [54, 55]. Below 23.9 at.% Mn, disordered NiMn is a reentrant ferromagnet, behaving as a ferromagnet above the freezing temperature and as a

![Magnetic phase diagram of disordered NiMn](image_url)
mixed ferro-spin-glass (FSG) below. For higher compositions, the system behaves as a spin glass (SG) with $T_g$ decreasing with Mn concentration above 25 at.% Mn. The properties of reentrant NiMn have been the topic of numerous studies [56–61].

Of particular interest has been the influence the introduction of non-magnetic defects has on the anisotropy of reentrant NiMn systems. After a report from Prejean et. al [62] that the addition of very small amounts of Au defects resulted in an enhancement of coercivity of CuMn spin glass, Öner and coworkers [58, 63] investigated the magnetism of a quenched NiMn alloy near the multicritical point, doped with 2 at.% Pt. The NiMnPt ternary alloy exhibited enhanced coercivity and a greater extent of uniaxial and unidirectional anisotropy than a NiMn sample with the same Mn concentration and prepared with the same procedure. Subsequent studies of reentrant NiMn doped with non-magnetic defects confirmed the enhancement of coercivity and anisotropy and also showed that doping has minimal effect on the transition temperature and saturation magnetization [64–67]. This is interpreted as the doping atoms inducing a large spin-orbit coupling, which enhances magnetic anisotropy through a Dzyaloshinskii-Moriya type interaction [65, 67, 68].

Fewer studies have been concerned with the effects of doping NiMn in its pure spin glass state. Durusoy and Öner [63] showed that as Ni is replaced by Pt in Ni$_{72-x}$Mn$_{28}$Pt$_x$ for $x$ between 0 and 10 at.% Pt, the glass temperature increases slightly with Pt concentration, but the susceptibility at $T_g$ decreases significantly.

### 2.3 Analogues between exchange bias systems and spin glasses

A number of reports where unidirectional anisotropy, arising from mixed exchange interactions, has been used to account for the low-temperature magnetism of micromagnetic materials have been highlighted in the previous section. More recently, there has been an increasing recognition in the literature of spin-glassy behaviour exhibited by slightly disordered exchange bias materials consisting of interfaces between components of mostly ordered ferromagnetic and antiferromagnetic regions.
One of the most remarkable examples was reported by Ali et al. [69], in which CuMn was substituted for the antiferromagnet in a set of exchange bias Co/CuMn bilayers. For bilayers using a Cu$_{94}$Mn$_{6}$ layer, behaviours canonically associated with exchange bias systems such as displaced hysteresis loops and training were observed. The exchange bias field, $H_{EB}$, increased in magnitude with the spin glass layer thickness and decreased in magnitude with temperature as expected but, unusually, positive exchange bias was observed in a temperature range approaching the blocking temperature. This was accounted for within a model based on a long-ranged oscillating RKKY interaction between the ferromagnet and spins in the spin glass component, whereby, at a certain temperature and provided the spin glass concentration is sufficiently low, the ferromagnetic interaction between the ferromagnet and spins in the spin glass close to the interface overcomes the mostly antiferromagnetic interaction between those spins and the rest of the spin glass, resulting in a reversal of unidirectional anisotropy.

Spin-glassy behaviour, such as sharp cusps in the temperature dependent magnetization and strong sensitivity to cooling field, has been observed in magnetic nanoparticulate systems with mixed exchange interactions, such as antiferromagnetic particles with canted surface spins [70–72] and FM-core/AFM-shell surface oxidized nanoparticles [73, 74]. Fiorani and coworkers [75–78] interpreted the cooling field sensitivity and cluster-glass-like properties of Fe nanoparticles dispersed in a FeO matrix as evidence for magnetic frustration and disorder within the antiferromagnetic oxide. If the antiferromagnet has a number of local, energetically stable configurations, they may become frozen as the system is cooled through its transition temperature, which accounts for the cooling field dependent behaviour [75].

Many of the properties of slightly disordered exchange bias systems may be understood within the domain state model [79, 80], in which exchange bias is dependent on the formation of domains within the antiferromagnetic component, and domain walls form preferentially at defect sites, which aid to pin the ferromagnet. Within this model, exchange bias is enhanced by disorder within the antiferromagnet.

Hysteresis loops that exhibit asymmetric reversal have been observed in mictomagnets [25] and exchange bias systems [81–85] alike. Asymmetric reversal, which is discussed in more detail in section 4.5, generally refers to asymmetry between the magnetization
reversal mechanisms on the “down” branch and the “up” branch of a hysteresis loop [86]. In exchange bias systems, this is thought to arise from the misalignment of cluster or domain easy axes, associated with their own shape anisotropy (uniaxial in the simplest approximation), with each other and the field. Models based on a distribution of shape easy axes have been used to successfully account for asymmetric reversal [87–91].
Chapter 2 References


Chapter 3

Experimental Techniques

3.1 Overview

In this chapter, the experimental apparatus used in this work will be introduced. Much of the apparatus has been designed and assembled specifically for this work and this will be discussed in detail. This chapter will deal with the design and capabilities of a vibrating sample magnetometer (VSM), and its performance and limitations will be reported. Sample preparation methods used in this investigation will also be considered, while sample characterization techniques, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) will be briefly introduced.

3.2 Vibrating Sample Magnetometer

A vibrating sample magnetometer was designed and built for measurements of magnetization, based on a commercial cryostat and superconducting magnet supplied by Cryogenic Ltd. The magnetometer consists of a system of excitation and detection coils, positioned coaxially, as well as a superconducting magnet capable of generating a magnetic field as large as 82 kOe (or, equivalently a magnetic flux density or \( B \) field of 8.2 T) in either direction along the vertical axis. The sample space and excitation and detection coil system are contained within a closed-cycle refrigerator (CCR) cryostat supplied by Cryogenic Ltd with a temperature range of 3.8 to 350 K.
Figure 3.1: Block schematic of the connections in the VSM system. A lock-in amplifier generates the frequency that drives the linear motors (after being amplified by the servoamplifier) and then detects that specific frequency in the detection coil system. The excitation and detection system, 8 Tesla magnet and sample space is contained within a helium cryostat. A scanner in conjunction with a digital multimeter sequentially scans the temperatures at various stages of the cryostat. The entire system is controlled and automated via software on a PC written in Labview. Communication links between the PC and various instruments are established over USB, RS232 and IEEE ports on the PC. Green is used to highlight instruments that control and monitor temperatures, red represents instruments that set the field and blue colours apparatuses that measure detection coil signals and control the drive system.
A Kollmorgen Direct Drive Ironless Linear motor provides the drive for oscillatory motion of the sample. The linear motor is typically operated at a low frequency of 6.3 Hz, allowing higher amplitude of oscillation for the same drive force.

A VSM measures magnetic moment by mechanically oscillating a magnetized sample in the presence of a set of carefully positioned detection coils. The time variant dipole field observed by the detection coils induces a electromotive force across the coils. The technique was pioneered by Foner [1–3] several decades ago, and differed from previously common flux integration techniques in that the time variant dipole field was produced by motion of the sample, as opposed to motion of the detection coils [4], or oscillation of the applied field.

Innovations in VSM design have subsequently improved sensitivity and versatility. Drive systems have evolved from Foner’s modified loudspeaker transducer [1, 3], with more recent reports detailing VSM instruments based on crank shafts [5, 6], stepper motors [7], and piezoelectric actuators [8, 9], the latter being commonly used in commercial instruments. Superconducting magnets have become ubiquitous for generating applied fields, due to their ability to apply and maintain very high fields while requiring smaller power supplies than magnets made of turns of resistive materials. However, the use of superconducting magnets requires care to compensate for parasitic effects such as flux creep and image effects [10, 11]. Halbach-type arrays of permanent magnets have been proposed as one of the more novel solutions [12, 13], although these tend to be limited in the maximum field they can apply. A multitude of different detection coil configurations have been explored both in theory and practice [4, 14–19], each sensitive to components of sample magnetization in different ways.

The measurement of magnetization of a sample by VSM works on the principle of measuring an electromotive force, $\epsilon = V(t)$, induced by a time variant magnetic flux density, $B(t)$, in the detection coils, as described by Lenz’s law

$$\epsilon = V(t) = -\frac{d}{dt} \sum_{i=0}^{n} \int_{S} B(t) \cdot dS$$

$$= -\sum_{n} \int_{S} \frac{dB(t)}{dt} \cdot dS$$  \hspace{1cm} (3.1)
Figure 3.2: Two coaxial detection coils configured in Smith’s geometry [4]. The $\mathbf{k}$ and $\mathbf{n}$ vectors are both parallel to the vertical $z$-axis, which, in this investigation, is aligned with the applied field. The $x$-$y$ plane is given by the gray region. The initial position vector of the sample, $\mathbf{R}(0)$, defines the origin. The signal from the detective coils is sensitive only to the $z$-component of magnetization.
where \( \mathbf{dS} \) is the open surface element vector. A summation over all \( n \) turns in the detection system is denoted. A magnetized sample is held within the vicinity of the detection system, and vibrated mechanically. As the magnetized sample emits a magnetic \( \mathbf{B} \) field, its movement in space translates to a temporal variation in field at the stationary detection coils. For simplicity, we consider a single turn detection system lying in the \( x-y \) plane, with \( \mathbf{dS} = \mathbf{dSn} \) parallel to the (vertical) \( z \)-axis. We may approximate the sample as an arbitrary point source vector dipole, emitting a \( \mathbf{B} \) field

\[
\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \left( \frac{3(\mathbf{\mu} \cdot \mathbf{r}) \mathbf{\hat{r}}}{r^5} - \frac{\mathbf{\mu}}{r^3} \right)
\]

where \( \mathbf{\mu} = (\mu_x, \mu_y, \mu_z) \) is the dipole moment and \( \mathbf{r} = (x, y, z) \). This dipole is then allowed to vibrate, in this case along the vertical axis, parallel to the applied field, thus inducing an observable electromotive force in the detection coils. Following Pacyna’s [17] general analysis of a signal induced by a vibrating moment, the time dependent position vector of the sample is described as

\[
\mathbf{R}(t) = \mathbf{R}(0) + \mathbf{\hat{k}} \delta \sin(\omega t)
\]

where \( \mathbf{\hat{k}} \) represents the direction of motion, in this case the vertical, \( \delta \) gives the amplitude of oscillation, \( \omega \) is the angular frequency and \( \mathbf{R}(0) \) is the initial position vector, which defines the origin for convenience. The configuration used in this case, where the normal to the coils, \( \mathbf{\hat{n}} \) and direction of motion, \( \mathbf{\hat{k}} \) both lie parallel with the \( z \)-axis, the coils are all positioned coaxially with the \( z \)-axis and the initial position vector of the dipole moment points to the origin is known as Smith’s geometry [4, 17], and is shown in Figure 3.2.

Then

\[
\frac{d\mathbf{B}(t)}{dt} = \frac{d\mathbf{R}(t)}{dt} \cdot \nabla \mathbf{B}(\mathbf{r})
\]

where \( \nabla \mathbf{B}(\mathbf{r}) \) is a \( 3 \times 3 \) tensor that is essentially

\[
\nabla \mathbf{B}(\mathbf{r}) = \text{grad} \mathbf{B}(\mathbf{r}) = \begin{bmatrix}
\frac{\partial B_x}{\partial x} & \frac{\partial B_x}{\partial y} & \frac{\partial B_x}{\partial z} \\
\frac{\partial B_y}{\partial x} & \frac{\partial B_y}{\partial y} & \frac{\partial B_y}{\partial z} \\
\frac{\partial B_z}{\partial x} & \frac{\partial B_z}{\partial y} & \frac{\partial B_z}{\partial z}
\end{bmatrix}.
\]

The identity in equation (3.4) conveniently allows separation of the time and spatial
dependencies of the $B$ field. Thus, the voltage response from this single turn system is,

$$V_i(t) = -\int_S \frac{dR(t)}{dt} \cdot \nabla B(r) \cdot dS.$$  \hfill (3.6)

Performing this integration in Smith’s geometry, where all relevant vectors are parallel to the $z$-axis, we find that, for a single coil

$$V_i(t) = -\omega \delta \cos(\omega t) \frac{3}{2} \mu_0 \mu_z \frac{a^2}{(a^2 + z^2)^\frac{3}{2}}$$  \hfill (3.7)

where $a$ is the radius of the turn and $z$ is its position on the $z$-axis. The important result is that this observable signal is proportional to the $z$-component of the sample’s moment, from which its magnetization may be calculated. It also indicates that the signal is proportional to the magnitude of the velocity of the sample, $\omega \delta$, meaning that a higher velocity is desirable in order to maximize the signal. To determine the total response of a set of coils, $V_i(t)$ must be summed over the $n$ individual turns that comprise the detection coils.

The VSM employed in this investigation uses two sets of coaxially wound detection coils configured in Smith’s geometry. The sample is driven by a linear motor that may be positioned along a 500 mm magnet way, allowing for flexible locating of the sample. During measurement, the sample vibrates at relatively low frequency, usually 6.3 Hz, but over a relatively large amplitude of 5 mm. Low frequency, large amplitude was chosen as the linear motor is force limited. For a given constant available force, $F_{\text{limit}} = m\omega^2\delta$, the velocity can be increased by decreasing $\omega$ and increasing $\delta$. Low frequency vibration also limits the reaction forces on the cryostat. The sample may be oscillated in a region where both the applied field and detection coil response are approximately constant.

### 3.2.1 Detection coil system

The detection coil system consists of two coaxial solenoids (pickup coils), placed above and below the origin, each consisting of 9470 turns of 0.0598 mm diameter superconducting wire. A calculated response of the detection system was derived by integrating equation (3.6) over the length of both pickup coils. The response of the
coils, as shown in Figure 3.3, is approximately constant, to within 4.5%, in a ∼ 20 mm region between the two coils. While a sinusoidal vibration of a sample in this region would result in a minimal amount of harmonic distortion in the measured pickup coil response, the size of this region also limits the acceptable amplitude of vibration.

The output of the pickup coils is amplified by a factor of 100 using a low noise pre-amplifier, and then processed using a lock-in amplifier tuned to the frequency of motion of the drive system.

### 3.2.2 Vibration drive

A Kollmorgen Direct Drive Ironless Linear motor drives a carbon fibre sample rod which carries the sample and provides the oscillatory motion of the sample. A linear motor was chosen over alternative drive systems because its centre of vibration is entirely programmable. This allows samples of differing sizes to be centred on the pickup coils by scanning the drive rod along the z-axis. The linear motor is force
limited to a maximum force of 76 N. Carbon fibre was chosen for the sample rod for its high stiffness, relative to its density, which minimizes any undesired lateral vibrations. A PCTFE (fluoropolymer, also referred to as “Kel-F”) section at the bottom end of the sample rod minimizes its contribution to the signal, owing to the material’s particularly low magnetic susceptibility.

The linear motor communicates with a servoamplifier, which is commanded via the RS232 interface of a PC, in conjunction with a 24 V linear motor interface unit designed to switch the Configurable I/O Interface of the servoamplifier. The servoamplifier controls the current to the linear motor, and gathers feedback from an encoder fixed to the linear motor, which reads its relative position from a strip of marked stainless steel tape. After tuning the control parameters of the linear motor system, the fidelity of its motion was verified using supplied calibration software, and shown to be only slightly frequency dependent up to 10 Hz, decreasing in amplitude by 5% between 3 Hz and 10 Hz. During measurement, an analogue signal generated by the lock-in amplifier and fed to the servoamplifier controls the position of the linear motor. This signal consists of a DC component, which positions the motor such that the sample sits in the centre of the pickup coils, added to an AC voltage which vibrates the sample sinusoidally. The lock-in amplifier is then tuned to the linear motor drive frequency.

While the linear motor has a relatively large available force, its velocity is limited by the requirement to dissipate heat. The linear motor is, in effect, an inductive load, and its heat generation can be approximated as $\omega^3$. This enforces a severe limit on the range of frequencies that can be used during operation without risking overheating the linear motor.

The linear motor is contained within the top-works of the VSM, an open-faced aluminium case referred to as the “head” (Figure 3.4). The head is sealed with an o-ring and a perspex door and is connected directly to the sample space through a hole in its base plate, which accommodates the sample rod. The head and sample space are flushed and charged with a low pressure helium atmosphere prior to operation, within an approximate range of 0.3 to 0.5 bar when the sample space is above room temperature.
Figure 3.4: Schematic of the VSM head. A perspex door seals the head and sample space under a helium atmosphere during operation. Motor current and encoder signals are carried using flexible ribbon cables, which are connected to a set of vacuum tight sockets that sit in the base plate. A carbon fibre tube is used for the sample rod, with an aluminium top-piece glued on, which screws into a threaded sample rod holder.
3.2.3 Superconducting magnet and excitation coil system

A superconducting magnet capable of generating 82 kOe is used to apply a field to the sample. The magnet, manufactured by Cryogenic Limited, consists of a long solenoid of superconducting wire and produces an approximately constant field in a region between the pickup coils (a 0.23% variation in a 60 mm region in the centre of the solenoid was reported by the manufacturer). The magnet is powered by a commercial 93 A single quadrant magnet power supply (MPS) manufactured by Cryogenic Limited. In order to give the magnet bipolar capabilities for measuring hysteresis loops, a digitally controlled magnet polarity switch was designed and connected to the output of the magnet power supply (a circuit diagram is shown in Appendix B). The magnet polarity switch works by switching a set of high current relays connected in parallel so that, when a control bit is active, the connection terminals from the MPS to the superconducting magnet are reversed. Safety features are built into the magnet polarity switch which lock the relays into their current state whenever a current through the superconducting magnet is detected. If power is lost to the magnet polarity switch, all inputs and outputs are shorted together, so that the output impedance as seen from the MPS remains zero.

The superconducting magnet is housed within the cryostat and connected in parallel to a superconducting switch which, when cooled below its critical temperature, allows for a persistent current to flow through the magnet. A switch heater, controlled by the magnet power supply, is placed in the vicinity of the superconducting switch, allowing for control of its superconducting state.

A small offset current produced by the commercial MPS makes it unsuitable for low field measurements, where it is important to know when the applied field is zero. A 20 A current supply was designed with versatility in mind (a conceptual circuit diagram is given in Appendix B). A relatively high current output gives it the capability of setting fields in the superconducting magnet up to 17 kOe, which is suitable for most samples investigated in this work, while its positive and negative rails give it bipolar capabilities without requiring a magnet polarity switch at the output which may abruptly interrupt the flow of current. The circuit works by taking feedback of the output current from a grounded reference resistor, and setting the
gate voltage of a set of two high current MOSFETs which are connected in series at the output, and each to their respective power rails. Capacitors are strategically placed across the rails and inputs of the regulating op-amp circuits to reduce high frequency noise. The constant output current is set by an input voltage generated from the 16-bit DAC of a USB controlled data-acquisition device (DAQ). The output current is monitored from the voltage across the reference resistor, measured by a digital multimeter. This 20 A current supply was used whenever fields outside the range of ±17 kOe were not required.

When a field of 1 kOe or more is removed from the superconducting magnet, a remanent field in the opposite direction to the removed field often persists, which is typical of superconducting magnets [10, 11, 20]. This remanent field can be removed by training the magnet, which involves applying alternating fields with decreasing magnitude until the field generated by the magnet is zero. Where an experiment allowed, the superconducting magnet was trained prior to low field measurements, generally resulting in remanent fields less than ∼0.8 Oe. During training, the sample was often warmed above its critical or transition temperature, which acts to reset any memory effects within the sample.

3.2.4 Cryostat and variable temperature insert

The entire excitation and detection coil system, as well as the sample space and superconducting magnet are contained within a helium cryostat capable of cooling to below liquid helium temperatures. Helium gas is cooled with a 2-stage Gifford-MacMahon mechanical refrigerator. The sample space itself is contained within a stainless steel variable temperature insert (VTI). The VTI temperature is established by a helium spray from a needle valve connected to the cooling circuit and monitored by a calibrated Cernox temperature sensor. The spray is heated with a heater controlled by a Lakeshore Model 340 Temperature Controller. The temperature control loop was manually tuned in ten zones between 4 K and 400 K to optimize the stabilizing time after changing the set temperature.

A thin walled insert which houses the sample space was designed by the author with two purposes in mind. The first was to permanently isolate the VTI and cooling
Figure 3.5: Schematic of the VTI and sample space. The sample space is contained within a thin-walled stainless steel insert with a copper extension connected to the bottom, chosen for its superior thermal conductivity. A PCTFE extension tube is connected to the bottom of the carbon fibre sample rod. PCTFE is used for the sample rod extension and sample holder due to its low susceptibility. A Cernox temperature sensor is used to monitor the temperature close to the sample. The temperature sensor is carefully positioned so that, when the sample induces a maximum signal in the pick-up coils, the contribution to the signal from the temperature sensor is negligible.
circuit from impurities introduced via the sample space to prevent capillary blockage by ice. The second was to allow for the most efficient transfer of heat from the sample space into the cooling system possible in this configuration, while minimizing heat leak up through the walls of the insert out of the cryostat. This was done by making the insert out of two parts. The upper part consists of thin walled stainless steel. Stainless steel was chosen for its relatively poor thermal conductivity for a metal, which minimizes the thermal conduction between the sample space and the upper works of the VTI and drive head. The lower part, which houses the sample space, was made of copper, chosen for its high thermal conductivity and high Debye temperature of 343.5 K (when the temperature, $T$, of a solid is significantly less than the Debye temperature, $T_D$, its specific heat drops quickly with $T^3$). The insert thus allows for efficient cooling of the sample space (cooling the VTI from room temperature to 5 K typically takes 4 hours) and facilitates good agreement between the sample space temperature and the VTI temperature. An earlier design of this insert, made entirely from thin walled stainless steel, required 17 hours for the VTI to cool from room temperature to 5 K.

A second calibrated Cernox temperature sensor is attached to the sample rod to measure the sample space temperature. This allows for very good measurement of the sample temperature, as the sample space temperature is approximately isothermal within the vicinity of the copper attachment of the insert. However, as the sensor is attached to the sample rod, it contributes to the signal measured by the VSM. To bypass this, the default sample rod position is chosen such that the sensor is close to a null response position, meaning that its contribution to the signal is negligible. Figure 3.3 shows that there are two null response positions that coincide closely with the centres of each of the two pickup coils.

### 3.2.5 Calibration

The VSM was calibrated using a nickel sphere and a lead rod. Nickel is a well known ferromagnet with a considerable saturation magnetization, low coercivity and high susceptibility in low field. Lead is a Type-1 superconductor with a susceptibility of $-1$ below its critical temperature, $T_c = 7.2$ K [21].
Figure 3.6: Measured $z$-profile of pickup coils using a 0.273 g nickel sphere in 6 kOe at 315 K. The sample was oscillated at 6.3 Hz with an amplitude of 5 mm. A mismatch between the measured and calculated responses reveal an imbalance between the two pickup coils in the detection coil system.

The $z$-profile of the detection coil response was gauged by measuring a 0.273 g nickel sphere in 6 kOe at 315 K. The agreement between the measured and calculated responses is shown in Figure 3.6 and verifies the positions of the pickup coils. However, the magnitudes of the two maxima differ by approximately 14%, suggesting that the pickup coils are imbalanced, presumably in the number of turns contained in each.

Magnetization curves were measured for the nickel sphere at several temperatures between 4.1 K and 315 K, and a conversion factor between the signal response of the pickup coils and the moment of the sample was extracted using known temperature dependent values for the saturation magnetization of nickel [22]. The magnetization of the nickel sphere as a function of field at 4.1 K is shown in Figure 3.7, both before and after correcting for demagnetizing field.

A critical temperature of $6.9 \pm 0.13$ K was extracted from temperature dependent
Figure 3.7: Magnetization loop for a 0.273 g nickel sphere measured at 4.1 K. Loop shown with and without corrections for demagnetizing fields.

Figure 3.8: (a) Temperature dependent magnetization of a 0.701 g lead rod in 100 Oe after cooling in zero field (ZFC). (b) Magnetization of lead rod at 4.4 K after ZFC, measured between ±100 Oe and corrected for demagnetizing fields.
measurements of superconducting lead (99.9999% rod), which disagrees with the accepted value of 7.2 K. The discrepancy is attributed to a small temperature gradient between the sample and temperature sensor. The linear magnetic response of lead in its superconducting state was used to calibrate the output of the 20 A current supply when it was connected to the superconducting magnet. The superdiamagnetic response of lead at 4.4 K is displayed in Figure 3.8(b). However, there is a small discrepancy between the measured magnetization and the expected value (given a susceptibility of $-1$) of 5%. This is presumed to be a discrepancy in the actual value of applied field per supplied current compared with that given by the manufacturers.

### 3.2.6 Lessons learned

During the commissioning process of the VSM, a number of problems were encountered that were not anticipated during conceptualization. In this section, a handful of these problems will be briefly discussed and their eventual solutions reported, with a focus on highlighting some of the limitations of this particular VSM design (the importance of which is raised by Foner in reference [3]).
The detection coil system is sensitive to any change in the magnetic $B$ field observed by the pickup coils. There are two particularly notable sources of parasitic contributions to the detection coil signal: the signal due to magnetization of any object on the sample rod [23] and the signal due to flux creep in the superconducting magnet [10, 24, 25]. In order to minimize the contribution of sample rod magnetization to the signal, the sample rod must be constructed from low susceptibility materials. In the first instance, copper was trialed for the sample holder, but induced a parasitic signal at low temperatures, which was presumed to be due to magnetic impurities. PCTFE was used subsequently for the sample holder and the region of the sample rod close to the pickup coils, due to its low susceptibility compared with carbon fibre, which demonstrated a linear response to field, presumably due to impurities in the binder epoxy.

The soft ferromagnetic response of the temperature sensor shown in Figure 3.9 was unanticipated and unavoidable. In order to give a good measure of the sample temperature, the temperature sensor should be positioned close to the sample, which requires that it be placed on the sample rod. However, as its motion is equivalent to that of the sample, the pickup coils are also sensitive to its magnetization. As the “home” position of the linear motor was programmed such that it corresponded to a maximum response in the pickup coils from the sample, this problem was solved by placing the temperature sensor in a null response position above the sample (about 13 mm from the sample). Subsequent trials with no sample showed that, when the linear motor was oscillated about its home position and the temperature sensor was placed close to a null response position, the signal was negligible, relating to a magnetic response of $\sim 2 \times 10^{-3}$ emu.

A second problem highlighted in Figure 3.9 is that of flux creep in the superconducting magnet. When the set field in the superconducting magnet is changed, flux lines must redistribute themselves into a new equilibrium configuration. If a magnetized sample oscillates while this occurs, the motion of the flux lines is disturbed by the motion of the field originating from the sample, which induces a parasitic signal in the pickup coils. To overcome this problem, a wait time of approximately 60 s was included in the measurement routine. This significantly improved reproducibility of
Figure 3.10: Temperature dependent magnetization of an irradiated CuMn_{16.4\%} alloy sample labeled “2I2” in 100 Oe with solder on the sample rod. The solder contributes to the measurement below its superconducting critical temperature (approximately 7 K) in a manner which is cooling field dependent.

The measurements, as seen from the reduced scatter in Figure 3.9(b), which relates to a magnetic response of $\sim 2.5 \times 10^{-3}$ emu.

It was found that solder (tin 60\%, lead 40\%), which was used to connect the temperature sensor leads to the temperature sensor, shows a magnetic response akin to a Type-2 superconductor at low temperatures which is cooling field dependent. In this investigation, this was first observed as an unexpected “kick” in the cooling field dependent behaviour of samples of interest below the critical temperature of solder, that either decreased or increased with temperature depending on whether the sample was field cooled or not. Where possible, solder was replaced with silver bearing epoxy for connecting leads.

While operating under a low pressure helium atmosphere, the linear motor would occasionally trigger an arc between two of its connection terminals on the connection termination board, setting off an error condition in the servoamplifier, which
would stop the linear motor. Breakdown of gas at low pressures is well described by Paschen’s Law [26], which states that, generally, the electric field required to breakdown a gas decreases as the pressure of the gas decreases until, approximately, rough vacuum. To prevent this from happening, the linear motor was generally operated at a pressure above 0.1 bar, which was found to be safe. Additional care was taken to conceal as many connection terminals as possible from exposure to the helium atmosphere. It should be noted that, when the VTI and sample space are cooled to low temperature, the pressure in the head drops and therefore, needs to be sufficiently charged so that a safe pressure is always present in the head.

3.3 Sample preparation

3.3.1 Argon arcing and alloy sample preparation

An argon-arc furnace with a water cooled hearth and titanium getter was used to make alloy samples for this investigation. Samples were generally flipped and remelted three times to improve homogeneity.

Some alloy samples were cold worked, to create vacancies, and remelted in the arc in order to induce homogeneity. After repeating the process a number of times (usually three), the samples were cut and/or ground into defined shapes with known demagnetization factors (see section 1.5). As cutting samples perturbs the homogeneity of the distribution of the constituent elements throughout the alloy, the samples were sealed in evacuated quartz tubes and homogenized at temperatures close to their liquidus temperature, before being quenched in water. In the case of the NiMn and NiMnCu alloys reported in Chapter 8, quenching in water also followed the aging process.

3.3.2 High energy ball mill

A SPEX 8000 high energy mixer mill was used to mechanically mill and grind powder samples in this investigation. A tool steel vial was made, that contains the sample and balls under an argon atmosphere during milling. The hardness of the vial was measured at HRC 60 on the Rockwell scale. Either 316 stainless steel or 440 stainless
Figure 3.11: X-ray diffraction in Bragg-Brentano geometry. X-rays are emitted from an X-ray source and diffract from the sample. After scattering from the sample, constructive interference occurs at angles given by Bragg’s law. The sample holder sits on a rotating stage at an angle of $\theta$ with respect to the direction of the incoming radiation, while the detector sweeps a range of $2\theta$.

Steel were used for the balls. 440 stainless steel was generally preferred for the material of the balls because it is harder. To prevent metallic particles within the sample from congealing during the milling process, a buffer was occasionally included, such as NaCl or teflon powder. After milling, the sample was potted in low concentration by volume in Epofix, an epoxy resin, which was allowed to set in a defined shape. The magnetic properties of Epofix were measured at low temperature, and found to be negligible.

3.4 Structural characterization

3.4.1 X-ray diffraction

X-ray diffraction (XRD) in Bragg-Brentano mode (Figure 3.11) was used to characterize the crystal structure, lattice parameters and particle size distributions of samples prepared for this investigation. The instrument used for the crux of this work was a GBC MMA X-Ray diffractometer emitting CuKα radiation.
Information about short range order, strain effects and particle size distributions can be determined from diffuse scattering, which is scattering that doesn’t align with a Bragg peak. Decreasing the mean particle size results in an increase in the width of Bragg peaks. When the mean particle size is sub-micron, it may be approximated using the Scherrer equation [27]

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

(3.8)

where \( L \) is the mean linear dimension of the particles, \( \beta \) is the full-width half-maxima of the Bragg peak at \( \theta \), and \( K \) is the shape factor, which depends on the geometry of the particles, and is usually taken as 0.93 rad [27].

3.4.2 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to characterize the chemical composition and surface topology of alloy samples. The chemical composition at the sample’s surface can be determined from the number of electrons that are backscattered elastically from the surface. A JEOL 840A Electron Probe Microanalyzer scanning electron microscope was used to measure SEM images and compositions in this investigation, to a spatial resolution of approximately 1 micron.
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Chapter 4

Models

4.1 Introduction

Modeling of magnetic behaviour is widely used in research on magnetic systems in order to broaden the understanding of such systems within increasingly generalized frameworks, and examine properties of interest, such as transition temperatures, susceptibilities and exchange bias fields and their dependencies on the underlying driving mechanisms, structures and internal interactions [1–9]. Many of the commonly used models involve a minimization of energy of microscopic magnetic entities, such as domains and clusters, taking into account the external and internal fields, interactions among neighbouring entities, particularly at the interfaces, and the entity’s own magnetic moment and anisotropy. Such models vary widely in their complexity, and are all dependent on their own unique set of underpinning assumptions. The methods by which they are applied to real, experimental data must vary accordingly.

Several models are used to extract parameters of interest from the magnetic measurements reported in this thesis. The assumptions and derivations that underpin these models, as well as their ability to account for a range of observed phenomena, are examined and discussed in this chapter. To aid understanding of the measured magnetic behaviours of samples exhibiting exchange bias, several phenomenological models were developed during this project and are described in sections 4.4 and 4.5. The aim was to first describe the complex magnetic behaviour observed and then to relate model parameters to physical quantities.
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4.2 Temperature dependent magnetization

Temperature dependent measurements of magnetization are performed on magnetic systems in order to characterize transition or Curie temperatures in materials such as spin glasses, superparamagnets, ferromagnets and exchange bias composites. A Curie-Weiss law is often used to approximate the temperature dependence of magnetization measurements well above the transition temperature, when such systems behave as a paramagnet,

\[ M (T) = \frac{N_v \mu_{\text{eff}}^2 \mu_0 H}{3k_B (T - \Theta)} \]  

(4.1)

where \( N_v \) is the concentration of magnetic species per unit volume, \( \mu_{\text{eff}} \) is their effective moment and \( \Theta \) is the Weiss constant, which is related to the transition temperature. The magnetic species may either be isolated atomic spins or clusters, but in the following derivation, we consider single spins with no anisotropy for simplicity.
The origin of the Curie-Weiss law arises by considering the following expression for paramagnetism

\[ M(H) = N_v g_J j \mu_B \mathfrak{B} \left( \frac{g_J j \mu_B \mu_0 H}{k_B T} \right) \]  

(4.2)

where \( g_J \) is the Landé g-factor, \( j \) is the total angular momentum quantum number, \( \mu_B \) is the Bohr magneton and \( \mathfrak{B}(y) \) is the Brillouin function, with an argument of

\[ y = \frac{g_J j \mu_B \mu_0 H}{k_B T}. \]  

(4.3)

The effective atomic moment is written as

\[ \mu_{\text{atom}} = gJ \sqrt{j(j+1)} \mu_B. \]  

(4.4)

In the high temperature, low field limit, where \( g_J j \mu_B \mu_0 H \ll k_B T \), the Brillouin function may be approximated by a Taylor expansion

\[ \mathfrak{B}(y) \approx \frac{1}{3} y \left( \frac{2j+1}{2j} \right)^2 - \frac{1}{2j} \left( \frac{1}{2j} \right)^2 = y \frac{(j+1)}{3j} \]  

(4.5)

and, therefore, the temperature dependent magnetization becomes

\[ M(T) = \frac{N_v \mu^2_{\text{atom}} \mu_0 H}{3k_B T}. \]  

(4.6)

This model of paramagnetism does not account for interaction between magnetic species. In the simplest circumstances, interactions may be modeled using a molecular field. The expression for low field magnetization then becomes the Curie-Weiss Law in equation (4.1), in the high temperature regime.

This expression is used to estimate the effective atomic moment in some of the systems explored in this investigation, by taking the gradient of the inverse magnetization at high temperatures, where it becomes linear. The values of \( \mu_{\text{atom}} \) extracted using this equation are reasonable estimates, but the assumptions innate to the model, such as weak magnetic interactions which are treated as a molecular field and a linear magnetic response in low field, must be kept in mind. Furthermore, the assumption that the magnetic species is an atom in known concentration \( N_v \) is invalid for systems
like the classic superparamagnet, in which internally ferromagnetic clusters that are stable far above the blocking temperature are the magnetic species.

### 4.3 Kouvel model

In an experimental investigation of magnetic hysteresis loops in concentrated CuMn and AgMn spin glass alloys, Kouvel [5] proposed a simple model based on inhomogeneity consisting of regions of ferromagnetically aligned and antiferromagnetically aligned spins that interacted with each other, in order to account for the exotic behaviour observed in these systems, such as displacements of the loop along the field axis after cooling in a field, linear dependency at higher field and an increasing remanent magnetization with increasing cooling field. Determining that the observed magnetic behaviour could only be accounted for by considering an exchange anisotropy mechanism, Kouvel considered the hysteresis loops as the sum of a linear component and an asymmetrical component, and proposed that the area enclosed under the shift of the asymmetrical component is related to the unidirectional anisotropy energy within Mickeljohn and Bean’s model for exchange anisotropy [2, 3],

$$ J = \frac{H_{0}}{2} \int_{-H_{\text{max}}}^{0} (M + M_s) \, dH $$

where $M$ and $M_s$ are the magnetization and saturation magnetization after the linear component has been subtracted from the displaced loop. (A more sophisticated model.
for describing displaced hysteresis loops will be introduced in section 4.5.)

Kouvel expanded this model in a theoretical treatise [6], where he considered a system of interacting ferromagnetic and antiferromagnetic domains. By considering intra- and inter-domain interactions, and arguing that the exchange interactions within domains must be considerably stronger than the interactions between domains, he could treat the effective field on each domain as the sum of the applied field and a molecular field, and derived an angle-dependent energy expression for each domain in terms of the magnetization of the ferromagnetic domains, the uniaxial anisotropy energy per domain and the molecular field. The system has zero net magnetization in its ground state, but a non-zero net moment is introduced by cooling in a field (or “field cooling”). The properties of the system then depend strongly on the difference between the number of spin pairs that align across the domain boundary interfaces and the number of spin pairs that anti-align at the interfaces. Within this model, Kouvel accounted for hysteresis, hysteresis displacement, asymmetric reversal and a peak in the temperature dependent susceptibility.

4.4 Langevin model

4.4.1 Two component model

A simple, empirical model based on an approximation of non-interacting, monodisperse, superparamagnetic clusters against a paramagnetic background was developed to fit single branches of minor hysteresis loops:

\[ M(H) = M_r + \chi_{H\rightarrow H_{\text{max}}}H + N_v \mu_{\text{eff}} \mathcal{L} \left( \frac{\mu_{\text{eff}} \mu_0 (H - H_c)}{k_B T} \right) \]  

(4.8)

Following Kouvel’s method of splitting hysteresis loops into linear and asymmetric components [5], the first two terms describe the linear, paramagnetic background of the hysteresis loop that is typically observed at high fields. In this model, \( M_r \) is labeled the pseudo-remanent magnetization and \( \chi_{H\rightarrow H_{\text{max}}} \) is the high field susceptibility, which is taken as the gradient of \( M \propto H \) near the maximum field, \( H_{\text{max}} \). It is assumed that the susceptibility is equal at the positive and negative extreme fields,
M-H loop within Langevin model. (b) M-H loop after linear component is subtracted.

Figure 4.3: $M-H$ curve within the Langevin model showing the $M_r$, $H_c$ and $M_{st}$ parameters, given in equations (4.8) and (4.9).

which is approximately valid in most of the following measurements of spin glasses. The other component is proportional to the Langevin function $\mathcal{L}(y)$ (the classical or high-spin limit of the Brillouin function), and describes the magnetic non-linearity or “step”. A Langevin function is often used to model the magnetism of ensembles of monodisperse, superparamagnetic particles [4, 10–15]. $N_v$ is the cluster concentration, either in per unit volume or per unit mass, depending on the units of magnetization used, $\mu_{\text{eff}}$ is the effective cluster moment in Bohr magnetons ($\mu_B$) while $H_c$ is the pseudo-coercive field, which represents the shift in the hysteresis loop along the field axis.

The first two terms describing the paramagnetic background are referred to as the “linear component”, and the term containing $\mathcal{L}(y)$ the “Langevin component”. When the Langevin component is zero, the pseudo-remnant magnetization reduces to the remnant magnetization; similarly, when the linear component is zero, the pseudo-coercive field reduces to the coercive field.

The height of the non-linearity in magnetization, $2M_{st}$ can be described explicitly within this model by removing the linear component and taking the field to infinity,

$$M_{st} = N_v \mu_{\text{eff}}. \quad (4.9)$$
This value, sometimes referred to as the “step” magnetization [16, 17], is generally approximated using the remanent magnetization. The step magnetization is a parameter of great interest in this investigation.

Equation (4.8) is limited in the types of hysteresis loops it can describe. Its composition of symmetric functions renders it insufficient to fit loops exhibiting asymmetric reversal, and the implicit assumption of superparamagnetic clusters means that it is better suited for describing systems where non-interacting groups of spins rotate coherently with field, while maintaining a constant magnitude of moment. This means that it cannot be accurately fitted to loops in systems where domains play a prominent role in the reversal mechanisms, and sudden flipping of spins happens when these domains overcome the transition barrier. This model also says nothing about the origin of hysteresis loops shifts or the role of uniaxial and unidirectional anisotropy. To model this, the pseudo-coercive field is added to the argument of the Langevin component ad hoc.

4.4.2 Three component model

The above model is not suitable for describing hysteresis loops where the magnetization changes suddenly, as is the case for CuMn in high measuring fields, or at moderate temperatures well above 0 K, where the susceptibility has increased, but well below the glass temperature, where the effects of cluster anisotropy have all but disappeared [6] (refer to sections 6.3.2 and 6.3.3 for examples). Under these conditions, a third component, fitted as a step function, is introduced ad hoc to describe the region of the loop where the magnetization flips suddenly.

\[
M(H) = M_r + \chi_{H\rightarrow H_{\text{max}}} H + N_v \mu_{\text{eff}} L \left( \frac{\mu_{\text{eff}} \mu_0 (H - H_c)}{k_B T} \right) + \begin{cases} 
-M_F & \text{if } H < H_F \\
M_F & \text{if } H > H_F 
\end{cases}
\]

(4.10)

\(M_F\) and \(H_F\) are two new parameters describing the height of the transition and the field at which it is triggered respectively. As there are now seven free parameters, some of which may be interdependent, this model can only be used practically by fitting each component successively. The two parameters within the linear component, \(M_r\) and \(\chi_{H\rightarrow H_{\text{max}}} \) are extracted from fits to the high field portion of the loop, then
the entire linear component $M_r + \chi_{H \rightarrow H_{\text{max}}} H$ is subtracted from each data point. The value for the flipping field, $H_F$ is gauged from the peak in instantaneous susceptibility, and the flipping magnetization, $M_F$ is estimated by iteratively subtracting a step function with increasing magnetization until the remaining loop only exhibits a smooth change in susceptibility across $H_F$. The remaining parameters are fitted simultaneously using a Levenberg-Marquardt algorithm in Labview.

### 4.5 Monte Carlo simulations using a modified Stoner-Wohlfarth model

The Langevin model described above is unsuitable for fitting hysteresis loops that display significant asymmetric reversal, such as those observed in aged Cu$_{81.2}$Mn$_{18.8}$ alloy (see section 5.3.3). Asymmetric reversal is defined in general either as an asymmetry between the magnetization reversal mechanisms from positive to negative saturation and the reversal mechanisms in the other direction, or as an asymmetry of the magnetization curve with respect to the origin [18]. In CuMn, it typically takes the form of a sharp, high curvature transition on the positive side of the hysteresis step (which may be interpreted as due to stochastic domain wall motion), and a low curvature, gradual decrease in magnetization, signature of coherent domain rotation on the negative side of the step in loops [19]. Asymmetric reversal is generally explained by misalignment of local easy axes with respect to the field [20–25].

Monte Carlo simulations involving an ensemble of ellipsoid shaped, ferromagnetically aligned clusters that each have their own unique easy axis and each experience a molecular field due to exchange interactions with the local spin glass, are run to fit the non-linear component of hysteresis loops where noticeable asymmetric reversal is observed. As for the two and three component Langevin models, the linear component is fitted in the high field region to extract values for the $M_r$ and $\chi_{H \rightarrow H_{\text{max}}}$ parameters, and the linear component is then subtracted from the loop. $M_{st}$ is taken as the magnetization at the positive maximum field, and the non-linear component is normalized.
Figure 4.4: Labview was used to run Monte Carlo simulations because of the high-level functions available in its mathematics package. A single branch of a measured hysteresis loop is normalized and shown as a series with white data points in the XY graph, while a simulated $M-H$ branch is generated as red data points. The controllable parameters are adjusted until the simulation coincides with the experimental data, and the green “difference” line is optimized.

The simulations are run using an energy expression based on a modified Stoner-Wohlfarth model [1, 23, 26], involving the sum of a single cluster’s Zeeman energy, shape (uniaxial) anisotropy energy and exchange (unidirectional) anisotropy energy due to its interaction with the local spin glass:

$$E(\theta) = -\mu_{\text{eff}}\mu_0 H \cos \theta + KV \sin^2(\phi - \theta) - JV \cos(\alpha - \theta).$$ (4.11)

Here, $\theta$ is the angle between the applied field and the alignment of the cluster moment, $\mu_{\text{eff}}$ is the magnitude of the effective cluster moment, $K$ is the uniaxial cluster anisotropy energy per unit volume in J/m$^3$, $\phi$ gives the direction of the easy axis, $J$ is the total energy per unit volume of all exchange interactions between the cluster and the immediate, neighbouring spin glass moments in J/m$^3$ and $\alpha$ is the angle between the effective molecular field observed by the cluster due to the local spin glass and the applied field. The volume of the cluster, $V$, is approximated as

$$V \approx \frac{\mu_{\text{eff}}}{\mu_{\text{atom}}} X na^3$$ (4.12)

where $\mu_{\text{atom}}$ is the effective atomic moment of the magnetic species (estimated from equation (4.1)), $X$ is the concentration of magnetic species within the cluster, $a$ is...
Figure 4.5: Cluster energy as a function of $\theta$, as described by equation (4.11), for positive and negative fields, when $\phi$ and $\alpha$ align with the field. The exchange interaction parameter $J$ introduces an asymmetry such that the $\theta = 0^\circ$ state is much more favourable in positive field than the $\theta = 180^\circ$ state is in negative field. As was the case in Figure 1.2, the uniaxial anisotropy energy $KV$ acts as a barrier between the $\theta = 0^\circ$ and $\theta = 180^\circ$ states.

The lattice parameter and $n$ is the number of atoms per unit cell, which is 1 in simple cubic (SC) lattices, 2 in body-centered cubic (BCC) lattices, and 4 in face-centered cubic (FCC) lattices.

The probability of a certain alignment of $\theta$ is given by a Boltzmann distribution over all angles between $0^\circ$ and $180^\circ$

$$p(\theta) = \frac{e^{-\frac{E(\theta)}{kBT}}}{\sum_{\theta=0^\circ}^{180^\circ} e^{-\frac{E(\theta)}{kBT}}}. \quad (4.13)$$

$N$ simulations are run to generate a value of magnetization for a given field. A random number is generated which corresponds with an orientation of $\theta$ within the above probability distribution. The resultant value of normalized magnetization is
(a) Paramagnetic distribution in low field.  
(b) Paramagnetic distribution in high field.

**Figure 4.6:** Simulated paramagnetic distribution of the alignment of an ensemble of spins with respect to the field (blue dots) fitted to a Gaussian distribution with a peak at 0° (red line). The fit shows reasonable agreement at both high and low fields.

Then taken as the sum of the projections of the simulated values for \( \theta \) on the measuring axis (which, in this investigation, is aligned with the field axis)

\[
\frac{M'(H)}{M_{st}} = \frac{1}{N} \sum_{i} \cos \theta_i
\]  

(4.14)

where \( M'(H) \) is the magnetization after the linear component has been subtracted.

There are seven important parameters in this model: \( \mu_{\text{eff}}, V, K, \phi, J, \alpha \) and \( T \), the temperature, which is taken as the temperature at which the hysteresis loop was measured, using a sensor placed adjacent to the sample (see section 3.2.4). Assumptions about each parameter differ from sample to sample, and will be discussed in their relevant sections, however, one particular assumption is discussed here.

In order to account for asymmetric reversal, \( \phi \) must be allowed to deviate from the direction of the cooling field. Many of the samples reported in subsequent chapters display asymmetric reversal which depends strongly on the cooling field. It has been proposed that this implies a system that has a number of local, energetically stable configurations that become frozen as the sample is cooled in constant field through its transition temperature [27].
Such systems are considered in this model in terms of the distribution of $\phi$ for a given cooling field. If the magnetic correlations in such a system are low-dimensional and disordered, as is the case for micromagnetic $\text{CuMn}$ [28], then the easy axes of such entities must be dependent on both the direction and intensity of the cooling field, because it is energetically favourable for them to be so. Two alternative models for the distribution of easy axes were considered, the first involving a step function, in which orientations for which $\phi < \phi_{\text{max}}$ are forbidden. This model was applied to a handful of hysteresis loops reported in subsequent sections, but reasonable fits could not be achieved. A second model involved a paramagnetic distribution of easy axes with respect to the cooling field. Figure 4.6 shows that simulated paramagnetic distributions can be approximated using Gaussian distributions. Further simulations (not shown) confirmed the validity of this approximation for all tested cases. A Gaussian distribution for easy axes, with a mean value of 0° and normalized probability over 180°, was adopted here for simplicity. This model has been used with success here to account for much of the data to which it has been applied. The parameter $\phi$ then becomes $\phi_{\text{std dev}}$, the standard deviation of the distribution. If $\phi_{\text{std dev}} = \infty$, the alignment of easy axes is random between 0° and 180°, if $\phi_{\text{std dev}} = 0$, only alignment with the cooling field is allowed.

Given the large number of interdependent variables within this model, physically reasonable values can only be extracted if assumptions are made about one or more of the parameters, owing to correlations between parameters. $M_r$, $\chi_{H \rightarrow H_{\text{max}}}$ and $M_{\text{st}}$ are extracted first using fitting algorithms, leaving the normalized, non-linear component of the loop. The other parameters are adjusted manually, one at a time, until the simulated loop coincides with the processed data, and the difference between the real and simulated data sets are minimized.

Figure 4.7 shows the dependence of simulated $M$-$H$ loops on the parameters $\mu_{\text{eff}}$, $J$, $K$ and $\phi_{\text{std dev}}$. Increasing the effective cluster size increases the curvature of the loop around the step, while increasing $J$ shifts the loop along the field axis in the negative direction. Increasing $K$ while pinning the cluster easy axis to align with the field also has the effect of increasing the curvature of the loop, but once the variable reaches appreciable values, of the order of $1 \times 10^5 \text{ J/m}^3$, the model becomes relatively insensitive to even large changes in $K$. However, once $\phi$ is allowed to deviate from
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(a) Effects of changing $\mu_{\text{eff}}$.

(b) Effects of changing $J$.

(c) Effects of changing $K$ with $\phi_{\text{stdev}} = 0^\circ$.

(d) Effects of changing $K$ with $\phi_{\text{stdev}} = 30^\circ$.

Figure 4.7: Simulated $M$-$H$ curves, demonstrating the effect of adjusting each parameter in the Monte Carlo model. Comparing (c) and (d) shows the effect of adjusting $\phi_{\text{stdev}}$.

the field axis, changes in $K$ have a drastic effect on the asymmetry of the simulated loops.

$\phi_{\text{stdev}}$ has its greatest effect on the magnetic behaviour on the negative side of the step. By moving the peak of the energy barrier due to uniaxial anisotropy away from the $\theta = 0^\circ$ state, the $\theta = 180^\circ$ state becomes less energetically favourable. To give a simplistic, qualitative description of the mechanism, in order to undergo the transition from the $\theta = 0^\circ$ to the $\theta = 180^\circ$ state during the “down” branch of a hysteresis loop, as the field decreases from the positive extreme to the negative extreme, a cluster
Figure 4.8: Simulated temperature dependent magnetization in low field illustrating the effects of using large and small values of $J$ and $K$. In this regime, the resultant magnetization is most sensitive to the $J$ parameter.

will align with $\theta = 0$ and then with $\theta = \phi$, which is a low susceptibility transition if $\theta - \phi$ is small and $\cos \theta \approx \cos \phi$. Once the field becomes sufficiently negative so that $\theta = \phi$ and $\theta = 180^\circ$ become energetically comparable, the cluster still must overcome the energy barrier due to uniaxial anisotropy to make the transition. The higher the energy barrier, the slower this transition will be with respect to field (hence, a decrease in curvature). The distribution of easy axis orientations requires that this transition will happen at a distribution of fields. This accounts for the low curvature on the negative side of the step, while the fact that the distribution centres around $\phi = 0$ being the most popular orientation for easy axis explains why the curvature is high on the positive side of the step: these clusters do not pass through the $\theta = \phi$ state because they occupy it to begin with.

Simulated runs of temperature dependent magnetization were performed in low field,
in a temperature range of interest in this investigation (Figure 4.8). While the simulated values for \( \frac{M'}{M_{st}} \) showed an approximately \( T^{-1} \) dependence, a peak in susceptibility reminiscent of spin glass and superparamagnetic systems was not observed, demonstrating a shortcoming in the model. The model is not sophisticated enough to describe the critical behaviour that takes place at \( T_g \), which in a number of ways resembles a magnetic phase transition in the spin glass itself [29–33]. In this model, only the interaction between clusters and the spin glass component are considered. Low field values have a considerable sensitivity to the parameter \( J \), which makes sense physically, as exchange anisotropy only becomes observable in magnetic behaviour in the presence of a cooling field, and the field cooled branch always has a greater magnetization than the zero field cooled branch.

It is recognized that some of the assumptions that drive this model are tenuous. No system in this investigation consists of an ensemble of monodisperse coherent clusters and a distribution of clusters would more accurately reflect reality. Similarly, \( X \) is unknown for some samples, and values have either been estimated or taken from the literature. As the cluster volume depends on \( X \), and \( J \) and \( K \) scale with \( V \), this means that the uniaxial energy and exchange interaction energy can only be treated as relative values. Both the cluster size distribution and \( X \) can be determined experimentally from techniques such as small angle neutron scattering [28, 34].

Some of the parameters, particularly \( \mu_{eff} \), \( K \) and \( \phi_{\text{stdev}} \), are highly interdependent, and in some cases different combinations of them can result in reasonable fits to the same data set. In order to extract physical trends that depend on the experimental conditions of interest, different assumptions are made depending on the sample that, at times, are not physically justified. These assumptions will be discussed in detail in their relevant sections.

Finally, there exists an implicit duality regarding the definition of “cluster” within this model: firstly as a region that contains a higher concentration of magnetic impurities than the system average, and secondly as a system of spins whose configurations are correlated. The first describes an entity which cannot be cooling field dependent, but is instead dependent on preparations methods such as aging [19, 34–36] and irradiation [37–39]. The second, however, is field dependent, particularly in systems where the correlations are low-dimensional, and different correlations become energetically
favourable in different conditions. Small-angle neutron studies in CuMn have shown that magnetic clustering and chemical clustering are separate phenomena \[28, 40\]. This duality makes it simple to build a rigid physical construct around something which is metastable and disordered, and it also highlights one of the intrinsic shortcomings of this model.
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Chapter 5

Magnetic properties of aged high concentration CuMn alloy

5.1 Introduction

The magnetic behaviour of concentrated, “mictomagnetic” CuMn alloys at temperatures well below the glass temperature, $T_g$, has been a topic of interest among researchers for several decades [1–5]. Much of the behaviour observed in magnetic hysteresis loops at low temperatures are analogous to behaviour observed in exchange bias systems, such as displaced hysteresis loops owing to field cooling [2], asymmetric reversal mechanisms [6, 7], and field dependent unidirectional anisotropy [2, 8, 9]. This analogue was shown explicitly in a recent experimental paper on a thin film system consisting of an interface between a ferromagnetic cobalt layer and a low concentration CuMn spin glass layer [10].

Kouvel first proposed a model to account for unidirectional anisotropy in CuMn, consisting of ferromagnetically (FM) and antiferromagnetically (AFM) aligned domains that interact at the interfaces [3]. Subsequent understanding developed in terms of clusters that had giant magnetic moments [6] in the presence of a so-called “infinite” cluster, which is blocked at low temperatures [11], with interactions taking place through an indirect exchange mechanism. The strong dependence of the magnetism of CuMn alloys on preparation techniques such as aging [6, 12] and irradiation [13]
was explained by atomic short range ordering processes, which lead to an increase in ferromagnetic correlations within finite clusters [14]. The topology of finite clusters in CuMn has also been probed by small angle scattering techniques [15, 16], which suggest that such clusters are low-dimensional and ramified and contain about 100 - 200 Mn atoms in zero field.

In this chapter, behaviour normally associated with exchange bias systems consisting of FM-AFM interfaces [17, 18], such as displaced hysteresis loops and asymmetric reversal, is explored in micromagnetic CuMn. The magnetic properties of an 18.8 at.% CuMn alloy sample are shown to be strongly dependent on cooling field at temperatures well below the glass temperature. Monte Carlo simulations run using a modified Stoner-Wohlfarth model (section 4.5) are successfully able to account for much of the observed behaviour at low temperatures.

### 5.2 Experimental method

The dependence of the magnetic properties of an alloy sample of 18.8 at.% CuMn on cooling field, was investigated within a range of temperatures between 5 K and 315 K. The alloy was prepared by argon arc melting copper (99.99+% rod) and manganese (99.98+% flake) at a nominal concentration of 20 at.% Mn. The sample was cold worked in a mechanical press between two copper sheets, and remelted in the arc. This process was repeated three times before the sample was machined and ground into a 10 mm diameter, 3 mm thick disc. After being sealed in an evacuated quartz tube, the sample was homogenized at 850°C for two hours before quenching in water at room temperature. The sample was then aged in an oven at 75°C for six days, removed in order to perform measurements of temperature dependent magnetic susceptibility, before being replaced in the oven until the aging time reached a total of 62 days. An aging temperature of 75°C was chosen in light of a study suggesting that a relatively low aging temperature, of the order of 100°C, is optimal for increasing the low-field susceptibility of CuMn by thermal treatment [13]. The crystal structure of the aged sample was confirmed with a GBC MMA X-Ray diffractometer (XRD) in Bragg-Brentano geometry using CuKα radiation. The composition was checked with a
JEOL 840A Electron Probe Microanalyzer scanning electron microscope (SEM) and, through analysis of backscattered electrons, was found to be Cu$_{81.2}$Mn$_{18.8}$.

Measurements of magnetization were performed using the vibrating sample magnetometer (VSM) described in section 3.2. Temperature dependent magnetization was measured in three branches, zero-field cooled (ZFC), field cooled (FC) and thermoremanent magnetization (TRM), between 5 K and 310 K in fields of 100 Oe, 1000 Oe and 6000 Oe. $M-H$ hysteresis loops were measured at a set of temperatures between 5 K and 315 K after cooling in various fields between zero and 8 kOe from 220 K, ie, well above the measured glass temperature in order to reset any memory effects in the spin glass. Several minor loops were measured consecutively in fields between ±6 kOe, ±50 kOe and ±75 kOe, and other, variable maximum fields, in order to examine any training effects. Most results reported in this chapter pertain to the loops measured between ±6 kOe. Not all hysteresis loops measured in this investigation are displayed here, but Monte Carlo modeling on these loops, following the method outlined in section 4.5, as well as qualitative descriptions of their behaviour, will be presented. All displayed loops have been corrected for demagnetizing fields, as outlined in section 1.5.

5.3 Results

5.3.1 Structural characterization from XRD and SEM

An X-ray diffraction (XRD) pattern from aged Cu$_{81.2}$Mn$_{18.8}$ alloy was collected between a range of 20° and 100° 2θ at a wavelength of 1.54 Å. An FCC structure with a lattice parameter of 3.69 ± 0.03 Å was fitted to the pattern using Rietveld refinement. This is comparable with a previous investigation, where a 3.66 Å lattice parameter was observed for a Cu$_{82.5}$Mn$_{17.5}$ alloy sample [1].

Backscattered images of the sample’s surface generated via scanning electron microscopy (SEM) were used to quantify the alloy composition. Trace amounts of nickel (0.04 at.%) and silicon (0.10 at.%) were observed, most likely introduced through grinding during the sample preparation process. A manganese concentration of 18.84 ± 0.15 at.% was given using a Standard Quantitative Analysis method.
Figure 5.1: Lab source XRD pattern of aged Cu$_{81.2}$Mn$_{18.8}$ alloy taken in Bragg Brentano mode using CuK$\alpha$ radiation ($\lambda = 1.54$ Å). Diffraction shows a FCC structure with a lattice parameter of 3.69 Å.

Using the composition determined from SEM backscattered images and the lattice parameter measured from XRD, a X-ray crystal density of $8.178\pm0.07$ g/cm$^3$ was calculated (which is a slight overestimate owing to the unavoidable presence of defects, vacancies and vacancy clusters).

### 5.3.2 Temperature dependent magnetization

Figure 5.2 shows the ZFC, FC and TRM branches for Cu$_{81.2}$Mn$_{18.8}$ alloy, measured after aging at 75°C for six days and 62 days. Measurements in a field of 100 Oe show that the low field susceptibility has increased by a factor of 2.2 over this aging time, with the peak magnetization in the respective ZFC branches increasing from $0.057\pm0.001$ emu/g to $0.128\pm0.001$ emu/g. The glass temperature (determined from the peak in $M(T)$ in the ZFC branch) has also increased slightly, from $83.59\pm0.18$ K after six days of aging to $85.67\pm0.08$ K after 62 days.
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Figure 5.2: Temperature dependent magnetization of Cu$_{81.3}$Mn$_{18.8}$ alloy measured after aging at 75°C for six days and 62 days in 100 Oe, 1000 Oe and 6000 Oe. Aging causes the low field susceptibility to increase by a factor of 2.2, while the glass temperature increases from 83.59 ± 0.18 K after six days of aging to 85.67 ± 0.13 K after 62 days.

The sample was also measured in 1000 Oe after aging for 62 days (Figure 5.2(c)). A peak magnetization of 1.101 ± 0.005 emu/g is seen at a temperature of 83.21 ± 0.13 K in the ZFC branch. Peak broadening is observed when compared with measurements at smaller fields, while the peak susceptibility has decreased, typical for spin glass systems [19]. This effect becomes more extreme in 6000 Oe, where the peak in temperature has decreased to 59.52 ± 0.20 K, and the peak magnetization has increased to 4.53 ± 0.02 emu/g.
Figure 5.3: Minor hysteresis loops of aged Cu$_{81.2}$Mn$_{18.8}$ alloy measured at 5 K between ±6 kOe after cooling in various low fields, specified above, where an approximately linear response is observed.

5.3.3 Minor hysteresis loops at 5 K

Minor $M$-$H$ loops for Cu$_{81.2}$Mn$_{18.8}$, aged for 62 days, were measured between ±6 kOe at 5 K after cooling in various fields. For a cooling field, $H_{FC}$, of 167 Oe, or below, loops measured between ±6 kOe show an approximately linear (resembling paramagnetic) response. For the ZFC curve, shown in Figure 5.3(a), the sample exhibits a linear susceptibility of $2.16 \times 10^{-4}$ emu.g$^{-1}$.Oe$^{-1}$. Coercive fields of $-162$ Oe and $-14$ Oe are observed on the “down” ($H_{c\downarrow}$) and “up” ($H_{c\uparrow}$) branches respectively, resulting in a small exchange bias field ($H_{EB}$) of $-88$ Oe. As the cooling field increases,
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Figure 5.4: Minor hysteresis loops of aged Cu$_{81.2}$Mn$_{18.8}$ alloy measured at 5 K between ±6 kOe after cooling in various fields, specified above, where non-linearity and coercivity begin to develop in the negative quadrant. Asymmetric reversal also develops.

\( H_{\downarrow} \), \( H_{\uparrow} \) and \( H_{EB} \) all increase in magnitude, while the linear susceptibility decreases very slightly. This results in an imbalance between the values of magnetization measured at \( H = 6000 \) Oe and \( H = -6000 \) Oe and, by extension, an increase in the remanent magnetization, \( M_r \). A small amount of non-linearity is noticeable in the negative quadrant of loops measured after non-zero cooling fields.

This non-linearity becomes much more apparent as the cooling field is increased to 200 Oe. The “up” branch of the \( M-H \) loop displayed in Figure 5.4(a) shows a jump in susceptibility at approximately \(-3400 \) Oe, which is preceded by a visible departure
from the path followed by the “down” branch, which itself exhibits minor non-linearity at larger negative fields. This hysteretic effect increases for $H_{FC} = 250$ Oe. The non-linearity is referred to as a “step” magnetization ($M_{st}$), which was defined in section 4.4.1 and equation (4.9). This step appears to be asymmetric: on the positive side of the transition, the curvature is sharp, suggesting a spin-flip event accompanied by domain wall motion, while on the negative side of the transition, the curvature is smoother, suggesting coherent domain rotation. As the cooling field increases, the magnitude of the step also becomes larger, while the field that it occurs at decreases in magnitude. While the loop measured after $H_{FC} = 450$ Oe shows an enhanced coercivity (as defined by the difference between coercive fields), in actuality, both the width and area of the hysteresis loop have decreased. The linear susceptibility at high, positive fields continues to decrease slightly with cooling field, while the asymmetry on either side of the step has become more pronounced. The imbalance between $M(H = 6$ kOe) and $M(H = -6$ kOe) decreases until $H_{FC} = 750$ Oe, where it becomes insignificant.

In Figure 5.5, the step continues to increase in magnitude as the cooling field is increased and, above cooling fields of 1000 Oe, it becomes the dominant feature of the hysteresis loops. The curvature on either side of the step increases, significantly so on the negative side, resulting in a decrease in asymmetry, which is also accompanied by a decrease in coercive and exchange fields, as well as hysteresis.

Differential susceptibility as a function of field, $dM/dH$, for the “up” branches of some of the above hysteresis loops is shown in Figure 5.6(a). A few noteworthy trends become apparent from the differential susceptibility. The peaks in susceptibility represent the step magnetization, which increases in sharpness as the cooling field increases. The fields at which the step occurs also decrease in magnitude with the cooling field, as do the breadth of the peaks in susceptibility. All displayed peaks show a similar, asymmetrical shape: on the positive side of the step, the susceptibility changes rapidly, while it decays with smoother curvature on the negative side. While the differential susceptibility for “down” branches is not displayed here, it exhibits the same asymmetry. There is some hysteresis induced by moderate cooling fields ($200 \lesssim H_{FC} \lesssim 1000$ Oe), but the asymmetry itself remains relatively independent of path, suggesting that its origin lies in a frozen component of magnetization created
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Figure 5.5: Minor hysteresis loops of aged Cu$_{81.2}$Mn$_{18.8}$ alloy measured at 5 K between ±6 kOe after cooling in various larger fields, specified above. The coercivity and asymmetric reversal begins to become suppressed, but the magnitude of the step increases significantly.

During field cooling, minimal training effect was measured at 5 K between ±6 kOe for this sample, suggesting that, during the experiments described above, the maximum measuring fields were insufficient to disturb any frozen spin configurations.

The high field susceptibility ($\chi_{H\rightarrow H_{\text{max}}}$) shown in Figure 5.6(b) was taken as the gradient towards the positive maximum measuring field of the above hysteresis loops. From ZFC to $H_{\text{FC}} = 6000$ Oe, the high field susceptibility decays monotonically by approximately 12%, but increases for $H_{\text{FC}} = 8000$ Oe. The linear or paramagnetic
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(a) Differential susceptibility.  
(b) High field susceptibility.

**Figure 5.6:** (a) Differential susceptibility for the “up” branches of minor loops at 5 K after cooling in various fields, highlighting the asymmetry of the step. (b) High field susceptibility for minor loops measured at 5 K between ±6 kOe, graphed as a function of cooling field.

The component present in all of the above hysteresis loops is attributed to a component of single spins and small clusters which interact only weakly with the rest of the sample. The decrease in high field susceptibility suggests that some quantity of these small clusters have left the paramagnetic component. The subsequent increase at $H_{FC} = 8000$ Oe can only be sensibly interpreted in the context of the increase of the step magnetization at the same cooling field (Figure 5.8(b)), and, as such, is understood as an unfreezing of a fraction of spins that were blocked at lower cooling fields.

The coercive field at 5 K depends linearly on the cooling field until $H_{FC} = 450$ Oe. For larger cooling fields, the coercive field decreases in magnitude as $H_{FC}$ is increased. There is little observed hysteresis about $M = 0$ (ie, coercivity), except for loops where $H_{FC}$ is of the order of 450 to 1000 Oe. Interestingly, $H_c$ doesn’t decay to zero for the observed loops, with an exchange bias shift persisting up to $H_{FC} = 8000$ Oe.

The imbalance between the two values of magnetization at the extremes of a given loop at 5 K, as a function of cooling field, is displayed in Figure 5.8(a). This value, defined as the difference between $M(H = 6000 \text{ Oe})$ and the magnitude of $M(H = -6000 \text{ Oe})$ as a fraction of $M(H = 6000 \text{ Oe})$ for a single loop, increases rapidly and linearly with
Figure 5.7: Coercive field for the “down” branches of minor hysteresis loops measured at 5 K between ±6 kOe, graphed as a function of cooling field.

Figure 5.8: (a) Imbalance between $M(H = 6000 \text{ Oe})$ and $M(H = -6000 \text{ Oe})$ as a fraction of $M(H = 6000 \text{ Oe})$, for loops measured at 5 K between ±6 kOe. (b) Remanent magnetization, $M(H = -6000 \text{ Oe})$ and step magnetization graphed as a function of cooling field for loops measured at 5 K between ±6 kOe. The step magnetization follows a Langevin-type function above $H_{FC} \approx 200 \text{ Oe}$, and is comparable with $M(H)$ at $T_g$. 
low cooling fields, up to $H_{FC} = 167$ Oe, before falling off to an insignificant value after $H_{FC} \geq 750$ Oe.

Figure 5.8(b) shows both the step magnetization and $M_r$ as a function of cooling field, as well as the magnetization at the positive maximum field, $M(H = 6000$ Oe), at 5 K. The three curves run approximately parallel, demonstrating that, on the scale of the observed magnetization in the measured hysteresis loops, the contribution to the magnetic behaviour from the paramagnetic component varies only slightly. While faint non-linearity becomes noticeable in loops measured after cooling in fields as low as 50 Oe (Figure 5.3(b)), the size of that step is negligible on the scale shown in Figure 5.8, until $H_{FC} \geq 200$ Oe. For higher cooling fields, there is very little difference between $M_{st}$ and $M_r$.

A comparison between the cooling field dependence of these three parameters and $M v H$ measured at the glass temperature shows that the quantities are similar, and the latter is slightly larger, by 22% at 6 kOe.

$M-H$ loops that exhibited significant imbalance were remeasured, with the negative maximum field extended until the magnetization either balanced or exceeded the magnetization measured at the positive maximum. A subset of these loops is shown in Figure 5.9. Many of the same behaviours are observed here, with non-linearity developing in the negative quadrant after cooling in small-to-moderate fields, which develops into strong asymmetry at larger cooling fields.

For $M-H$ loops that showed paramagnetic behaviour, the negative maximum field increased in magnitude with cooling field. This negative maximum field value peaked at $H_{FC} = 200$ Oe, which coincided with the development of apparent non-linearity. The value reduces in magnitude for a cooling field range of $750 \leq H_{FC} \leq 3000$ Oe, indicating an approximately balanced loop, but increases again upon $H_{FC} \geq 6000$ Oe.

Given the imbalance of the $M-H$ loops reported above, coercivity is not a good indicator of the hysteresis loop width. Non-linearity tends to develop in the negative quadrant, for negative values of magnetization. The loop width, taken as the greatest difference in field in the “down” and “up” branches that result in the same magnetization, is displayed as a function of cooling field in Figure 5.10(b). The loop width, which is indicative of hysteretic behaviour, peaks about $H_{FC} = 250$ Oe. For lower
cooling fields, the sample behaves as a paramagnet, while, for much higher cooling fields, strongly bistable behaviour is observed, and in both these cases there is little hysteresis.

As reported above, for $M-H$ loops with balanced maximum fields, only faint non-linearity was observed when $H_{FC} \leq 200$ Oe. To help understand the apparent upward “shift” in loops for small but increasing values of cooling field, the possibility that a step may appear in the unbalanced loops beyond the originally measured negative
Figure 5.10: (a) The maximum negative field in $M-H$ loops where the negative maximum was extended until the largest negative magnetization either balanced or exceeded the largest positive magnetization, as a function of cooling field. (b) The width of the same loops at their widest point. Errors displayed in both graphs were estimated from the field step size on the “down” loop at the points of measurement, as determined by Smartloop (see Appendix A).

maximum field, that increased in magnetization but decreased in magnitude of field with $H_{FC}$, was considered. The field for which the step occurs, $H_{st}$ is approximated as the field at which the differential susceptibility peaks in a given loop branch in Figure 5.11. A noticeable step did not appear in extended loops at low cooling fields, and there was little difference in the general behaviour, dependent on cooling field, between loops with balanced and imbalanced maximum fields.

Once a step becomes apparent ($H_{FC} \geq 200$ Oe), the step field decreases with cooling field, and the step field for the “up” branch is greater than that for the “down” branch. Values for the step field displayed for low cooling fields, in the paramagnetic regime, are only indicative (as indicated by the large error), as they are extracted from a parameterization of non-linearity, which struggles with data that are nearly linear.

5.3.4 Minor hysteresis loops at other temperatures

The general dependence on cooling field at 10 K is very similar to the behaviour described above for 5 K. Up to a cooling field of 130 Oe, a linear relationship is
observed between magnetization and field for minor loops between ±6 kOe, and the loops appear to “shift” upwards as the cooling field increases, displaced by an amount that depends linearly on $H_{FC}$. As the cooling field increases to 200 Oe, non-linearity begins to form in the negative quadrant, which develops into bistability, exhibiting the same asymmetric step which has significantly higher curvature on the positive side of the step than on the negative side, independent of whether the loop is on an “up” or “down” branch. This asymmetry relaxes as the cooling field approaches the same order as the positive maximum field of the measured loops.

Training becomes noticeable at 25 K, after being absent in loops measured at lower temperatures. Each training iteration appears to activate higher degrees of non-linearity about the step on both paths of each loop, and the effect is observably stronger on the “down” path. Exchange bias and coercivity decrease slightly with each training iteration. All loops measured at 25 K show noticeable coercivity and
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Figure 5.12: Minor hysteresis loops of aged Cu_{81.2}Mn_{18.8} alloy measured at 10 K between ±6 kOe after cooling in various fields. Small coercivity is already present upon ZFC, and noticeable non-linearity develops at $H_{FC} = 250$ Oe. A step is noticeable for $H_{FC} = 6000$ Oe.

Hysteresis, and the magnetization measured at the maximum positive field, $M(H = 6000$ Oe), shows only slight dependence on $H_{FC}$ for low to moderate cooling fields.

The initial loop shown in Figure 5.13(d), measured at 25 K after $H_{FC} = 6000$ Oe does not close when the field returns to the positive maximum. The first iteration is also significantly unbalanced at the extremes, with an imbalance value (defined in section 5.3.3) of 0.083, and the magnetization at each maximum continues to decrease slightly in magnitude after successive loops.
Figure 5.13: Minor hysteresis loops of aged Cu$_{81.2}$Mn$_{18.8}$ alloy measured at 25 K between ±6 kOe after cooling in various fields. Successive loop iterations show a training effect: the non-linearity and curvature of the step tend to increase with each cycle. Note that, for $H_{FC} \geq 6000$ Oe, the first loop does not close.

The particularly exotic magnetic behaviour at 25 K may be accounted for by considering components of magnetization frozen at lower temperatures, and thus, only passively influencing magnetic behaviour, freeing up and becoming susceptible to sufficiently high fields at 25 K, which is a significant fraction of $T_g$.

If the frozen, highly frustrated configuration created by moderate cooling fields and responsible for the exchange bias and asymmetric reversal at very low temperatures begins to unfreeze at a higher temperature, one can imagine high fields aligning this
component. Successive training iterations may then have a similar effect to slight increases in the cooling field, which, as shown in section 5.3.3, results in enhanced non-linearity, step magnetization and asymmetric reversal, but decreases in coercivity and exchange bias.

Then, the imbalance in the values of $M(\pm H_{\text{max}})$ with $H_{\text{FC}} = 6000$ Oe, and the subsequent decrease in $M(H_{\text{max}})$ with each iteration could be accounted for by the opposite happening. Here, the sample exists in a regime where $H_{\text{FC}} \geq H_{\text{max}}$, and the “frozen” component may be disordered by the negative maximum field, rather than being ordered by the positive maximum field, as happens when $H_{\text{FC}} < H_{\text{max}}$. This explains the decrease in $M(H = \pm 6000$ Oe), but it fails to account for the consistent decrease in exchange bias and coercivity after each loop. Given the minimal amount of training along the step in the “up” branch, it is possible that $H_{c_{\downarrow}}$ is decreased by small amounts of increasing aligning or unblocking of spins in the paramagnetic component at the positive maximum field that are completely reversible by negative maximum fields.

Loops measured at higher temperatures are shown in Figure 5.14, and no longer demonstrate training, asymmetry or a significant dependence on cooling field. Coercivity persists at 50 K, but disappears at higher temperatures. At temperatures well above $T_g$, the magnetization decreases and only paramagnetic behaviour is observed within the bounds of the measured minor loops.

Figure 5.15(a) shows that the exchange bias field consistently peaks around $H_{\text{FC}} \approx 450$ Oe for low $T \leq 25$ K. For loops measured at higher temperatures, $H_{\text{EB}}$ decays to zero, becoming independent of cooling field.

$M(H = 6000$ Oe) increases slightly between 5 K and 10 K for measured loops at all cooling fields, as does the step magnetization (Figure 5.16(a)). $M(H = 6000$ Oe) still shows an increasing dependence on cooling field up to 25 K, but behaves as a constant with varying $H_{\text{FC}}$ at higher temperatures. This confirms the view that the magnetic behaviour is independent of cooling field at and above $T_g$, where the magnetization is completely reversible. The behaviour with respect to temperature resembles a ZFC branch for low cooling field, and a FC branch for $H_{\text{FC}} = 6000$ Oe.
The Monte Carlo model described in section 4.5 was used to simulate minor $M-H$ loops measured at 5 K, after cooling fields of 250 Oe and greater (loops measured after lower cooling fields display insufficient non-linearity for this model to be applicable), in order to extract values for the parameters $\mu_{\text{eff}}$, the average cluster moment, $K$, the uniaxial cluster shape anisotropy energy per unit volume, $J$, the exchange interaction energy per unit volume and $\phi$, the angle between cluster easy axes and the field. A Gaussian distribution of easy axes was assumed, centred around a peak at $\phi = 0$, with
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Figure 5.15: (a) Exchange bias field as a function of cooling field at various temperatures. (b) Exchange bias field dependent on temperature after cooling in various fields.

Figure 5.16: (a) Step magnetization and $M(H = 6000 \text{ Oe})$ vs $H_{\text{FC}}$. (b) $M(H = 6000 \text{ Oe})$ vs $T$. The displayed dependencies closely follow the FC and ZFC branches in 6000 Oe for high and low values of cooling field respectively.
a standard deviation of $\phi_{\text{stdev}}$. For simplicity, it was assumed that the clusters are ferromagnetic in alignment and interact only with the spin glass but not with each other. The spin glass was modeled as quasi-isotropic by allowing the angle between the applied field and the molecular field felt by the cluster owing to the surrounding spin glass, $\alpha$ to take random orientations between $\alpha = 0^\circ$ and $\alpha = 180^\circ$. As the observed exchange bias fields are negative, positive values for $J$ were assumed.

The volume occupied by a cluster was estimated using equation (4.12), using the lattice parameter of 3.691 Å, determined from XRD (see section 5.3.1). No experimental techniques are available for directly determining the concentration of Mn within a cluster, $X$, and as such, a value of 0.25 was assumed, which is based on theoretical predictions [20] and calculations from neutron experiments [15, 21] for comparable, slightly lower concentrations of CuMn. The Mn atomic moment was assumed to be 4.2 $\mu_B$, in close agreement with the value of 4.19 $\mu_B$ extracted from the temperature dependent magnetization in the region where the inverse magnetization is linear.

With the assumptions made above, $\mu_{\text{eff}}$, $K$, $J$ and $\phi_{\text{stdev}}$ become the parameters of interest. Due to the high interdependency between the $\mu_{\text{eff}}$, $K$ and $\phi_{\text{stdev}}$ parameters, it is possible to arrive at a fitted loop from different combinations of parameters, and, as such, further assumptions are required. The “up” branch of each loop was first fitted four times, with the following assumed values for parameters: $\mu_{\text{eff}} = 579.5$ $\mu_B$ for the first simulation, $\mu_{\text{eff}} = 2000$ $\mu_B$ for the second, $K = 0.65 \times 10^6$ $J/m^3$ for the third and $K = 2.7 \times 10^6$ $J/m^3$ for the fourth. A final fit was performed using starting values extracted from the first four fits, and fitted parameters $\mu_{\text{eff}}$, $KV$, $JV$ and $\phi_{\text{stdev}}$ with no assumptions made about the dependencies of these parameters on cooling field, or about $X$ or $V$. The goodness of fit was quantified using coefficient of determination $R^2$ values, which were typically in the range of 0.994 to 0.999.

The resultant parameters for the first two runs, where $\mu_{\text{eff}}$ was treated as a constant with respect to cooling field, are shown in Figure 5.17. $K$ increases quickly at lower cooling fields, before saturating to an approximately constant value after $H_{\text{FC}} \approx 3000$ Oe, and is significantly larger for the smaller value of $\mu_{\text{eff}}$. $J$ decreases as a power law (straight line on a log-log graph), approximately following $H_{\text{FC}}^{-0.78}$. The breadth of the distribution of easy axes decreases with $H_{\text{FC}}$, indicating that the cooling field has an effect on the alignment of clusters, pulling them increasingly towards the direction
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Figure 5.17: $K$, $J$, $\phi_{\text{std}}$, and $N_v$ as a function of cooling field for two sets of Monte Carlo model fits on loops measured at 5 K and after cooling fields between 250 and 8000 Oe. $\mu_{\text{eff}}$ is set constant at 579.5 $\mu_B$ for the first set of fits and 2000 $\mu_B$ for the second set of fits.

of the field. The cluster concentration, $N_v$, calculated using equation (4.9), increases proportionally with $M_{\text{st}}$ (Figure 5.8(b)), as $\mu_{\text{eff}}$ is constant.

In general, $\mu_{\text{eff}} = 579.5$ $\mu_B$ resulted in better fits for loops measured after cooling in low to moderate fields, between 250 and 450 Oe, while $\mu_{\text{eff}} = 2000$ $\mu_B$ resulted in better fits for higher cooling fields, $H_{\text{FC}} \geq 750$ Oe. Two subsequent runs were performed, setting $K$ as a quantity independent of cooling field. The two values of $K$ used were taken from $K(H_{\text{FC}} = 3000$ Oe) for the previous two runs, where $K$ starts to saturate.
Figure 5.18: $\mu_{\text{eff}}$, $J$, $\phi_{\text{stdev}}$ and $N_v$ as functions of cooling field for two sets of Monte Carlo model fits on loops measured at 5 K and after cooling in fields between 250 and 8000 Oe. As opposed to the parameters displayed in Figure 5.17, this time $K$ is set constant, with $K = 0.65 \times 10^6 \text{ J/m}^3$ for the first run and $K = 2.7 \times 10^6 \text{ J/m}^3$ for the second.

Figure 5.18(b) shows that, when $K$ is treated as a constant with respect to cooling field, and $\mu_{\text{eff}}$ is allowed to vary freely, the two resultant parameter dependencies for $J$ on $H_{\text{FC}}$ superimpose. This is interpreted as $J$ dissociating from $K$, and essentially showing only a dependence on the cooling field. There is insufficient evidence to assess whether this is a physically realistic scenario. It is plausible, but could be an artifact of the model, in that the coercive field is determined by a combination of both the exchange interaction energy and the distribution of cluster easy axes, and that the latter has a more extreme influence on the magnetic behaviour if the uniaxial
anisotropy energy is large (Figure 4.7(d)). If $K$ is moderate, or $\phi_{\text{stddev}}$ changes only slightly, then the value of $H_{EB}$ is predominantly driven by changes in $J$.

While the dependence of $J$ on $H_{FC}$ makes no clear statement on the physical validity of $K$ being independent of cooling field for the values tested, the behaviour of $\phi_{\text{stddev}}$ (Figure 5.18(c)) and $N_v$ (Figure 5.18(d)) may be interpreted as evidence against it. $\phi_{\text{stddev}}$ peaks about $H_{FC} \approx 450$ Oe, before decreasing with large cooling fields, again an indication that large cooling fields act to align the easy axes of clusters with the field. However, the tendency for easy axes to align at low cooling fields cannot be accounted for without considering some driving mechanism that acts to align them, which is only apparent at low cooling fields. It would be more reasonable to suppose that $K$ must depend on cooling field in some manner, similar to that observed in Figure 5.18(a) for constant values of $\mu_{\text{eff}}$. The model also isn’t strongly sensitive to $\mu_{\text{eff}}$ for small changes in $H_{FC}$ for the values of $K$ tested, resulting in variations for $N_v$ with $H_{FC}$ that aren’t monotonic.

The resultant parameters for the final run are shown in Figure 5.19. The effective cluster moment appears to increase monotonically with cooling field, displaying a dependency similar to that of $M_{st}$ on $H_{FC}$ at 5 K. $KV$, the uniaxial anisotropy energy per cluster, increases quickly at lower cooling fields, before saturating to an approximately constant value after cooling with $H_{FC} \geq 1000$ Oe. $JV$, the exchange anisotropy energy per cluster, decreases as a power law, approximately following $H_{FC}^{-0.21}$. The distribution of easy axes again narrows at higher values of $H_{FC}$.

5.5 Discussion

Minor $M$-$H$ loops measured on the aged Cu$_{81.2}$Mn$_{18.8}$ alloy between $\pm 6$ kOe at 5 K and 10 K, well below $T_g$, exhibit a remarkable sensitivity to $H_{FC}$, with the sample displaying behaviours that range from paramagnetic to ferromagnetic over the span of applied cooling fields. In the paramagnetic regime, where the cooling field is low, the loop is displaced by an amount that depends linearly on $H_{FC}$. At $H_{FC} \approx 200$ Oe, a non-linearity or “step” develops in the negative quadrant, which increases in magnetization and differential susceptibility, but decreases in magnitude of field at which it triggers, with $H_{FC}$. These observations are explained by considering the
magnetic entities within the sample in terms of two interacting components, the first consisting of an ensemble of large, coherent clusters that are ferromagnetically aligned, and the second consisting of a quasi-isotropic spin system that resembles a ZFC spin glass [22] that becomes frozen when the sample is cooled through $T_g$ [23], the so-called “infinite cluster” [11, 14]. This spin glass component is frozen at low temperatures. It has been proposed that, generally, sensitivity of magnetic behaviour to the intensity of cooling field is due to the presence of a magnetically disordered phase that has a
number of local, energetically stable configurations that are established by the cooling field, and that become frozen below the transition temperature [24]. This picture is qualitatively consistent with the present results, as will be discussed below.

The two components interact with each other via an indirect exchange mechanism, which is responsible for stabilizing the ferromagnetic component as the system is cycled around a hysteresis loop until \( H = H_{\text{st}} \). The monotonic increase in \( M_{\text{st}} \) with \( H_{\text{FC}} \) must be considered either in terms of the average size of the ferromagnetic clusters increasing, or their concentration increasing, or both. If the spin glass component appears magnetically randomized, it must have a considerably smaller susceptibility than the ferromagnetic component. If ferromagnetic clusters either grow or nucleate with \( H_{\text{FC}} \), then one may suppose they do so at the expense of the spin glass. Since the configuration of the spin glass freezes due to magnetic frustration, and moderate cooling fields have the effect of partially aligning spins at \( T_g \), ferromagnetic correlations created at \( T_g \) by the cooling field presumably persist below \( T_g \). In other words, the cooling field has the effect of increasing the ferromagnetic component by creating ferromagnetic correlations that are less likely to be frustrated at low temperatures, and depleting the spin glass component.

This depletion of the spin glass component can also account for the decrease in \( H_{\text{EB}} \) with \( H_{\text{FC}} \). A disordered magnetic component, akin to a spin glass component, has the effect of stabilizing the ferromagnetic component due to an exchange interaction [25–28]. The fact that it’s “frozen” explains why hysteresis is only observed at low to moderate cooling fields, where \( H_{\text{FC}} \ll H_{\text{max}} \), and the positive maximum field is more likely to influence and align the spin glass configuration. The small amount of training observed in low temperature \( M-H \) loops (especially compared with the irradiated CuMn sample investigated in Chapter 6) suggests that whatever small changes have been made to the spin glass configuration by the negative maximum field have essentially been reversed by the positive maximum field.

While the cooling field acts to create a net magnetization at the glass temperature, only a fraction of this results in ferromagnetic correlations that persist below the glass temperature, as observed in Figure 5.8(b). The effect is considerably weaker here than it is in the irradiated 16.4% alloy, where \( M_{\text{st}} (H_{\text{FC}}) \) at 5 K follows \( M (H) \) near the glass temperature more closely (see section 6.4.1). This suggests that clusters form
much more readily in the irradiated sample than they do in the aged Cu$_{81.2}$Mn$_{18.8}$ alloy, even despite the significant aging time and higher Mn concentration.

A considerable amount of asymmetric reversal is observed in non-linear hysteresis loops (Figures 5.4 and 5.5). This is understood in terms of a distribution of alignments of cluster easy axes within the ferromagnetic component, and fits using Monte Carlo simulations based on a modified Stoner-Wohlfarth model in section 5.4, where Gaussian-distributed easy axes are used, support this viewpoint. The asymmetric reversal paths are attributed to the spin glass component freezing with a configuration that favours positive magnetization in the ferromagnetic branch over negative magnetization on both the “up” and “down” hysteresis branches.

Similar behaviour is often observed in exchange bias systems [29–34], and is understood in terms of competition between uniaxial and unidirectional anisotropy energy. Asymmetric reversal has been observed in CuMn alloys well below $T_g$, both directly from hysteresis loops [2, 7, 22] and, more distinctly, in field-dependent measurements of AC susceptibility [8], where behaviour similar to that displayed in Figure 5.6(a) was observed in Cu$_{91.75}$Mn$_{8.25}$. Generally, lower concentrations of CuMn produce squarer hysteresis loops at $T \ll T_g$ [2, 8, 35]. To the author’s knowledge, only Kouvel and coworkers [2, 5] have investigated the dependence on cooling field of this particular concentration of CuMn at temperatures well below the glass temperature. Kouvel’s sample was quenched from 800°C, but not aged, and the asymmetric reversal was not as apparent as it is here. A highly concentrated Cu$_{75}$Mn$_{25}$ sample studied by Mukhopadhyay and Beck [6] showed a comparable extent of asymmetric reversal to the present sample after aging at 100°C for three weeks.

Two sets of assumptions were tested using the model proposed above, the first involving constant values of effective cluster moment with respect to cooling field, and the second involving constant values for cluster (uniaxial) anisotropy energy. Both assumptions were shown to be simplistic, the first due to the fact that the lower value for effective cluster moment, $\mu_{\text{eff}} = 579.5 \mu_B$ couldn’t produce good fits for high cooling field loops. This value for $\mu_{\text{eff}}$ is based on a ZFC finite cluster size close to that calculated from small angle neutron scattering (SANS) data for an aged Cu$_{83.3}$Mn$_{16.7}$ alloy [15], and assuming a proposed Cu$_3$Mn cluster phase, which has yet to be directly observed [20, 21]. The fact that this value is evidently too small to account for high
cooling field hysteresis loops within this model may be interpreted as evidence that the effective cluster moment depends on and grows with cooling field. However, it is also possible that the interdependence between $\mu_{\text{eff}}$ and $K$ leads to an overestimate of the effective cluster moment. For simplicity, the model relies on an assumption of a single value for the cluster moment, but a distribution would be more physically realistic, which also undermines the validity of the $\mu_{\text{eff}}$ parameter. A way to resolve this would be to probe the average effective cluster moment and cluster distribution with a technique such as SANS, dependent on the cooling field and the magnetic state along the hysteresis loop.

The second set of assumptions, based on a constant cluster anisotropy energy with cooling field, was dismissed on the basis that the resulting dependencies of easy axis distribution and effective cluster moment on cooling field appeared unphysical, although this could be due to the model’s relative insensitivity to $K$ at very large values of $K$. Schwink and coworkers have argued in several papers that both the uniaxial anisotropy energy [36, 37] and unidirectional anisotropy energy [7] are field dependent values based on measurements of multi-stepped hysteresis loops in CuMn after successively increasing the magnitude of the maximum negative measuring field after each training iteration [9, 22]. Increasing the magnitude of the negative maximum field did not result in multi-stepped hysteresis loops, or even single stepped loops for low cooling field loops at low temperatures in this investigation, but it seems plausible that single steps would have been observed had the negative maximum field been increased in magnitude further, which would account for the apparent upward “shift” in low cooling field loops. Varying the cooling field is a more explicit method for probing the relationship between anisotropy and field in CuMn systems, as both methods result in a partial aligning of the spin glass component. Application of a cooling field aligns the spin glass above $T_g$, where the susceptibility of the spin glass component is much higher, while increasing the maximum negative field does so below $T_g$. The training effect observed in the present data at 25 K, where the spin glass component is much more susceptible to high field, also supports the viewpoint that the unidirectional anisotropy depends on both the measuring field and cooling field, and is extremely sensitive to the configuration of the spin glass.

In the data sets displayed here, the values for $K$ and $J$ are extremely high, and
$K$ in particular is comparable with high anisotropy materials such as SmCo$_5$ [38], which has a crystal anisotropy of roughly $1\times10^7$ J/m$^3$. Within the model used, $J$ and $K$ are both scaled by $V$, which is underpinned by assumptions about the cluster phase and topology and the atomic manganese moment. As such, $V$ is most likely underestimated in this model, and $K$ and $J$ are overestimated.

The tendency to local ferromagnetic coupling arises in correlated atomic and magnetic short range order [39, 40]. At the length scale of a cluster containing thousands of atoms, there is no evidence to prove that the Mn concentration is the global average or the theoretical value of the predicted ordered solid. The truth probably lies between these schemes and furthermore, high fields may substantially change the spin alignments. Fits using parameters $KV$ and $JV$ avoid the need to assume or guess a value for $X$, and are therefore felt to be much more satisfactory.

Parameters extracted from a final set of fits are displayed in Figure 5.19, in which no assumptions were made except that the parameters should approximate those generated by the more physically plausible scenarios that resulted from the earlier sets. $KV$, the uniaxial anisotropy energy per cluster and $JV$, the exchange interaction energy per cluster, are used here instead of $K$ and $J$ because the former quantities are independent of any assumptions made about the composition and topology of clusters, as expressed in equation (4.12), particularly the concentration of magnetic entities, $X$. The assumption of a single value for $X$ is used for convenience in the prior simulations, but is simplistic for a number of reasons, the most pertinent of which is that it implies a tightly packed, homogeneously ordered agglomeration of spins, but small angle neutron analysis of magnetic clusters in CuMn suggest that they are strongly diffuse and ramified [15, 16], and likely contain an inhomogeneous distribution of atomic moments.

The resulting dependencies for $\mu_{\text{eff}}$, $JV$ and $\phi_{\text{stdev}}$ on cooling field appear to be physically plausible and can all be qualitatively accounted for. $\mu_{\text{eff}}$ increases like a Langevin function with cooling field, while $N_v$ (not shown here) increases in a similar manner. Much like the behaviour of $H_{\text{EB}}$, the decrease in $JV$ may be accounted for by the depletion and alignment of the spin glass component, while the rapid decrease of $\phi_{\text{stdev}}$ to moderate $H_{\text{FC}}$ may be seen as the cooling field dragging the alignment of cluster easy axis to align with the field.
The dependency of $KV$ on $H_{FC}$ is not as intuitive, given that it saturates in moderate cooling field, while $\mu_{\text{eff}}$ continues to grow at higher cooling field values. Two alternative explanations are offered. The first is that it is due to the model’s relative insensitivity to $K$ at very large values of $K$. The second is that, due to the ramified nature of magnetic clusters in CuMn [15], cluster shape anisotropy energy saturates at a certain cluster size.

5.6 Conclusion

At 5 K, well below $T_g$, the magnetism of aged Cu$_{81.2}$Mn$_{18.8}$ alloy is strongly dependent on the cooling field, demonstrating a paramagnetic dependence on field for $H_{FC} \lesssim 200$ Oe, ferromagnetic bistability for $H_{FC} \gtrsim 1000$ Oe and mixed behaviour in between, with marked asymmetric reversal. The magnetism was explained in terms of two interacting components, one consisting of ferromagnetically aligned clusters, and the other consisting of a quasi-isotropic configuration of spins, resembling a ZFC spin glass. $M_{st}$ increases monotonically with cooling field, which is interpreted as ferromagnetic clusters evolving in volume and/or concentration. Similarly, the decrease in high field susceptibility up to $H_{FC} = 6000$ Oe is interpreted as a depletion of the spin glass component, while the increase at $H_{FC} = 8000$ Oe is attributed to the cooling field starting to align the spin glass component.

The occurrence of an exchange bias field in all low temperature hysteresis loops with a non-zero cooling field is clear evidence for a unidirectional anisotropy mechanism, which was successfully modeled using an exchange interaction between an ensemble of monodisperse, ferromagnetic clusters and a randomly orientated spin glass. The parameter representing this exchange interaction, $J$, showed a $H_{FC}^{-0.78}$ dependence on cooling field at 5 K. The model was modified to account for the observed asymmetric reversal. Asymmetric reversal was accounted for by ascribing to all clusters a uniaxial anisotropy energy due to cluster shape, and allowing the easy axes of this anisotropy to deviate from the field with a Gaussian distribution. Two main assumptions were tested within this model; firstly, that the cluster moment is independent of cooling field and, secondly, that the uniaxial anisotropy energy is independent of cooling field. Neither assumption could account for all observed behaviour in hysteresis loops across
the range of cooling fields to which they were applied, but $\mu_{\text{eff}} = 579.5 \, \mu_B$ resulted in a better account of low cooling field loops, and $\mu_{\text{eff}} = 2000 \, \mu_B$ yielded better fits to loops measured after cooling in a high field. A final set of fits in which all parameters were allowed to vary freely resulted in $\mu_{\text{eff}}$ and $N_v$ exhibiting a Langevin-like dependency on $H_{\text{FC}}$, while $J V$, showed a $H_{\text{FC}}^{-0.21}$ dependence. This strongly suggests that the effective cluster moment in aged Cu$_{81.2}$Mn$_{18.8}$ alloy is dependent on both the measuring field and cooling field.

It is therefore of interest to experimentally investigate the dependence of cluster moment in aged Cu$_{81.2}$Mn$_{18.8}$ alloy on cooling field using a technique such as SANS. Once the dependence of cluster moment on cooling field is known, it could be implemented into Monte Carlo simulations, which could be used to determine the cooling field dependencies of $K$, $J$ and $\phi_{\text{stddev}}$. 
Chapter 5 References


Chapter 6

Field cooling dependence of neutron irradiated CuMn alloy

6.1 Introduction

Atomic short range order (SRO) in CuMn alloys can be drastically modified through aging [1–5], leading to the growth of magnetic clusters when the temperature is less than the characteristic glass temperature ($T_g$), which play a significant role in the low temperature magnetism. Gray [6] demonstrated in a CuMn alloy sample with 16.4 at.% Mn concentration that the SRO process may be driven to equilibrium through neutron irradiation of the alloy, leading to an observed magnetic susceptibility over 20 times greater than the as-quenched value at the glass temperature. He attributed this to the neutron irradiation acting as a continuous supply of vacancies, which drives the ordering process through vacancy migration. Subsequent studies by Cussen and coworkers [7, 8] showed that neutron irradiation induces the onset of long range order in CuMn at a slightly higher concentration.

In this chapter, a study of the low temperature magnetic properties of a sample of Cu$_{83.6}$Mn$_{16.4}$ alloy exposed to the neutron irradiation process described in reference [6] is reported, with a particular focus on the cooling field dependence of minor hysteresis loops at 5 K. Three models of increasing complexity are applied to the data, which each result in scenarios for the dependencies of the effective cluster moment, cluster
concentration, uniaxial (shape) anisotropy and unidirectional (exchange) anisotropy on cooling field. These scenarios are then considered in terms of their physical plausibility.

6.2 Experimental method

In this series of experiments, the dependence on cooling field of the magnetization of a sample of Cu$_{83.6}$Mn$_{16.4}$ alloy that had previously been exposed to neutron irradiation was investigated. The sample was prepared by Gray for a previous investigation [6], and was labeled “2I2”. 2I2 was cut from an ingot made from 99.999% copper and 99.98% manganese arc melted together under argon, and homogenized at 850°C in an evacuated, sealed quartz tube before being quenched in an ice-water slurry. After aging in air at 100°C for 10 days, 2I2 was exposed for 89 hours to a fast-neutron flux of $3.6 \times 10^{12}$ neutrons.cm$^{-2}$.s$^{-1}$ in Rig X-33 at HIFAR, the old reactor of the Australian Nuclear Science and Technology Organisation.

Measurements of magnetization were performed using the vibrating sample magnetometer (VSM) described in section 3.2. Measurements of the temperature dependent magnetization between 4 K and 310 K in 100 Oe and 6000 Oe were used to determine the glass temperature, which agreed with Gray’s previously reported value. $M-H$ hysteresis loops were measured at a set of temperatures between 5 K and 315 K after cooling in various fields between $\pm 8$ kOe from 220 K, ie, well above the glass temperature in order to reset any memory effects in the spin glass. Several minor loops were measured consecutively in fields between $\pm 6$ kOe, $\pm 50$ kOe and $\pm 75$ kOe, in order to examine any training effects. The number of recorded data points was decreased with each loop iteration. Most results reported in this chapter pertain to the loops measured between $\pm 6$ kOe. Not all hysteresis loops measured in this investigation are displayed here, but modeling of these loops, following the methods outlined in sections 4.4 and 4.5, as well as qualitative descriptions of their behaviour, will be discussed. All displayed loops have been corrected for demagnetizing fields.
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6.3 Results

6.3.1 Temperature dependent magnetization

Figure 6.1(a) shows the ZFC, FC and TRM branches for sample 2I2 measured with a 100 Oe applied field. A glass temperature \( T_g \) of 81.57 ± 0.24 K was extracted from the average of the peak magnetization temperatures of the ZFC branch and FC branches (which agree to within the resolution of the instrument). The peak magnetization in 100 Oe is 0.808 ± 0.01 emu/g.

The temperature dependent magnetic properties of 2I2 in 100 Oe can be directly compared with those of aged Cu\(_{81.2}\)Mn\(_{18.8}\) in the same conditions, as reported in section 5.3.2. The peak susceptibility of 2I2 is considerably larger than that of aged Cu\(_{81.2}\)Mn\(_{18.8}\), by a factor of 6.3, showing the dramatic effect irradiation has on the magnetic response of CuMn [6]. However, \( T_g \) is slightly larger for the aged Cu\(_{81.2}\)Mn\(_{18.8}\) sample (85.67 K, compared with 81.57 K for the irradiated sample) demonstrating that composition plays a more important role in determining the glass temperature than aging [4].

As was the case for aged Cu\(_{81.2}\)Mn\(_{18.8}\) alloy, peak broadening and decreased susceptibility are observed when the sample is measured in larger cooling fields. The peak
magnetization for 2I2 in 6 kOe is $10.426 \pm 0.008$ emu/g, reached at $43.31 \pm 0.03$ K, which is more than double the magnetization of aged Cu$_{81.2}$Mn$_{18.8}$ alloy under the same conditions. Values of $\mu_{\text{atom}} = 4.89 \, \mu_B$ and $\Theta = 186.1$ K were extracted from the ZFC branch using equation (4.1). The small negative magnetization around $T_g$ in the TRM branch is attributed to a negative remanent field in the superconducting magnet after the cooling field was removed.

### 6.3.2 Minor hysteresis loops at 5 K

The magnetic behaviour of sample 2I2 can be vastly altered depending on cooling field ($H_{\text{FC}}$). Figure 6.2 shows the variation in behaviour between ±6 kOe at 5 K after cooling in fields from zero to 133 Oe. The magnetization depends approximately linearly on field after cooling in zero field, suggesting that paramagnetism is the dominant mechanism, and that the interaction between free spins is relatively weak. It is noted that, even after cooling in zero field, hysteresis is apparent between the two branches, which wasn’t the case for aged Cu$_{81.2}$Mn$_{18.8}$ alloy (section 5.3.3). This is consistent with a small amount of non-linearity at the extremes of the loop.

When a small cooling field of 50 Oe is applied (Figure 6.2(b)), noticeable non-linearity begins to develop in the negative quadrant of the $M$-$H$ loop. The coercive fields for the “down” ($H_{c\downarrow}$) and “up” ($H_{c\uparrow}$) branches are both non-zero and negative. The coercive fields continue to increase in magnitude when $H_{\text{FC}} = 90$ Oe, and a training effect in iterative loops becomes apparent (Figure 6.2(c)). The behaviour in the positive field quadrant still resembles that of a paramagnetic system, but the non-linearity in negative fields appears as a “step” magnetization (section 4.4.1). The curvature of the step increases with each loop iteration, while the step field, ie, the field at which the step occurs, decreases in magnitude. A similar behaviour is observed for loops where $H_{\text{FC}} = 133$ Oe but the curvature has increased again and the height of the step magnetization is much larger.

The onset of asymmetric reversal also appears on either side of the step. The curvature on the positive side of the step is sharp, which is reminiscent of sudden, stochastic domain wall motion [9, 10], while the curvature on the negative side of the step is much smoother, suggesting coherent domain rotation. Asymmetric reversal was also
Figure 6.2: Minor hysteresis loops measured between ±6 kOe at 5 K after cooling in (a) zero field, (b) 50 Oe, (c) 90 Oe and (d) 133 Oe. Insets in (c) and (d) highlight the changes in the loop paths due to training in iterative loops. The lines display a fit using the two component Langevin model (section 4.4.1).

observed in aged Cu$_{81.2}$Mn$_{18.8}$ alloy, as reported in section 5.3.3, but not for such low values of cooling field.

Figure 6.3(a) displays the effect of increasing the cooling field to 250 Oe. The step becomes sharper and more well defined, becoming the dominant feature of the hysteresis loop. The relatively large height of the step is indicative of bistability, which continues to increase with cooling field. Asymmetric reversal becomes more apparent for loops with cooling fields between $\sim$ 250 Oe and $\sim$ 1000 Oe, however the extent of
(a) $T = 5\ \text{K},\ H_{FC} = 250\ \text{Oe}$.

(b) $T = 5\ \text{K},\ H_{FC} = 1000\ \text{Oe}$.

(c) $T = 5\ \text{K},\ H_{FC} = 3000\ \text{Oe}$.

(d) $T = 5\ \text{K},\ H_{FC} = 6000\ \text{Oe}$.

**Figure 6.3:** Minor hysteresis loops measured between $\pm 6\ \text{kOe}$ at 5 K after cooling in (a) 250 Oe, (b) 1000 Oe, (c) 3000 Oe and (d) 6000 Oe.

the effect isn’t as extreme as it was for aged Cu$_{81.2}$Mn$_{18.8}$. The effect disappears in 212 at about $H_{FC} = 3000\ \text{Oe}$, but persists in the aged sample up to $H_{FC} = 8000\ \text{Oe}$, which was the highest cooling field investigated.

The loops displayed in Figure 6.3(c) and 6.3(d), where the cooling field is at least 3000 Oe, show little to no asymmetric reversal; in fact, when $H_{FC} = 6000\ \text{Oe}$, the curvature entering and exiting the transition is comparatively smooth, evidencing coherent domain rotation as a significant magnetization reversal mechanism under these conditions. In each case, the coercive field decreases as the cooling field increases,
while the amplitude of the step increases. Training effects and hysteresis become negligible above cooling fields of about 500 Oe.

Hysteresis loops of sample 2I2 at 5 K measured after applying negative cooling fields (ie, the cooling fields point in the opposite direction to the first measuring fields in the hysteresis loops) are displayed in Figure 6.4. Loops measured after cooling in moderate to high fields, where training effects are negligible, are essentially equal and opposite to loops measured in equivalent positive fields, and display many of the same features, such as asymmetric reversal, shifted hysteresis and bistability. Successive
Figure 6.5: Minor hysteresis loops measured between at 5 K between maximum fields of (a) ±50 kOe and (b) ±75 kOe. Insets show the original branch and first two hysteresis loops to demonstrate a slight training effect. The lines display a fit using the three-component model discussed in section 4.4.2.

Loop iterations have a training effect on the sample after cooling in −90 Oe, but this effect isn’t as pronounced as it was when the sample was cooled in the analogous positive field. This suggests that the training effect is induced by the application of either a large positive or negative measuring field, but the effects due to either maximum field on the spin glass configuration are unbalanced.

The sample was measured at 5 K between fields of ±50 kOe and ±75 kOe (or ±5 T and ±7.5 T) after cooling in zero field (shown in Figure 6.5). Even at these extreme fields, the magnetization has not fully saturated. The initial branch, starting from zero field, changes smoothly up to the positive maximum field, however once the system enters its first hysteresis loop, it retains a significant positive magnetization until it reaches its coercive field, at which point it very quickly flips to a large negative magnetization. With each training iteration, the curvature of the loops increases slightly, and the “down” branches always have more positive magnetization than the “up” branches at a given field. There exists a small, non-zero coercive field for each branch. The coercive fields for the first iteration of the ±75 kOe hysteresis loop, determined from a fit to the three component Langevin model (section 4.4.2) were measured as −142 ± 150 Oe and −429 ± 421 Oe for the “down” and “up” branches respectively. At ±75 kOe, the magnetization of 2I2 is 21.7 ± 0.1 emu/g.
6.3.3 Minor hysteresis loops at other temperatures

The first ZFC loop measured at 10 K shows low curvature (as seen in Figure 6.6(a)), but significantly more coercivity than the loop measured at 5 K under the same conditions. Training is already noticeable in subsequent loops, even without a cooling field, and the curvature of the step increases with each iteration. The coercive fields of both the “down” and “up” branches decrease in magnitude with each iteration, while the magnetization at the maximum measuring field increases slightly with each.
cycle. When $H_{FC} = 50$ Oe, the loop again shifts in the negative field direction, and subsequent loop iterations again see the curvature around the step increase, while the coercivity decreases. The same is evident of loops measured after $H_{FC} = 90$ Oe, and the magnetization at the negative maximum measuring field also increases in magnitude with each iteration (Figure 6.6(c)). The “down” branch of the first loop shows only slight curvature, but each subsequent branch displays steps that are significantly more pronounced. The increase in magnetization of each branch in the positive quadrant after successive loops is also noteworthy, and is a feature which is observable for all cooling fields at 10 K that display training. Asymmetric reversal is also a feature of loops at 10 K for cooling fields between 90 Oe and 1000 Oe, but, again, the effect is not as striking as it was for aged Cu$_{81.2}$Mn$_{18.8}$ alloy (see section 5.3.4). However, the cooling fields required to induce the effect in 212 are significantly lower.

Bistability becomes apparent in the loops measured at 10 K after $H_{FC} = 450$ Oe. Both $|H_c^\downarrow|$ and $|H_c^\uparrow|$, as well as coercivity ($H_c^\uparrow - H_c^\downarrow$) decrease as the cooling field is increased to 6000 Oe. The magnitude of the step magnetization also increases with cooling field. Training becomes insignificant when $H_{FC} \gtrsim 1000$ Oe, and while hysteresis disappears within the step, it manifests in the paramagnetic component in the positive quadrant when $H_{FC} = 6000$ Oe.

Hysteresis loops recorded at various temperatures between 25 K and 150 K after cooling in 90 Oe are displayed in Figure 6.8. $H_{FC} = 90$ Oe is significant, as this is the cooling field which has tended to result in the most apparent demonstrations of training and enhanced coercivity in this investigation. The dependence of magnetic behaviour on cooling field is significantly suppressed at 25 K and negligible above $\sim 50$ K. Training is still apparent in loops at 25 K, reducing coercivity with each iteration. Unlike loops measured between $\pm 6$ kOe at lower temperatures, the observed behaviour at 25 K is not well described by the two component Langevin model (section 4.4.1).

At 50 K, bistability is suppressed, and the sample mostly follows a reversible, paramagnetic path. A small amount of irreversibility persists at very low fields, and there exists a small, but non-zero coercivity. This disappears at 75 K, as the sample follows a reversible path on both branches of the loop. Values for $M(H_{max})$ of
Figure 6.7: Minor hysteresis loops measured between ±6 kOe at 10 K after cooling in (a) 250 Oe, (b) 750 Oe, (c) 3000 Oe and (d) 6000 Oe.

10.11 ± 0.10 emu/g, 10.42 ± 0.12 emu/g and 10.22 ± 0.08 emu/g are observed at 25 K, 50 K and 75 K respectively, showing very little change in this temperature range, and a slight increase between 25 K and 50 K. These values are consistent with temperature dependent magnetization measurements made in 6 kOe, as shown in Figure 6.1(b).

Figure 6.9 displays $H_{c\downarrow}$ and $H_{c\uparrow}$ for the first three hysteresis loops measured at 5 K and 10 K, as functions of cooling field. Both $H_{c\downarrow}$ and $H_{c\uparrow}$ tend to decrease in magnitude with each iteration, although the effect is stronger in the “down” branches. At 5 K, $H_{c\downarrow}$ is greatest in magnitude in loops where $H_{FC} = 133$ Oe, peaking at a value of $-1457$ Oe in the first loop, while $H_{c\uparrow}$ peaks at $-1138$ Oe in the first loop when
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(a) $T = 25 \text{ K}, H_{FC} = 90 \text{ Oe}$.

(b) $T = 50 \text{ K}, H_{FC} = 90 \text{ Oe}$.

(c) $T = 75 \text{ K}, H_{FC} = 90 \text{ Oe}$.

(d) $T = 150 \text{ K}, H_{FC} = 90 \text{ Oe}$.

**Figure 6.8:** Minor hysteresis loops measured between $\pm 6 \text{ kOe}$ at various temperatures after cooling in $90 \text{ Oe}$. The inset in (a) shows a fit of three consecutive hysteresis loops to the model discussed in section 4.4.2.

$H_{FC} = 100 \text{ Oe}$. The coercivity is generally larger at 10 K, but the magnitude of values for $H_{c\downarrow}$ have decreased compared with loops at 5 K. In the first loop, $H_{c\downarrow}$ is greatest in magnitude when $H_{FC} = 100 \text{ Oe}$, at a value of $-1246 \text{ Oe}$. $H_{c\uparrow}$ is most negative for the first loop when $H_{FC} = 133 \text{ Oe}$, but remains relatively steady for all loops between $100 \lesssim H_{FC} \lesssim 450 \text{ Oe}$. At very high cooling field values, both at 5 K and 10 K, hysteresis and training are suppressed, and both coercive fields converge and asymptote to a small negative field.

At both 5 K and 10 K, the exchange bias field ($H_{EB}$) of each first hysteresis loop shows
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Figure 6.9: $H_{c\downarrow}$ and $H_{c\uparrow}$ for the first three hysteresis loops measured at 5 K and 10 K, as a function of cooling field. There is a more significant training effect at 10 K, and the coercivity is greater after low to moderate cooling fields.

Figure 6.10: Exchange bias field as a function of cooling field for the first hysteresis loop at various temperatures, between 5 K and 150 K.
Figure 6.11: (a) Exchange bias field for the first hysteresis loop as a function of temperature for various $H_{FC}$. (b) The width of the first loop at its widest point, as a function of temperature. Errors were estimated from the field step size on the “down” loop at the points of measurement, as determined by Smartloop (see Appendix A).

A similar, negative peak slightly above $H_{FC} = 100$ Oe when plotted as a function of cooling field (Figure 6.10). By fitting a quadratic around the negative peak in $(H_{EB})$ at 5 K on a log ($H_{FC}$)-linear($H_{EB}$) scale, a peak exchange bias field of $-1240$ Oe is found when $H_{FC} = 129.3$ Oe. The same method applied to $H_{EB}$ v log ($H_{FC}$) at 10 K gives a peak of $-771$ Oe for $H_{FC} = 117.5$ Oe. Above about $H_{FC} \gtrsim 250$ Oe, $|H_{EB}|$ v $H_{FC}$ is straight on a log-log scale, giving a power law relationship. For loop 1, $|H_{EB}|$ decays as $H_{FC}^{-0.61}$ at 5 K and $H_{FC}^{-0.54}$ at 10 K. Exchange bias is strongly suppressed at 25 K, and reduces to zero within uncertainty above 50 K, which reaffirms the observation of cooling field independence when 2I2 is warmed to temperatures approaching $T_g$.

$H_{EB}$ decreases in magnitude monotonically with temperature for all cooling fields. Of the four cooling fields displayed, $H_{EB}$ is greatest in magnitude for $H_{FC} = 90$ Oe up to 25 K, after which the cooling field dependence decays rapidly, disappearing when $T \geq 75$ K. There exists a small positive exchange bias field at 50 K when $H_{FC} = 25$ Oe, however this is likely due a remanent field in the superconducting magnet at low field.

The width of the first loop at its widest point is displayed as a function of temperature.
for four cooling fields in Figure 6.11(b). For low cooling fields, the loops width is
greatest at 10 K, and is greatest at 25 K for \( H_{FC} \geq 450 \) Oe. Hysteresis is still
noticeable up to 50 K, but becomes negligible once \( T > T_g \).

6.4 Models

6.4.1 Two component Langevin model

The two component Langevin model introduced in section 4.4.1 was used to fit minor
hysteresis loops measured between ±6 kOe at 5 K and 10 K. Values for the high
field susceptibility, \( \chi_{H\rightarrow H_{max}} \), pseudo-coercive field, \( H_c \), effective cluster moment, \( \mu_{eff} \)
and cluster concentration, \( N_v \) were extracted from best fits of the model to mea-
sured hysteresis loops. The parameters were fitted simultaneously using a Levenberg-
Marquardt algorithm. The step magnetization, \( M_{st} \), was calculated using equation
(4.9).

Figure 6.12 displays the resultant parameters as a function of cooling field for both the
“up” and “down” branches of the second hysteresis loop measured at 5 K. The second
loop is displayed as the system is much closer to a training-independent equilibrium
than it is during the first loop, ie, changes between the first and second loop tend to
be more volatile than they are between the second and third and subsequent loops.

\( \chi_{H\rightarrow H_{max}} \) decreases monotonically with cooling field in both the “down” and “up”
branches, however, at large cooling fields, the values diverge, showing that the “down”
branches have a higher susceptibility. The decrease in high field susceptibility is
significant across the range of applied cooling fields, decreasing by 58% between ZFC
and \( H_{FC} = 8000 \) Oe, compared with 12% for aged Cu\(_{81.2}\)Mn\(_{18.8}\) alloy over the same
range (see section 5.3.3).

The magnitude of the pseudo-coercive field increases rapidly in both branches up to
\( H_{FC} = 50 \) Oe, before decreasing, the “down” branch as \( H_{FC}^{-0.76} \) and the “up” branch
as \( H_{FC}^{-0.59} \). The behaviour of the pseudo-coercive field can be compared with the
behaviour of the coercive field displayed in Figure 6.9(a), which doesn’t increase as
rapidly in either branch, or exhibit as sharp a cusp at low cooling field. The two
values don’t coincide at low to moderate cooling fields because the pseudo-coercive field describes the activation of the step, which occurs completely within the negative quadrant in this cooling field range. Above $H_{FC} \approx 250$ Oe, when the step comprises a transition from a positive magnetization to a similar negative magnetization on the “down” branch (or vice-versa on the “up” branch), the pseudo-coercive field and the coercive field are in close agreement.

The model gauges $\mu_{eff}$ from the curvature of the step. Both values of $\mu_{eff}$ and $N_v$ peak in $H_{FC}$, but the peak in cluster concentration happens at the comparatively low
cooling field of 70 Oe, as seen in Figure 6.12(c). This suggests that the number of clusters increases rapidly to $H_{\text{FC}} = 70$ Oe before falling, while their effective moments increase much slower. $N_v$ reaches a minimum at $H_{\text{FC}} = 70$ Oe, which approximately coincides with a broad peak in $\mu_{\text{eff}}$. At high cooling field, $N_v$ increases and $\mu_{\text{eff}}$ decreases, suggesting that the existing clusters are breaking up. This coincides with a disappearance of asymmetric reversal effects in the loops themselves. The curvature of the loops as they enter and exit the step decreases with cooling field above $H_{\text{FC}} \gtrsim 1000$ Oe, and appears symmetrical. Effects typical of exchange bias systems are suppressed in this cooling field range.

$M_{\text{st}}$ as a function of cooling field at 5 K is compared with $M (H)$ at $T_g$ in Figure 6.12(d). As was the case for aged Cu$_{81.2}$Mn$_{18.8}$ alloy, the two relationships are similar, following a Langevin-like function (Figure 5.8(b)). In 2I2, the values for both parameters at 6000 Oe differ by just 12%. This is markedly closer than the 22% disagreement found for aged Cu$_{81.2}$Mn$_{18.8}$ alloy (section 5.3.3), suggesting that the nature of clusters in 2I2 at 5 K is even more sensitive to the frozen magnetic configuration established as the sample passes through the glass temperature, than clusters are in aged Cu$_{81.2}$Mn$_{18.8}$. On close inspection, $M_{\text{st}}$ is greater on the “up” branch than on the “down” branch, but the difference between the quantities is within uncertainty.

The resultant parameters of fits to loops measured during a second iteration after cooling in various fields at 10 K are shown in Figure 6.13. The behaviour of $\chi_{H \to H_{\text{max}}}$ has changed in two noticeable aspects between 5 K and 10 K. The first is that it doesn’t decrease monotonically from a maximum at ZFC. Instead, in both branches, it increases rapidly until $H_{\text{FC}} \geq 70$ Oe. However, the loops themselves don’t display marked changes in high field susceptibility between ZFC and $H_{\text{FC}} = 90$ Oe in Figure 6.2. Given the differential susceptibility remains comparable throughout the entire loop after low cooling field, the model has seemingly not been able to distinguish between the linear component and step, causing it to grossly overestimate the step magnetization, and therefore underestimate the high field susceptibility.

The second is that, between cooling fields of 3000 Oe and 6000 Oe, $\chi_{H \to H_{\text{max}}}$ increases slightly on the “down” branch, and remains constant within uncertainty on the “up” branch. This increase in high field susceptibility induced by high cooling field is similar to the dependency observed in aged Cu$_{81.2}$Mn$_{18.8}$ at 5 K, shown in Figure
5.6(b), though the effect in 2I2 is not as extreme. In aged Cu$_{81.2}$Mn$_{18.8}$, this was interpreted as spins frozen into frustrated configurations by low cooling fields, and therefore blocked, becoming aligned by high cooling fields, and it is surmised that the same effect is happening here.

The separation between the $H_c$ values of the “up” and “down” branches is significantly greater after cooling in small fields at 10 K than it is at 5 K, at its greatest at 1482 Oe after ZFC, and decreasing with $H_{FC}^{-0.89}$ when larger positive cooling fields are applied. $H_c$ is most sensitive to cooling field in the “up” branch while $H_{FC} \leq 90$ Oe, shifting
along the field axis in the negative direction before both branches start tracking in
the positive field direction and converge at higher cooling fields. This demonstrates
that hysteresis is much greater at 10 K than at 5 K, across the entire range of cooling
fields investigated, suggesting an increased frozen magnetization component [11].

The values for $\mu_{\text{eff}}$ and $N_v$ extracted from 10 K loops appear to anti-correlate when
plotted as a function of cooling field on a log-log scale (Figure 6.13(c)). For almost
all applied cooling fields, the curvature of the “up” branch is greater than that of
the “down” branch. The effective cluster moment increases from just a few hundred
Bohr magnetons after low cooling field to 37031 $\mu_B$ after $H_{\text{FC}} = 133$ Oe, remaining
approximately constant between $133 \leq H_{\text{FC}} \leq 300$ Oe before decreasing for larger
cooling fields. The “down” branch values of $\mu_{\text{eff}}$ do not increase as rapidly, and do
not remain stagnant across an appreciable range of cooling fields.

Given that $N_v$ tends to reciprocate this behaviour, this suggests that there are more
clusters on the “down” branch, but the effective moments of these clusters are larger
on the “up” branch. The important observation is that the cluster configuration
changes after reversal. However, Figure 6.13(d) suggests that, while the nature of the
clusters changes throughout a hysteresis loop, the total magnetization due to the clus-
ter component only depends on $H_{\text{FC}}$, and is branch independent. $M_{\text{st}}$ has decreased
at 10 K in the cooling field range investigated, compared with same parameter at 5 K,
and with $M_v H$ at $T_g$. The spike in $M_{\text{st}}$ at low cooling fields supports the view that
the model struggles to distinguish between the two components when the curvature
of the step is slight, leading it to overestimate the step component.

6.4.2 Three component Langevin model

Minor hysteresis loops measured at 25 K between ±6 kOe and at 5 K between very
high measuring fields of ±50 kOe and ±75 kOe show particularly rapid reversals of
magnetization near the coercive field, which cannot be accounted for within the two
component Langevin model. The three component Langevin model, introduced in
section 4.4.2, is used to analyze these loops. Given that the model fits seven free
parameters, sensible values could only be extracted when each component was fitted
sequentially. The model requires very good data sets for accurate, meaningful fits,
Figure 6.14: Resultant parameters from fits using the three component Langevin model to the first three hysteresis loops measured between ±6000 Oe at 25 K after cooling in various fields. (a) $H_c$, (b) $H_F$, (c) $M_F$.

particularly around the region where the magnetization flips suddenly. This is why many of the parameters reported in this section, especially those extracted from loops after the second iteration where fewer data points were recorded, are accompanied by large uncertainty.

At 25 K, the separation between $H_c$ in the “up” and “down” branches is approximately double the separation between $H_F$ across the branches. Figure 6.14(b) shows that this separation in $H_F$ tends to decrease with both cooling field and loop iteration. The imbalance between $H_F$ in the “down” and “up” branches suggests that even
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Figure 6.15: (a) $H_F$ v loop iteration at 5 K. (b) $M_F$ v loop iteration at 5 K.

at 25 K, there exists a small exchange bias effect, shifting hysteresis loops in the negative field direction. This effect appears to decrease with cooling field. $M_F$ tends to increase both with cooling field and loop iteration, however the relatively large associated uncertainty makes it difficult to be confident about this.

Meaningful values for $H_c$ and $H_F$ couldn’t be extracted from minor loops measured at 5 K between ±50 kOe and ±75 kOe due to a lack of data points in the region of the magnetization flip. $H_F$ is displayed in Figure 6.15(a), which suggests that the coercivity of these loops increases dramatically with each training iteration. This is in fact false – the number of data points has decreased throughout the region of the magnetization flip, leading to an incorrect estimate of $H_F$ based on the recorded data. $M_F$ appears to increase with loop iteration, and while visual inspection of the loops displayed in Figure 6.5 suggests this is the case, the extent of this increase displayed in Figure 6.15(b) is questionable.

6.4.3 Monte Carlo simulation

While the extent of asymmetric reversal is not as apparent in 2I2 as it is in aged Cu$_{81.2}$Mn$_{18.8}$ alloy (section 5.4), it is still noticeable, particularly for minor loops measured at 5 K between ±6 kOe with a cooling field range of $90 \lesssim H_{FC} \lesssim 1000$ Oe.
As the two component Langevin model is unable to account for asymmetric reversal, a modified Stoner-Wohlfarth model introduced in section 4.5 was used to fit the first “up” branch of loops measured at 5 K after cooling in fields between 90 Oe and 8000 Oe, using Monte Carlo simulations.

Fits were used to extract cooling field dependencies for the parameters $\mu_{\text{eff}}$, the effective cluster moment, $K$, the uniaxial cluster shape anisotropy energy per unit volume, $J$, the exchange interaction energy per unit volume, $\phi$, the angle between the cluster easy axis and the applied field, and $N_v$, the cluster concentration. As was the case for aged Cu$_{81.2}$Mn$_{18.8}$ alloy in section 5.4, a Gaussian distribution was assumed for $\phi$, centred around $\phi = 0$, and with a standard distribution of $\phi_{\text{stdev}}$. The clusters are treated as ferromagnetic entities that interact only with a quasi-isotropic spin glass and not with each other. $\alpha$, the angle between the applied field and a given cluster’s observed molecular field due to the local spin glass, was assigned random values between $\alpha = 0^\circ$ and $\alpha = 180^\circ$. Positive values for $J$ were assumed. Assumptions about $a$, $n$, $\mu_\text{atom}$ and $X$ in equation (4.12) were guided by the literature [7, 12–14]. The values used for these four parameters were $a = 3.661$ Å, $n = 4$, $\mu_\text{atom} = 4.2 \mu_B$ and $X = 0.25$.

The interdependence between parameters requires that further assumptions are made. Six assumptions were tested initially, in each case fixing one of either $\mu_{\text{eff}}$, $N_v$ or $J$ as cooling field independent. In the first two trials, $\mu_{\text{eff}}$ was set to 2000 $\mu_B$, then 7000 $\mu_B$; in the next two trials, $N_v$ was set to $1.029 \times 10^{17}$ g$^{-1}$, then $5.0 \times 10^{17}$ g$^{-1}$, and in the final two trials, $K$ was set to $0.5 \times 10^6$ J/m$^3$, then $1.75 \times 10^6$ J/m$^3$. Finally, as was the case for aged Cu$_{81.2}$Mn$_{18.8}$ alloy, additional fits were performed using $KV$ and $JV$, the uniaxial anisotropy energy per cluster and exchange interaction energy per cluster in place of $K$ and $J$, utilizing a set of starting parameters determined to be plausible from the previous fits, in which no other assumptions were made about their dependence on cooling field. The goodness of fit was quantified using coefficient of determination $R^2$ values, which were typically in the range of 0.993 to 0.998, except when the simulations failed to converge with the data.

$K$ is displayed in Figure 6.16(a) as a function of cooling field for constant values of $\mu_{\text{eff}}$. The lesser value of $\mu_{\text{eff}} = 2000 \mu_B$ sees $K$ increase with $H_{\text{FC}}$ up to a value of $2.3 \times 10^6$ J/m$^3$ when $H_{\text{FC}} \geq 1000$ Oe, which coincides with a decrease in asymmetric
reversal in the hysteresis loops displayed in Figure 6.3. The greater value of \( \mu_{\text{eff}} = 7000 \ \mu_B \) results in a more volatile dependence of \( K \) on \( H_{\text{FC}} \). \( K \) decreases rapidly by more than an order of magnitude when \( H_{\text{FC}} \) is increased from 90 Oe to 133 Oe, before saturating to 35000 J/m\(^3\) when \( H_{\text{FC}} = 3000 \) Oe, decreasing exponentially with \( H_{\text{FC}} \) thereafter.

In both cases of constant \( \mu_{\text{eff}} \), \( J \) decreases as a power law with \( H_{\text{FC}} \). There is very little change in \( J \) between \( \mu_{\text{eff}} = 2000 \ \mu_B \) and \( \mu_{\text{eff}} = 7000 \ \mu_B \), although \( J \) is generally slightly larger for the greater value of \( \mu_{\text{eff}} \). \( J \) decreases with \( H_{\text{FC}}^{-0.57} \) and \( H_{\text{FC}}^{-0.55} \) for \( \mu_{\text{eff}} = 2000 \ \mu_B \) and \( \mu_{\text{eff}} = 7000 \ \mu_B \) respectively.
Asymmetric reversal occurs as a consequence of misalignment between the easy axes of domains and the applied field [15–21]. Given this, Figure 6.16(c) suggests that 2000 $\mu_B$ is a more physically reasonable estimate for $\mu_{\text{eff}}$, as $\phi_{\text{stdev}}$ decreases to zero for high cooling fields, which coincides with symmetric hysteresis loops. However, $\phi_{\text{stdev}}$ falls to zero at $H_{\text{FC}} \geq 750$ Oe, and hysteresis loops measured with $750 \leq H_{\text{FC}} \leq 1000$ Oe show that some asymmetry still persists even after cooling in these fields. The increase of $\phi_{\text{stdev}}$ with high cooling fields indicates that $\mu_{\text{eff}} = 7000$ $\mu_B$ is not a reasonable value for the effective cluster moment, and is most likely an overestimate. This disagrees with the values generated by the two component Langevin model in section 6.4.1, which peaked in $\mu_{\text{eff}} \approx 13600$ $\mu_B$ for $H_{\text{FC}} = 300$ Oe before decaying to $\mu_{\text{eff}} \approx 7000$ $\mu_B$ once $H_{\text{FC}} \geq 3000$ Oe (Figure 6.12(c)).

Setting $\mu_{\text{eff}}$ independent of $H_{\text{FC}}$ is akin to assuming that $N_v$ increases proportionally with $M_{\text{st}}$, which is observed explicitly in the Langevin-like dependence on $H_{\text{FC}}$ in Figure 6.16(d). In this picture, increases in $M_{\text{st}}$ are driven entirely by cluster nucleation, rather than cluster growth.

Of the two cooling field independent values for cluster concentration tested, only $N_v = 1.029 \times 10^{17}$ $g^{-1}$ could simulate all loops over the investigated range of cooling fields. When $N_v = 5.0 \times 10^{17}$ $g^{-1}$, the fits would not converge at low to moderate cooling fields, between 100 Oe and 300 Oe, likely due to $\mu_{\text{eff}}$ being underestimated. The observed behaviours for $K$, $J$ and $\phi_{\text{stdev}}$ when $N_v = 1.029 \times 10^{17}$ $g^{-1}$, displayed in Figure 6.17, are similar to those extracted for constant $\mu_{\text{eff}} = 7000$ $\mu_B$ which, as mentioned above, is thought to be an overestimate. For this reason, it is inferred that $N_v = 1.029 \times 10^{17}$ $g^{-1}$ is generally an underestimate, particularly at high field where physically unlikely trends such as a decrease in $K$ and an increase in $\phi_{\text{stdev}}$ are seen.

$N_v = 1.029 \times 10^{17}$ $g^{-1}$ generates a Langevin-like dependence in $\mu_{\text{eff}}$ on $H_{\text{FC}}$, which varies from 756 $\mu_B$ to 10000 $\mu_B$ over the investigated cooling field range. It is noted that the values for $J$ in Figure 6.17(b) (which shows a $H_{\text{FC}}^{-0.57}$ dependence) are very similar to those in Figure 6.16(c) for constant $\mu_{\text{eff}}$, which suggests that $J$ has somewhat dissociated from the other parameters over this range of values. The sensitivity of $J$ only to cooling field and not to other parameters supports its validity.
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Setting $K$ to $1.75 \times 10^6$ J/m$^3$, independent of cooling field, generates the most physically believable dependencies of $\phi_{\text{stdev}}$, $N_v$ and $\mu_{\text{eff}}$ on $H_{\text{FC}}$ of the tested values. $J$ is again reasonably insensitive to changes in the other model parameters, increasing slightly with $K$ and decaying as a power law with $H_{\text{FC}}^{-0.54}$ when $K = 1.75 \times 10^6$ J/m$^3$ and $H_{\text{FC}}^{-0.58}$ when $K = 0.5 \times 10^6$ J/m$^3$. The values for $\phi_{\text{stdev}}$ are much smaller for the two constant values of $K$ tested, because larger values of $K$ require smaller deviations in easy axis orientation to produce the same extent of asymmetric reversal (as demonstrated in Figure 4.7(d)). For both runs of $K$, $\phi_{\text{stdev}}$ decreases as one would expect up to high cooling field, where the effects of asymmetric reversal disappear, but above $H_{\text{FC}} \geq 1000$ Oe, $\phi_{\text{stdev}}$ increases again for the lower value of $K$. $\phi_{\text{stdev}}$
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Figure 6.18: $J$, $\phi_{\text{std dev}}$, $N_v$ and $\mu_{\text{eff}}$ as a function of cooling field for two sets of Monte Carlo model fits on loops measured at 5 K between ±6000 Oe. $K$ is set constant at 0.5×10^6 J/m^3 and 1.75×10^6 J/m^3.

decreases monotonically when $K = 1.75 \times 10^6$ J/m^3, but it never decays to zero, settling at $\phi_{\text{std dev}} = 0.3^\circ$ once the loops appear symmetric.

The higher value $K$ implies a greater value for $N_v$ for high cooling fields. The nature of the dependency of $N_v$ on $K$ is similar for both tested values, fluctuating about $1\times10^{17}$ g$^{-1}$ before growing approximately as $H_{FC}^{0.5}$ once $H_{FC} \gtrsim 300$ Oe. While extrapolating $H_{FC}^{0.5}$ doesn’t suggest saturation, it is at least consistent with a lower rate of growth in $N_v$ at higher cooling fields. One would expect a term or component that tends to saturation, such as an exponential cutoff, to become apparent at higher cooling fields.
While the values for $\mu_{\text{eff}}$ shown in Figure 6.18(d) are significantly less than those generated using the two component Langevin model for the same loops, the two models both suggest a decrease in the cluster moment above $H_{\text{FC}} \geq 1000 \text{ Oe}$, again coinciding with the suppression of asymmetric reversal by high cooling fields.

It is much more likely that none of the parameters are cooling field independent, but by testing assumptions based on a single cooling field independent parameter, the cooling field dependence of the other parameters can be qualitatively probed, allowing scenarios to be considered based on plausibility. All tested assumptions agree that $J$ depends on $H_{\text{FC}}$ as a power law, decaying with an index in the range of $-0.54$ to $-0.58$. It is also likely that $\phi_{\text{stdev}}$ decreases monotonically with $H_{\text{FC}}$ from a high deviation of easy axes alignments at low cooling field, to strong (but not total) alignment with the field at high cooling field, once the effects of asymmetric reversal are no long noticeable. It would be reasonable to infer that $\mu_{\text{eff}}$ increases linearly with cooling field to $H_{\text{FC}} \approx 300 \text{ Oe}$, peaking about $H_{\text{FC}} \approx 1000 \text{ Oe}$, while $N_v$ varies only slightly, but at higher cooling fields, the clusters break up, causing their effective moments to decrease, but their concentration to increase at a great rate. The rate at which $\mu_{\text{eff}}$ increases with $H_{\text{FC}}$ in the low cooling field regime is most likely much higher than the Langevin-like dependency generated for a constant cluster concentration of $5.0 \times 10^{17} \text{ g}^{-1}$. $K$ would increase slightly with low cooling field, saturating to a very high value once $H_{\text{FC}} \approx 1000 \text{ Oe}$.

These dependencies are qualitatively supported by the final set of fits, in which no assumptions are made about the way each parameter depends on cooling field. Figure 6.19 again suggests that $\mu_{\text{eff}}$ peaks about $H_{\text{FC}} \approx 1000 \text{ Oe}$ and $KV$, the uniaxial anisotropy energy per cluster (as opposed to the $K$ parameter, uniaxial anisotropy energy per unit volume used in the previous sets of fits) saturates towards the same cooling field. $JV$ exhibits a different behaviour, decreasing only slightly in the low to moderate cooling field range, and decreasing as $H_{\text{FC}}^{-0.87}$ when $H_{\text{FC}} \geq 1000 \text{ Oe}$. $\phi_{\text{stdev}}$ rapidly decreases to less than $2^\circ$ once $H_{\text{FC}} \geq 300 \text{ Oe}$, again suggesting strong alignment of cluster easy axes with the cooling field.
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Figure 6.19: (a) $\mu_{\text{eff}} \propto H_{\text{FC}}$ with free parameters. (b) $KV \propto H_{\text{FC}}$ with free parameters. (c) $JV \propto H_{\text{FC}}$ with free parameters. (d) $\phi_{\text{stdev}} \propto H_{\text{FC}}$ with free parameters.

6.5 Discussion

The magnetism and dependence on cooling field displayed by sample 2I2 during investigation of its hysteretic behaviour at temperatures well below $T_g$ are, in many ways, analogous to an exchange bias system [22–25]. Much like aged Cu$_{81.2}$Mn$_{18.8}$ alloy, discussed in section 5.5, the magnetism of 2I2 shows a remarkable sensitivity to cooling field at temperatures well below $T_g$. However, despite a lower Mn concentration, 2I2 tends more towards ferromagnetic behaviour than aged Cu$_{81.2}$Mn$_{18.8}$ alloy. Much of the observed behaviour is common between the two samples, but aspects such as
the development of an asymmetric step in minor hysteresis loops with cooling field, exchange bias and training effects are activated by either lower cooling fields or lower temperatures in 2I2 than are required for aged Cu_{81.2}Mn_{18.8} alloy. The susceptibility and magnetization of 2I2 are significantly larger than those of aged Cu_{81.2}Mn_{18.8} alloy, by a factor of 6.3 in low field at $T_g$ and a factor of 2.3 in 6000 Oe at 5 K after cooling in 6000 Oe.

It is argued again that the existence of two interacting components, the first consisting of internally ferromagnetic clusters that are highly anisotropic in nature (presumably, with respect to shape), and the second quasi-isotropic, internally frustrated and akin to a ZFC spin glass, can account for much of the observed behaviour. The difference between 2I2 and aged Cu_{81.2}Mn_{18.8} alloy is the extent of ferromagnetism, which is significantly stronger in 2I2. This may be interpreted as spins being much more susceptible to being drawn from the spin glass component and into the ferromagnetic cluster component.

At 5 K, the observed cooling-field dependence of the cluster component in 2I2 can be gauged from the height of the step magnetization in minor hysteresis loops. The strong correlation between the behaviour of the step magnetization as a function of cooling field at 5 K and the magnetization at $T_g$ in Figure 6.12(d) suggests that the configuration of the spin glass component becomes metastable as the sample is cooled below $T_g$. It is inferred that correlations form between spins that have been aligned by the cooling field, which persist as the system is cycled about a minor hysteresis loop.

The various models applied to the present data in section 6.4 indicate that magnetic clusters nucleate and grow at different rates, dependent on cooling field. The two component Langevin model (section 6.4.1) suggests a rapid nucleation of clusters at $H_{FC} = 70$ Oe, followed by a decrease in cluster concentration to mirror an increase in cluster moment up to $H_{FC} = 300$ Oe, after which clusters break up and the cluster concentration increases again. The modified Stoner-Wohlfarth model (section 6.4.3) indicates an approximately constant number of clusters up to $H_{FC} = 300$ Oe, followed by a $H_{FC}^{0.5}$ increase with higher cooling fields when $K$ is set constant, which is considered one of the more plausible of the investigated scenarios. The presence of hysteresis and non-linearity after ZFC at 5 K (Figure 6.2(a)) supports a viewpoint in
which clusters precipitate from the spin glass as the sample passes through $T_g$, even after cooling in very low fields [24, 26]. The existence of ZFC clusters in CuMn has been corroborated by neutron studies of aged samples with similar compositions to 2I2 [13, 27].

$\chi_{H \rightarrow H_{\text{max}}}$ may be extracted from the high-field part of hysteresis loops, where the differential susceptibility is generally constant, and used to estimate the configuration of the spin glass component. At 5 K, $\chi_{H \rightarrow H_{\text{max}}}$ decreases monotonically with $H_{\text{FC}}$, coinciding with the Langevin-like increase in $M_{\text{st}}$. The decrease in $\chi_{H \rightarrow H_{\text{max}}}$ in 2I2 is significant (58% between ZFC and $H_{\text{FC}} = 8000$ Oe) compared with the same decrease noted in aged Cu$_{81.2}$Mn$_{18.8}$ at the same temperature and cooling field range (12% between ZFC and $H_{\text{FC}} = 6000$ Oe, followed by an increase at higher $H_{\text{FC}}$). The significant decrease of $\chi_{H \rightarrow H_{\text{max}}}$ with $H_{\text{FC}}$ in 2I2 and the tendency for $M_{\text{st}}(H_{\text{FC}}, 5$ K) to follow $M(H, T_g)$ more closely, together support the existence of a ferromagnetic cluster component that grows when spins otherwise contained in frustrated configurations within the spin glass component are aligned by the cooling field.

Coercive fields, pseudo-coercive fields, the exchange bias field and the unidirectional anisotropy energy are all informative of magnetization reversal phenomena, and, at 5 K in 2I2, all follow power law relationships with $H_{\text{FC}}$ above a given cooling field (usually $H_{\text{FC}} = 300$ Oe or lower), with indices between $-0.87$ and $-0.54$. Within the domain state model for materials with FM-AFM interfaces [28, 29], introducing defects into the AFM phase acts to pin AFM domain boundaries, enhancing the stability of AFM domains, which causes increases in exchange bias fields [30–32]. An analogous phenomenon is presumed to occur in 2I2, with the spin glass component likened to a disordered AFM phase. As the spin glass component is aligned by the cooling field, the exchange bias field decreases.

Domain structures and pinning sites are thought to play a significant role in coercivity [33, 34]. In general, aligning the easy axes of an ensemble of single domain particles, such as non-interacting ferromagnetic clusters, with the field, leads to enhanced coercivity when they have unidirectional anisotropy, but aligning the easy axes of adjacent interacting domains decreases the coercivity [35, 36]. The increase in step magnetization and decrease in coercivity suggest that domains play a significant role in reversal at higher cooling fields, which is possibly due to the clusters having grown sufficiently.
large in volume that they exceed the critical domain size and no longer behave as single domain particles. This would be consistent with the break up of clusters at high cooling fields suggested by both the two component Langevin model and Monte Carlo simulations. It is also consistent with the step function-like flips that dominate hysteresis loops at 5 K between ±50 kOe and ±75 kOe, characteristic of unrestricted domain wall motion [34, 37].

Equation (4.12), along with the assumptions made in section 6.4.3, may be used to approximate the average diameter of coherent magnetic entities (either clusters or domains) in 2I2. Using the results for $\mu_{\text{eff}}$ in Figure 6.18(d) with $K$ assumed as $1.75 \times 10^6$ J/m$^3$ (which was determined to be one of the more physically plausible scenarios), the cluster diameter saturates at $\sim 2.0$ nm when $H_{FC} = 1000$ Oe before decreasing to $\sim 1.7$ nm once $H_{FC} = 6000$ Oe. While this is significantly smaller than the typical critical size of elemental ferromagnets, it is comparable with the critical size of superparamagnetic CuCo, which is about 6.5 nm [38].

Asymmetric reversal is observed in 5 K and 10 K hysteresis loops between $90 \leq H_{FC} \leq 1000$ Oe, and is attributed to a distribution of easy axis orientations. For $H_{FC} > 1000$ Oe, asymmetric reversal becomes significantly reduced, which coincides with a gradual alignment of a portion of the spin glass component due to the increasing cooling field. The extent of asymmetric reversal in 2I2 at 5 K is noticeably less than that observed in aged Cu$_{81.2}$Mn$_{18.8}$ alloy under the same conditions, which evidences a more narrow distribution of easy axes alignments in 2I2, supporting the view that it has comparatively greater ferromagnetic order and enhanced susceptibility.

Training is observed in 2I2’s minor hysteresis loops at 5 K (most noticeably when $70 \leq H_{FC} \leq 300$ Oe) and higher temperatures, up to 25 K. At 5 K, there are three key observations to consider when attempting to explain the training effect in 2I2. Firstly, successive loop iterations generally have the effect of increasing the curvature of $M$-$H$ around the step, which is associated with an increase in the effective cluster moment. Secondly, the step magnetization increases on the "down" branch with loop iteration, but decreases slightly on the "up" branch, which implies a decrease in cluster concentration. Finally, training decreases the magnitude of the pseudo-coercive field.
Training is attributed to the influence the maximum applied fields have on the configuration of the spin glass component. The influence training has on the magnetic behaviour is similar to that of increasing the cooling field, suggesting that the positive maximum field has a greater effect on the spin glass configuration. Training, and hysteresis in general, can only occur if there is an irreversible component of magnetization on the time scale of the measurement [36, 39, 40]. In 2I2, the spin configuration induced by a positive cooling field appears to be partially aligned by the positive maximum field. Likewise, the magnetic behaviour displayed in Figure 6.4 suggests that negative cooling field configurations are more susceptible to alignment from negative maximum fields.

Training has been studied in CuMn previously by Schwink and coworkers [41, 42], who demonstrated that unidirectional anisotropy could be increased by increasing the magnitude of the negative maximum field with successive loop iterations [43]. In contrast, this study shows that in 2I2, where (presumably) clusters are sufficiently large for domain formation, successive loop iterations in which both the positive and negative maximum fields are held constant results in a decrease in the magnitude of unidirectional anisotropy.

Minor hysteresis loops at 10 K are still reasonably well described as the sum of a step magnetization due to ferromagnetic clusters and a high field paramagnetic response, attributed to the magnetism of the spin glass component. Again, the interaction between the two components influences the shift of the step field, creating an exchange bias field, and the asymmetry of the cluster component’s reversal, while the cooling field draws spins from the spin glass component into the cluster component through alignment, creating new correlations by gradually overcoming local minima induced by frustration typical of a quasi-isotropic spin glass. However, the extent of ferromagnetic behaviour declines at 10 K. The step magnetization has decreased compared with 5 K, accompanied by a decrease in cluster concentration within the two component Langevin model. Interestingly, $\mu_{\text{eff}}$ increases at 10 K, due to temperature being in the denominator of the Langevin function argument in equation (4.8). Visual inspection of loops at 10 K shows that the curvature around the step has decreased with temperature. The high field susceptibility is higher at 10 K, another indication
of reduced ferromagnetism. This is either indicative of increased “free” magnetization [11], or fewer spins involved in clusters.

Coercivity at 10 K is significantly enhanced compared with 5 K, but Figure 6.10 shows that the exchange bias field decreases in magnitude with temperature. This suggests that unidirectional anisotropy decreases with temperature, but the spin glass component is more readily and symmetrically reversible at the positive and negative maximum fields at higher temperatures, where it has more thermal energy to escape “frozen” configurations. It is also consistent with a greater proportion of single domain clusters, which disagrees with the results of the two component Langevin model. It is likely that the expression for temperature in the denominator of the argument of the Langevin function requires a correction term to account for configurations that are irreversible when \( T \ll T_g \), such as a \((T - \Theta)\) term, where \( \Theta \) is the Weiss constant.

At 10 K, when \( H_{FC} = H_{\text{max}} = 6000 \) Oe, hysteresis can be observed in the positive quadrant of the loop (Figure 6.7(d)), in a region usually associated with a paramagnetic response. In this instance, the step magnetization is greater on the “down” branch, while the high-field susceptibility in the positive quadrant is greater on the “up” branch. Here, hysteresis has occurred due to changes in the spin glass configuration induced by the negative maximum field, which act to increase the distribution of spin alignments.

Gray [6] attributed the significant increase in 2I2’s low field susceptibility (a factor of 20 over quenched-in Cu_{83.6}Mn_{16.4}) to the irradiation process during sample preparation driving the atomic short range ordering (SRO) to equilibrium via vacancy migration, in which irradiation causes continuous nucleation of fixed vacancies, around which vacancy clusters would grow at the aging temperature (estimated to be 100°C). In the previous reference, Gray compared the low-field susceptibility of 2I2 at \( T_g \) with the aging dependent susceptibility of another Cu_{83.6}Mn_{16.4} sample and showed that, with the best aging procedure tested (quenching in ice-water, followed by aging at 100°C up to 96 hours), the susceptibility eventually saturates, with non-exponential kinetics, at only one-third of 2I2’s, suggesting Cu_{83.6}Mn_{16.4} cannot attain this susceptibility by aging alone.
The extent of short range ordering (SRO), favouring ferromagnetic interactions between neighbouring spins [1, 44], means that the transition from the spin glass component to the cluster component happens more readily in 2I2 than it does in CuMn samples of similar concentration that are treated thermally, rather than through irradiation. Magnetic SRO parameters in CuMn and their influence on macroscopic magnetic behaviour has been a topic of interest in several investigations [12, 45, 46]. As has been stated above, the behaviour of 2I2 is strongly suggestive of ferromagnetic ordering.

The onset of long range order has been achieved in higher concentrations of CuMn through exposure to neutron irradiation during the preparation process [7, 8], but few magnetic studies have been performed on such systems [6]. It is expected that long range ordering would see an increase in the susceptibility of CuMn. Small-angle neutron scattering (SANS) investigations on such systems would also be of interest, in order to probe the magnetic cluster topology as a function of cooling field at temperatures well below $T_g$, and correlate it to the observed magnetic behaviour.

### 6.6 Conclusion

Neutron irradiation significantly increases the low-field susceptibility of a sample of Cu$_{83.6}$Mn$_{16.4}$ alloy, labeled 2I2. The dependence of the magnetic behaviour of 2I2 on cooling field at 5 K, has been investigated through measurements of hysteresis loops, and compared with that of an aged Cu$_{81.2}$Mn$_{18.8}$ sample. It is noted that 2I2 is significantly more inclined towards ferromagnetic behaviour than aged Cu$_{81.2}$Mn$_{18.8}$ alloy. Aspects that are typically associated with exchange bias systems consisting of FM-AFM interfaces, such as shifted hysteresis loops, asymmetric reversal and training, are displayed by 2I2. Three models were applied to hysteresis loops measured between 5 K and 25 K, in order to estimate the dependence of magnetic clusters on cooling field. While the specific nature of cluster evolution is inconsistent between the various models, the most plausible scenario is that clusters grow approximately linearly with low cooling field, before peaking in volume and breaking up in higher cooling fields. This is interpreted as evidence for domain structures forming when the clusters have grown sufficiently large that it is no longer favourable for them to exist.
as single domain particles. The break-up of clusters coincides with a suppression of asymmetric reversal, which is modelled within Monte Carlo simulations as the alignment of cluster easy axes with the cooling field. The step magnetization as a function of cooling field at 5 K very closely follows the magnetization at \( T_g \), within 12%. Training consecutive hysteresis loops appears to have an effect analogous to slightly increasing the cooling field, and is interpreted as the maximum field, \( H_{\text{max}} \) aligning a portion of the frozen spin glass component.

At 5 K, parameters related to magnetization reversal, such as coercive field, pseudo-coercive field, exchange bias and unidirectional anisotropy energy, tend to decay with cooling field as a power law above a given cooling field, with indices between \(-0.87\) and \(-0.54\). This is understood qualitatively within the domain state model for exchange bias materials. \(|H_{\text{EB}}|\) peaks in cooling field about \( H_{\text{FC}} = 129.3 \) Oe at 5 K, and decreases with temperature. Loop width increases with temperature to 10 K after cooling in low to moderate fields, and 25 K for high cooling fields, before decreasing at higher temperatures and becoming negligible once hysteresis disappears above \( T_g \). No cooling field dependence was observed in hysteresis loops where \( T \geq 50 \) K.

Of the proposed models, the modified Stoner-Wohlfarth model, applied using Monte Carlo simulations, gives the best account of the present experimental data. By testing a set of assumptions, in which certain parameters are treated as independent of \( H_{\text{FC}} \) at 5 K, scenarios could be extracted for the cooling field dependence of parameters within the model, particularly the effective cluster moment, cluster concentration, cluster uniaxial anisotropy energy, cluster easy axis distribution and unidirectional (exchange) anisotropy energy. The results from the model suggest that clusters precipitate as the system is cooled through \( T_g \) in zero field, and grow as the cooling field is increased, but become multi-domain when the cooling field is high. This is considered a plausible qualitative description of the cluster evolution within 2I2, but small angle neutron scattering experiments at \( T \ll T_g \) in which both the cooling field and applied fields are varied would allow a quantitative dependence to be determined, which will aid in the understanding of CuMn in an equilibrium SRO configuration.

It would also be of interest to measure the magnetic properties of irradiated CuMn samples at higher concentration in which the onset of long range order has been induced, such as the one reported in reference [7]. A comparison of the cooling field
dependent behaviour with that observed in 2I2, with a particular focus on uniaxial and
unidirectional anisotropy, the size and curvature of the step magnetization, and the
extent of asymmetric reversal, would enhance the understanding of the relationship
between atomic short range and long range ordering, and the macroscopic magnetic
properties.
Chapter 6 References


Chapter 7

Summary of findings of investigations on CuMn

The following observations can be drawn from the results of experiments performed on the two micromagnetic CuMn samples outlined in the previous two chapters:

- Both samples exhibit a “step” magnetization, $M_{st}$, at 5 K which increases with cooling field, $H_{FC}$. The dependence of $M_{st}$ on $H_{FC}$ resembles a Langevin function and is comparable to the magnetization at the glass temperature, $T_g$, moreso for 2I2. The step magnetization is attributed to the magnetism of finite magnetic clusters.

- Both samples exhibit asymmetric reversal in minor $M$-$H$ loops measured at 5 K for a moderate range of cooling fields, but this is more apparent in aged Cu$_{81.2}$Mn$_{18.8}$ alloy. Asymmetric reversal is understood to occur as a result of a distribution of cluster easy axis alignments with respect to the field, and is successfully simulated using Monte Carlo simulations based on a modified Stoner-Wohlfarth model with a Gaussian distribution of easy axes. According to these simulations, this distribution tends to narrow with higher cooling field. High cooling fields suppress asymmetric reversal in 2I2 which, along with a decrease in the parameter relating to effective cluster moment, is interpreted as possible evidence for the formation of multi-domain particles.
2I2 exhibits a greater degree of ferromagnetic behaviour compared with the aged Cu$_{81.2}$Mn$_{18.8}$ alloy. It has a greater low-field susceptibility, greater magnetization, greater step magnetization at lower cooling fields and also exhibits a training effect at 5 K, unlike aged Cu$_{81.2}$Mn$_{18.8}$ alloy, which doesn’t exhibit training below 25 K. This is understood to be a consequence of the neutron irradiation driving the short-range order within 2I2 to equilibrium during the preparation process.

For both samples, the magnitude of the exchange bias field, $|H_{EB}|$ peaks at a moderate cooling field at 5 K ($H_{FC} \approx 450$ Oe for aged Cu$_{81.2}$Mn$_{18.8}$ alloy and $H_{FC} \approx 129$ Oe for 2I2). $|H_{EB}|$ also decreases with temperature, while coercivity is greatest in both samples at about 25 K. This is understood in terms of the degree of alignment of the “spin glass” component established by the cooling field.
Chapter 8

Magnetic properties of NiMn and NiMnCu alloys

8.1 Introduction

Research in NiMn has been driven by an interest in understanding the exchange bias effect in disordered systems where the constituent elements are ferromagnetic and antiferromagnetic in bulk respectively. Additionally, NiMn has applications in magnetic microelectromechanical systems (MEMS) [1] and spin valve devices [2], due to the considerable exchange bias field and high blocking temperature of certain NiMn phases. NiMn alloys with concentrations about 25 at.% Mn have received particular attention over the decades [3–5], due to the sensitivity to composition and thermal treatment of the system in this region of the phase diagram [6, 7], shown in Figure 2.1. Below 23.9 at.% Mn, NiMn is a reentrant spin glass [5, 8, 9], and above 25 at.% it behaves as a spin glass [10, 11]. The ordered Ni$_3$Mn phase is ferromagnetic, but thermal treatment at temperatures approaching the liquidus (approximately 900 - 1100°C) causes an order-disorder transition [12–15], inducing Mn-Mn nearest neighbour pairs which interact antiferromagnetically. The coexistence of regions of ferromagnetically and antiferromagnetically interacting spins leads to an exchange bias effect in NiMn.

More recent work on alloyed systems has been concerned with doping NiMn with small amounts of non-magnetic defects, which enhances unidirectional anisotropy,
resulting in increased exchange bias [16–21]. When the system is reentrant, addition of palladium or platinum results in enhanced exchange bias with minimal changes in the reentrance temperature and the saturation magnetization at low temperatures [17, 18, 22]. When the system is a spin glass, addition of platinum increases the glass temperature, but decreases the susceptibility [11].

This chapter reports an investigation of the magnetic properties of a set of Ni$_{71}$Mn$_{29}$ spin glass alloys at low temperature, made in order to probe their cooling field dependence, and study the effects of aging. A separate set of alloys consisting of the same concentration of Mn, but an addition of 3 at.% Cu in substitution of Ni, was also measured, in order to examine the effects that the addition of non-magnetic defects has on NiMn when it is in a highly concentrated spin glass phase.

### 8.2 Sample preparation and experimental method

The magnetic properties of a set of Ni$_{71}$Mn$_{29}$ alloy samples and a set of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples were investigated between 5 K and 315 K, with a focus on probing the dependence of the magnetic behaviour on composition and aging time. The Ni$_{71}$Mn$_{29}$ alloy sample set was prepared by argon arc melting nickel (99% foil) and manganese (99.98+% flake) at a nominal concentration of 29 at.% Mn. The resultant melt was cold worked in a mechanical press between two stainless steel sheets, and remelted in the arc. This process was repeated three times before rectangular rods were cut with dimensions of approximately $10 \times 2.5 \times 1.5$ mm$^3$.

Four rods were sealed in an evacuated quartz tube and annealed at 1000°C for two hours. The samples were then quenched in water. Three samples were then sealed separately in evacuated quartz tubes, aged at a nominal temperature of 500°C for periods between 3 and 27 minutes, then quenched in water. A drift in furnace temperature of the order of $\sim 30$°C was noted over the course of approximately 3 min.

The Ni$_{68}$Mn$_{29}$Cu$_3$ sample set was prepared by argon arc melting nickel (99% foil), copper (99.99+% rod) and manganese (99.98+% flake) at a nominal concentration of 3 at.% Cu and 29 at.% Mn. The subsequent preparation process was the same as it was for the Ni$_{71}$Mn$_{29}$ alloy sample set. The samples were labeled depending on their
composition and the amount of time they were aged at 500°C, nominal, as seen in Table 8.1. Unless otherwise specified, the rider “at 500°C, nominal” is taken as read for all subsequent references to aging times in this chapter.

Composition measurements were performed on two samples from each set by scanning electron microscopy, through analysis of backscattered electrons. The crystal structures of all samples were measured by X-ray diffraction (XRD) as described in section 3.4.1.

Measurements of magnetization were performed using the vibrating sample magnetometer (VSM) described in section 3.2. Temperature dependent magnetization was measured in three branches, zero-field cooled (ZFC), field cooled (FC) and thermoremanent magnetization (TRM), between 5 K and 310 K in fields of 10 Oe, 100 Oe and 1000 Oe. $M-H$ hysteresis loops were measured at a set of temperatures between 5 K and 315 K after cooling in various fields between zero field and 8 kOe from 300 K, ie, well above the measured peak temperature in order to reset any memory effects in the spin glass. Several minor loops were measured consecutively in fields between ±200 Oe, ±8 kOe, ±20 kOe and ±75 kOe, in order to examine any training effects. All displayed loops have been corrected for demagnetizing fields, as outlined in section 1.5.

### Table 8.1: Labels and descriptions of preparation procedures for $\text{Ni}_{71}\text{Mn}_{29}$ and $\text{Ni}_{68}\text{Mn}_{29}\text{Cu}_3$ alloy samples.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ni}<em>{71}\text{Mn}</em>{29}.\text{Q}$</td>
<td>Quenched from 1100°C.</td>
</tr>
<tr>
<td>$\text{Ni}<em>{71}\text{Mn}</em>{29}.\text{A3}$</td>
<td>Quenched from 1100°C, aged 3 min at 500°C, quenched.</td>
</tr>
<tr>
<td>$\text{Ni}<em>{71}\text{Mn}</em>{29}.\text{A9}$</td>
<td>Quenched from 1100°C, aged 9 min at 500°C, quenched.</td>
</tr>
<tr>
<td>$\text{Ni}<em>{71}\text{Mn}</em>{29}.\text{A27}$</td>
<td>Quenched from 1100°C, aged 27 min at 500°C, quenched.</td>
</tr>
<tr>
<td>$\text{Ni}<em>{71}\text{Mn}</em>{29}\text{Cu}_3.\text{Q}$</td>
<td>Quenched from 1100°C.</td>
</tr>
<tr>
<td>$\text{Ni}<em>{71}\text{Mn}</em>{29}\text{Cu}_3.\text{A3}$</td>
<td>Quenched from 1100°C, aged 3 min at 500°C, quenched.</td>
</tr>
<tr>
<td>$\text{Ni}<em>{71}\text{Mn}</em>{29}\text{Cu}_3.\text{A9}$</td>
<td>Quenched from 1100°C, aged 9 min at 500°C, quenched.</td>
</tr>
<tr>
<td>$\text{Ni}<em>{71}\text{Mn}</em>{29}\text{Cu}_3.\text{A27}$</td>
<td>Quenched from 1100°C, aged 27 min at 500°C, quenched.</td>
</tr>
</tbody>
</table>
Figure 8.1: Lab source XRD patterns of Ni\textsubscript{71}Mn\textsubscript{29} alloy samples taken in Bragg-Brentano mode using CuK\textalpha{} radiation (\(\lambda = 1.54\ \text{Å}\)). Diffraction shows two FCC-like phases with slightly different lattice parameters. The phase with the larger lattice parameter produces broad peaks, signifying smaller crystallite sizes.

8.3 Results

8.3.1 Structural characterization from XRD and SEM

The compositions of Ni\textsubscript{71}Mn\textsubscript{29} Q and Ni\textsubscript{71}Mn\textsubscript{29} A27, along with Ni\textsubscript{71}Mn\textsubscript{29}Cu\textsubscript{3} Q and Ni\textsubscript{71}Mn\textsubscript{29}Cu\textsubscript{3} A27 were determined from backscattered images of the samples’ surfaces generated via scanning electron microscopy (SEM). For the two Ni\textsubscript{71}Mn\textsubscript{29} alloy samples, a Mn concentration of 28.88 ± 0.11 at.% was found, while for the two Ni\textsubscript{68}Mn\textsubscript{29}Cu\textsubscript{3} samples, concentrations of 29.03±0.17 at.% Mn and 3.33±0.16 at.% Cu were observed. Several positions were probed on each sample's surface at the micron scale, but the observed variations in composition were insignificant and comparable with the uncertainty of the measurement. Trace amounts of silicon were found on the samples’ surfaces (< 0.1 at.% in each case), which was presumed to have been introduced during the grinding and cutting process.
X-ray diffraction patterns were collected from each Ni$_{71}$Mn$_{29}$ and Ni$_{68}$Mn$_{29}$Cu$_3$ alloy sample using a lab source XRD. For Ni$_{71}$Mn$_{29}$Q and Ni$_{68}$Mn$_{29}$Cu$_3$.Q, the samples were mounted on an aluminium sample holder using Blu-Tack. The other samples were mounted on the aluminium sample holder using Kapton tape, which resulted in an increased background at lower angles.

XRD patterns for the Ni$_{71}$Mn$_{29}$ alloy sample set reveal two coexistent FCC-like phases with slightly different lattice parameters, which are given in Table 8.2 alongside mean crystallite sizes estimated using the Scherrer equation (see equation (3.8)). The phase with the smaller lattice has significantly sharper peaks, signifying larger crystallite sizes. The lattice parameter, $a$, of this phase is virtually insensitive to thermal treatment. Despite the fact that no variation in composition was discernible in Ni$_{71}$Mn$_{29}$ alloy samples on the scales probed via SEM, the ordered phase in the above XRD pattern has a similar lattice parameter to bulk nickel (3.520 Å), and appears to be a nickel-rich phase. This phase is subsequently referred to as the “Ni-rich phase”. The samples exhibited unusual magnetic behaviour, reported in section 8.3.3, which justified further investigation.

The peaks which result from the larger FCC lattice are much broader, and more diffuse, suggesting small crystallite sizes. Aging tends to have the effect of increasing the sharpness of the peaks in both phases, resulting in increases of $L$, the parameter relating to the mean linear dimension of particles in the Scherrer equation. The relative heights of peaks in the Ni-rich phase increase with aging time, coinciding with a decrease in the peak heights of the second phase (referred to as the “NiMn phase”), suggesting that aging drives the system towards an ordered state. In Ni$_{71}$Mn$_{29}$.A9, the lattice parameter for the NiMn phase has increased sufficiently that the two phases are resolvable, however, when $t_{age} = 27$ min, $a$ decreases to a similar value

<table>
<thead>
<tr>
<th>Aging time (min)</th>
<th>$a$ (Ni-rich) (Å)</th>
<th>$L$ (Ni-rich) (nm)</th>
<th>$a$ (NiMn) (Å)</th>
<th>$L$ (NiMn) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.525±0.002</td>
<td>26.8±8.2</td>
<td>3.545±0.004</td>
<td>7.0±1.9</td>
</tr>
<tr>
<td>3</td>
<td>3.528±0.002</td>
<td>26.2±3.9</td>
<td>3.549±0.005</td>
<td>7.5±2.1</td>
</tr>
<tr>
<td>9</td>
<td>3.526±0.002</td>
<td>56.6±14.9</td>
<td>3.565±0.012</td>
<td>7.6±1.2</td>
</tr>
<tr>
<td>27</td>
<td>3.528±0.002</td>
<td>64.0±6.9</td>
<td>3.543±0.018</td>
<td>9.8±2.7</td>
</tr>
</tbody>
</table>

Table 8.2: Lattice parameters and estimated crystallite sizes of the ordered (Ni-rich) and diffuse (NiMn) phases in Ni$_{71}$Mn$_{29}$ alloy samples.
as that of the samples with lesser aging times. A peak is observed in all patterns at $2\Theta \approx 77.5^\circ$ that cannot be attributed to either of the two phases, or the sample holder.

The relative phase proportions, as well as the composition of the NiMn phases, were determined using Quantitative Phase Analysis (QPA) and are given in Table 8.3. The fraction of the Ni-rich phase increases slightly with aging time for the first three samples, but increases significantly for Ni$_{71}$Mn$_{29}$A27, suggesting that nickel dissociates from the NiMn phase. As there is an excess of Ni within the Ni-rich phase, the concentration of Mn within the NiMn phase must be higher than the global Mn concentration. Few studies have investigated the structure of NiMn close to 40 at.\% Mn, but the crystal structure reported for ordered NiMn with 50 at.\% Mn isn’t consistent with the structure of the NiMn phase observed here [23].

Compositions of the NiMn phases based on the lattice parameters and the linear relationship between $a$ and Mn concentration reported by Hauser and Bernardini [4] are also displayed in Table 8.3. A similar linear relationship between lattice parameter and Mn concentration in the relevant concentration range is reported elsewhere [24]. It is clear that a significant discrepancy exists for the value for Mn concentration within the NiMn phase between the two methods used to determine it. The values determined using QPA are more likely to be reliable, as this method takes into account the global concentrations of the samples, which were verified using SEM, while the calculations based on lattice parameters implicitly assume a simple structure with a single phase.

<table>
<thead>
<tr>
<th>Aging time (min)</th>
<th>Ni-rich phase (at. %)</th>
<th>NiMn phase (at. %)</th>
<th>Mn concentration from QPA (at. %)</th>
<th>Mn concentration from reference [4] (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22.3±1.2</td>
<td>77.7±4.3</td>
<td>37.4±2.1</td>
<td>8.6±0.6</td>
</tr>
<tr>
<td>3</td>
<td>25.1±1.8</td>
<td>74.9±5.5</td>
<td>38.7±2.8</td>
<td>10.3±0.7</td>
</tr>
<tr>
<td>9</td>
<td>26.1±1.0</td>
<td>73.9±2.7</td>
<td>39.3±1.5</td>
<td>16.8±0.8</td>
</tr>
<tr>
<td>27</td>
<td>48.8±1.4</td>
<td>51.2±1.4</td>
<td>56.6±1.6</td>
<td>7.8±0.6</td>
</tr>
</tbody>
</table>
A single phase FCC-like pattern is observed in diffraction patterns from Ni₆₈Mn₂₉Cu₃ alloy samples, as shown in Figure 8.2. The lattice parameter in Ni₆₈Mn₂₉Cu₃ is notably different to either of those observed in the two Ni₇₁Mn₂₉ phases. The lattice parameter of Ni₆₈Mn₂₉Cu₃ is virtually independent of aging, increasing from 3.605 Å to 3.609 Å after 3 min of aging, and stabilizing after that. These values are comparable with NiMn systems in the literature with similar Mn concentrations [4]. Aging also has a slight, but discernible, effect on crystallite size, with peaks tending to sharpen with aging time.

**Figure 8.2:** Lab source XRD patterns of Ni₆₈Mn₂₉Cu₃ alloy samples using CuKα radiation. An FCC-like pattern is observed. Aging induces minute changes in the lattice parameter, and the peaks tend to sharpen with aging time.

<table>
<thead>
<tr>
<th>Aging time (min)</th>
<th>( a ) (Å)</th>
<th>( L ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.605±0.003</td>
<td>18.4±5.4</td>
</tr>
<tr>
<td>3</td>
<td>3.609±0.003</td>
<td>21.2±6.5</td>
</tr>
<tr>
<td>9</td>
<td>3.609±0.003</td>
<td>20.3±5.5</td>
</tr>
<tr>
<td>27</td>
<td>3.609±0.002</td>
<td>22.0±6.4</td>
</tr>
</tbody>
</table>

**Table 8.4:** Lattice parameters and estimated crystallite sizes of Ni₆₈Mn₂₉Cu₃ alloy samples.
Chapter 8. Magnetic properties of NiMn and NiMnCu alloys

Figure 8.3: Temperature dependent magnetization of Ni\textsubscript{71}Mn\textsubscript{29}A\textsubscript{27} measured in (a) 10 Oe and (b) 100 Oe. The peak temperature in 10 Oe is 79 ± 1.3 K and in 100 Oe is 70 ± 1.7 K.

As $t_{age}$ increases. Again a peak is observed at $2\Theta \approx 77.5^\circ$ that cannot be attributed to any of the observed phases. This peak is greatest when Kapton was not used to mount the sample to the sample holder.

Using the composition and crystal structure data, crystal densities of 8.59 g/cm$^3$ and 8.19 g/cm$^3$ were calculated for Ni\textsubscript{71}Mn\textsubscript{29} and Ni\textsubscript{68}Mn\textsubscript{29}Cu\textsubscript{3} alloy samples respectively.

8.3.2 Temperature dependent magnetization of NiMn

The temperature dependent magnetizations of four Ni\textsubscript{71}Mn\textsubscript{29} alloy samples were measured in applied fields of 10 Oe and 100 Oe. In 10 Oe, a broad peak around $\sim 80$ K is seen in the ZFC branch of Ni\textsubscript{71}Mn\textsubscript{29}A\textsubscript{27} in Figure 8.3(a). Above the peak temperature, the temperature dependence of the magnetization doesn’t appear Curie-like, suggesting that interactions persist even above the peak temperature ($T_{pk}$). For a 100 Oe applied field, the peak in the ZFC branch broadens further, while the ZFC and FC branches overlap above $\sim 100$ K. In both applied fields, a small temperature dependence is exhibited in the TRM branch at temperatures approaching room temperature. While this may be attributed to a small negative remanent field persisting in the superconducting magnet (see section 3.2.3), it also suggests that a positive remanent magnetization is the equilibrium state after removing a positive applied
field, right up until room temperature. A low but measurable remanent magnetization is indicative of a system that is ferromagnetic even at room temperature. The ferromagnetic response is attributed to the magnetism of the Ni-rich phase.

The Curie-Weiss law (equation (4.1)) was applied to the measured ZFC branches for each Ni$_{71}$Mn$_{29}$ sample in the region where the inverse magnetization was approximately linear (i.e., well above the peak temperature), but the resultant values for effective moment per spin ($\mu_{atom}$) were both field dependent and too large to be physically feasible. This supports the view that the system is ferromagnetic, even as it approaches room temperature.

### 8.3.3 Minor hysteresis loops of NiMn

A magnetization curve of Ni$_{71}$Mn$_{29}$A27 measured above room temperature, seen in Figure 8.4(a), explicitly demonstrates the ferromagnetic behaviour suggested by the temperature dependent behaviour reported in section 8.3.2. There is little hysteresis, and the response is approximately linear in high field, but a non-linear “step” magnetization, $M_{st}$, (defined in section 4.4.1) is observed as the magnetization reverses. The high field susceptibility increases slightly when the sample is cooled in zero field to 5 K, but the height of the step increases significantly (Figure 8.4(b)). When a low positive cooling field of 200 Oe is applied, a small amount of asymmetric reversal becomes apparent, with the curvature of the magnetization response being greater on the positive side of the step than the negative side. The step magnetization is $3.62 \pm 0.02$ emu/g, and stays constant within uncertainty between $0 \leq H_{FC} \leq 1000$ Oe.

However, within this range of cooling fields, both magnetization values at either end of the loops, $M(H_{max})$ and $M(-H_{max})$, increase approximately linearly with $H_{FC}$, resulting in the magnetization curve appearing to shift up along the magnetization axis with cooling field. The magnetization at the positive maximum field increases at a slightly greater rate with $H_{FC}$ than the magnetization at the negative maximum field, meaning that the average of the two values also increases with cooling field.

When $H_{FC} = 8000$ Oe, a secondary step develops in hysteresis loops for all Ni$_{71}$Mn$_{29}$ alloy samples, as seen in Figure 8.5 (subsequently, the step which appears in all nonlinear magnetization curves close to $H = 0$ Oe will be referred to as the “primary”
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(a) \( t_{\text{age}} = 27 \) min, \( T = 315 \) K, ZFC.  
(b) \( t_{\text{age}} = 27 \) min, \( T = 5 \) K, ZFC.  
(c) \( t_{\text{age}} = 27 \) min, \( T = 5 \) K, \( H_{\text{FC}} = 200 \) Oe.  
(d) \( t_{\text{age}} = 27 \) min, \( T = 5 \) K, \( H_{\text{FC}} = 1000 \) Oe.

Figure 8.4: Minor hysteresis loops of Ni\(_{71}\)Mn\(_{29}\)A\(_3\) between \( \pm 8 \) kOe at (a) 316 K after ZFC, (b) 5 K after ZFC, (c) 5 K after \( H_{\text{FC}} = 200 \) Oe and (d) 5 K after \( H_{\text{FC}} = 1000 \) Oe.

step). Hysteresis becomes apparent in the region of the secondary step, and there is an observable training effect which sees a slight decrease in the magnitude of the field at which the secondary step is triggered (\(|H_{\text{st2}}|\)) with each loop iteration. With the exception of Ni\(_{71}\)Mn\(_{29}\)-A\(_3\), \(|H_{\text{st2}}|\) decreases with aging time, while the magnetization and curvature of the secondary step increases with aging time. The differential susceptibility (\(dM/dH\)) at \( H_{\text{st2}}\) also increases with aging time. It is also noteworthy that the secondary step is strongly asymmetric. The curvature on the negative side of the secondary step is much higher compared with that on the positive side.
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Figure 8.5: Minor hysteresis loops of Ni$_{71}$Mn$_{29}$ alloy samples aged for various times, measured at 5 K between ±8 kOe after $H_{\text{FC}} = 8000$ Oe, where a secondary step develops. The insets highlight the changes in loop path due to training.

The behaviour of the secondary step in Ni$_{71}$Mn$_{29}$A3 appears to be inconsistent compared with that of the other samples. The secondary step only manifests on the “down” branch and is almost completely suppressed on the “up”. The curvature of the secondary step is greater on the positive side, as opposed to the negative side, while the magnitude of $H_{\text{st}}$ is much lower than that of Ni$_{71}$Mn$_{29}$A27, despite the lesser aging time. $M(H_{\text{max}})$ after $H_{\text{FC}} = 8000$ Oe is also much greater for Ni$_{71}$Mn$_{29}$A3 than it is for the other samples in the same sample set.
Minor hysteresis loops of Ni_{71}Mn_{29}A_{27} measured between nominal fields of ±200 Oe, displayed in Figure 8.6, highlight the way in which the primary step changes with cooling field. The primary step appears to shift upwards along the magnetization axis by an amount which depends on cooling field (which is supported by other $M$-$H$ loops cooled after various fields, not shown here). A training effect develops in negative fields once a cooling field is applied, but only on the “down” branches, and a small amount of asymmetry is apparent which seems to favor negative magnetization.

Figure 8.7 shows minor hysteresis loops of Ni_{71}Mn_{29}A_{27} between 10 and 20 K. At 10 K, after cooling in zero field a small amount of hysteresis is induced, and the magnetization at $H_{\text{max}}$ has increased slightly compared with the equivalent loop at 5 K (Figure 8.4(b)). When $H_{\text{FC}} = 8000$ Oe, $M(H_{\text{max}})$ increases significantly, and a secondary step becomes apparent again. The width of the hysteresis around the secondary step has also increased significantly compared with 5 K, with $H_{\text{sat}}$ on the “up” branch changing much more than $H_{\text{sat}}$ on the “down” branch from 5 K to 10 K.

Hysteresis loops measured at 20 K are shown in Figures 8.7(c) and 8.7(d). At 20 K, hysteresis becomes enhanced in the high field region of the loop after ZFC, and $M(H_{\text{max}})$ again increases with temperature. After cooling in 8000 Oe, training is clearly apparent on the “down” branch, but has negligible effect on the “up” branch.
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(a) $t_{age} = 27$ min, $T = 10$ K, ZFC.
(b) $t_{age} = 27$ min, $T = 10$ K, $H_{FC} = 8000$ Oe.
(c) $t_{age} = 27$ min, $T = 20$ K, ZFC.
(d) $t_{age} = 27$ min, $T = 20$ K, $H_{FC} = 8000$ Oe.

**Figure 8.7:** Minor hysteresis loops of Ni$_{71}$Mn$_{29}$A27 measured between ±8 kOe at 10 K and 20 K after ZFC and $H_{FC} = 8000$ Oe.

$H_{st}$ decreases with each loop iteration, while $M(H_{max})$ decreases by 5.6% between the first and second iteration and by a further 0.99% between the second and third loops.

After cooling in 8000 Oe, the differential susceptibility as a function of field shows two peaks on the “down” branches of minor hysteresis loops for all Ni$_{71}$Mn$_{29}$ alloy samples at 5 K, which coincide with each of the steps. Generally, as $|H_{st2}|$ decreases, the differential susceptibility at $H_{st2}$ increases. Also, with the exception of Ni$_{71}$Mn$_{29}$A3, $|H_{st2}|$ decreases with aging time, while the differential susceptibility peak shape around the secondary step sharpens with aging time. However, of the
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(a) Differential susceptibility.

(b) High field susceptibility.

Figure 8.8: (a) Differential susceptibility for the first “down” branches of minor loops of Ni$_{71}$Mn$_{29}$ at 5 K after $H_{FC} = 8000$ Oe. (b) High field susceptibility for minor loops of Ni$_{71}$Mn$_{29}$ measured at 5 K as a function of cooling field.

The high field susceptibility ($\chi_{H\rightarrow H_{max}}$) for all Ni$_{71}$Mn$_{29}$ alloy samples at 5 K is displayed in Figure 8.8(b) as a function of cooling field. Generally, $\chi_{H\rightarrow H_{max}}$ decreases with cooling field and increases with aging time. The exception, again, is for Ni$_{71}$Mn$_{29}$ A3, which has a greater high field susceptibility than each of the other samples for all measured variations of cooling field.

The dependence of $M_{st}$ for the primary step on cooling field at 5 K varies from sample to sample. For Ni$_{71}$Mn$_{29}$ Q, $M_{st}$ increases only slightly between ZFC and $H_{FC} = 1000$ Oe, before growing from 3.53 emu/g to 4.22 emu/g when $H_{FC}$ is increased to 8000 Oe. Ni$_{71}$Mn$_{29}$ A9 and Ni$_{71}$Mn$_{29}$ A27 show similar dependencies on cooling field. Ni$_{71}$Mn$_{29}$ A3 is again anomalous compared with the other Ni$_{71}$Mn$_{29}$ alloy samples. In this case, $M_{st}$ dips sharply when $H_{FC} = 1000$ Oe.
Figure 8.9: Step magnetization as a function of aging time, extracted from minor loops of Ni$_{71}$Mn$_{29}$ alloys measured at 5 K after various cooling fields. The dashed line displays the height of the secondary step which develops in loops after cooling in 8000 Oe.

The dashed line in Figure 8.9 shows the total height of the secondary step (as opposed to the step magnetization, which is half of the total height of the step in the case of the primary step) as a function of aging time. The height of the secondary step, $M_{s12}$ is greatest for Ni$_{71}$Mn$_{29}$.A3. For the other samples, aging has the effect of increasing the height of the secondary step, which can be seen explicitly in the minor hysteresis loops shown in Figure 8.5.

Figure 8.10(a) shows the secondary step field for the “up” and “down” branches of the first loop measured after $H_{FC} = 8000$ Oe at 5 K, as a function of aging time. The width of these loops, displayed in 8.10(b), is taken as the width of the hysteresis loop at its widest point, which coincides with the difference between the secondary step fields on the “up” and “down” branches, as this was the only region where significant hysteresis was observed at 5 K. The loop width decreases with aging time.
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8.3.4 Temperature dependent magnetization of NiMnCu

The ZFC branches of four Ni\textsubscript{68}Mn\textsubscript{29}Cu\textsubscript{3} alloy samples measured in 1000 Oe are shown in Figure 8.11. The peaks of the ZFC branches are flat, somewhat resembling the low field magnetization of NiMn in its reentrant spin glass state [7]. However, the broadness of the plateau is smaller than that typically observed in reentrant NiMn, spanning approximately 20 K for each sample except Ni\textsubscript{68}Mn\textsubscript{29}Cu\textsubscript{3}_A3, where the plateau extends for 37 K. The temperature where the ZFC and FC branches converge is labeled the freezing temperature here ($T_f$), while the glass temperature is taken as the temperature where the ZFC magnetization begins to decay. $M$ ($T_{pk}$) is greatest for Ni\textsubscript{68}Mn\textsubscript{29}Cu\textsubscript{3}_A3, and decreases for longer aging times. The presence of 3 at.\% Cu has caused a factor of 82 decrease in the susceptibility at $T_{pk}$ in the $t_{age} = 3$ min sample, as seen by comparing the peak susceptibility of Ni\textsubscript{68}Mn\textsubscript{29}Cu\textsubscript{3}_A3 with that for Ni\textsubscript{71}Mn\textsubscript{29}_A3 reported in section 8.3.2.

The Curie-Weiss Law, given in equation (4.1), was applied to Ni\textsubscript{68}Mn\textsubscript{29}Cu\textsubscript{3} ZFC branches well above $T_{pk}$, where the inverse magnetization is approximately linear, and values for the effective moment per spin were extracted. $\mu_{atom}$ tends to decrease with aging time. Values for $\Theta$ were also extracted, but behaved erratically with respect to aging time, owing to a small amount of non-linearity in the low field magnetization,
Figure 8.11: ZFC magnetization branches of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples measured in 1000 Oe. The peak temperatures and magnetizations are given in Table 8.5.

Table 8.5: Peak temperatures, moment per atom, $T_{pk}$ and $M(T_{pk})$ parameters of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples, extracted from temperature dependent ZFC magnetization branches measured in 1000 Oe. The temperature at which the FC and ZFC branches converge is labeled $T_f$, the freezing temperature, while $T_g$ gives the temperature at which the magnetization begins to decay.

<table>
<thead>
<tr>
<th>Aging time</th>
<th>$T_f$</th>
<th>$T_g$</th>
<th>$\mu_{\text{atom}}$</th>
<th>$M(T_{pk})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>85.2 K</td>
<td>105.5 K</td>
<td>4.48 $\mu_B$</td>
<td>0.232 emu/g</td>
</tr>
<tr>
<td>3 min</td>
<td>88.0 K</td>
<td>125.8 K</td>
<td>3.85 $\mu_B$</td>
<td>0.346 emu/g</td>
</tr>
<tr>
<td>9 min</td>
<td>81.3 K</td>
<td>109.7 K</td>
<td>3.85 $\mu_B$</td>
<td>0.260 emu/g</td>
</tr>
<tr>
<td>27 min</td>
<td>83.3 K</td>
<td>108.3 K</td>
<td>2.54 $\mu_B$</td>
<td>0.225 emu/g</td>
</tr>
</tbody>
</table>
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Figure 8.12: Minor hysteresis loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples measured between ±8 kOe at 5 K after ZFC (red and blue circles) and $H_{FC} = 8000$ Oe (green and yellow triangles). (a) $t_{age} = 0$ min, (b) $t_{age} = 3$ min, (c) $t_{age} = 9$ min, (d) $t_{age} = 27$ min.

as will be shown explicitly in hysteresis in section 8.3.5. As the Curie-Wei"{s}s Law assumes a linear magnetization response when the applied field is low, these values for $\Theta$ hold little meaning.

8.3.5 Minor hysteresis loops of NiMnCu

The magnetization loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples at 5 K between ±8 kOe are largely linear in both the absence and presence of a cooling field, with the exception
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(a) $t_{age} = 0$ min, $T = 5$ K, $H_{max} = 20$ kOe.

(b) $t_{age} = 3$ min, $T = 5$ K, $H_{max} = 20$ kOe.

(c) $t_{age} = 9$ min, $T = 5$ K, $H_{max} = 20$ kOe.

(d) $t_{age} = 27$ min, $T = 5$ K, $H_{max} = 20$ kOe.

**Figure 8.13:** $M$-$H$ loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples measured between $\pm 20$ kOe at 5 K after ZFC (red and blue circles) and $H_{FC} = 20$ kOe (green and yellow triangles). (a) $t_{age} = 0$ min, (b) $t_{age} = 3$ min, (c) $t_{age} = 9$ min, (d) $t_{age} = 27$ min.

of Ni$_{68}$Mn$_{29}$Cu$_3$-A3, which develops a significant step magnetization and hysteresis in negative fields. Small steps are observable in low fields for Ni$_{68}$Mn$_{29}$Cu$_3$-Q (Figure 8.12(a)) and Ni$_{68}$Mn$_{29}$Cu$_3$-A9 (Figure 8.12(c)), in both the ZFC and $H_{FC} = 8$ kOe loops.

When $H_{max}$ is increased to 20 kOe, all samples exhibit a step magnetization in negative fields upon cooling in field, as well as appreciable hysteresis, asymmetric reversal, and an exchange bias effect (Figure 8.13). As well as a large step in negative fields, which is the dominant feature of magnetization loops measured for
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$H_{\text{max}} = H_{\text{FC}} = 20$ kOe, a smaller non-linearity is observable in low fields for samples where $t_{\text{age}} = 0$ min, $t_{\text{age}} = 9$ min and $t_{\text{age}} = 27$ min, which is noteworthy because it also appears in the linear, paramagnetic region of loops measured after field cooling as well. Its absence from other, equivalent measurements indicates that it is not a systematic error. For loops measured after ZFC, $\chi_{H \rightarrow H_{\text{max}}}$ follows a similar trend with aging time as that of $T_g$, as reported in section 8.3.4, peaking at $t_{\text{age}} = 3$ min.

A step appears when $H_{\text{FC}} = 20$ kOe. Its curvature increases sharply from $t_{\text{age}} = 0$ min to $t_{\text{age}} = 3$ min, while the field that the step occurs at, $H_{\text{st}}$, decreases in magnitude between the two samples. $|H_{\text{st}}|$ increases again for samples with larger aging times, while the height of the step decreases. While the magnetization loops for Ni$_{68}$Mn$_{29}$Cu$_3$.A9 and Ni$_{68}$Mn$_{29}$Cu$_3$.A27 are similar, the latter sample exhibits a slightly larger extent of asymmetric reversal, in which the curvature on the negative side of the step is sharper than that on the positive side of the step.

Magnetization loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples measured between ±75 kOe at 5 K are displayed in Figure 8.14. In general, loops measured upon ZFC exhibit exchange bias. This exchange bias effect is greatest for Ni$_{68}$Mn$_{29}$Cu$_3$.A3, in which an exchange bias field of approximately $-2400$ Oe is induced in the first loop measured after ZFC. It is worth noting that for each sample, the “up” branch of the first loop measured after ZFC has a greater curvature than the “down” branch, suggesting that the maximum negative field enhances the effective cluster moment.

When a cooling field of 75 kOe is applied, a step develops in negative fields, resulting in an exchange bias field in the range $-2900$ to $-1600$ Oe. $|H_{\text{EB}}|$ is greatest for Ni$_{68}$Mn$_{29}$Cu$_3$.Q, and least for Ni$_{68}$Mn$_{29}$Cu$_3$.A3, while the step magnetization is greatest for Ni$_{68}$Mn$_{29}$Cu$_3$.A3 ($M_{\text{st}} = 3.12$ emu/g) and least for Ni$_{68}$Mn$_{29}$Cu$_3$.A27 ($M_{\text{st}} = 2.82$ emu/g).

Figure 8.15(a) shows the first magnetization loop of Ni$_{68}$Mn$_{29}$Cu$_3$.A27 measured after ZFC between ±20 kOe at 10 K. The response is still mostly linear, with the susceptibility increasing by $\sim 14\%$ compared with that observed at 5 K. However, a small amount of hysteresis is noticeable in the low field region of the loop, with the non-linearity about the coercive field and the coercivity both increasing with temperature. When a cooling field of 20 kOe is applied (Figure 8.15(b)), coercivity
and hysteresis increase significantly from 5 K to 10 K. A slight training effect becomes apparent on the “down” branches of consecutive loops, resulting in small, iterative decreases in $M(H_{\text{max}})$ and $|H_{c\downarrow}|$.

At 20 K, coercivity and high field susceptibility continue to increase. A training effect is apparent on the “down” branch after cooling in 20 kOe, as seen in Figure 8.15(d). The effect is greatest between the first and second loops, resulting in marked decreases in $M(H_{\text{max}})$ and $|H_{c\downarrow}|$. While the branches of the magnetization loops are non-linear,
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(a) $t_{\text{age}} = 27\ \text{min},\ T = 10\ \text{K},\ \text{ZFC}$.

(b) $t_{\text{age}} = 27\ \text{min},\ T = 10\ \text{K},\ H_{\text{FC}} = 20\ \text{kOe}$.

(c) $t_{\text{age}} = 27\ \text{min},\ T = 20\ \text{K},\ \text{ZFC}$.

(d) $t_{\text{age}} = 27\ \text{min},\ T = 20\ \text{K},\ H_{\text{FC}} = 20\ \text{kOe}$.

**Figure 8.15:** $M$–$H$ loops of Ni$_{68}$Mn$_{29}$Cu$_3$A27 measured between ±20 kOe at 10 K and 20 K after various cooling fields.

at 20 K there is no distinct step.

Figure 8.16(a) shows the differential susceptibility of the first “down” branches of loops displayed in Figure 8.13, where $T = 5\ \text{K}$ and $H_{\text{max}} = H_{\text{FC}} = 20\ \text{kOe}$. The peak in differential susceptibility coincides with the step, while the area under the peak gives the height of the step, $2M_{st}$. The peak in differential susceptibility for Ni$_{68}$Mn$_{29}$Cu$_3$Q is significantly lower and broader than it is for the other samples, while the magnitude of the field it occurs at is higher. $|H_{\text{st}}|$ decreases significantly when $t_{\text{age}} = 3\ \text{min}$, while the peak in differential susceptibility increases by more
than a factor of 11 compared with \( t_{\text{age}} = 0 \) min. The step field changes only slightly between \( t_{\text{age}} = 9 \) min and \( t_{\text{age}} = 27 \) min, but the peak differential susceptibility increases significantly with aging time for the last two samples. Within each peak, there is a small dip in differential susceptibility, which coincides with the coercive field. This is attributed to noise in the measured signal at very low magnetization values.

The high field susceptibility of loops measured at 5 K is displayed in Figure 8.16(b) as a function of aging time. \( \chi_{H \rightarrow H_{\text{max}}} \) tends to peak around an aging time of 3 min, and decrease as cooling field and maximum field are increased.

The step magnetization exhibits a similar dependence on aging time, as seen in Figure 8.17(a). When \( H_{\text{max}} = 75 \) kOe, the step magnetization peaks with 3 min of aging, and decreases with longer aging times. \( M_{\text{st}} \) behaves similarly when \( H_{\text{max}} = H_{\text{FC}} = 20 \) kOe, but increases slightly between aging times of 9 min and 27 min; however, this increase is insignificant, and is less than the uncertainty in the measurements. Loops measured between \( \pm 8 \) kOe or \( \pm 20 \) kOe after ZFC are predominantly linear, yielding small values for step magnetization.

The magnitude of the step field decreases sharply at an aging time of 3 min on each of the branches shown in Figure 8.17(b). For samples with longer aging times, \( H_{\text{st}} \)
Figure 8.17: (a) Step magnetization extracted from minor loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples at 5 K, shown as a function of aging time. The blue series highlight loops measured upon ZFC. Other colours symbolize loops where $H_{FC} = H_{max}$. Circles are for loops measured between ±8 kOe, triangles are for loops measured between ±20 kOe and squares are for loops measured between ±75 kOe. (b) Step field for the first “down” and “up” branches of loops measured at 5 K for $H_{FC} = 20$ kOe and $H_{FC} = 75$ kOe.

varies only slightly with $t_{age}$.

Coercivity at 5 K is displayed in Figure 8.18(a) as a function of aging time for various combinations of $H_{max}$ and $H_{FC}$. The amount of coercivity is relatively small in all samples in loops measured between ±20 kOe after ZFC, where the response of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples is largely paramagnetic. Coercivity increases when a cooling field of 20 kOe is applied and hysteresis develops around the step between the “down” and “up” branches. A large amount of coercivity develops when $M-H$ loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples are measured between 75 kOe after ZFC, where the response is non-linear but there is no distinct step. A step develops in loops measured after cooling in a field of 75 kOe. These loops exhibit a greater degree of hysteresis in the high field region, away from the step, and as such, the amount of coercivity decreases.

The exchange bias field is relatively small in loops measured after ZFC, although there is a slight increase in $|H_{EB}|$ at $t_{age} = 3$ min when $H_{max} = 20$ kOe and a significant increase when $H_{max} = 75$ kOe. The latter is due to the fact that the curvature of the response on the “up” branch is much greater than the curvature on the “down”
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8.4 Discussion

In this investigation the magnetic properties of a set of four Ni$_{71}$Mn$_{29}$ alloy samples and a set of four Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples were studied and, in both sample sets, a sensitivity to aging time during the preparation process and cooling field during an experiment was observed. The magnetic behaviour of Ni$_{71}$Mn$_{29}$ is vastly different to the magnetic behaviour found in Ni$_{68}$Mn$_{29}$Cu$_3$ with the former system tending towards a mixture of ferromagnetic and exchange bias behaviour, and the latter exhibiting aspects of disordered magnetism. Some of the results are difficult to reconcile with other aspects of the observed behaviour. Speculative explanations for the observed behaviour will be considered in this section.

The presence of a Ni-rich phase in the Ni$_{71}$Mn$_{29}$ alloy samples can account for much of their magnetic behaviour. Presumably, a portion of nickel did not alloy during the arcing process, but the inhomogeneities were not detected in SEM scans, possibly because the 1 micron resolution of the instrument was insufficient to discern them. In

![Figure 8.18: (a) Coercivity of minor loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples at 5 K as a function of aging time. The blue series symbolize loops measured upon ZFC, while other colours give loops where $H_{FC} = H_{max}$. (b) Exchange bias fields of the same set of $M-H$ loops.](image-url)
diffraction terms, in contrast, 1 micron corresponds to a large particle size. The Bragg peaks in Figure 8.1 from the NiMn phase are broader, which is likely due to a combination of small crystallite sizes and a concentration gradient within the NiMn phase. The lattice parameter of NiMn has been shown to increase with Mn concentration [4, 24], but the observed value for the NiMn phase here is less than, and therefore inconsistent with, those reported in other studies of NiMn between 29 and 40 at.% Mn. The heights of the Bragg peaks from the Ni-rich phase increase dramatically with aging. Ordering of Ni$_3$Mn has been shown to occur near 500°C [12]. Ordered Ni$_{50}$Mn$_{50}$ forms a tetragonal structure with a $c_0$ lattice parameter similar to that of nickel [23], but the observed pattern here does not support the presence of ordered Ni$_{50}$Mn$_{50}$. Quantitative phase analysis appears to suggest that nickel has somehow dissociated from the NiMn phase in Ni$_{71}$Mn$_{29}$, but it is difficult to reconcile this with an aging temperature of 500°C. The nickel-manganese phase diagram [25] suggests that a $\zeta$ phase with unknown structure forms at $\sim$ 29 at.% Mn just below 500°C, while an $\eta$ phase with a simple cubic lattice forms near $\sim$ 50 at.% Mn below 500°C. Between these concentration ranges, the system passes through a number of phase transitions as it is cooled below 500°C, which may account for the unusual aging dependence exhibited by the structure of the Ni$_{71}$Mn$_{29}$ alloy samples. However, a simple cubic structure wasn’t observed here, which discounts the possibility of an $\eta$ phase existing in these samples.

While a peak is observed in the temperature dependent magnetization of Ni$_{71}$Mn$_{29}$, magnetization curves of each sample after cooling in low fields indicate ferromagnetic behaviour both well above and well below $T_{pk}$, which is likely due to the Ni-rich phase. The discrepancy between the ZFC and FC magnetizations above $T_{pk}$ in a small field of 10 Oe, as seen in Figure 8.3(a), is evidence for magnetic irreversibility even at these temperatures. As the magnetization of the Ni-rich phase is highly nonlinear in low fields (shown explicitly in Figure 8.6), it is difficult to model its direct contribution to the temperature dependent magnetization. When the temperature dependent magnetization is fitted to a Curie-Weiss law well above $T_{pk}$, where the inverse magnetization is approximately linear, the resultant parameters for the effective atomic moments in each sample are unphysically large, which is a result of the strong ferromagnetic interactions that persist even at these temperatures.
The application of low cooling fields results in $M-H$ loops that shift slightly upwards along the magnetization axis. The upward shift may be attributed to the NiMn phase, which is presumed to be mostly antiferromagnetic if the compositions suggested by Table 8.3 are accurate [24, 26]. It is likely that, for low cooling fields, the NiMn phase behaves similarly to the aged Cu$_{81.2}$Mn$_{18.8}$ alloy reported in section 5.3.3, which exhibits linear $M-H$ loops that are offset along the negative field axis by an amount that is proportional to the cooling field. For this reason, it is plausible that a secondary step might appear if the magnitude of the negative maximum field was increased sufficiently.

After cooling in 8000 Oe, a secondary step forms in the negative field region of the hysteresis loop, which is also attributed to the NiMn phase and is again analogous with the behaviour of aged Cu$_{81.2}$Mn$_{18.8}$ alloy reported in Chapter 5. The step field, $H_{st2}$, is very likely related to the unidirectional anisotropy of the NiMn phase. If we momentarily disregard Ni$_{71}$Mn$_{29}$A3, both the height and differential susceptibility of the secondary step in the other three samples increase with aging time, while $|H_{st2}|$ decreases with $t_{age}$. The decrease of $|H_{st2}|$ in particular is significant of a decrease in unidirectional anisotropy and is consistent with the ordering effect that the structural data suggest aging has on the samples. Figure 8.8(a) shows that, while there is very little change in the differential susceptibility around the primary step between each sample (i.e., the magnetism of the Ni-rich phase), the differential susceptibility of the secondary step increases noticeably with aging time (again, disregarding Ni$_{71}$Mn$_{29}$A3), which may also be attributed to the ordering of the NiMn phase.

With regard to its magnetic behaviour, Ni$_{71}$Mn$_{29}$A3 is an outlier compared with the other Ni$_{71}$Mn$_{29}$ alloy samples. The magnitude of the secondary step field is significantly lower than it is in the other Ni$_{71}$Mn$_{29}$ alloy samples, and only manifests itself on the “down” branch of the hysteresis loop, suggesting that unidirectional anisotropy is suppressed in this sample. In the first instance, this appears inconsistent with the link between ordering and unidirectional anisotropy proposed above to account for the behaviour of the other Ni$_{71}$Mn$_{29}$ alloy samples, because the XRD pattern of Ni$_{71}$Mn$_{29}$A3 is not remarkably different to those of the other samples.

The large magnetization of Ni$_{71}$Mn$_{29}$A3 may possibly be reconciled with the behaviour of the other samples by considering the nature of domains within the NiMn
The XRD data in Table 8.2 appear to suggest that the crystallite sizes in the NiMn phase coarsen. If the crystallite sizes are below the critical domain size for NiMn in the two samples where \( t_{\text{age}} \leq 3 \text{ min} \), and above it for the samples with longer aging times, the large secondary step magnetization (Figure 8.9) and differential susceptibility (Figure 8.8(a)) of Ni\(_{71}\)Mn\(_{29}\)A3 could be explained in terms of single domain particles with giant, coherent moments. If the particles then break up into multi-domains for longer aging times and coarser crystallite sizes, this might account for the decrease in secondary step magnetization and differential susceptibility when \( t_{\text{age}} > 3 \text{ min} \).

This picture may also account for the dependence of the secondary step field on aging time (Figure 8.10(a)). If single domain particles in the NiMn phase in the sample aged for 3 minutes are coarser than they are in Ni\(_{71}\)Mn\(_{29}\)Q, this means the domains have a smaller relative surface through which the NiMn and Ni-rich phases can interact, which accounts for the decrease in \( H_{\text{st2}} \) at \( t_{\text{age}} = 3 \text{ min} \). If these particles break up into multiple domains that are mostly antiferromagnetic, these domain structures tend to be more stable and act to pin interacting ferromagnetic components [27, 28], which, in this case, are probably neighbouring nickel domains. Qualitatively, this is consistent with an enhancement of the exchange bias effect in samples with aging times longer than 3 min.

The shoulder in the differential susceptibility of the primary step in Figure 8.8(a) highlights asymmetry in the reversal of the primary step. As asymmetric reversal often results from a competition between unidirectional and uniaxial anisotropy energies [29–32], this strongly suggests that an exchange interaction occurs between the Ni-rich phase (mostly ferromagnetic) and NiMn phase (mostly antiferromagnetic).

The Ni\(_{68}\)Mn\(_{29}\)Cu\(_3\) alloy samples contain 3.33 ± 0.16 at.% more copper and a similar quantity less nickel than the Ni\(_{71}\)Mn\(_{29}\) alloy samples, determined from backscattered images of the samples’ surfaces generated via scanning electron microscopy (SEM). The addition of a small concentration of non-magnetic defects into the system and a commensurate decrease in nickel resulted in a factor of ~82 decrease in the low field susceptibility at the peak temperature. This can be explained by the absence of a ferromagnetic phase in Ni\(_{68}\)Mn\(_{29}\)Cu\(_3\).
A single phase is observed in Ni$_{68}$Mn$_{29}$Cu$_3$, with a lattice parameter that is virtually uninfluenced by aging. Aging appears to have a sharpening effect on the peaks in the XRD pattern (Figure 8.2), but the increase in crystallite size determined by the Scherrer equation is comparable with the uncertainty of the parameter. The Scherrer equation itself likely yields an underestimate of the crystallite size, given that other broadening effects, particularly local strain effects, haven’t been accounted for.

The peak magnetizations of each Ni$_{68}$Mn$_{29}$Cu$_3$ alloy sample given in Table 8.5 coincide with the general trend in magnetic behaviour observed within all samples in this set: the sample aged 3 min has the greatest magnetic order, while samples exposed to further aging have a decreased susceptibility. This evidently makes it difficult to draw a direct link between the magnetic properties of the Ni$_{68}$Mn$_{29}$Cu$_3$ alloy sample set and the crystal structures determined from XRD. It would be of interest to investigate these samples using a combination of neutron powder diffraction and small-angle neutron scattering (SANS) in order to determine the relationship between structure and magnetism in this system.

The moment per atom reported in Table 8.5 was determined by applying equation (4.1) to the slope of the inverse of temperature dependent magnetization well above $T_{pk}$. This value is an average of the moment of all atoms in the system, but typically, in NiMn a greater moment is localized on the Mn atoms than the Ni atoms, which leads to the observed spin-glassy behaviour [24, 33, 34]. Similarly, in CuMn, the moment is almost entirely localized on the Mn atoms [35–37]. Thus, it may be presumed that in Ni$_{68}$Mn$_{29}$Cu$_3$, most of the moment is localized on the Mn atoms, with the remainder on the Ni atoms, and a negligible amount (if any) on the Cu atoms. There is insufficient data to speculate what proportion of the moment is localized to which atoms, but this could be determined using polarized neutron analysis. The values calculated from the temperature dependent magnetizations appear to be significantly larger than those typically reported in the literature for similar NiMn samples with comparable concentrations, determined from neutron measurements (eg, $\sim 4.8 \, \mu_B$ per atom here compared with $\sim 4 \, \mu_B$ per Mn atom in reference [24]). This discrepancy may be attributed to the small non-linearity seen in the low field region of hysteresis loops reported in section 8.3.5.
Minor hysteresis loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloys appear analogous to those exhibited by aged Cu$_{81.2}$Mn$_{18.8}$ alloy at low temperature. A step develops in the $M$-$H$ loop of Ni$_{68}$Mn$_{29}$Cu$_3$.A3 after cooling in 8000 Oe (Figure 8.12(b)), while, for the other Ni$_{68}$Mn$_{29}$Cu$_3$ alloys, cooling in field results in a linear (paramagnetic) response that has been shifted along the field axis in the negative direction. This suggests that unidirectional anisotropy is significantly suppressed in Ni$_{68}$Mn$_{29}$Cu$_3$.A3 compared with the other samples. It is presumed that, if the negative maximum field was extended, a step would develop in the other samples, which is essentially what is seen in loops where the cooling and maximum measuring fields were increased to 20 kOe (Figure 8.13).

As with the Ni$_{71}$Mn$_{29}$ alloys, the relatively large high-field susceptibility (Figure 8.16(a)), step magnetization (Figure 8.17(a)) and decreased step field (Figure 8.17(b)) in Ni$_{68}$Mn$_{29}$Cu$_3$.A3 compared with other Ni$_{68}$Mn$_{29}$Cu$_3$ samples may also be possibly understood by considering the way in which domain structures depend on aging. If aging causes short-range order in Ni$_{68}$Mn$_{29}$Cu$_3$, magnetic clusters may form that increase in size with aging time. The observed dependencies of $\chi_{H\rightarrow H_{\text{max}}}$, $M_{\text{st}}$ and $|H_{\text{st}}|$ on aging time are qualitatively consistent with clusters growing sufficiently large that they break up into multi-domain particles once $t_{\text{age}} > 3$ min.

The dependence of the exchange bias field and step magnetization in Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples on cooling field suggest the presence of a magnetically disordered phase which has a number of local, energetically stable configurations that are established by the cooling field [38]. However, more data detailing the dependence of $H_{\text{EB}}$ and $M_{\text{st}}$ on $H_{\text{FC}}$ are needed to determine whether this is the case with a reasonable degree of confidence.

The modified Stoner-Wohlfarth model used to extract parameters relating to effective cluster moment, uniaxial anisotropy and unidirectional anisotropy from $M$-$H$ loops of CuMn alloys in sections 5.4 and 6.4.3 would not converge to hysteresis loops of Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples. This was because the asymmetric reversal observed in hysteresis loops in section 8.3.5 appears to favour negative magnetizations; the curvature of $M$-$H$ loops is greater on the negative side of the step than it is on the positive side. As a distribution of easy axes is required to model asymmetric reversal [30, 31, 39, 40], Ni$_{68}$Mn$_{29}$Cu$_3$ hysteresis loops may be modeled using the Gaussian
distribution of easy axes utilized in previous chapters, along with negative values of effective cluster moment, but this would be unphysical. Evidently, the model needs to be modified further to account for the present data. It is possible that a distribution of easy axes centred around alignment in the opposite direction of the field would be more successful in accounting for the type of asymmetric reversal observed in this sample set. However, whether this is a physically realistic scenario is open to discussion.

Similar behaviour is observed in the secondary step of Ni$_{71}$Mn$_{29}$ alloy samples, though the extent is not as apparent, possibly obscured by the ferromagnetic Ni-rich phase. One might model the hysteresis loops in Figure 8.5 by assuming the ferromagnetic Ni-rich phase and spin glass NiMn phase do not interact, and subtracting the nickel contribution. However, this is a naive assumption because the asymmetry about the primary step in high cooling field hysteresis loops suggests that some interaction occurs between the ferromagnetic and spin glass phases.

Doping of reentrant [16–18, 41] and spin glass [11] NiMn systems with non-magnetic defects has been performed in the past. When small concentrations of Pt or Pd dopants between 1 and 5 at.% are introduced in reentrant NiMn systems, the result is enhanced coercivity and exchange bias in hysteresis loops at low temperature, but minimal change in the peak temperature or the saturation magnetization. This is explained by the fact that the dopant atoms induce a large spin-orbit coupling, which enhances magnetic anisotropy through a Dzyaloshinskii-Moriya type interaction [17, 18, 22]. When NiMn is a spin glass, introduction of Pt results in a decrease in susceptibility, but increase in peak temperature [11], which also occurred in this investigation when copper was used as a non-magnetic dopant. The addition of copper also appears to result in an enhancement of magnetic anisotropy, as expected within the domain state model [27, 28]. When the contribution from the Ni-rich phase is subtracted from Ni$_{71}$Mn$_{29}$ hysteresis loops, $M_{st}/2$ for Ni$_{71}$Mn$_{29}$ in Figure 8.9 is significantly larger than $M_{st}$ in Ni$_{68}$Mn$_{29}$Cu$_{3}$ in Figure 8.17(a). The high field susceptibility is also much larger in Ni$_{71}$Mn$_{29}$, suggesting that the addition of copper decreases the magnetic order of the spin glass. However, the high field susceptibility in Ni$_{71}$Mn$_{29}$ is likely enhanced by the presence of a ferromagnetic Ni-rich phase, making it difficult to draw a direct comparison.
8.5 Conclusion

The structural and magnetic properties of Ni$_{71}$Mn$_{29}$ and Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples were explored in this chapter. Structural characterization was performed using XRD and SEM. Scans on the micron scale using SEM revealed that the average composition was close to the nominal composition, within uncertainty and no local variations in composition were clearly visible. However, XRD revealed the presence of a Ni-rich phase in Ni$_{71}$Mn$_{29}$, resulting in mixed ferromagnetic and spin glass behaviour in $M$-$H$ loops at low temperature. A primary step in the low-field region of the loops was attributed to the magnetism of the Ni-rich phase, while a secondary step that appeared after cooling in high field was attributed to the Ni$_{Mn}$ phase. Aging Ni$_{71}$Mn$_{29}$ alloys at 500°C tended to result in the growth of clusters within a Ni$_{Mn}$ phase, coinciding with an increase in the magnetism of a secondary step which appeared after cooling in a high field. The asymmetric shape of the differential susceptibility near the primary step was interpreted as evidence that the two phases interact, resulting in a unidirectional anisotropy. Given the composition of the Ni$_{Mn}$ phase suggested by QPA, the observed crystal structure of the Ni$_{Mn}$ phase was not consistent with any previous report of Ni$_{Mn}$ with comparable compositions, and a satisfactory explanation for the observed dependence of structure and phase quantity on aging time remains elusive.

The Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples were single phase according to both XRD and SEM measurements. Ni$_{68}$Mn$_{29}$Cu$_3$ displayed behaviour typical of a spin glass system, and had, on average, a significantly lower susceptibility than Ni$_{71}$Mn$_{29}$, as well as enhanced unidirectional anisotropy. $M$-$H$ loops at low temperature exhibited asymmetric reversal which favoured negative magnetization, which could not be modeled using the modified Stoner-Wohlfarth model with a Gaussian distribution of easy axes that successfully accounted for aged Cu$_{81.2}$Mn$_{18.8}$ alloy (section 5.4) and 2I2 (section 6.4.3), both of which exhibited asymmetric reversal that favoured positive magnetizations. A different distribution of easy axes may have more success for Ni$_{68}$Mn$_{29}$Cu$_3$. A similar type of asymmetric reversal was also observed in Ni$_{71}$Mn$_{29}$ alloys, but this was partly obscured by the presence of nickel. As questions remain about the nature of asymmetric reversal in both sample sets, particularly how it depends on aging time...
and composition, it may be of interest to synthesize new disordered $\text{Ni}_{71}\text{Mn}_{29}$ samples in order to investigate asymmetric reversal at low temperatures as a function of cooling field and aging time.

For both sample sets, aging for 3 min resulted in the greatest enhancement of susceptibility and step magnetization, and the greatest suppression of exchange bias. A qualitative explanation involving single domain particles in samples where $t_{\text{age}} \leq 3$ min fragmenting into multi-domain particles when $t_{\text{age}} > 3$ min was proposed.
Chapter 8. Magnetic properties of NiMn and NiMnCu alloys

Chapter 8 References


Chapter 9

Conclusions

9.1 Overview

The focus of this thesis has been on exchange bias behaviour exhibited by Mn containing alloys. The aim of this project was to investigate the analogues between exchange bias and spin glass systems in materials that have been found to exhibit strong sensitivity to short range order of magnetic entities. Magnetic measurements were performed on a set of concentrated spin glass samples, and close attention was paid to observed phenomena that are canonically associated with exchange bias systems, such as shifted hysteresis loops, training effects and asymmetric reversal. In general it was found that, in these samples, such phenomena are strongly sensitive to the cooling field, and an interpretation based on a frozen component of magnetization was proposed. The results and findings of this work are summarized in this chapter.

9.2 Summary of results and findings

The magnetic properties of an aged Cu_{81.2}Mn_{18.8} alloy were investigated below the glass temperature ($T_g$), and were reported in Chapter 5. Minor hysteresis loops at 5 K were found to be linear for cooling fields below 200 Oe, and developed a “step” magnetization, $M_{\text{st}}$, that increased with cooling field above $H_{\text{FC}} = 250$ Oe. At 5 K, $M_{\text{st}}$ varied with $H_{\text{FC}}$ as a Langevin function, closely matching the magnetization at
The discrepancy between $M_{\text{st}}(H_{\text{FC}}, 5 \text{ K})$ and $M(H, T_g)$ was 22% at 6 kOe. Below 25 K, the magnitude of the exchange bias field, $|H_{\text{EB}}|$ peaked about $H_{\text{FC}} \approx 450$ Oe, decaying monotonically for higher cooling fields. The monotonic behaviour of both $M_{\text{st}}$ and $H_{\text{EB}}$ with $H_{\text{FC}}$ strongly suggests the “spin glass” component is magnetically disordered, and has a number of stable configurations that become frozen as the sample is cooled through $T_g$.

The step exhibited asymmetric reversal, which was successfully accounted for within a modified Stoner-Wohlfarth model using a Gaussian distribution of easy axes, introduced in Chapter 4. Monte Carlo simulations were run to simulate hysteresis loops of aged Cu$_{81.2}$Mn$_{18.8}$ alloy measured at 5 K by varying parameters related to the effective cluster moment, $\mu_{\text{eff}}$, the uniaxial anistropy energy, $K$, the exchange anisotropy energy, $J$ and the standard deviation of the distribution of the easy axes directions, $\phi_{\text{stdev}}$. Two competing scenarios were tested, the first with $\mu_{\text{eff}}$ independent of $H_{\text{FC}}$ and the second with $K$ independent of $H_{\text{FC}}$; the first resulted in parameters that were more physically plausible. The success of the Stoner-Wohlfarth model, incorporating distributed easy axes, in simulating minor hysteresis loops strongly suggests that, if the cooling field dependence of $\mu_{\text{eff}}$ was experimentally known, the behaviours of $K$, $J$ and $\phi_{\text{stdev}}$ could be determined within the model.

Measurements of minor hysteresis loops of a neutron irradiated Cu$_{83.6}$Mn$_{16.4}$ alloy (2I2) that was prepared for a prior investigation [1], in which neutron irradiation was shown to cause a factor of 20 increase in susceptibility at $T_g$ compared with the as-quenched sample, were reported in Chapter 6. 2I2 exhibited enhanced ferromagnet-like behaviour compared with aged Cu$_{81.2}$Mn$_{18.8}$ alloy, with $M_{\text{st}}(H_{\text{FC}}, 5 \text{ K})$ following $M(H, T_g)$ to within 12% at 6000 Oe. The sample also displayed greater susceptibility, a greater step magnetization, a greater training effect and suppressed exchange bias compared with aged Cu$_{81.2}$Mn$_{18.8}$ alloy. Slight asymmetric reversal was observable in a range of moderate cooling fields, but not to the extent observed in aged Cu$_{81.2}$Mn$_{18.8}$ alloy, and the effect was suppressed by cooling in high fields. Hysteresis loops measured at 5 K in high fields ($\pm 50$ and $\pm 75$ kOe) and at 25 K between $\pm 6$ kOe did not saturate, but did show a high susceptibility “flip” at the coercive field, $H_c$. The enhanced tendency towards ferromagnetic behaviour observed in 2I2 is consistent with the findings of other investigations that suggest that aging drives short range
ordering among the nearest neighbour atoms so that ferromagnetic interactions are enhanced [2–5].

A simple Langevin model applied to minor hysteresis loops of 2I2 suggested that, at both 5 and 10 K, $\mu_{\text{eff}}$ decreases slightly for high cooling fields (ie, $H_{\text{FC}} \geq 1000$ Oe). Monte Carlo simulations based on a number of possible scenarios suggested a similar dependency, particularly for the scenario where $K$ is independent of $H_{\text{FC}}$, which resulted in the most physically plausible parameters. The decreases in $\mu_{\text{eff}}$ suggested by these models coincided with the suppression of asymmetric reversal, and was interpreted as possible evidence for the break up of clusters into multi-domain entities. Parameters related to the coercive field (such as pseudo-coercive fields, exchange bias fields and exchange anisotropy energies) tended to decrease as a power law with $H_{\text{FC}}$ above a certain cooling field (usually about 300 Oe), with indices between $-0.76$ and $-0.54$. This was understood as the alignment and depletion of the “spin glass” matrix component by the cooling field, which is qualitatively consistent with the domain state model [6, 7].

Chapter 8 detailed the work performed on a set of Ni$_{71}$Mn$_{29}$ and Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples. A Ni-rich phase was observed in XRD diffraction patterns from the Ni$_{71}$Mn$_{29}$ alloy samples, but was not discerned in backscattered SEM images, and was presumed to have been a result of insufficient alloying during the argon arc melting stage of sample preparation. This sample exhibited unusual magnetic behaviour, particularly in minor hysteresis loops at low temperature, which displayed mixed ferromagnetic and spin glass behaviour, particularly after cooling in a high field, when double-stepped hysteresis loops were observed. The two steps were attributed to the Ni-rich and NiMn phases respectively.

The Ni$_{68}$Mn$_{29}$Cu$_3$ alloy samples were characterized as single phase using XRD, with a structure consistent with similar samples [8, 9], and the observed magnetic behaviour at low temperatures was akin to that of a spin glass. In both sample sets, the sample aged for 3 min showed a peculiarly large magnetization and decreased unidirectional anisotropy (consistent with a greater extent of ferromagnetism) compared with the other samples. This was interpreted as a particularly large effective cluster moment in samples aged for 3 min decreasing once the coarsening of crystallites due to aging caused the clusters to exceed their critical domain size and break up into
multi-domain particles. As well as a factor of $\sim 82$ decrease in the low field susceptibility, the addition of copper caused an enhancement of coercivity and exchange bias compared with the magnetism of the NiMn phase in the Ni$_{71}$Mn$_{29}$ samples, which is qualitatively consistent with the domain state model and was interpreted as the copper enhancing the unidirectional anisotropy energy. However, the presence of the Ni-rich phase, along with evidence for interaction between the two phases, in the Ni$_{71}$Mn$_{29}$ samples made a direct comparison difficult. Questions remain about the aging dependence and structure of the Ni$_{71}$Mn$_{29}$ samples which may only be resolved by remaking samples with the same nominal composition and ensuring the samples are sufficiently disordered during the early stages of sample preparation. Asymmetric reversal was noted in minor hysteresis loops of Ni$_{68}$Mn$_{29}$Cu$_3$, though its nature differed from that observed in the two CuMn alloys, and could not be simulated using Monte Carlo simulations with a Gaussian distribution of easy axes. Time constraints prevented this being done as part of the project.

9.3 Future work

Hysteresis loops of aged Cu$_{81.2}$Mn$_{18.8}$ alloy have been shown to exhibit cooling field dependent asymmetric reversal, which was modeled using a series of scenarios tested for their physical plausibility. If the effective moment of magnetic clusters could be experimentally measured at low temperature as a function of cooling field, parameters relating to cluster shape effects, such as the uniaxial anisotropy energy and distribution of easy axes, could be determined within the model with greater confidence. The effective moment of magnetic clusters can be measured using small angle neutron scattering (SANS). It would be of interest to measure SANS profiles of aged Cu$_{81.2}$Mn$_{18.8}$ alloy at low temperature, after cooling in various fields, and at various points around each minor hysteresis loop, in order to determine how magnetic clusters depend on cooling field. An application for SANS beam time at the OPAL research reactor to perform this experiment was not successful, and the SANS instrument was subsequently unavailable.

Neutron irradiation had a profound effect on the magnetic properties of 2I2. A similar sample prepared by Cussen and coworkers [10, 11] with a higher Mn concentration
exhibited the onset of long-range order. Given the extent of ferromagnetism reported for 2I2 in this thesis, it would be expected that the sample made by Cussen would show significantly enhanced magnetic properties compared with an as-quenched sample with the same composition. Due to difficulties accessing and handling the sample, no macroscopic magnetic measurements have been performed on this previously radioactive sample and it would therefore be of interest to submit it to a range of measurements similar to those performed on 2I2.

While theoretical predictions of the relationship between the lattice parameter and concentration of disordered NiMn exist [9], few reports have been concerned with verifying the dependency with a series of careful measurements of samples in a region around the multi-critical point at 23.9 at.% Mn [12, 13]. Documenting the crystal structure of disordered NiMn in this region of the phase diagram would be a relatively straightforward measurement that would help fill a hole in the literature.
Chapter 9 References


Appendix A

Smartloop

Smartloop is a predictive control algorithm written with the aim of generating experimental isothermal $M-H$ loops such that the distribution of data points is approximately even across the page. In isotherms where bistability occurs, the differential susceptibility near the coercive field is much higher than that of the rest of the loop, and if the iterations of the independent variable (ie, the field) are too large near the coercive field, it may become difficult to accurately determine the coercive field with confidence, or observe all the important aspects related to a sample’s magnetic reversal mechanisms.

If we consider an array of data points $(x_i, y_i)$ which form a smooth curve described by the function $y(x)$, the points are distributed evenly along the curve if the separation of points, s.o.p., is a constant, given by

$$s.o.p. = \sqrt{(k\Delta x)^2 + (\Delta y)^2} \tag{A.1}$$

where $\Delta x = x_{i+1} - x_i$ and $k$ is the aspect ratio,

$$k = \frac{y_{\text{max}}}{x_{\text{max}}} \tag{A.2}$$

If the data points are sufficiently close, we can approximate the gradient between two adjacent points as the derivative of the function at the first point

$$\Delta y \approx \Delta x \frac{dy(x)}{dx} \tag{A.3}$$
and, therefore
\[
s.o.p. = \sqrt{\left(\frac{y_{\text{max}}}{x_{\text{max}}} \Delta x\right)^2 + \left(\Delta x \frac{dy(x)}{dx}\right)^2}. \tag{A.4}
\]

The next iteration of \(x_i\) can be estimated from the derivative at the current position along the curve,
\[
\Delta x = \text{s.o.p.} / \sqrt{1 + \left(\frac{x_{\text{max}}}{y_{\text{max}}} \frac{dy(x)}{dx}\right)^2}. \tag{A.5}
\]

To divide the curve into \(2N\) evenly distributed data points between \(x_{\text{max}}\) and \(-x_{\text{max}}\), we must know the length of the curve, which is
\[
l = \int \sqrt{(k \, dx)^2 + (dy)^2} \, dx = \int \sqrt{1 + \left(\frac{x_{\text{max}}}{y_{\text{max}}} \frac{dy(x)}{dx}\right)^2} \, dx. \tag{A.6}
\]

The length of the curve depends on \(y(x)\), but for the simplest case, a straight line through the origin that extends from \(x_{\text{max}}\) to \(-x_{\text{max}}\), we find \(l = 2\sqrt{2}x_{\text{max}}\). Then
\[
\Delta x = \frac{\sqrt{2x_{\text{max}}}}{N} / \sqrt{1 + \left(\frac{x_{\text{max}}}{y_{\text{max}}} \frac{dy(x)}{dx}\right)^2}. \tag{A.7}
\]

As an estimation for the length of the curve based on a straight line will always underestimate the length of any experimentally measured function, using equation A.7 to anticipate each iteration of the controlled variable will require slightly more than \(2N\) data points to traverse a curve that extends from \(x_{\text{max}}\) to \(-x_{\text{max}}\). While this means slightly more time is required to measure the curve, obtaining more data points increases the level of confidence in the observed nature of the function.

Where there is interest in regions of the curve where the second derivative varies rapidly, a perturbation can be added based on a quadratic approximation of \(y(x_{i+1})\),
\[
y(x + \Delta x) = y(x) + \Delta y \approx y(x) + \Delta x \frac{dy(x)}{dx} + \frac{1}{2} (\Delta x)^2 \frac{d^2 y(x)}{dx^2}, \tag{A.8}
\]

which leads to a separation of points given by
\[
s.o.p. = \sqrt{\left(\frac{y_{\text{max}}}{x_{\text{max}}} \Delta x\right)^2 + \left(\Delta x \frac{dy(x)}{dx} + \frac{1}{2} (\Delta x)^2 \frac{d^2 y(x)}{dx^2}\right)^2}. \tag{A.9}
\]
While equation A.9 can be solved exactly for $\Delta x$, a simpler but satisfactory result is obtained by using the approximation

$$(\Delta x)^2 \approx 2 \frac{x_{\text{max}}^2}{N^2}, \quad (A.10)$$

which, along with the approximation for s.o.p based on a straight line, gives

$$\Delta x \approx \sqrt{\frac{2x_{\text{max}}}{N}} \sqrt{1 + \left(\frac{x_{\text{max}}}{y_{\text{max}}} \left(\frac{dy(x)}{dx} + \frac{x_{\text{max}}^2}{N^2} \frac{d^2y(x)}{dx^2}\right)\right)^2}. \quad (A.11)$$

In a measurement of a real $M-H$ loop, $x_{\text{max}}$ and $y_{\text{max}}$ are determined from the first data point, and $N$ is a control parameter for the (nominal) number of data points in each quadrant of the hysteresis loop, chosen by the experimenter. The first three points of a branch are measured with Smartloop turned off, in order to gather enough data to make initial estimates of the first and second derivatives; after that, Smartloop uses the first and second derivatives at the most recent data point. The accuracies of the predictions made by Smartloop are susceptible to the validity of the approximation in equation A.3. Therefore, in regions of $M-H$ loops where the susceptibility increases suddenly, such as at the beginning of a “step”, Smartloop will often overestimate $\Delta x$ for one data point, missing a small region of the curve, before correcting itself for the rest of the high susceptibility region of the loop. If there is no hysteresis, this region of the loop can be measured with more data points on the return branch, but this is not feasible for loops that exhibit hysteresis, where memory effects are of interest. If $N$ is sufficiently high, these regions are generally negligible. It is particularly important to measure hysteresis loops with considerable detail near the coercive fields, especially when applying models to such data that are descriptive of reversal mechanisms.
Appendix B

Electronic circuits

In this appendix, simplified schematic circuit diagrams of electronic apparatus designed and built specifically for this project are displayed. Details such as power supply designs and most component values are left out to save space. The circuit diagrams shown here serve to supplement the discussion of experimental apparatus in section 3.2.

An analogue signal adder (Figure B.1) was used to add the DC and AC components of the analogue signal that commands the position of the linear motor (see section 3.2.2). The AC component of the signal was generated by the lock-in amplifier and also used as the reference frequency to measure the signal from the pickup coils. The DC component of the signal commands the stationary position of the linear motor.

![Figure B.1: Analogue signal adder. The circuit consists of two op-amps, the first configured to add the two incoming voltages, and the second inverting the added signal, which ensures $V_{out} = \sum V_{in}$.](image-url)
along the magnet way, thus determining the centre of vibration of the sample along the $z$-axis.

The superconducting magnet described in section 3.2.3 was powered by a commercial 93 A single quadrant magnet power supply (MPS) manufactured by Cryogenic Limited. While the MPS is capable of generating very high currents in one direction, it lacks bipolar output, which is necessary for measuring hysteresis loops. A magnet polarity switch, shown in Figure B.2, was designed to allow the direction of the current to the superconducting magnet to be reversed when commanded. The magnet polarity switch uses an array of six high-current relays that are configured so that the current from the magnet power supply flows through the superconducting magnet either in the positive or negative direction, depending on the input from a logical control bit. If power is lost, either to the logic circuit or the relays, all connections to the magnet power supply and superconducting magnet are instantly shorted, to ensure the load to the MPS remains zero. This means that, in the case of a power failure, the superconducting magnet can be safely de-energized. An additional safety feature which prevents the magnet polarity switch from changing state while there is an output current from the magnet power supply, is not shown here.

A small offset current from the MPS means that even in conjunction with the magnet polarity switch, it cannot train the field in the superconducting magnet to zero. A 20 A current supply (Figure B.3) was designed to power the superconducting magnet when only moderate fields (approximately $\pm 17$ kOe) were required. Bipolar capabilities were built into the 20 A current supply, allowing it to reverse and remove the field from the superconducting magnet without requiring the magnet polarity switch. Assuming a superconducting load, the output current is proportional to the input voltage, and is determined using the following equation:

$$I_{out} = \frac{R_2}{R_1 + \frac{R_2}{R_{ref}}} V_{in}.$$  \hspace{1cm} (B.1)
Figure B.2: The magnet polarity switch was designed to allow the superconducting magnet to generate fields in both the positive and negative directions using the magnet power supply.
Figure B.3: 20 A current supply. The circuit is powered by a set of ±5 V rails capable of delivering ±20 A.
Appendix C

Labview diagrams for VSM

In this appendix, block diagrams of Labview software developed and compiled to control and automate the vibrating sample magnetometer (VSM) are displayed. The main control VI for the automated VSM, “Sequence editor.vi” consists of a number of sequential stages, most (but not all) of which are shown here. In the main control loop, the current command is passed to the primary subVI, “Compile sequence into function.vi” which executes a function depending on the current command. “Compile sequence into function.vi” is divided into several cases for each allowable command, some of which will be shown here. Cases for syntax related commands are left out to save space. Lower level subVIs are also left out.
Figure C.1: The Labview block diagram of “Sequence editor.vi” showing sequence 0. All local and global variables are reset.
Figure C.2: The Labview block diagram of “Sequence editor.vi” showing sequence 2. An error check is performed on the sequence to ensure consistency, and that the commanded parameters are experimentally allowed.
Figure C.3: The Labview block diagram of “Sequence editor.vi” showing sequence 3. All local and global variables are reset again, and instrumentation such as the linear motor and lock-in amplifier, are initialized. Communication links with these instruments are established.
Figure C.4: The Labview block diagram of “Sequence editor.vi” showing sequence 4, which contains the main control loop. The current line of the sequence is selected and parsed by the “Compile sequence into function.vi”. The status of all instruments and sensors is checked and reported continuously.
Figure C.5: The Labview block diagram of “Sequence editor.vi” showing sequence 5. When all lines of the sequence have been executed, the experiment is concluded and all instrumentation initialized previously by the VI are brought to a safe halt and turned off and/or their communication links closed.
Figure C.6: The block diagram of case 8 of “Compile sequence into function.vi”, which is activated when a change of temperature is commanded.
Figure C.7: The block diagram of case 9 of “Compile sequence into function.vi”, which is activated when a change of field is commanded.
Figure C.8: The block diagram of case 10 of “Compile sequence into function.vi”, in which the position of the linear motor is changed.
Figure C.9: The block diagram of case 11 of “Compile sequence into function.vi”. The linear motor is commanded to oscillate about its current position, and a measurement is recorded from the lock-in amplifier, which is then converted to a value for magnetization and recorded in a spreadsheet.
Figure C.10: The block diagram of case 15 of “Compile sequence into function.vi”, which controls the state of the superconducting switch on the superconducting magnet (see section 3.2.3).
Figure C.11: The block diagram of case 16 of “Compile sequence into function.vi”, which uses the Smartloop algorithm described in Appendix A to anticipate the next value of field in a hysteresis loop such that the distribution of data points across the screen remains approximately constant.
Appendix D

Labview diagrams for Monte Carlo simulations
Figure D.1: The Labview block diagram of “Monte Carlo GUI.vi”, which is the main virtual instrument (VI) for running Monte Carlo simulations, as described in section 4.5. The raw data is passed through a subVI called “Remove linear component and normalize trans magnetization.vi” which processes and normalizes the data. Another subVI in the main loop, called “Energy simulation.vi”, determines the energy landscape in the current field, and simulates a magnetization based on that landscape, as determined in equations (4.13) and (4.14).
Figure D.2: The block diagram of “Remove linear component and normalize trans magnetization.vi”. The linear component of the $M-H$ curve is subtracted, and the remaining component is then normalized.
Figure D.3: The block diagram of “Energy simulation.vi”, which determines the energy landscape, as given by the modified Stoner-Wohlfarth model in equation (4.11) and simulates a magnetization based on that.
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