Optimisation of atomistic model parameters for $Nd_2Fe_{14}B$ type rare earth ferromagnets

ANDREW JON NADEN (MPHys)

DOCTOR OF PHILOSOPHY

The University of York SCHOOL OF PHYSICS, ENGINEERING AND TECHNOLOGY

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ABSTRACT

Rare earth ferromagnets are an important region of study due to their importance in electric motors, low maintenance magnetic resonance imaging scanners, and hard drive actuators, with Neodymium based magnets being of frequent use. Rare earth ferromagnets sharing the structure of $Nd_2Fe_{14}B$ have been previously parameterised for atomistic models manually taking many researcher hours for the parameterisation of one aspect of one alloy. This work provides a framework for evaluating atomistic parameters programmatically, using Python and numerical optimisation methods to automate and vastly speed up the parameterisation process.

Several Curie Temperature Measurement Protocols were implemented and evaluated for their reliability and consistency in calculating Curie temperatures in rare earth alloys from VAMPIRE atomistic model simulation data.

The atomistic spin exchange constants for the Iron–Iron interaction, and the Iron–Rare earth interaction have been parameterised using the Nelder-Mead and Brent-Dekker numerical optimisation methods, using the calculated Curie temperature of the simulation as the optimising objective function. The exchanges parameterised yield a calculated Curie temperature of within 4 Kelvin for the +3 oxidation state rare earths.

The higher order anisotropy constants for $Nd_2Fe_{14}B$ were evaluated in a single-spin and multi-spin model and comparisons were made to prior empirical and theoretical work. The First Order Magnetic Phase Transition present at low temperatures and high (> 15 Tesla) magnetic field was reproduced qualitatively, but quantitatively the spin direction simulated differs as much as 30% from the empirical behaviour.

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With thanks to my mother Frances and my father Mark for their unparalleled support, and to Alice, without whom the journey would have been far more arduous.

AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the requirements of the University's Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the thesis are those of the author.

I declare that this thesis is a presentation of original work and I am the sole author. This work has not previously been presented for an award at this, or any other, University. All sources are acknowledged as References. SIGNED:ANDREW NADEN DATE:NOVEMBER, 2023 'It's still magic even if you know how it's done.'

Terry Pratchett

CONTENTS

		Pag	şe		
Ab	Abstract i				
Ac	knov	wledgments	ii		
Au	Author's declaration iii				
Qu	iote	i	iv		
Ta	ble o	of Contents	v		
Li	st of	Tables	iii		
List of Figures ix					
List of Source Codes xi					
1	Intr	oduction	1		
	1.1	Magnetism for Motors	2		
	1.2	Methods of Modelling of Magnets	5		
		1.2.1 Programmatic analysis of data	7		
		1.2.2 Parameterisation of magnetic materials	8		
2	Met	hodology	10		
	2.1	Atomistic Model	10		
	2.2	Heisenberg model	12		
		2.2.1 Metropolis Hastings	16		
		2.2.2 LLG and Dynamics of systems	18		
	2.3	Structure of $Nd_2Fe_{14}B$	20		
3	Exc	hange optimisation 2	21		
	3.1	Fixed and variable parameters in body-centred-cubic Iron	22		
	3.2	Optimisation path	25		

3.3 Optimisation software		isation software	26			
3.4 Low temperature rescaling		Low te	emperature rescaling	28		
	3.5	Optim	ising Iron-Iron exchange in bcc-Fe	29		
	3.6	Curie '	Temperature Measurement Protocols	31		
		3.6.1	Measuring magnetisation with VAMPIRE	32		
		3.6.2	Fitting Ms(T)	33		
		3.6.3	Moskowitz extrapolation	33		
		3.6.4	Grommé's 2 tangent method	34		
		3.6.5	Tauxe differential method	36		
		3.6.6	Measuring peaks in other macroscopic parameters	37		
		3.6.7	Quality of methods listed	38		
		3.6.8	Linear regression	40		
		3.6.9	VAMPIRE Curie temperature simulation	40		
		3.6.10	Additional methods	40		
		3.6.11	Results in context	40		
	3.7	Rare e	arth ferromagnet exchange parameters	41		
		3.7.1	Low temperature rescaling	41		
		3.7.2	Limitation of the optimiser	42		
		3.7.3	Optimising rare earth-Iron exchange in Lanthanum based $La_2Fe_{14}B$	43		
	3.8	Optim	isation methods:Nelder-Mead and Brent-Dekker	43		
		3.8.1	Nelder Mead	43		
		3.8.2	Optimisation Flow Chart	44		
		3.8.3	Brent's method	46		
		3.8.4	Rare earth Iron exchange	50		
4	Opt	imisati	on paths for Exchange Parameters of $RE_2TM_{14}B$ alloys	53		
	4.1	Tempe	erature residuals along the optimisation paths for Rare earth ferro-			
		magne	ts	62		
		4.1.1	Error in Exchange estimate	65		
		4.1.2	Results in context	71		
5	Magnetic Anisotropy in $RE_2TM_{14}B$ alloys					
	5.1	1 Empirical results and work by Cadogan et al.				
	5.2	Replic	ating empirical anisotropy with spin models	73		
		5.2.1	Single spin model of anisotropy in $Nd_2Fe_{14}B$	78		
		5.2.2	Multi-spin model	85		
		5.2.3	Conversion between VAMPIRE and spherical harmonics	89		
	5.3	Multi-	spin model of anisotropy, in comparison to Cadogan et al.	90		

		5.3.1 Yamada et. al: Crystal electric field calculations as a method to				
		calculate anisotropy constants	91			
	5.4 Measuring anisotropy					
		5.4.1 Results in context	95			
6 Conclusion			96			
	6.1	Future work	97			
A	Арр	endix A	99			
	A.1	VAMPIRE - input files	99			
		A.1.1 Curie temperature monte carlo simulation	99			
	A.2	2 Wyckoff Positions for 2:14:1 type ferromagnets				
		A.2.1 Implementation of CTMP methods	103			
	A.3	VAMPIRE	113			
		A.3.1 Implementation of VAMPIRE statistics methods	113			
Glossary of Terms 11						
Bi	Bibliography					

LIST OF TABLES

TABLE

Page

 4.1 Rare earth-transition metal exchange 4.2 Sm range in used CTMPs	al. Digitised	66 69 69 70
5.1 Legendre polynomial expansion	r purposes	70
 5.2 Spherical harmonic expansion 5.3 Table of factors for converting anisotre 5.4 Table of CEF coefficients from Yamad 	py constants to VAMPIRE inputs et al	76 77 90 93

LIST OF FIGURES

FIG	URE Pa	age
2.1	Unit cell of $Nd_2Fe_{14}B$	20
3.1	Temperature dependent cubic anisotropy scaling in bcc-Fe	23
3.2	Grommeé's Curie temperature method illustrated	35
3.3	Susceptibility of Neodymium Iron Boron	38
3.4	The peak in the susceptibility at the Curie temperature for $Nd_2Fe_{14}B$	38
3.5	Specific heat capacity of Neodymium Iron Boron	39
3.6	The peak in the specific heat capacity at the Curie temperature for $Nd_2Fe_{14}B$.	39
3.7	Curie Temperature Measurement Protocol, (CTMP) calculated Curie tempera-	
	ture against temperature resolution	39
3.8	Fe-Fe exchange versus Curie Temperature	41
3.9	Exchange optimisation method flow chart	45
3.10	Dekker's method flowchart	49
4.1	Magnetisation curve for $Sm_2Fe_{14}B$ with a system size of $(6nm)^3$	56
4.2	Magnetisation of $Nd_2Fe_{14}B$ with an exchange scaled to account for finite size	
	effects	57
4.3	Magnetisation curve for $Nd_2Fe_{14}B$ at 4nm and 6nm $\ldots \ldots \ldots \ldots \ldots$	59
4.4	Optimisation route for Pr- and Nd-Fe exchange	60
4.5	Optimisation route for Tm- and Yb-Fe exchange	61
4.6	The result of the objective function, or Curie temperature residuals, for Sm-	
	and Gd-FeB during the optimisation of their exchange	62
4.7	The result of the objective function, or Curie temperature residuals, for Tb- and	
	Dy-FeB during the optimisation of their exchange.	63
4.8	The result of the objective function, or Curie temperature residuals, for LuFeB	
	during the optimisation of its exchange	64
4.9	Curie temperature and exchange of rare earth compounds	67
5.1	Computed magnetisation curves from Cadogan et al. [72]	74
5.2	Example canting and high field behaviour for an anisotropy constant set	82

5.3	Canting angle simulation of $Nd_2Fe_{14}B$	83
5.4	Anisotropic behaviour of a single spin model of $Nd_2Fe_{14}B$	84
5.5	Forms of anisotropy curves in the spherical harmonic basis	86
5.6	Energy contribution to spins due to external field	87
5.7	Reproduction of $Nd_2Fe_{14}B$ anisotropic behaviour using VAMPIRE, varying k_6^4 .	88
5.8	Reproduction of $Nd_2Fe_{14}B$ anisotropic behaviour using VAMPIRE	94

LIST OF SOURCE CODES

1	Curie simulation input file
2	Moskowitz' CTMP, impl Andrew Naden
3	Grommé's CTMP, impl Andrew Naden
4	Linear regreesion CTMP, impl Andrew Naden
5	Bloch's law CTMP, impl Andrew Naden
6	Tauxe's CTMP, impl Andrew Naden
7	SciPy linear regression
8	VAMPIRE magnetisation calculation
9	VAMPIRE magnetic susceptibility calculation
10	VAMPIRE specific heat calculation

CHAPTER

INTRODUCTION

Magnetic materials have been examined for thousands of years with naturally occurring permanent magnets such as magnetite (Fe_3O_4) being regarded as 'magic' for its ability to gather other iron particles [1]. Rare earth ferromagnets are an important area of study, due in part to their application in electric motors, medical magnetic resonance imaging, and data storage, with Neodymium based magnets of frequent use due to their high magnetocrystalline anisotropy. Research in this area is aimed at better understanding characteristic behaviours of the magnets, often to create stronger, less massive magnets with more tunable magnetic properties. A range of techniques are used to experimentally examine, mathematically model and computationally simulate both current and novel magnetic materials. These can include density functional theory; atomistic modelling; mean field theory; x-ray crystallography; transmission electron microscopy and others. Each of these methodologies has significant advantages and drawbacks, and so a combination of methods are used collaboratively to examine prospective materials for use. Similarly data driven approaches can be employed to evaluate trends across materials.

This work focuses on the atomistic modelling methodology; a computational technique for modelling larger cell structures with lower computational complexity compared to electron based approximations. This domain of research is limited by the parameterisation of the simulations; currently relying on computationally expensive ab initio calculations, or manual trial and error performed by researcher.

Reducing the time spent on evaluating these parameters through programmatic methods is the main subject of this work. More directly, in relation to the $RE_2Fe_{14}B$ type rare earth ferromagnets.

1.1 Magnetism for Motors

Permanent magnets are the class of magnetic materials with a persistent magnetic field. This permanent field is macroscopic, generated by the quantum scale electronic behaviour of the material. The permanent magnetic field is caused by the alignment of magnetic moments of the constituent electrons that make up the material. These magnetic moments correspond to the spin and orbital momentum of the electrons, which are quantum mechanical properties[2]. The total magnetic moment is related via angular momentum coupling to the sum of the individual orbital's angular momenta (related to the allowed orbitals for each electron's energy levels), and the sum of the individual electron's momenta (spin) which are confined to $\pm 1/2$. The energetic preference for these magnetic moments to align is termed the exchange interaction.

The exchange interaction is a quantum mechanical effect of the Pauli exclusion principle and Coulomb interactions[3]. The Pauli exclusion principle states that fermions (particles with half integer spin, such as electrons) must not have the same set of 4 quantum numbers; referring each to the electron shell, the subshell, the orbital and the spin. This is due to the requirement for a quantum system to be antisymmetric under exchange of two fermions. This results in electrons being required to enter higher energy states/orbitals under compression in space. For example, in an electron gas, the exchange symmetry causes a hole in the vicinity of an electron which other electrons with the same spin avoid due to the Pauli exclusion principle. The Coulomb interaction states that same charged bodies experience a repulsive force. As a result of this hole local to the electron, there is an energetic preference (by reduction in the Coulomb force) for particles with the same spin, as they are at a greater distance. This can be demonstrated by establishing the wave function in one dimension for two identical particles at positions x_1, x_2 in two states ψ_a, ψ_b :

$$\psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1) \tag{1.1}$$

Under exchanging the positions (swapping x_1 and x_2) either a symmetric combination of states or an antisymmetric combination is recovered.

The requirement for half integer spin particles (such as electrons) to behave as Fermions, with wave functions that are antisymmetric under exchange of two particles, is formed from the Spin Statistics theorem[4, 5]. The different recovered combinations yield different physical behaviour, with the expectation value of distance squared given by Griffiths and Schroeter[6]:

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2$$
(1.2)

With the final term increasing the expected distance for Fermions (and comparatively decreasing for Boson). This assertion of antisymmetry must still hold when the spin term is included. The possible spin states for a two electron system are given by one of four states, three triplet states with total spin 1, and one singlet state with total spin 0. The triplet states are symmetric under exchange and therefore require an asymmetric positional wave function, while the singlet state is asymmetric under exchange and requires a symmetric positional wave function. As a result the Pauli exclusion principle allows two electrons in the same position state, provided their spin state is different. This recovers the expected energetic preference for the same spin configuration. This results in an energetic preference for spins to align in a simple electronic gas. This equation clearly does not explain the whole set of nanoscale magnetic effects and so increasing abstractions are required.

This quantum mechanical effect can be approximated with a scalar exchange constant^[7]. This interaction and the associated Heisenberg model represent the culmination of a large body of work describing magnetism and magnetic materials, with a history of magnetic materials presented in as early as the year 1600 by Gilbert [8, translation] [referenced in 9]. Subsequent examinations of the nature of magnetic materials include the investigation of the earth's magnetism by Carl Friedrich Gauss in 1839 [10] an early quantitative measurement of natural magnetic phenomena. The quantitative study of the inverse square law for the electromagnetic force by Charles Coulomb in 1785 [11] and the theoretical unification of magnetism and electricity by James Clerk Maxwell in 1865 [12] allow for the creation of motors and generators, fundamental to the modern world. Modern advances in the theory of magnetism involve smaller and smaller scales. In the early 20th century, the theory of ferromagnetism was developed by Pierre Weiss [13] in collaboration with Pierre Curie [14]. Curie examined the critical temperature of a magnet, now called the Curie temperature, defined as the temperature at which a permanent magnet loses its cohesive magnetic ordering. The thermal excitation of the spins is large enough to overcome the ordering of the magnetic moments in the material, leaving a disordered "paramagnetic" state. Weiss developed the theory of a molecular field, a precursor to mean field theory, which drives the magnetic behaviour of magnetic materials, to describe the ordering behaviour of the magnetic moments. Following this work, Ernest Ising and Werner Heisenberg formed the present day understanding of magnetic materials, through examination of the Ising model [15], and its extension into three dimensions; the Classical and Quantum Heisenberg models. These models lay the foundation for the examination of macroscopic properties of complicated material structures. These models underpin the

simulation-based description of thermal behaviour in magnets by defining the exchange interaction between magnetic sites [2].

Magnetic materials experience a reduction in coercivity, the ability for a magnetic material to resist an external demagnetising field, at non-zero temperatures. This is due to the reduced alignment of the magnetic moments of the material due to thermal excitation. Thermal excitation overcomes the energy barrier to switch the magnetic field direction of the activation volume of the material[16, 17, 18]. The temperature dependent properties of magnetic materials is an important factor in their construction, as the working temperature of many magnets is sufficient to greatly reduce their magnetic performance. The design and modelling of current and novel magnetic structures is important to increase their efficiency at working temperatures. In addition, the anisotropic properties of a magnet are reduced at temperature, further reducing the capacity for work a given permanent magnet has.

Rare earth magnets are permanent magnets formed from alloys containing rareearth elements (in addition to other metallic and non-metallic elements). The rare earth elements comprise the 15 lanthanides (or lanthanoids), elements with atomic numbers 57-71, and Yttrium and Scandium, elements adjacent to the lanthanides. Historically and by convention Yttrium and Scandium are included due to their similar electronic properties [19]. Early research into the magnetic properties of these rare earth elements began after the discovery of the high anisotropy alloy YCo₅ in 1966 by K. J. Strnat and G. Hoffer [20], and in 1984 the Neodymium based rare earth ferromagnet $Nd_2Fe_{14}B$ was independently discovered by 2 industrial research teams [21, 22]. These Neodymium based magnets have the greatest magnetisation under typical working temperatures due to the 3-d transition metal content, and exhibit large magnetocrystalline anisotropy due to the rare earth[23], making them ideal candidates for electric motor applications. The critical nature of the rare earths in these materials, whether the prototypical neodymium or a substituted dysprosium, requires a directed modelling approach. This is doubly important due to the large effect on the macroscopic magnetic properties and the small proportion of the material they comprise. With respect to rare earth magnets, $Nd_2Fe_{14}B$ type ferromagnets and their macroscopic properties have been modelled with first principles approaches[24, 25] as well as using machine learning based [26] and phenomenological approaches. These approaches have varying accuracy for varying properties and computation times^[23], and often a balanced approach with a multiscale model is required. The materials have a large irreducible unit cell, making atomistic scale modelling a good choice for examining their behaviour and prototyping new magnets.[27, 7]

With global electric vehicles sales reaching 10 million in 2022 [28] and global electric

motor sales projected to reach 982 Million units by 2023 [29], efficiency of motor design, and the efficiency of permanent magnets encompassed within the motor is of paramount importance as global electricity demand increases the demand for fossil fuels [30]. The International Energy Agency (IEA) has made policy recommendations regarding the increased usage of high efficiency motors [31, 32] demonstrating the importance of these materials on a global scale. Due to their importance for the efficiency of motors and usage in electric and hybrid-electric vehicles, it is increasingly important to effectively estimate the performance of novel magnetic materials and structures, without engaging a complete manufacturing pipeline, thereby avoiding the increased lag time in the prototyping cycle.

1.2 Methods of Modelling of Magnets

The selection of modelling methods revolves primarily around the scale of the simulation and its computation time. Beginning at a small scale, Density Functional Theory is a computational quantum mechanical modelling method used for investigating the electronic and nuclear structure of many-electron systems. The principle of Density Functional theory was first formalised by Walter Kohn and Pierre Hohenberg in 1964 [33], where the two Hohenberg-Kohn theorems demonstrated that the ground state of a many electron system can be described using a density functional dependent on only 3 spatial coordinates, instead of the 3N coordinates of the N electrons, and that this is definitionally the electronic ground state.

Density functional theory has historically been used for the approximation and exploration of electronic ground states in atoms, molecules and solid materials, although time dependence has allowed for the studying of excited states. By definition the model is only exact when the functional describing the electronic density of the system is known. The approximate nature of the model comes from the fact that density functionals are not known exactly (excluding the free electron gas case), but are approximated from assumptions about the electronic state. These assumptions are only viable for certain electronic structures and are expensive to evaluate.

In 1987 similar theorems were presented for systems in arbitrarily strong magnetic fields [34]. The Kohn-Shan extension to this work changes the framework, using an exchange-correlation term, to represent the interaction with the external potential and the Coulomb interaction between electrons. There are many approximations to this term, varying in complexity, and in viability for different materials, but this approximation is often the most computationally expensive part of this methodology [35]. Specifically in regard to the 4-f electrons present in rare earth materials, Self-Interaction Corrected (SIC) Local Spin Density Approximation (LSDA-SIC) Functionals have been used. In order

to evaluate macroscopic properties from this approach however, requires an additional approximation to account for temperature, often Mean Field Theory (which overestimates Curie temperature) or Disordered Local Moment approach, creating another separation from macroscopic empirical results.[36]

Density Functional Theory can be prohibitively expensive for larger systems, especially regarding larger magnetic systems, with 3000 atom systems requiring approximately 10^6 core-seconds (seconds on a single core) to complete [37]. Rare earth metal alloys have on the order of 71 atoms per cubic nanometre and larger magnetocrystalline anisotropy energy driven effects, such as the large star shaped domains in NdFeB which have ordering on the scale of 1000nm, make DFT prohibitively expensive for modelling certain phenomena [38].

Increasing in scale from the electronic level to the atomic level yields atomistic modelling. The classical atomistic spin model, in contrast to the quantum Density Functional Theory, is an extension of the Classical Heisenberg model, to include anisotropy constant with orbital quantum number n, and magnetic quantum number m effects. Magnetic anisotropy refers to the energetic preference for a magnetic moment to align in a particular direction. Usually there are four types of anisotropy: shape anisotropy, caused by the shape of the grain of magnetic material; magnetoelastic or stress anisotropy, caused by tension applied to the material's structure; exchange anisotropy or exchange bias, caused by the interaction between antiferro- and ferro-magnetic materials; and magnetocrystalline anisotropy [39]. Magnetocrystalline anisotropy energy is the expression for the energetic preference for a materials magnetic moment to align along certain crystallographic directions. Simply put, the system requires more energy to magnetise in certain directions when compared with others due to the shape and composition of the unit cell of the material. This magnetocrystalline anisotropy energy usually relates to high coercivity of a material, and the high magnetic performance of 2:14:1 type ($Nd_2Fe_{14}B$) rare earth ferromagnet rare earth is attributed to the high anisotropy it exhibits [40]. It is important therefore to accurately model the anisotropic behaviours of this class of rare earth. The model occupies the nanoscale regime, with individual treatment of atomic sites in a fixed lattice, but no treatment of individual electrons and their orbitals. The magnetic moment of a site is an aggregate magnetic moment for all the electrons' magnetic moment associated with that atom. The model is one of the few models with the ability to evaluate magnetic behaviours of complex unit cell structures while still being computationally efficient enough to model them in bulk materials [7]. VAMPIRE [7] is the implementation of the model used throughout this work, as a parallel compute enabled flexible open source codebase.

Increasing in scale again, from the atomic to the microscale yields the micromagnetic approach [41]. Similar to the atomistic model, micromagnetic modelling examines the behaviour of aggregate magnetic moments, but, instead of the aggregate relating to a particular atomic site on a fixed lattice, the aggregate is over a larger volume in the material. This volume is sufficiently large to not treat the underlying atomic structure of the material directly (using the continuum approximation). While computationally efficient, this is an extra approximation that must be parameterised to compare to empirical results. This relates the underlying structure to the micromagnetic domain, and cannot always reliably examine complex structures (i.e. non-cubic materials).

In order to effectively manage different models at different scales, and to use the data they create effectively, automated exploration of parameter spaces is not only more efficient for researchers, it is required for effective large scale research.

1.2.1 Programmatic analysis of data

As the quantity of data produced daily increases exponentially, reaching 64.2 zettabytes in 2020 [42], it is becoming increasingly important to evaluate experimental and simulation data automatically, and in a programmatic manner where possible. Currently, much data analysis of raw magnetisation data and parameterisation of material simulations is performed manually creating a lag time between experiment or simulation and results driving subsequent experiments or manufacturing. Current atomistic parameterisation of magnetic materials involves computationally expensive ab initio calculations at zero temperature [43], or guided manual trial and error by a researcher. A systematic approach to this parameterisation lends itself to the increased compute power available to modern researchers.

Mathematical optimisation has roots in the work of Pierre de Fermat [44], introducing methods for finding maxima and minima analogous to calculus (which could be considered an unknown in 1629 in the West, 14 years prior to Isaac Newton's birth), methods which are still relevant in physics today. Similarly relevant, was the work of Dantzig [45], introducing simplex methods of optimisation and linear programming. The sum of these and other works forms the field of mathematical optimisation, provide methods for finding the best available values of an objective. The field of mathematical optimisation is ubiquitous in physics, computer science and engineering, as it allows for the automation of guided parameterisation, increasing the rate of the experimental cycle, and freeing researchers to work on less rote tasks. Mathematical Optimisation therefore provides for a convenient and automatic approach to estimating parameters of a system. Using the macroscopic output information of the simulation (in our case, the magnetisation), and transforming the data to examine a value related to the input parameter (in our case, the Curie temperature, as detailed in section 3.6) an optimiser can iterate the input parameter until a desired accuracy of output parameter is reached. This methodology allows parameters that would take many researcher-hours to be achieved with one optimisation program, freeing researchers to examine other information.

Future work in the field will likely lean even more heavily on Machine Learning and Neural Networks. These are similar to mathematical optimisation, except the researcher is required to provide less initial information regarding the relationship between input and output data. Neural networks and other data driven machine learning models requires a lot of data to compensate. For example, SciKit Learn [46], (a free software machine learning library for the Python programming language, and the fifth most imported package for machine learning projects on GitHub in 2019 [47]), illustrates the quantity of data required, with the order of one hundred thousand samples suggested for regression between data sets. Mathematical optimisation however, due to the strength of coupling between the input parameters and output data, can allow a researcher with knowledge of the domain to select optimisation variables to reduce the amount of data required to become effective.

1.2.2 Parameterisation of magnetic materials

The focus of this work was driven by the need for a robust parameterisation of the atomistic modelling of magnetic materials and rare earths as they relate to high performance motor applications. In order to yield appropriate macroscopic behaviour using the atomistic model, the atomistic parameters, such as exchange and anisotropy constants must be carefully selected. This work is an attempt to characterise a permanent magnet's atomistic parameters programmatically, using numerical optimisation methods to establish these parameters, and subsequently compare the macroscopic equilibrium behaviour of the magnets to experimental work. In order to increase the rate of novel material development, the automated numerical optimisation of these parameters becomes a more viable option, when compared with individual researchers' manual work. For example, to appropriately characterise a magnetic alloy's Curie temperature, the exchange constants, the measure of energetic preference for spins to align, between constituent atoms must be known. In simple systems, the relationship is trivial with exchange constant *J* is proportional to the Curie temperature T_C :

$$J \propto T_C$$
 (1.3)

For complicated systems however, this relationship is not easily extracted, and numerical optimisation can more rapidly evaluate the appropriate exchange for a given system and Curie temperature.

Methodology

In this chapter the atomistic model will be introduced as a methodology for simulating magnetic structures, both statically and dynamically. In order to computationally model a permanent magnetic structure of significant size, certain approximations must be established, and parameters must be set. For the atomistic model, the core assumption is that the magnetic moments of individual atoms are located at crystal sites occupied by the magnetic atoms in the material. The significant parameter set contains: the crystallographic structure (which can be established through means such as x-ray crystallography); the exchange constant between spin sites, the anisotropic angular energy dependence of the spin sites and the computational factors, such as interaction cut-off distances. Throughout this chapter the atomistic model is explored mathematically, and its implementation in VAMPIRE is detailed.

2.1 Atomistic Model

The atomistic spin model, as detailed in [7], is a classical model for modelling nanoscale magnetic interactions and structures in solids. The atomistic model, and other adjusted classical Heisenberg models, have been used for the evaluation of both a breadth and depth of magnetic phenomena. The thermal response of permanent magnets has been examined in relation to their spontaneous magnetisation and their anisotropy constants, using Monte Carlo methods to establish equilibrium properties [7, 48, 49]. Similar work by Gong et al. [50], and related to the materials examined in this thesis, uses ab initio parameters to inform the choice of parameters in 2:14:1 type rare earth ferromagnet [50] examining many microscopic parameters such as exchange stiffness. Domain wall

movement (regions separating magnetic domains in crystals) in 2:14:1 type rare earth ferromagnet type rare earth has been examined by Nishino et al. [51] using parameters calculated using the first principles Korringa-Kohn-Rostoker (KKR) method [52] and statistical properties of magnets used for energy transfer, such as remanence coercivity, have been examined in model magnets by Evans et al. [7] and in a rare earth ferromagnet by Toga et al. [27]. Complex magnetic structures, such as the vortex-like skyrmions [53, 54] have had properties such as lifetime and thermal response exposed by atomistic modelling [55], important for any experimental application of the structures. Dynamic properties used in Heat Assisted Magnetic Recording, and induced magnetic switching have been established areas of examination for atomistic modelling [56, 57, 58].

The vast array of empirical work that has been replicated using this scheme of models proves the associated adjusted Heisenberg models a reliable choice for the simulation of magnetic behaviour of complicated crystal structures, with significant atomic scale magnetic interactions.

In relation to the work presented in this thesis the atomistic model is used for the evaluation of macroscopic equilibrium properties (including the Curie temperature and the magnetocrystalline anisotropy energy) via the estimation of the atomistic parameters of the simulation, the magnetic exchanges and all relevant orders of anisotropy constants k_n^m . These constants are non-trivially linked to the macroscopic and experimentally verifiable behaviours of a magnetic system, and this linkage means that it isn't readily possible to establish the sub-nano-scale parameters by means of a simple mathematical formula or transformation. The core assumption of the atomistic spin model is that the spin moment of any atom is localised to its magnetic site [7]. This assumption dictates the scale of the simulation, sitting between the electron focused ab initio methods, and Density Functional Theory, and the larger aggregated models of micromagnetics. The atomistic model can be used within a multiscale model, with some parameters provided by ab initio calculations, and subsequently providing parameters to larger scale micromagnetics simulations [59]. By treating each atomic site independently, complex magnetic structures can be examined without treatment of individual electrons, vastly reducing the computational effort required to evaluate the magnetostatics and magnetodynamics of the material [7].

The assumption of atomistic spin locality is rooted in the Ising model proposed by Wilhelm Lenz in 1920 and solved analytically in one dimensions in 1924 by Ising [15] and in two dimensions in 1944 by Onsager [60].

The Ising model is a translationally invariant, ferromagnetic model with magnetic spin states confined to plus or minus one at each spin site. Each magnetic spin state is confined to a fixed lattice, analogous to the position of atoms in a unit cell and the resultant atomistic model's fixed atomic sites. The Ising model has an analytical solution in two dimensions only in the case of a square lattice in zero external magnetic field [60]. However, the equilibrium of the system can be relatively easily evaluated using the Metropolis Monte-Carlo method, allowing for the examination of equilibrium properties.

The Ising model Hamiltonian is given by

$$H = -\sum_{\langle i,j \rangle} J_{ij}\sigma_i\sigma_j - \mu \sum_j h_j\sigma_j \tag{2.1}$$

where $\langle i, j \rangle$ is the pairs neighbouring spins; J_{ij} is the exchange constant between i and j, σ_i is the spin at site i; fixed to +1 or -1, σ_j is its neighbouring spin; μ is the magnetic moment of the site; and h_j is the externally applied magnetic field.

While this incredibly simply Ising system reproduces some interesting magnetic phenomena, including being one of the simplest models to demonstrate a phase transition [61], it is markedly separate from a functional model of real world materials. The model cannot replicate spin waves (as the binary nature of the model prevents the smoothing of a disturbance in a spin over a range of spins), and the magnetisation of the system as a function of temperature doesn't replicate real world systems.

2.2 Heisenberg model

In order to more appropriately model real world materials, the Ising model can be extended to allow the spin moments at each site to point in any direction on the unit sphere.[62, 63] This extension forms the basis of the classical Heisenberg model. As observed by Stanley [64], the classical Heisenberg model is the n=3 case of the n-vector model, used for statistical modelling of ferromagnetism. In this n-vector model, classical unit-length spins s_i are placed at each vertex, v of a d-dimensional lattice. In specific relation to atomic structures, and in the atomistic model, these spins are placed at vertices at the atomic positions of the unit cell.

The spins in the classical Heisenberg model are a set of spins placed at each lattice vertex and fulfil:

$$\vec{S}_i \in \mathbb{R}, |\vec{S}_i| = 1 \tag{2.2}$$

The model's Hamiltonian is defined:

$$\mathcal{H} = -J_{ij} \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - H \sum_i \mu_i \vec{S}_i$$
(2.3)

(2.4)

12 of 142

where

$$J_{ij} = \begin{cases} J, & \text{if } i \text{ and } j \text{ are neighbours,} \\ 0, & \text{otherwise} \end{cases}$$
(2.5)

where

 J_{ij} is the exchange constant, energies due to the exchange between spins; \vec{S} is the normalised atomic spin vector; $\langle i, j \rangle$ is the pairs neighbouring spins; H is the applied magnetic field strength; μ_i is the magnetic moment of spin i. Fundamentally this is similar to the Ising model presented above, without a binary fixed spin direction of +1 or -1 in the direction out of the lattice structure. This model more accurately approximates the freedom of rotation for spin moments in magnetic systems and can replicate spin wave behaviour, but the model has previously been shown to be incapable of spontaneous magnetisation at temperature in two infinite dimensions, via the Mermin-Wagner theorem [65], although for finite size systems the theorem does not apply [66]. As in the Ising model, the magnetostatics of the system are investigated via the Monte-Carlo family of methods. In order to evaluate the dynamics of this class of fixed magnetic moment site systems however, the Landau-Lifshitz-Gilbert (LLG) and Landau-Lifshitz-Bloch (LLB) equations, which describe precession of magnetic moments in solids, with intrinsic damping of the material, and neglecting and approximating appropriate thermal noise respectively are employed, see section 2.2.2.

The atomistic model is a further extension to the Heisenberg model. Fundamentally, the model is extended via the Hamiltonian. The exchange constant J as described in section 2.2 extends to more than the immediate neighbours of a spin site and additional terms are added to the Hamiltonian related to magnetocrystalline anisotropy energy. The description of an individual spin remains the same as the Heisenberg model, but the spins are explicitly localised to atomic sites. The introduction of a non-scalar exchange constant reflects the complex atomic structure of crystalline solids, with many spin moments able to interact at different ranges and across different atom types. In this context, the exchange constant becomes a matrix of interaction distances and atom types, with each referring to a different J. The exchange can be further complicated with anisotropic exchange (including 2-ion anisotropy [67]) and antisymmetric exchange (Dzyaloshinskii-Moriya interaction [68, 69]) via the replacement of J with an exchange tensor, J_{ij} .

$$J_{ij} = \begin{bmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{bmatrix}$$
(2.6)

13 of 142

Throughout this work, this exchange tensor is a diagonal tensor, with off diagonal terms being zero. These terms relate to additional antisymmetric exchange terms [7, 70]. This extra asymmetric exchange is typically very weak, with measurements on Nd doped crystals giving exchange constants of approximately 4-5 orders of magnitude less than a symmetric exchange constant $(2.24 \times 10^{-25} J$ for the asymmetric exchange in Nd doped YVO_4 crystals, versus 5×10^{-21J} for the symmetric exchange in $Nd_2Fe_{14}B$) [71]. This also means that the exchange between atomic sites is symmetric, it depends only on their relative orientation (the dot product of spins), and not on their crystallographic orientations. The single ion anisotropy in 2:14:1 type rare earth ferromagnet is accounted for in the magnetocrystalline anisotropy energy terms forming the anisotropy Hamiltonian, H_{ani} , relevant to chapter 5.

Combining these extensions, the atomistic model's Hamiltonian is given by,

$$H = H_{exch} + H_{ani} + H_{app} \tag{2.7}$$

Composed of the components

$$H_{exch} = -\sum_{\langle i,j \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

$$H_{ani} = -\sum_i [k_2^0 \sin^2\theta + (k_4^0 + k_4^4 \cos 4\phi) \sin^4\theta + (k_6^0 + k_6^4 \cos 4\phi) \sin^6\theta - \dots] \qquad (2.8)$$

$$H_{app} = -\sum_i \mu_s \vec{S}_i \cdot H$$

where:

 H_{exch} = energy from the exchange interaction between spins

 H_{ani} = magnetic anisotropy in the spherical harmonics basis set

 H_{app} = Energy from the applied magnetic field

 \mathbf{B}_{app} = Applied magnetic field strength from external fields

i, j = neighbouring atomic sites

 $\mathbf{J}_{i,j}$ = exchange constant between atomic sites i and j (tensor component)

$$\mathbf{S}_i$$
 = The spin on site i

 θ = the polar angle (from the z-axis) of the spin

 ϕ = the azimuthal angle (from the x-axis in the x-y plane) of the spin

 $k_{2.4.6}^0$ = the easy axis anisotropy constants of second, fourth and sixth order

 $k_{2,4,6}^4$ = the rotational anisotropy constants of second, fourth and sixth order; in this instance chosen to match the tetragonal symmetry of $Nd_2Fe_{14}B$. Note that the anisotropy Hamiltonian can be formed by any orthonormal basis set, but the spherical harmonics

presented are chosen to match the symmetries in the materials examined.

$14 \ {\rm of} \ 142$

The atomistic model formalism treats the unit cell of the required material as the minimum repeating unit, as opposed to the single atom in the Ising Model. The spin sites are placed at the atomic positions, these are then translated along the unit vectors of the crystal, left, right, up, down, and into and out of the page. This translation can be extended infinitely, dependent on compute resources. Within the atomistic class of models, two atoms labelled A and B, while distinct from each other, would be characterised the same regardless of their cell's position in the larger structure. It is possible instead to generate a much larger "macro-cell" with individual characteristics for each site, and this way of decomposing the material becomes more relevant in the work done by Cadogan et al. [72] detailed in section 5.1. For macroscopic properties, the finite larger crystal structure is treated as an infinite bulk crystal through the use of periodic boundary conditions. Here the material's edges are treated as wrapping around to the opposite face, essentially preventing any section of the material being on the "surface". Care must be taken in this instance to ensure that the finite structure which is repeated via periodic boundary conditions is of sufficient size to prevent finite size effects from dominating the performance of the magnet. Traditionally this systematic effect is countered by repeated iterations of the same material at larger and larger (or inversely, smaller and smaller) system sizes until any trend in macroscopic property is removed.

The atomistic Hamiltonian is broadly similar to the classical Heisenberg model, with each spin localised to atomic sites subsequently dictating the lattice of the model. The addition of magnetocrystalline anisotropy energy to the model allows for examination of more empirical effects than is possible with a fully isotropic system. The atomistic model also allows for the introduction of different exchange constants for different interactions, with each element in the material comprising its own sublattice, with its own magnetic inter and intra sub-lattice interaction.

Given that J_{ij} is the exchange constant between atoms i and j, an isotropic calculation of the spin exchange energy is given by:

$$\begin{aligned} H_{exch} &= -\sum_{\langle i,j \rangle} J_{ij} \overrightarrow{S}_i \cdot \overrightarrow{S}_j \\ &= -\sum_{\langle i,j \rangle} \left[S_x^i \quad S_y^i \quad S_z^i \right] \begin{bmatrix} J_{ij} & 0 & 0 \\ 0 & J_{ij} & 0 \\ 0 & 0 & J_{ij} \end{bmatrix} \begin{bmatrix} S_x^j \\ S_y^j \\ S_z^j \end{bmatrix} \\ &= -\sum_i \sum_{j < i} J_{ij} \overrightarrow{S}_i \cdot \overrightarrow{S}_j \\ &= -\sum_i \sum_{j < i} J_{ij} \left(S_x^i, S_y^i, S_z^i \right) \cdot \left(S_x^j, S_y^j, S_z^j \right) \end{aligned}$$
(2.9)

The classical 3d-Heisenberg model has been used successfully to model materials

which fit into the so-called Heisenberg universality class. Experimental measurements of the specific heat, spontaneous magnetisation at temperature, isothermal susceptibility and coordination length can be used to assign materials to this universality class (with similar classes for the Ising model and 2 dimensional XY model). Antiferromagnets which the Heisenberg model produces good agreement for include $KMnF_3$, $KNiF_3$ and $RbMnF_3$ while the similar $KCoF_3$ is less well modelled[73, 74, 75], with anisotropy causing deviations and spin orbit coupling causing larger deviation still. Rare earth materials have been held to be good candidates for this style of model, when compared with metals with more itinerant d-electrons[76]. Other materials do not exhibit good agreement with this model at all however, when compared with the flexibility of the atomistic model, especially in its description of magnetic anisotropy, paradoxically extremely relevant for the $RE_2Fe_{14}B$ type materials. The Heisenberg model allows for examination of tertiary magnetic effects, such as second order phase order transitions.

The atomistic model has historically created good agreement with experimental data for macroscopic properties, albeit with some phenomenological scaling performed[7, 77], and due to the flexible nature of the anisotropy implementation, anisotropic effects can be matched more readily to experiment.

2.2.1 Metropolis Hastings

The aims for this work were to replicate equilibrium measurements of the rare earth ferromagnets and as such the Metropolis Hastings Monte Carlo method was used to "evolve" the system to an equilibrium state. The Metropolis-Hastings algorithm is traditionally used to numerically solve the Ising model [78] and has been used repeatedly in applying the atomistic model to magnetostatics or equilibrium measurements. The Metropolis-Hastings algorithm is a Markov Chain Monte Carlo method.

Markov Monte Carlo methods are a collection of algorithms designed for sampling from a probability distribution when uniformly sampling the entire distribution would be prohibitively difficult; being both computationally and empirically expensive [79]. The principle of these methods, is that by separating the system into a Markov chain, and sampling the steps in this chain sufficiently, the overall distribution, or in our case the static behaviour of the magnet can be established [7, 80]. The requirement for a Markov chain is that it is composed of stochastic states that can undergo a series of probabilistic state changes, where the probability is dependent only on the previous state. That is it satisfies the Markov property, akin to "memorylessness" of the system [79]. In the atomistic model of a magnetic system, the energy of the system at any state is only dependent on the current state, and the probability of movement between states is only dependent on the energy difference in states, satisfying the Markov property [81, 82]. For this model, the chain is also countably infinite, and dependent on discrete rather than continuous time steps. Throughout this work, the stopping time of the Monte Carlo method, is a fixed rule, counting a number of "time-steps", rather than evaluating any set of criteria of the system. While a stopping time could be evaluated using derivatives of simulation properties, this reduction in total computation time could be counteracted by the increase in calculations made.

It should be noted that this approach only allows examination of the statics of the system, as magnetic systems can exhibit a memory in their dynamics (e.g. hysteresis) and this memory means that any dynamical effects are only recovered in a system that does not satisfy the Markov property. Static systems however (those at equilibrium) are memory-less and can be evaluated using the method. The steps in this chain yield the Monte Carlo "time" steps in our simulation using VAMPIRE.

The Metropolis algorithm is presented as follows:

- 1. Given the current state of the system m, select a new possible state n using selection probability f(m,n)
- 2. Evaluate the acceptance probability of this change in system a(m,n)
- 3. Accept the new state and repeat with n as the current state, or
- 4. Reject the new state and repeat with m as the current state

By imposing a restriction on the number of spin flips allowed to change between states to one, the energy change between systems is limited by the coordination number and the exchange constant. This energy change is assumed to be smaller in magnitude than the thermal energy for fluctuation in the system (of the order k_BT). For the Ising model, the selection probability is simply uniform. The selection probability for any site to flip is 1/Lwhere L is the number of lattice sites. The acceptance probability is more complicated. Given a spin flip changing the system from state m to state n the acceptance probability is given by

$$g(m,n) = \begin{cases} e^{-\beta(H_n - H_m)}, & \text{if } H_n - H_m > 0\\ 1, & \text{otherwise} \end{cases}$$
(2.10)

Where the probability $e^{-\beta(H_n-H_m)}$ is enforced to preserve detailed balance [78]. Detailed balance requires that in kinetic systems with elementary steps, at equilibrium each process is in equilibrium with its inverse.

That is that, in the case of a Markov chain, any closed loop of the chain must have the same probability in either direction. This holds in our case, as any combination of individual spin flips can return to the initial state, and the sum of probabilities will hold.

The acceptance probability for the atomistic model during a Monte-Carlo simulation is similarly defined.

$$g(m,n) = \begin{cases} e^{\left(\frac{-(E_{new} - E_{old})\mu_s}{\mu_B}\right) \cdot R_T}, & \text{if } E_{new} - E_{old} > 0\\ 1, & \text{otherwise} \end{cases}$$
(2.11)

where:

 E_{new}, E_{old} = calculated energies after and before the spin state changes μ_s = Atomic magnetic moment

 μ_B Bohr magneton

 R_T = Temperature rescaling constant (detailed in [7, 77])

2.2.2 LLG and Dynamics of systems

The Metropolis Monte Carlo methods established in section 2.2.1 are relatively rapid methods for establishing the equilibrium magnetic state of an atomistic model, but they are incapable of calculating appropriate dynamic information, as the "time steps" in VAMPIRE's Monte Carlo methods are metaphorical, they refer to the steps through the Markov Chain of the system. Advancement through this chain does not advance through time, but rather, advances in aggregate towards the equilibrium of the system. In order to calculate dynamic properties of a material either a series of Monte Carlo simulations can be carried out in sequence, with small changes to the conditions of the system before allowing to re-equilibrate, or a dynamical method can be used. The common dynamical method for evaluating spin systems is the Landau-Lifshitz Gilbert equation [83, 84]. The Landau-Lifshitz equation was first presented in 1935 [83].

$$\frac{d\mathbf{M}}{dT} = -\gamma \mathbf{M} \times \mathbf{H}_{eff} - \lambda \mathbf{M} \times \left(\mathbf{M} \times \mathbf{H}_{eff}\right)$$
(2.12)

where:

- \mathbf{M} = the magnetisation
- γ = the electron gyromagnetic ratio

 $\hookrightarrow (1.76085963023 \pm 0.0000000053 \cdot 10^{11} s^{-1} T^{-1} \ [85])$

- \mathbf{H}_{eff} = the effective field accounting for applied magnetic field, the demagnetising field (magnetic field due to the magnetisation) formed by taking the variation in the Gibbs free energy with with respect to the magnetisation, [86]
- $\begin{array}{ll} \lambda & = \mbox{ A phenomenological damping ratio, inherent to the material defined as} \\ & \left(\lambda = \alpha * \frac{\gamma}{M_s}\right) \mbox{ where } \alpha \mbox{ is a dimensionless material damping factor,} \\ & \gamma \mbox{ is the electron gyromagnetic ratio and} \\ & M_s \mbox{ is the saturation magnetisation.} \end{array}$

$$\lambda = \alpha \cdot \frac{\gamma}{M_s} \tag{2.13}$$

2.2.2.1 Integrators

The LLG and LLB equations are first order differential equations, and they can be approximately solved numerically using a numerical integration scheme. The integrator most often used in VAMPIRE is Heun's method, a variant on Euler's explicit trapezium rule method, similar to a two stage Runge-Kutta method [87]. Heun's method is a numerical method for solving an ordinary differential equation with a given initial value.

The algorithm is as follows: For an initial value problem $y'(t) = f(t, y(t)), y(t_0) = y_0$, the two stage method is given here as,

- 1. Calculate an intermediate point, $a_{i+1} = y_i + hf(t_i, y_i)$
- 2. Calculate the next approximated point, $y_{i+1} = y_i + \frac{h}{2} [f(t_i, y_i) + f(t_{i+1}, a_{i+1})]$

where $t_i + 1 = t_i + h$, and a_{i+1} is an approximate solution for y_{i+1} .

VAMPIRE is an open-source atomistic magnetic modelling package developed primarily at the University of York [7, 88]. The package provides ready-made implementations of the LLG and Monte-Carlo methods of evaluating the magnetic behaviour of magnetic models. The atomistic model is explained in section 2.1. Example input files for the simulations provided are in the appendix appendix A.3.

2.3 Structure of $Nd_2Fe_{14}B$

The prototypical $Nd_2Fe_{14}B$ has the space group $(P4_2/mnm)$ [89]. This is primarily relevant as a computational concern, its relative irreducibility meaning better ab initio methods are prohibitively expensive; and in relation to the tetragonal symmetries that can be employed in the selection of anisotropic basis vectors to describe the anisotropic behaviours of $Nd_2Fe_{14}B$. The full space group's Wyckoff positions are presented in table A.1. Throughout this work, the cut-off radius for exchange interaction is fixed to 5Å, this radius is large enough to include the largest inter atom distances within the unit cell of $Nd_2Fe_{14}B$ [89] whilst not being prohibitively expensive. In energetic terms, the exchange coupling as calculated by Matsumoto and Akai [90] is reduced by one order of magnitude at a distance of 5Å comparatively. Longer cut-off radii for the exchange interaction is a focus of future simulations.



Figure 2.1: The unit cell of $Nd_2Fe_{14}B$ displaying only the magnetic atoms (Boron has been removed). This leaves 64 magnetic atoms with 1932 inter-atom interactions with a 5 angstrom cut-off radius, this radius is large enough to include the largest inter atom distances within the unit cell of $Nd_2Fe_{14}B[89]$. There are 11 Wyckoff sites with multiplicity ranging from 2 to 16 [91], see table A.1 Generated using Jmol [92] and Povray [93] and provided by Richard Evans.

CHAPTER CHAPTER

EXCHANGE OPTIMISATION

The atomistic parameters for different magnetic materials are not readily known, and are not always easily derivable from analytic expressions. Previously, parameterisation of the atomistic model has been performed manually, involving many cycles of parameter tweaks and manual examination of simulation properties. Using methods such as parameter sweeps to explore the state space of parameters is expensive due to the large parameter space. In order to accelerate this process, automatic mathematical optimisation of these parameters can be employed. This automation is demonstrated for the atomistic software VAMPIRE for single atom ferromagnets, before it can be extended for more complex systems in later chapters. As a prototypical example, the iron to iron exchange constant, X_{Fe-Fe} , in body-centred-cubic iron was to be optimised. This would lay a foundation for the implementation of a general optimiser for more complex systems, such as the 2:14:1 type rare earth ferromagnet rare earth ferromagnets.

This chapter details the parameterisation of the exchange constant in body-centredcubic iron. The parameterisation requires an accurate and reliable method of measuring the Curie temperature of a simulated magnetic material, and several Curie Temperature Measurement Protocols are examined and evaluated. These protocols are used as feedback for a numerical optimiser as it estimates the exchange constant by minimising the difference in empirical and simulated Curie temperature.

3.1 Fixed and variable parameters in body-centred-cubic Iron

The modelling parameter set for body-centred-cubic iron is presented in Table 3.1. The simulated material is generated as a body-centred-cubic crystal structure, which yields a coordination number (the number of atoms adjacent and linked directly to each atom) of 8, similarly this corresponds to 8 equidistant nearest neighbours. Additionally, the system is wholly isotropic with respect to the crystal structure, with each of the system's lattice constants equal at a = 2.866Å and all internal angles of the unit cell set at 90 deg. Each atomic site (where an iron is located) is place at one of these crystal sites. The magnetic "atom" at each atomic site has the same magnetic parameters (magnetic moment, anisotropy constant, exchange constant) as every other atom, with only position changed. This "atom" is the approximation to the effective local magnetic moment at this site. The nearest neighbour approximation to exchange is employed, and as such the exchange parameter between any two nearest neighbour atoms is the same scalar measured in Joules per link. This exchange parameter is the optimisation target, that is, the value we iterate towards. The system is defined with periodic boundary conditions, with each edge of the system interacting with the opposite edge. For example, the limit of the system in the positive x-direction interacts with the atomic sites on the limit in the negative x-direction. The system size was chosen to be 10nm in an attempt to minimise finite size effects in the magnetic behaviour, as used in similar atomistic simulations performed using VAMPIRE[94]. The magnetic "atoms" have a local moment of $2.22\mu_B$, and only cubic anisotropy, $k_c(S_x^4 + S_y^4 + S_z^4)^1$, with three easy axes (each of x, y, and z). The magnetocrystalline-anisotropy therefore cubic in nature and is weak in bcc-Fe, especially compared to exchange interaction. Given the literature value of $48kJ/m^3$ [95], each unit cell has 1.131×10^{-24} joules of energy contributed from the cubic anisotropy, when compared with approximately 4×10^{-20} joules due to the first nearest neighbour exchange interaction (assuming $5 \times 10^{-21} J$ exchange constant). The anisotropy is dependent on lattice expansion due to temperature, with the scaling constant at temperature presented in fig. 3.1. This has a negligible effect on calculated Curie temperature in comparison to exchange, as the energy due to exchange is significantly larger (of the order of 10000 times larger). Higher order anisotropy terms are similarly neglected, as the energy due to the next component of cubic anisotropy. No external field is applied.

The Hamiltonian used for calculating the energy for a given system state in this configuration is (as given in equation 2.7):

¹Equivalent to $k_c \left[\left(\cos \phi \sin \theta \right)^2 \left(\sin \phi \sin \theta \right)^2 + \left(\sin \phi \sin \theta \right)^2 \left(\cos \theta \right)^2 + \left(\cos \theta \right)^2 \left(\cos \phi \sin \theta \right)^2 \right]$ in polar coordinates



Anisotropy scaling due to lattice expansion of bcc-Fe

Figure 3.1: Cubic anisotropy scaling for bcc-Fe due to lattice expansion at temperature. This value is multiplied by the cubic anisotropy constant specified in VAMPIRE. Despite the factor of 2.5 at temperatures greater than 250K, the anisotropy energy is still of the order 10000 times smaller than the energy due to exchange interaction.

$$H = H_{exch} + H_{ani} + H_{app} \tag{3.1}$$

Composed of the components

$$H_{exch} = -\sum_{\langle i,j \rangle} J_{ij} \overrightarrow{S}_i \cdot \overrightarrow{S}_j$$

$$H_{ani} = -\sum_i \left[k_c (S_x^4 + S_y^4 + S_z^4) \right]$$

$$H_{app} = -\sum_i \mu_s \overrightarrow{S}_i \cdot H$$
(3.2)

In addition, the nearest neighbour approximation yields a simplified exchange term:

$$H_{exch} = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j$$
(3.3)

given that J_{ij} is a constant J for each of 8 Fe-Fe interactions.

Given that no field is applied in the measurement of Curie temperature, rendering the applied term zero ($H_{app} = 0$), and that the anisotropy is much less than the exchange energy ($H_{ani} \ll H_{exch}$) the full Hamiltonian is given by:

$$H = -J\sum_{i}\sum_{j=1}^{8} \vec{S}_{i} \cdot \vec{S}_{j}$$
(3.4)

where; J is the exchange constant between iron atoms, S_i is the spin at site i, and j refers to each of 8 neighbouring spins.

Parameter	Description	Value
Unit cell Structure	body centered cubic	"bcc"
Unit cell size	The length of the unit cell in	2.866\AA
	Ångströms, the same constant value	
	in x, y and z due to the cubic nature	
	of the unit cell.	
System size (x,y,z)	The total size of the system in x, y	10nm
	and z. Where this parameter would	
	cut a unit cell in half, the system is	
	rounded up to a full multiple of the	
	unit cell size.	
Coordination number	The number of atoms directly ad-	8
	jacent to an atom. Equivalent in	
	the nearest neighbour approxima-	
	tion to the number of atoms in the	
	neighbour-list.	
Exchange	The energy of the exchange inter-	e.g. $7.0e-21 J/link$
	action between each iron atom, in	
	Joules per link. This is the param-	
	eter that was varied to fit the sim-	
	ulation to the experimental Curie	
	temperature.	
Simulation type	The simulation program which is	curie-temperature
	evaluated. The Curie temperature	
	program built in to VAMPIRE was	
	used. This program equilibrates the	
	system at a start temperature (the	
	minimum temperature by default)	
	then calculates statistics such as	
	magnetisation over an averaging pe-	
	riod of loop-time-steps, before in-	
	crementing the temperature by a	
	temperature-increment.	
Minimum temperature	The start temperature of the Curie program simulation.	400K
--------------------------	--	--------------------
Maximum temperature	The end temperature of the Curie program simulation.	1600K
Temperature increment	The step size for the change in tem- perature at each step.	2K
Equilibration time steps	The number of Monte Carlo steps that the simulation steps through at the start temperature before be- ginning statistics accumulation and averaging.	25000
Loop time steps	The number of Monte Carlo steps the statistics at each temperature are averaged over.	5000
Boundary conditions	The system was generated with pe- riodic boundaries in x, y and z direc- tions. This treats the unit cells on one extreme of the system as con- nected to the other side directly.	Periodic
Atomistic spin moment	The magnetic moment per atom. As this is a single atom type system and the system is integrated stati- cally using the Monte Carlo method this value is unused. This parame- ter would be used during examina- tion of magneto dynamics, and in multi-atom systems as it is different for each magnetic atom type.	2.22µ _B

Table 3.1: Parameters for modelling body-centred-cubic Iron atomistically with VAMPIRE.

3.2 Optimisation path

Given the initial system configuration above, the system's equilibrium state at a given temperature is modelled using the Metropolis Hastings Monte Carlo method. The dynamical methods of magnet simulation (such as the Landau-Lifshitz-Gilbert equation) are not employed during the optimisation process, as the magnetostatics of the system at equilibrium are the properties being optimised for. The Metropolis Monte-Carlo method was therefore employed throughout this work, as detailed previously in section 2.2.1.

The equilibrium spin configuration at a specific temperature value can then be ascertained. Repeating this process for a series of values, ranging from well below the expected Curie temperature to above it, the spontaneous magnetisation as a function of temperature can be ascertained. Using the CTMPs referenced in section 3.6 the Curie temperature can be evaluated, and this can be used to alter the following estimate for the exchange constant. Given the positive relationship between exchange and Curie temperature in ferromagnets, if the Curie temperature is lower than experiment, then the exchange is increased. Similarly, the reverse is true.

3.3 Optimisation software

To prevent the additional complexity of designing a bespoke piece of atomistic modelling software, an external program used to control the behaviour of VAMPIRE was developed. This program, tentatively entitled vampire_opt, generates appropriate input files for VAMPIRE, at each stage of the exchange optimisation process, before running VAMPIRE on those input files; and then performing the Curie temperature analysis on the output data from the VAMPIRE simulation. The program is implemented in Python 3.6, a language chosen for its flexibility, compatibility and its readily available scientific libraries. In particular the libraries in use are:

- SciPy [96], for analysis methods and optimisers,
- numpy [97], for data structures used in the storage of simulation data, and the additional built-in libraries,
- shutil, for file handling when copying templated input files,
- os, multi-platform filesystem access,
- subprocess, for running VAMPIRE programmatically,
- random, for pseudo random number generation.

The final four libraries are included in the Lib section of Python installs.

The program stores the input exchange and output Curie temperature values from previous iterations in an optimisation sequence. This allows the program to be stopped and restarted, reusing earlier optimisation steps and preventing the repeat of expensive VAMPIRE simulations, reading the optimisation output data file. Future improvements to this lookup could include Bayesian methods to bias towards less well explored regions of the parameter space as the optimisation unfolds[23]. Although this increases the amount of state stored for each optimisation step, the number of additional variables would be minimal.

The program repository, located at https://github.com/a-naden/vampire_opt [98] uses the curie_calc repository [99] as a submodule. This submodule contains the implementations of the CTMPs outlined in sections 3.6.1 to 3.6.6 and 3.6.8 and listed in listings 2 to 7. This submodule is required for the functioning of vampire_opt, with each version of the program using a fixed commit of the submodule, ensuring reproducibility despite any upstream changes made to the CTMPs repository. This allows for parallel future development of the two code bases.

Python as a language is well suited for controlling another program's behaviours due to its flexible "duck" typing (typing of variables by the methods that can be applied to them, rather than an explicit declaration) and powerful interpreter. As an interpreted language, program state can be easily examined while the program is running. In future this should allow for a permanent "worker" program that controls VAMPIRE externally, vampy, with work progressing in this area. As the computation of the atomistic model is orders of magnitude more computationally expensive than the text based operations on input files, any reduction in speed compared to a lower level language is rendered moot in comparison to the prototyping speed, and the additional reach in the scientific community a Python script has. The program operated exclusively on input and output files for two reasons: firstly, the state of the optimiser could be readily examined without running VAMPIRE and additionally every state contains the input for a valid VAMPIRE simulation, and the corresponding output allowing for the decoupling of the computational work from the optimiser in the case of hardware failure requiring additional simulations.

Many changes will be required for this program to be reliable and robust for any exchange problem. The program is currently brittle software, making use of some hard coded parameters in relation to the specific materials examined in this thesis. In addition, the total program state is not always transparent, with optimisation data being converted to text and reinterpreted at a later date. In addition, with more resources, the program would have a simple setup script, as well as a collection of material examples from across magnetism.

Initially, only one dimensional optimisation was intended, and vampire_opt was written for assuming only a one dimensional optimisation problem such as demonstrated for bcc-Fe in fig. 3.8. The program has been developed to enable parallel multidimensional optimisation subsequently, however, due to the dimensionality reduction enabled through the use of a prototypical element (see section 3.7.3), this is not fully evaluated at the time of writing. While this 1-d optimisation of exchange is well suited for similar materials, different materials, such as ferro- and ferri-magnets rare earths have different phenomenological low temperature rescaling behaviour due to their different quantum stiffness behaviour. Work by Christopher Venn (BSc) [100] in his Dissertation, with support provided by the author, during his time at York, illustrates the range of values an exchange constant can take, with different low-temperature quantum rescaling constants (see section 3.4) vastly changing the interactions between sublattices, as they effectively experience a different quantum thermostatic heat bath. This results in different magnetisation behaviour, in addition to a different Curie temperature, for elements in a structure which do not behave similarly.

3.4 Low temperature rescaling

The classical spins of the Heisenberg and atomistic models do not have the same thermal behaviour as the quantum behaviour of the physical electrons due to their lack of quantisation. This causes a discrepancy in the low temperature behaviour of the magnetisation, and this is addressed using the low temperature rescaling detailed in [49, 77]. This rescaling uses a single parameter to map the magnetisation behaviour of the classical simulation, to the calculated behaviour in the quantum regime. As detailed by Evans, Atxitia, and Chantrell [49], the Curie-Bloch equation, relating temperature and magnetisation can be defined as:

$$m(\tau) = (1 - \tau^{\alpha})^{\beta} \tag{3.5}$$

Kuzmin [101] however presents an alternative description of the magnetisation:

$$m(\tau) = \left[1 - s\tau^{3/2} - (1 - s)\tau^p\right]^{\beta}$$
(3.6)

where τ is defined as $\frac{T}{T_C}$, or the fraction of the Curie Temperature, and s and p are fitting parameters.

By relating these equations, and fixing $\beta = 0.34$, the simulation temperature can be related to an experimental temperature using:

$$\frac{T_{sim}}{T_C} = \left(\frac{T_{exp}}{T_C}\right)^{\alpha} \tag{3.7}$$

This allows for the low temperature magnetisation to match empirical values and was evaluated for single-exchange systems [49]. Each magnetisation sublattice in a multi-atom system however, can have a different rescaling constant α .

It is important to note that the scaling constants are material specific, and that each sublattice in a multi sublattice system can be scaled differently. The automatic scaling of exchange presented in [49] does not preserve the relative behaviour of different sublattices, introducing an additional parameter that must be fitted for perfect empirical agreement.

3.5 Optimising Iron-Iron exchange in bcc-Fe

To establish the appropriateness of using a numerical optimisation method to find the atomistic exchange of a magnetic material, a simple test used was to calculate the Fe-Fe exchange for bcc-Iron. This material is modelled using only a single atomistic exchange constant [7] while reproducing the temperature dependence on the magnetisation and crucially, the Curie temperature. The single exchange value yields a simple one-dimensional optimisation problem, with the figure of merit, the Curie temperature of the material dependent on only one input variable and on the method of calculation. The Curie Temperature T_C is therefore given by

$$T_C = f(X_{Fe}) \tag{3.8}$$

where f is a function describing running the atomistic simulation with VAMPIRE, using the input of the function as the exchange constant, and then evaluating the Curie temperature of the simulation using the Curie methods detailed in 3.6. X refers to the exchange constant estimated by the optimiser.

The function f is exposed to the optimiser but is composed of the sub procedures g and h, where g is the calculation of the Curie temperature from output data, and h is the VAMPIRE Heisenberg model Monte-Carlo simulation. These functions must remain coupled throughout the optimisation, as they contain parameters invisible to the optimiser. For example, g contains parameters dictating the calculation of Curie temperature, including the subset of methods used, and h contains VAMPIRE input parameters, such as the size of the system simulated. If these parameters are changed in a manner invisible to the optimiser (i.e. by altering system size mid-optimisation) then the optimiser may fail.

The objective function of an optimiser is the function that maps the input variable to an associated variable which quantifies some "cost" associated with the system state. With the Curie temperature being the value we wish to iterate the optimiser towards, the objective function's associated cost is the numerical difference between the calculated Curie temperature and the empirically evaluated Curie temperature. This is therefore the value we wish to minimise. Explicitly, given an empirical value of the Curie temperature of the material, $T_{Fe} = 1043K$ [20], a calculated Curie temperature, T_C and an input exchange value of X_{Fe} ; the objective function of the optimisation problem is:

$$min(|T_c - T_{Fe}|)$$

$$min(|f(X_{Fe}) - T_{Fe}|)$$

$$min(|g(h(X_{Fe})) - T_{Fe}|)$$
(3.9)

where f is a fixed function consisting of; the calculation of magnetisation curves using VAMPIRE (h) and Calculating the Curie temperature based on that curve (g).

The methods used to calculate the Curie temperature of a material have been collectively labelled as Curie Temperature Measurement Protocols, (CTMPs). As these methods can vary substantially under differing conditions, the methods required some examination.

3.6 Curie Temperature Measurement Protocols

The evaluation of Curie temperature has often been established on a case by case basis, with several methods, presented in sections 3.6.2 to 3.6.6, providing less insight into complex materials[102, 103]. Comparisons of methods have been made for Iron-based compounds, but fewer evaluations have been made for complex ferromagnetic structures, such as the 2:14:1 type rare earth ferromagnets, or on the stability of these methods when applied to incomplete or noisy datasets. Additional complications in the determination of the Curie temperature, such as the inhomogeneity of the temperature of a sample material, can cause changes in the evaluated Curie temperature, and can smooth the phase transition over a temperature range [102]. Some first principles methods exist for the evaluation of simpler materials, such as bcc-Fe[43], but methods often over-report the empirical Curie temperature [104, 105, 106].

In order to reliably estimate the relationship between exchange and Curie temperature the Curie temperature must be evaluated at runtime of the optimiser. CTMP are defined here for the numerical estimation of the Curie temperature of a ferromagnetic material. Each CTMP operates on either the:

- $|\vec{M}(T)|$, Magnetisation as a function of temperature curve;
- $\chi(T)$, Susceptibility as a function of temperature; or
- c(T), the specific heat capacity as a function of temperature.

Each of these parameters is readily available from the output file of a Monte-Carlo VAMPIRE Curie temperature simulation, input referenced in at the VAMPIRE website[88, 107]appendix A.1.1, and methods referenced in section 3.6.9. Specifically, the commands

```
output:mean-magnetisation,
output:mean-susceptibility,
output:mean-specific-heat
```

return these values explicitly, as calculated in sections 3.6.1 and 3.6.6 and with VAM-PIRE's source listed in listings 8 to 10. This simulation involves a systematic raising of the temperature of the system, followed by an equilibration time, and then the calculation of the desired properties averaged over the "time" steps of the simulation. Prior to using a CTMP for the systematic evaluation of atomistic exchange constants, the CTMPs must be evaluated to find an acceptably consistent series of CTMPs to use throughout the optimisation process. In practice and in theory it would be preferable to use the same CTMP by which the Curie temperature is calculated in any particular academic experimental reference, in literature however, the specific methods are not always listed in an appropriate manner for extraction, or at all. As "Big Data" becomes more practical in materials science this is likely to change, with selection of individual CTMPs catered to match simulation to specific experimental results becoming the norm.

In addition, measurements of magnetic materials differ from optimal systems generated for simulation. The grain size of domains can alter the magnetic properties of a material, with saturation magnetisation and coercivity dependent on grain size and orientation[108, 109]. In addition experimental apparatus cannot fully remove the external fields from a material or reduce its temperature to absolute zero as in simulation. As a result, the properties of the magnet in these conditions are extrapolated via a series of measurements above these values. It should be noted however, that with the increased interest in low-field and low-temperature measurements, sub femtotesla magnetometers have been demonstrated[110, 111, 112] for the use in Zero or Ultra Low Field Nuclear Magnetic Resonance measurements.

Future work in this area should include an appropriate examination on the reliability of a method given the type and quality of data to be analysed. By, for example, measuring the smoothness, resolution, and range of the magnetisation data, the method that has been most accurate historically for that data type could be chosen. This would involve a much more comprehensive and multi-dimensional analysis of the quality of the methods outlined here, beyond the scope of this work. This could be a viable region for the use of machine learning, specifically data driven neural networks, due to the ease of creation of input data via VAMPIRE simulation and the high dimensionality of the state space to be explored. The methods in use throughout this work, by taking their arithmetic mean at each instance, are: the Bloch protocol, section 3.6.2[113]; Moskowitz's extrapolation method, section 3.6.3[114]; Tauxe's method, section 3.6.5[115]; the Specific Heat Capacity protocol, section 3.6.6; the Susceptibility protocol, section 3.6.6.

A brief outline of each method is available below, but greater detail on implementation and methodology is available in appendices A.2.1.

3.6.1 Measuring magnetisation with VAMPIRE

Throughout the work forming this thesis, magnetisation is measured directly in VAMPIRE simulations as

$$\vec{M} = \sum_{i} \vec{S}_{i} \cdot \frac{\mu_{i}}{\sum_{n} \mu_{n}}$$
(3.10)

where: \vec{M} is the normalised magnetisation vector; \vec{S} is the normalised atomic spin vector; i is iterating through the spin sites n and μ_i is the magnetic moment of spin i.

3.6.2 Fitting Ms(T)

Fitting a curve to the magnetisation data can be used to estimate the Curie temperature in ferromagnets[116]. Bloch's law can be used to relate the spontaneous magnetisation of a material (the magnetisation measured in absence of an external field) and temperature the material is equilibrated to. At low temperature the Bloch law was established as explicitly,

$$|\vec{M}(T)| = M(0) \cdot \left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right)$$
(3.11)

where M(T) is the magnetisation at zero external field at temperature T; M(0) is the magnetisation at zero external field and at zero temperature; T is the temperature and T_c is the Curie temperature[113]. In real magnets, close to the Curie temperature the following proportional relationship holds,

$$|\vec{M}(T)| \propto \left(1 - \left(\frac{T}{T_c}\right)\right)^{\beta} \tag{3.12}$$

The limits of each of these equations can be interpolated for systems with only one large phase transition, from ferro- to para-magnetic:

$$|\vec{M}(T)| = M(0) \cdot \left(1 - \left(\frac{T}{T_c}\right)^{\alpha}\right)^{\beta}$$
(3.13)

where β is a critical exponent of the system, and the other symbols are unchanged from 3.11. This is fitted using the Trust Region Reflective least squares algorithm implemented for the Python language as part of SciPy[117, 118, 119], with all of the parameters fixed by system type except for the Curie temperature. Finding the curve with the least difference from the data therefore yields the Curie temperature. This method has been adapted to account for system shapes, sizes and structures[103], but was originally developed for bulk materials[120].

3.6.3 Moskowitz extrapolation

While the full derivation is available in Moskowitz's 1981 work[114], the physical description is similar to Bloch's law, but the method is restricted to a temperature range of $T/T_c > 0.8$. The rearranging of 3.12, assuming some starting temperature T_0 , is given by,

$$[Ms(T)/Ms(T_0)]^2 = \frac{T_c}{T_c - T_0} - \frac{T}{T_c - T_0}$$
(3.14)

With symbols as defined in 3.11 and in addition taking T_0 to be some Temperature greater than approximately 80% of the expected Curie temperature, and $Ms(T_0)$ being the corresponding magnetisation. Note that T_0 does not indicate a temperature of 0 Kelvin.

Explicitly, the Curie temperature is calculated by taking the linear regression of the line formed by $[Ms(T)/Ms(T_0)]^2$ and T over the range just below the Curie temperature. The gradient, *m*, of this line is then related to the Curie temperature via,

$$T_c = \frac{-1}{m} + T_0 \tag{3.15}$$

Given the similar physical approach that Moskowitz extrapolation and Bloch's law take, it was expected that there would be good agreement in their Curie temperature estimations, but the separation in these methods could still be in the 3K range, see fig. 3.7.

3.6.4 Grommé's 2 tangent method

This method has often been used for Iron rich compounds, such as titanomaghemites and basalts [114]. This method is highly dependent on the choice of tangent position, and in this work, a similar method, using a linear regression of above and below the Curie temperature is also presented. While no physical basis for this method was presented by Grommé et al. it has been used with good agreement with the other methods previously[102], but is highly susceptible to noise in the magnetisation curve. The implementation covered in listing 3 uses a region from $0.1 \vec{M_s}$ to $0.4 \vec{M_s}$ for the calculation of the tangents to the magnetisation. The tangent to the curve below the Curie temperature is calculated over the range $(0.1 \overrightarrow{M_s}, T_0)$ to $(0.4 \overrightarrow{M_s}, T_u)$ and the tangent to the curve for $T > T_C$ is from $2 * T_u - T_0$ to the end of the data set. Two tangents are taken to the magnetisation curve, above and below the Curie temperature, and the temperature value at which they intersect is the calculated Curie temperature, see fig. 3.2. The tangents are calculated using the Central Difference Method at a point midway through the each of region 1 and 2. These gradients were than used to solve for the intercept, and as such, the two linear equations are formed. These are then treated as simultaneous equations, with their crossing point being at the Curie temperature.

For each region in the magnetisation as a function of temperature curve, with midpoint in the data set *mid*.

$$m = (M[mid + \delta] - M[mid - \delta])/(T[mid + \delta] - T[mid - \delta])$$
(3.16)

$$a = M[mid] - mT[mid] \tag{3.17}$$



Figure 3.2: The tangents to the Magnetisation curve calculated for Grommé's method, the first range is bounded in this implementation from the data points closest to a magnetisation of $0.1M_S < M < 0.4M_S$. This bound is selected based on the magnetisation to ensure proximity to the Curie temperature while remaining below it. The second range is bounded in this implementation by the end of the dataset and the total range of temperature values encompassed by range one, above the upper bound of range one. That is for the 1st range defined as $(T_{0.4}, 0.4M_S) - > (T_{0.1}, 0.1M_S)$ the second range is defined by $T_{0.1} + (T_{0.1} - T_{0.4}) - > EOD$. The second range begins at the temperature one range above the higher bound of the first range, and extends to the end of the data set.

where M[mid] refers to the element in the Magnetisation data set at the index "mid", δ is a small integer, m is the slope of the tangent, and a is the intercept.

Following this, given the two tangents C_1, C_2 with slopes and intercepts m_1, m_2 and a_1, a_2 respectively the Curie temperature can be found by solving the set of simultaneous equations:

$$M_1 = m_1 T_1 + a_1 \tag{3.18}$$

$$M_2 = m_2 T_2 + a_2 \tag{3.19}$$

The Curie temperature is thus calculated as:

$$T_{C,\text{Grommé}} = \frac{(m_1 - m_2)}{(a_2 - a_1)} \tag{3.20}$$

While using the central difference method at one point in the magnetisation curve is an inherently unstable method of generating a tangent, due to its reliance on a single data point, the method was not developed further due to problems with the behaviour of the method, with respect to its performance in noisy scenarios (e.g. with poor quality simulations), and with its performance with reduced resolution. In addition, it is the only method which requires a large region beyond the Curie temperature in the data set, otherwise, the method underestimates the Curie temperature by estimating a more negative gradient in the second region. The range parameters were chosen to maintain a guaranteed range above and below the Curie temperature, without moving away from the Critical region which the method is defined for.

While the method has an inherent reliance on the resolution of the data set (as δ is an integer, the smallest difference in the Central Difference Method is governed by the resolution), the solution to the two simultaneous equations is not fixed to the data set. It can be seen in fig. 3.7 that the method does not become significantly less reliable over the decrease in resolution, but it is substantially less consistent at all resolutions. Above 30K temperature steps it can calculate two tangents which do not have a common solution within the Temperature Domain.

The similar linear regression based method, created for this work, is more consistent, with overestimation fairly consistent across the resolution scale. While not useful as a CTMP in itself, it could be useful as a bounding method for other methods.

3.6.5 Tauxe differential method

The Tauxe differential method[115] seeks the greatest second differential of the magnetisation curve. By differentiating the Ms(T) curve numerically this is readily found as the peak in the magnitude of $|d^2M/dT^2|$. The differential thermal analysis has been shown to give an error in Curie temperature of rare earth ferromagnets of approximately 1%[121].

The implementation created for this work is listed in listing 6. The default operation does not perform any interpolation to find the data point with the greatest magnitude second derivative, that is, T_C is guaranteed to be a point in the data set, inherently limiting the Curie temperature by the resolution. If interpolation is enabled, as it will be throughout the rest of this work, the list of second gradients is interpolated cubically in 1 dimension. This interpolated function is then optimised to calculate the Curie temperature.

3.6.6 Measuring peaks in other macroscopic parameters

Both the susceptibility of the material and the specific heat capacity of the material, as functions of temperature, can be used to evaluate the Curie temperature[122, 123]. In both cases, there is a sharp peak at the Curie temperature as the material loses the spontaneous magnetisation present at low temperatures. The peak in specific heat capacity occurs as the thermal energy introduced to the system is used to break down the ferromagnetic order, and not to directly raise the temperature, analogous to a solid-liquid phase transition[124][125]. This peak is not symmetric. The peak in susceptibility [126] can be directly related to the Curie-Weiss Law for paramagnetic materials eq. (3.21) but has a similar peak (Hopkinson effect [127]) just prior to the Curie temperature as in the specific heat capacity. It has been shown that applying Grommé's two tangent method to the susceptibility curves yields erroneous results[128], but throughout this work no extrapolation on the susceptibility curve was performed.

$$\chi = \frac{C}{T - T_C} \tag{3.21}$$

where C is given as

$$C = \frac{\mu_0 \mu_B^2}{3k_B} N g^2 J (J+1)$$
(3.22)

where: k_B is the Boltzmann constant; N is the number of atoms per unit volume; g is the Landé's g-factor; μ_B is the Bohr magneton and J_{ij} is the exchange constant, energies due to the exchange between spins. Given that C is a material specific constant, it can be seen that the susceptibility will tend to infinity as T approaches T_C . This law is only applicable in the paramagnetic regime of the M(T) (magnetisation as a function of temperature curve) and becomes ill defined around the Curie temperature and below, but it can be seen in section 3.6.6 that the expected peak at $T = T_C$ is still present.

The susceptibility peak relates to the greatest rate of change of magnetisation in the simulation, similar to the Tauxe differential method section 3.6.5, but is calculated



Figure 3.3: The peak in the susceptibility at the Curie temperature for $Nd_2Fe_{14}B$. The red box surrounds the expanded image to the right.



Figure 3.4: The peak in the susceptibility at the Curie temperature for $Nd_2Fe_{14}B$.

directly at runtime, rather than post processing the magnetisation curve. Similarly to the Moskowitz/Bloch parallels above, the expectation would be for these two methods to have good agreement, but again, even at high temperature resolutions, the disagreement can be as much as 3K between these methods, see fig. 3.7. The susceptibility is calculated as,

$$\vec{\chi} = \sum_{i} \frac{\mu_{i}}{k_{B}T} \left(\langle m_{l}^{2} \rangle - \langle m_{l} \rangle^{2} \right)$$
(3.23)

where: χ is the susceptibility of the system; T is the Temperature in Kelvin; μ_i is the magnetic moment of spin i; k_B is the Boltzmann constant; and m_l is the length of magnetisation vector and the angle brackets denote a mean over the counter i. The length of magnetisation vector is given by,

$$m_l = \frac{\sum_i \mu_i \cdot S_i}{\sum_i \mu_i} \tag{3.24}$$

where symbols are defined as above. The specific heat is calculated as:

$$c = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2} \tag{3.25}$$

where: c is the specific heat of the system; E is the magnetic energy of the system; k_B is the Boltzmann constant; T is the Temperature in Kelvin and the angle brackets refer to an average over the atomic sites.

These methods are both implemented without any additional fitting or extrapolation, limiting the resolution of their calculated Curie temperature to that of the input data set.

3.6.7 Quality of methods listed

The range of CTMPs presented yield a range of Curie temperatures of approximately 60K. The most reliable methods, providing a Curie temperature both close to the empirical



Figure 3.5: The peak in the specific heat capacity at the Curie temperature for $Nd_2Fe_{14}B$. The red box surrounds the expanded image to the right.



Figure 3.6: The peak in the specific heat capacity at the Curie temperature for $Nd_2Fe_{14}B$.



Figure 3.7: Variability of the different CTMPs with respect to resolution of an example bcc-Fe VAMPIRE[88] simulation. The expectation that the CTMPs based on the Bloch Law (e.g. Fitting $M_s(T)$ and Moskowitz' method or Tauxe's method and Measuring peak susceptibility) would be similar is mostly borne out, but the variance between similar CTMPs even at high temperature resolution is still several Kelvin.

value and consistently doing so for non-ideal data sets, are visible as the tight cluster of the Moskowitz, Tauxe, Bloch and Susceptibility methods in fig. 3.7. These methods present a range of 10K. This is considered an acceptable level of error, given the imprecise nature of measuring the Curie temperature in complex systems. Due to the similar computation time for each of these methods, and the domination of compute being in the VAMPIRE atomistic spin simulation, these methods were chosen for an arithmetic mean to use as the canonical Curie temperature for the purposes of this optimisation work.

3.6.8 Linear regression

The linear regression method follows the same range finding protocol as Grommé's two tangent CTMP. The linear regression (using least squares regression) is used to calculate the pair of lines which meet near the Curie temperature, instead of a pair of calculated tangents. There is no physical basis for this method presented, and it was explored due to the ready availability of the required simulation data, and the similarity between tangents and least squares linearly regressed lines in the critical region around the Curie temperature.

3.6.9 VAMPIRE Curie temperature simulation

The methods were tested on a simple body centred cubic iron (bcc-Fe) one-exchange systemat varying temperature resolutions, and for varying numbers of total simulation "time" steps. The system was defined with the following parameters

Exchange Cutoff radius 5\AA System size (cubic) $64nm^3$

This methodology was designed to evaluate the consistency of the CTMPs on a range of possible simulation data sets, so as to give the most consistent information to the optimisation method.

3.6.10 Additional methods

Many additional estimators for the Curie temperature have been established[128] but were not considered in addition to the CTMPs presented in this thesis.

3.6.11 Results in context

The exploration of methods for calculating Curie temperature is poorly explored in the literature, with much of the examination of materials presented without detail as the the

methodology used to calculate this value. This becomes especially relevant when the Curie temperature is to be examined programmatically, as in the following chapters, and direct reference to literature data is required. The selection of methods presented here have not been directly compared on the same data set prior to this work. This work introduced a comparison of the methods and detailed their consistency when examining simple cubic systems. This comparison and the highlighting of the poor reporting practices in the literature are required to generate meaningful material data sets for parameterisation, machine learning and reproduceability moving forward.



Figure 3.8: Linear relationship between the Fe-Fe exchange in bcc-Iron and the resultant calculated Curie temperature evaluated from the output of a VAMPIRE monte carlo simulation.

3.7 Rare earth ferromagnet exchange parameters

3.7.1 Low temperature rescaling

VAMPIRE uses a low temperature rescaling to compensate for quantum spin effects which are not treated directly in VAMPIRE. Within VAMPIRE, the spin's orientation is not quantised as it is in Quantum Mechanics [49], but the quantitative low temperature behaviour is recovered using a single-parameter rescaling. A more detailed explanation is presented in section 3.4. This requires the Curie temperature of a simulation to be provided in advance of the simulation itself. This presents a problem when the Curie temperature is to be considered an output of the simulation. In order to estimate the Curie temperature in advance, a linear regression is performed on previous iterations of the optimiser. This line is then used to estimate the Curie temperature of the next simulation. It is possible that this isn't necessary, as the low temperature rescaling of the magnetisation does not affect magnetisation when $T \sim T_C$, and this is where the majority of the CTMPs operate. This additional estimation of the Curie temperature allows for the estimation of exchange to more quickly reach a more accurate magnetisation curve. However, the optimiser is blind to this additional variable, and as a result, 2 simulations at the same exchange input value, but at different times, and therefore different estimated input T_{C} s will yield different results. This can mean that the final iteration of the optimiser was not at the minima of the objective function. This forms a trade-off between improved CTMP performance earlier in the optimisation cycle, and improved locating of the final minima. Currently, the optimiser implements this method, as the expected runtime of these optimisations was high. As the runtime has been substantially shorter than expected (the optimisation methods are quicker than expected due to the broadly monotonically increasing relationship between Curie temperature and exchange) it is not necessarily a requirement going forward, and removing this additional hidden parameter could make the work easier for less simulation minded researchers, especially as the area of interest is near the Curie temperature, where the rescaling is lowest.

3.7.2 Limitation of the optimiser

As an early implementation of an exploratory piece of research software, the current version of vampire_opt has several limitations that will affect computational performance, generalisability to different materials and use cases; and, ultimately its adoption by researchers independent of this work. Limitations include:

- The optimiser has no preference for a ferro or ferri-magnetic final state, and as the Curie temperature can often be achieved via either regime, this can result in incorrect final system behaviour
- The optimiser doesn't account for any fluctuation in simulation results, the same exchange will not be re-verified, which can result in failure to optimise if the quality of the individual iterations' simulations (in terms of number of equilibration and averaging time steps) is not high enough.

• Restricted to a 2:14:1 type rare earth ferromagnet system, the optimiser is brittle in respect to changes in system type, number of exchanges and material type; and would need generalising to other materials.

3.7.3 Optimising rare earth-Iron exchange in Lanthanum based $La_2Fe_{14}B$

In order to reduce the dimensional complexity involved in approximating the exchange constants between Iron atoms (Fe-Fe), and between Iron and Rare earth atoms (Re-Fe), initially the Fe-Fe exchange was chosen as the optimisation goal. In order to remove the Re-Fe exchange as a parameter, to reduce the problem to one dimension, Lanthanum was chosen as the base rare earth $La_2Fe_{14}B$. Lanthanum has no outer 4f electron, resulting in very weak paramagnetism in comparison to Iron or the other rare earths studied [20, 129]. As a result, it is assumed that the Re-Fe exchange constant in $La_2Fe_{14}B$ can be neglected. This allows for the one dimensional optimisation of the Fe-Fe exchange in the material with the Curie temperature of the material used as the figure of merit for the objective function eq. (3.26)

$$obj(X) = |T_C(X) - T_{La}|$$
 (3.26)

where X is the exchange constant between Iron and Lanthanum; T_C is the ; and T_{La} is the empirical Curie temperature of $La_2Fe_{14}B$.

3.8 Optimisation methods:Nelder-Mead and Brent-Dekker

3.8.1 Nelder Mead

The Nelder Mead Simplex method is a numerical method for finding the minimum or the maximum of an objective function [130]. This method was the first implemented to optimise exchange constants for single constant systems (such as bcc-Fe). The method belongs to a class of methods known as direct search methods which do not require an explicit calculation of the gradient of the objective function [131, 132]. This allows for fewer function evaluations at each step in the optimisation process, but can be slower than methods incorporating a calculated gradient. Given that the bottleneck for the optimisation is the number of runs that can be parallelized in batch, the usage of a gradient method could greatly increase the rate of optimisation. As you calculate x Curie temps for each estimated exchange value to increase the accuracy of the next estimate and these would be batch parallelisable (i.e. these simulations could be run concurrently). In practice, however, the rate of finding exchanges is so high in comparison to other manual methods, and only needs to be done once for each material exchange, this was never implemented. The overall optimisation procedure was implemented with the goal of being indifferent to the underlying optimisation algorithm, to allow for comparison and, in future, choice of optimiser to suit the system type. While the Nelder-Mead method successfully optimised bcc-Fe, it was replaced with the Brent-Dekker method (or Brent's method) prior to optimisation of the set of rare earth alloys. This method is detailed in section 3.8.3.

3.8.2 Optimisation Flow Chart

The flow of the optimisation process is presented in fig. 3.9. Note that the calculation of Curie temperature and the atomistic simulation using VAMPIRE are separate, but must occur in sequence. This separation was a conscious decision driven by the aim to allow for the CTMPs to be used on empirical data in addition to simulation data. By definition the CTMPs do not use any internal state of the simulation, but only the data outputted by the program, in order to match the available data sets for empirical work.



Figure 3.9: Optimisation flowchart, where: X_{Fe-Fe} is the exchange constant between iron spins, multiplies the exchange function 3.37; T_{Fe} is the empirical Curie temperature of bcc-Fe, T_C is the calculated Curie temperature of bcc-Fe. Dekkers's method (the precursor to Brent's method) is detailed in the flowchart in fig. 3.10.

Trial Exchange, J/link	Calculated Curie Temperature, K	Exponent	$egin{array}{c} { m Residual} \ abs\Bigl({T-T_{C,emp}\over T_{C,emp}}\Bigr) \end{array}$
1.5e-21	356.262523053	0.350194817481	0.327806560278
3.5e-21	476.336658947	0.333663541736	0.101251586893
5.5e-21	586.721588862	0.324122416497	0.107021865777
2.736068e-21	376.212192436	0.385948312101	0.290165674649
4.263932e-21	486.352851904	0.356795993042	0.0823531096152
3.96688262326e-21	458.420524366	0.320044094433	0.135055614404
4.73606794969e-21	516.410766374	0.36176056842	0.0256400634445
5.02786401922e-21	536.468580409	0.35831234485	0.0122048686961
:	:	:	:
4.99180207763e-21	526.488093462	0.331498915834	0.00662623875185
4.99183603874e-21	526.458857826	0.332773772765	0.0066814003288

Table 3.2: The route for the optimisation of $La_2Fe_{14}B$'s Fe-Fe exchange, with La-Fe exchange fixed at 0. The rows represent the output from the vampire_opt optimisation program, the Curie temperature's calculated using the CTMPs above, and $T_{C,emp}$ representing the empirical Curie temperature from Herbst and Croat [133]. Optimisation was performed with the Nelder Mead simplex algorithm.

3.8.3 Brent's method

Brent's method, or commonly the Brent-Dekker method, is a hybrid root-finding algorithm, combining two root finding algorithms; the bisection method, which repeatedly bisects the previous interval around a root to create a new interval [134]; and interpolation (either linear interpolation, or the secant method, which uses successively generated pairs of points to form secants to the curve [135] or inverse quadratic interpolation, which uses the Lagrange interpolation formula for quadratic interpolation of the inverse of the curve [136]).

Each of these methods are employed at different points in the overall Brent's method algorithm [137], and the core of the method is in the selection of either the bisection method or interpolation method at each iteration point, as published by Dekker [138] in 1969. The bisection method is a more reliable root finder, but the secant and inverse quadratic interpolation methods are potentially much faster.

At each stage of the Dekker's method three points are labelled at each iteration n:

- b_n is the current estimate for the root
- a_n is the current contrapoint, a point such that a_n and b_n have opposite sign, and such that $f(b_n)$ is closer to zero

• b_{n-1} is the previous estimate (with an initial estimate of a_0 for n = 1).

The subsequent point is conditionally one of two values, s and m, given by the secant method, and the bisection method respectively:

$$b_{n+1} = \begin{cases} s = b_n - \frac{b_n - b_{n-1}}{f(b_n) - f(b_{n-1})} f(b_n), & if(f(b_n) \neq f(b_{n-1}) \& \text{ s is between } b_n \text{ and } m) \\ m = \frac{a_n + b_n}{2}, & else \end{cases}$$
(3.27)

Decker's method can perform very well when the function to optimise is well-behaved (that is, the function is smooth and finite in the optimisation region), but can repeatedly use the secant method in certain situations involving less well-behaved functions. This can be unnecessarily slow, necessitating an improvement to the method.

Brent [137] built on this algorithm making two improvements. Firstly, the secant linear interpolation method was replaced with the inverse quadratic interpolation method.

This redefines section 3.8.3 as

$$b_{n+1} = \begin{cases} s = q, & if(f(b_n) \neq f(b_{n-1}) \& \text{ s is between } (3a_n + b_n)/4 \text{ and } b_n) \\ m = \frac{a_n + b_n}{2}, & else \end{cases}$$
(3.28)

where q is the result of the inverse quadratic interpolation recurrence relation:

$$q = \frac{f_{n-1}f_n}{(f_{n-2} - f_{n-1})(f_{n-2} - f_n)} x_{n-2} + \frac{f_{n-2}f_n}{(f_{n-1} - f_{n-2})(f_{n-1} - f_n)} x_{n-1} + \frac{f_{n-2}f_{n-1}}{(f_n - f_{n-2})(f_n - f_{n-1})} x_n$$
(3.29)

where for brevity $f_n \equiv f(b_n)$. This interpolation method requires 3 starting bracket points, instead of the two of linear interpolation, but has the potential to be substantially faster than linear interpolation.

Secondly, two sets of inequalities to be satisfied were added to prevent the repeated interpolation method problem. The first set contains a pair of numerical tolerance inequalities. If the previous step used the bisection method, then the change in estimate must remain below a certain numerical tolerance δ for inverse quadratic interpolation to be

47 of 142

used:

$$\delta| < |b_n - b_{n-1}| \tag{3.30}$$

If the previous step used interpolation, then the change in the previous iteration's start and end estimates must be below the numerical tolerance δ to perform interpolation at the next step:

I

$$|\delta| < |b_{n-1} - b_{n-2}| \tag{3.31}$$

This requires a small amount of additional data to be held between optimisation steps.

The second set contains a pair of inequalities regarding the interpolation method's values. If the previous step uses bisection then the inequality,

$$|s - b_n| < \frac{1}{2} |b_n - b_{n-1}| \tag{3.32}$$

must hold to allow for interpolation at the next step. Similarly, if the previous step used interpolation then

$$|s - b_n| < \frac{1}{2} |b_{n-1} - b_{n-2}| \tag{3.33}$$

must hold to allow for interpolation. These conditions enforces a bisection step at most every $2log_2(|b_{n-1}-b_{n-2}|/\delta)$ iterations, preventing an endless series of interpolation steps.

Brent's method [137] was used as a faster alternative to the Nelder-Mead method. Prior to trialling this method, a gradient descent method was considered, but Brent's method proved sufficiently fast and simple enough to easily implement in Python.The implementation of Brent's method used throughout this work was from SciPy, a scientific Python library [96, 139].

3.8.3.1 Dekker's method flowchart

The control flow for Dekker's method [138] is presented in flow chart form in fig. 3.10. Note that at each iteration only one additional function evaluation is required (as the previous iteration has already calculated $f(b_{k-1})$).

The sign function presented in the flowchart is defined as:

$$sgn(x) := \begin{cases} -1, & x < 0\\ 0, & x = 0\\ 1, & x = 0 \end{cases}$$
(3.34)

and is used in Dekker's method, see fig. 3.10.

The Brent-Dekker's method has a similar control flow, with additional inequality tests as outlined in section 3.8.3 and as such is not repeated here.



Figure 3.10: Dekker's method algorithm flowchart, symbols in yellow are conditions, a_0, b_0 are the input bracket on the objective function f, which is to be optimised to 0. sgn is the sign function, defined in eq. (3.34).

3.8.4 Rare earth Iron exchange

Lanthanum was the first rare earth examined, using $La_2Fe_{14}B$ as the prototype for other rare earth alloys due to the reduced magnetic properties of Lanthanum, but maintaining the same electronic structure as other rare earths. Using $La_2Fe_{14}B$ as the prototype for the Fe-Fe exchange, the other rare-earth elements can be substituted. The Fe-Fe Exchange is kept constant throughout, but the interatomic distances change as there is a 7% change in unit cell volume throughout the lanthanide series due to Lanthanide contraction [90]. Matsumoto and Akai [90] demonstrate the change in trend for Curie temperature when the lattice contraction across the lanthanide series is not taken into account². As a result, the Curie temperature for the materials simulated is only dependent on the Rare earthiron exchange, and can be optimised similarly using a one dimensional optimiser. As noted in Matsumoto and Akai [90] Cerium has an exceptional 4+ state and corresponding reduction in lattice size. They demonstrate that this is responsible for the reduction in Curie temperature for this material by demonstrating the removal of the drop in T_C by enforcing a 3+ state on Cerium in their simulation and fixing the lattice size to that of $Nd_2Fe_{14}B$. The unit cell experimental lattice constants are presented in table 3.3 and are in use throughout this work.

Pajda et al. [140] demonstrated a methodology for evaluating the exchange curve functional for body centred cubic materials. Pajda et al. use the first principles tight binding linear muffin tin orbital method (TB-LMFTO[141]) to evaluate the symmetric exchange between iron atoms in bcc-Fe. The proportional relationship between inter atomic distance and exchange in bcc-Fe is presented in eq. (3.35) by evaluating the energy potentials for weak ferromagnets such as iron:

$$Ex(s) \propto \frac{\sin\left[\left(k_F^{\dagger} + k_F^{\downarrow}\right) \cdot R_{ij} + \phi^{\dagger} + \phi^{\downarrow}\right]}{R_{ij}^3}$$
(3.35)

Where $k_F^{\uparrow,\downarrow}$ corresponds to the Fermi wavevector for the up (\uparrow) and down (\downarrow) spin electrons, $\phi^{\uparrow,\downarrow}$ corresponds to a phase factor for the up (\uparrow) and down (\downarrow) spin electrons and R_{ij} is the distance between the two electrons i and j.

For a strong ferromagnet, or materials approaching strong ferromagnetism (no itinerant magnet is a strong ferromagnet due to sp-d hybridization [140]), one wave vector is imaginary, and as such there is an exponential term in the exchange function.

$$Ex(s) \propto \frac{\sin\left[k_F^{\downarrow} \cdot R_{ij} + \phi^{\uparrow} + \phi^{\downarrow}\right] \exp\left[-\kappa_F^{\uparrow} \cdot R_{ij}\right]}{R_{ij}^3}$$
(3.36)

 $^{^{2}}La_{2}Fe_{14}B$ has the largest volume at 959.958Å 3 , and $Lh_{2}Fe_{14}B$ the lowest at 896.926Å 3

Compounds	a / Å	c / Å	Volume / ${\rm \AA}^3$
$La_2Fe_{14}B$	8.82	12.34	959.958
$Ce_2Fe_{14}B$	8.76	12.11	929.292
$Pr_2Fe_{14}B$	8.8	12.23	947.091
$Nd_2Fe_{14}B$	8.8	12.2	944.768
$Sm_2Fe_{14}B$	8.8	12.15	940.896
$Gd_2Fe_{14}B$	8.79	12.09	934.123
$Tb_2Fe_{14}B$	8.77	12.05	926.800
$Dy_2Fe_{14}B$	8.76	12.01	921.619
$Ho_2Fe_{14}B$	8.75	11.99	917.984
$Er_2Fe_{14}B$	8.73	11.95	910.744
$Tm_2Fe_{14}B$	8.73	11.93	909.220
$Yb_2Fe_{14}B$	8.71	11.92	904.300
$Lu_2Fe_{14}B$	8.7	11.85	896.926
$Y_2Fe_{14}B$	8.76	12	920.851
$Th_2Fe_{14}B$	8.8	12.17	942.445

Table 3.3: The lattice constants of the Rare earth compounds unit cells [133]. c is the lattice constant in the easy axis direction, while a is the constant for the other two directions.

This approach has given accurate descriptions of magnetic systems previously[142, 143, 144]. This interatomic Fe-Fe exchange is used as an approximate basis for the shape of the exchange function in $La_2Fe_{14}B$ for VAMPIRE. The inter atomic exchange is converted to Joules from Rydberg energies, and the distance is measured in Angstrom's within VAMPIRE, and as such there are two conversion factors present. In addition, the Curie temperature estimation using the mean field approximation by Pajda et al. overestimates the Curie temperature (1414K compared to 1043K). There is a small discrepancy in the ratio in use by VAMPIRE and this ratio (0.5%). This corresponds to a 6K difference in the Curie temperature reported in Pajda et al. and the value used for compensation in this work. The ratio in VAMPIRE is used for consistency with other exchange calculations. The exchange energy curve as a function of inter-atomic distance for Fe-Fe exchange interaction in 2:14:1 type rare earth ferromagnet is given by eq. (3.37)

$$Ex(s) \propto 2 \cdot 2.179872 \cdot 10^{-21} \cdot (A \exp\{-Bs\} + C \cdot Fe_{ratio})$$
(3.37)

where: A=36.9434; B=1.25094;C=-0.229572; Fe_{ratio} =0.78444232559. Here, 2.1798782 is the Rydberg energy $\frac{e^4m_e}{8\epsilon_0^2h^2}$ where *e* is the elementary charge of an electron; m_e is the mass of an electron, ϵ_0 is the permittivity of free space; and *h* is Planck's constant. These constants were evaluated by manual fitting of the exponential portion of eq. (3.36) with the phenomenological behaviours of $La_2Fe_{14}B$. The sinusoidal portion of the exchange function was neglected as a longer range effect under the assumption that the exchange modelling of the material would remain under 5Å. The factor of 2 appears as the exchange energy calculation in VAMPIRE uses a factor of one half to reduce the summation required. The Fe_{ratio} is a scaling factor which reduces the Curie temperature calculated by Pajda et al. using the mean field approximation and this exchange functional.

This curve is then multiplied by the exchange constant presented throughout this work to parameterise the exchange for $RE_2Fe_{14}B$.

• Fe_{ratio} is a scaling factor which reduces the Curie temperature calculated by Pajda et al. using the mean field approximation and this exchange functional.

[140]. This curve is multiplied by the parameterised exchange value in calculating the total exchange interaction in the atomistic model.



Optimisation paths for Exchange Parameters of $RE_2TM_{14}B$ **alloys**

Using the optimisation method detailed above, the rare-earth iron exchange for a series of 2:14:1 type rare earth ferromagnet rare earth was established. The empirical Curie temperature and lattice constants for each magnet were taken from Herbst and Croat [133]. The structure of each magnet was fixed as that of $Nd_2Fe_{14}B$ but scaled by the appropriate lattice constants from Herbst and Croat [133]. No additional structural optimisation (for example via molecular dynamics) was performed for each unit cell.

It is important to note that large single crystal structures are very uncommon in 2:14:1 type rare earth ferromagnets. Instead, the total materials structure consists of multiple grains, of the order of $1 - 3\mu m$ in diameter. These grains are situated near each other but are not necessarily aligned creating instability in the crystal structure, and gaps for other phases to form. Typically, tertiary phases that fail the gaps between grains are formed from interfacial phases, with gradual deviations from the crystal structure, other rare earth ferromagnet phases and α -Iron (bcc-Iron). These phases are formed during the quenching process in the production of rare earth. While the evaluation of these phases would be beneficial for the simulation of complete empirical samples, the micrometer scale of the structures mean they are prohibitively computationally expensive for any sort of

53 of 142

iterative searching pattern with the atomistic model. As a result, properties for a pure crystal, or the inside of a grain, are evaluated first. These parameters can be used to guide micromagnetic simulations of grains, and, with a similar methodology, interfacial phases and α -Iron could be similarly evaluated with sufficient empirical data with respect to the interface structures. This forms the basis for a multiscale model involving atomistic parameters and micromagnetic simulations. Future iterations of the optimisation method of parameter evaluation presented in this work could make use of such a multiscale model, with separate atomistic simulations for the different regions; grain internal, interface, and α -Iron, being combined in a micromagnetic simulation with the macroscopic output of the micromagnetic simulation being used as the objective function for optimising the atomistic parameters.

The structure examined initially during the optimisation phase was a $(4 \times 4 \times 4)nm^3$ cell with periodic boundary conditions. This value was chosen as a compromise for the optimisation cycle, as smaller systems modelled atomistically have been found to greatly affect Curie temperature due to finite size effects with a grain size below 3.5nm [94]. Finite size effects are a class of systematic errors introduced in reducing the size of a simulation. In magnetic structures this is often manifested by reduced Curie temperature when compared to bulk materials. After the optimisation process, the final calculated exchange values can be used to calculate a large system's properties, with a high temperature resolution to measure the effects of optimising for a smaller system size. An example curve is given below, fig. 4.3. To confirm the validity of the 3.5nm threshold, the $(4nm)^3$ was compared with a larger $(6nm)^3$ system. Both were simulated with the final exchange value of $Nd_2Fe_{14}B$. The magnetisation as a function of temperature behaviour of the two systems is displayed in fig. 4.3 alongside empirical results from Hirosawa et al. [145] at 1T for a single domain inside a larger material. Hirosawa et al. grew crystals with size of order several millimetres rendering a full size comparison to the work performed unfeasible due to the theoretical computational expense. As demonstrated in figs. 4.1 and 4.3 the initial system size was not sufficient to remove finite size effects. The Curie temperature of the system falls as the system size is increased to $(6 \times 6 \times 6)nm^3$. This indicated that using the bulk Curie temperature (which is reduced compared with finite size systems) results in a reduced optimised exchange. An increase of 5% results in the 6nm system giving an appropriate Curie temperature (and subsequently, increasing the Curie temperature of the 4nm system). The calculated discrepancy in the Curie temperature due to finite size effects does not account for the discrepancy in shape of the empirical curve. The two sublattice model of the $RE_2Fe_{14}B$ alloys relies on two parameters for calculating the low temperature rescaling present in section 3.4. The rounder shape of the magnetisation curve in fig. 4.3 suggests that one or both rescaling exponents were too great, and subsequently, that the exponent must be separately optimised. Fortunately, at the Curie temperature is by definition unaffected by the exponent, the exchange constants calculated should remain fixed during this subsequent optimisation. The additional spin reorientation, the kink in the empirical curve of fig. 4.3 can be described by anisotropic effects, but at this stage, the temperature dependence of the anisotropic constants in $Nd_2Fe_{14}B$ have not been fully parameterised.

Hirosawa et al. [145] measured the single crystal in a 1*T* external applied magnetic field. Using the same CTMPs which pertain to magnetisation as in the optimisation method (i.e. Bloch law fitting section 3.6.2 [113]; Moskowitz's extrapolation method, section 3.6.3 [114]; Tauxe's method, section 3.6.5 [115]; but not the Specific Heat Capacity protocol, section 3.6.6 or the Susceptibility protocol, section 3.6.6 due to a lack of measurements of susceptibility and heat capacity presented) results in an average effective T_C under this applied field of 603.4*K* for the empirical curve. This is approximately 3% larger than the zero field Curie temperature from literature, and calculated in this thesis. The CTMP is not detailed by Hirosawa et al. [145], but it is expected that the Curie temperature at field would be higher than the temperature at zero field, as there is an additional energetic incentive to align.

These discrepancies suggest a need for greater transparency in the calculation of physical parameters such as the Curie temperature, as it is possible that the methods presented here are overly sensitive to changes near the Curie temperature when compared with regions further from T_C .

While the Curie Temperature is in good agreement with empirical work [133], the combination of critical exponents of the two sub-lattices do not produce the appropriate shape of the curve [145]. Similarly, as this work was undertaken prior to the establishment of higher order anisotropy constants in $Nd_2Fe_{14}B$, the spin reorientation temperature is not visible in the calculated curve, where empirically there is a small bump in the magnetisation in the 120K region, no such increase is present in the calculated curve. At a nominal working temperature of a motor, 450K, there is a discrepancy of approximately 15% between the



Sm₂Fe₁₄B with optimised exchange of 1.215x10⁻²¹

Figure 4.1: Magnetisation curve for $Sm_2Fe_{14}B$ with a system size of $(6nm)^3$ with a Sm-Fe exchange of 1.215×10^{-21} . Compared with the literature empirical curve measured by Hirosawa et al. [145] at 1*T* applied external field [145, digitized from print].

$56 ext{ of } 142$



Nd₂Fe₁₄B with optimised exchange of 0.9x10⁻²¹

Figure 4.2: Magnetisation curve for $Nd_2Fe_{14}B$ with a system size of $(6nm)^3$ with a Nd-Fe exchange of 0.9×10^{-21} in zero external field and at 1T in the easy axis (z) direction. Compared with the literature empirical curve measured by Hirosawa et al., digitized from print at 1T applied external field [145]. This exchange value is 5% greater than the optimised value, to compensate for finite size effects in the $(4nm)^3$ optimised system.

 $57 \ \mathrm{of} \ 142$

empirical and calculated data. Similar comparisons are made for $Sm_2Fe_{14}B$ in fig. 4.1.

The calculated Curie temperatures did not include: $La_2Fe_{14}B$ as it was the prototypical system, with iron-lanthanum exchanged fixed at zero; $Ce_2Fe_{14}B$ due to its additional +4 oxidation state and $Yb_2Fe_{14}B$ due to its +2 oxidation state. These additional states are available due to their different electronic structure. Elemental Cerium has an electronic structure of [Xe] $4f^1 5d^1 6s^2$, with the 4f electron's energy level being very comparable to the delocalised 5-d electrons. This is due to its early position in the series, and the relative stability of an empty 4-f shell, when compared to the other lanthanides, yielding a low enough nuclear charge [146]. Ytterbium similarly has a uniquely stable +2 state due to its penultimate position in the lanthanide series. Its base [Xe] $4f^{14} 6s^2$ electronic structure has a relatively stable +2 state due to the stability of the full f-orbital when the 6-s electrons are removed. The change in electronic state of these two elements creates a large change in their magnetic properties when compared to the other rare earth, causing $La_2Fe_{14}B$ to no longer be a good prototype for $Ce_2Fe_{14}B$ and $Yb_2Fe_{14}B$. Depicted below are the rare earth iron exchange values calculated at each iteration of the optimisation process. As stated in section 3.8 the optimiser in question is using Brent's method [137] to iterate through possible input exchange values. In general the iterator needs fewer than 10 iterations to be within the error margin of the Curie Temperature Measurement Protocols, (CTMPs), however, as can be noted in the graphs of temperature residual as a function of iteration number, the optimiser rarely exits at the lowest residual iteration. For example, in fig. 4.6, the $Gd_2Fe_{14}B$ optimisation path continues into a false minimum despite the temperature residual being much lower in the first 10 iterations. This is caused by the estimation in Curie temperature required as input for the low temperature rescaling, detailed in section 3.4. As the small error in the estimation of the Curie temperature can be larger than the change due to the optimiser altering the exchange in earlier iterations, the optimiser can explore the wrong region of the state space. Some optimisations coincidentally reach an exchange within the tolerance to exit very early, but this cannot be relied upon to happen in practice. The optimiser frequently missed the earliest within tolerance exchange constant, due in part to the Curie temperature estimation being performed to prime the low temperature rescaling at each step. As stated above it is likely that this rescaling could be ignored until post-exchange optimisation, as the rescaling tends to zero as the temperature tends to the Curie temperature. The simulation quality was kept low for improved computation time,



Figure 4.3: Magnetisation curve for $Nd_2Fe_{14}B$ at 4nm and 6nm simulation size with a Nd-Fe exchange of $0.85x10^{-21}$. The finite size of the smaller system results in a 1.7% difference to the calculated Curie temperature. Compared with the literature empirical curve measured by Hirosawa et al. [145].

$59 ext{ of } 142$

with a relatively small number of equilibration and temperature increment steps. This was mitigated for as the optimiser performed multiple similar simulations as the optimiser advanced, increasing the amount of sampling in the Monte-Carlo algorithm.



Figure 4.4: Optimisation route for Pr- and Nd-Fe exchange. Final calculated exchange: Pr = 1.19E - 21J/link, Nd = 0.850E - 21J/link


Figure 4.5: Optimisation route for Tm- and Yb-Fe exchange. Final calculated exchange: Tm = -0.343E - 21J/link, Yb = -0.2475E - 21J/link. Note that Ytterbium was not calculated using this method, as noted in section 3.8, due to its lower Curie temperature than Lanthanum in the 2:14:1 type rare earth ferromagnetic phase.

4.1 Temperature residuals along the optimisation paths for Rare earth ferromagnets

During the optimisation process, the objective function yields the residual of the calculated Curie temperature and the empirical. Using Brent's method [137]. As shown here, the simulation often passed the lowest Curie temperature residual, before circling another local minima. It is suggested that this is caused by the naive rescaling estimation performed at each optimiser step in concert with numerical noise from the simulation translating to slightly inconsistent Curie temperature measurements.



Figure 4.6: The result of the objective function, or Curie temperature residuals, for Smand Gd-FeB during the optimisation of their exchange. Final calculated exchange: Sm = 1.215E - 21J/link, Gd = 1.57E - 21J/link



Figure 4.7: The result of the objective function, or Curie temperature residuals, for Tband Dy-FeB during the optimisation of their exchange. Final calculated exchange: Tb = -1.208E - 21J/link, Dy = -0.63E - 21J/link



Figure 4.8: The result of the objective function, or Curie temperature residuals, for LuFeB during the optimisation of its exchange. Final calculated exchange: Lu = 0.0E - 21J/link

The resultant exchanges are presented in table 4.1, as are the calculated Curie temperatures from the resultant VAMPIRE simulation, the smooth $\vec{M}(T)$ curves are presented below. The systematic optimisation method provided Curie temperature values within 4 Kelvin of the empirical values recorded by Herbst and Croat [133]. As expected, the rare earths (except for Cerium) have an increased Curie temperature compared to the prototypical Lanthanum compound. An increase in Curie temperature between materials causes an increase in the magnitude of the rare-earth-iron exchange calculated, with some exception. $Lu_2Fe_{14}B$ has a smaller unit cell size than $La_2Fe_{14}B$, which means that the magnetic sites are closer together. Given this, the iron-iron exchange in $Lu_2Fe_{14}B$ is larger than in $La_2Fe_{14}B$ and as such the Curie temperature is increased without a corresponding increase in the rare-earth-iron exchange constant.

4.1.1 Error in Exchange estimate

Given that the calculation of Curie temperature can be performed with a variety of methods, without consensus in the literature as to the most appropriate, there is a large margin of error in the estimated Curie temperature. The range of Curie temperature's calculated using CTMPs is presented for a simple cubic Iron simulation in fig. 3.7. As is apparent, the range of Curie temperature's calculated exceeds 60K across all the implemented methods, and exceeds 5K for the 4 CTMPs selected for averaging (the Bloch protocol, section 3.6.2[113]; Moskowitz's extrapolation method, section 3.6.3[114]; Tauxe's method, section 3.6.5[115]; and the Susceptibility protocol, section 3.6.6]. This error range directly relates to an error range in the optimised exchange constants. This error is compounded with the error as a result of simulation quality, due to for example finite size effects and homogeneity of sample grain structure, but can be evaluated by calculating the range in exchange constants that yield a similar range in Curie temperatures. For each optimisation result from the average of the CTMPs results, there is an optimisation result for each CTMP separately. This relates a range in the exchange to the range in Curie temperatures that the set of CTMP calculates.

Given that the CTMPs produce different estimates of the Curie temperature, and that the Curie temperature used as the objective function is the arithmetic mean of the four CTMPs in use, the error in the calculated exchange is related to both the distance that the final simulation's Curie temperature is from the empirical temperature, and the spread of these methods. Fortunately, when examining the individual CTMPs which form components of the Curie temperature calculation the range of estimates is low. For example, for the $6nm Sm_2Fe_{14}B$ simulation whose magnetisation curve is presented in fig. 4.1, the range in exchange calculated is only 0.96K, detail in table 4.2. By assuming a linear relationship between exchange and Curie temperature, and taking the gradient of

Compound	<i>T_c</i> (K) [133]	4nm	
		Re-TM Exchange (× $10^{-21}J/link$)	Calculated $T_c(K)$
$La_2Fe_{14}B$	530	01	530 ± 1
$Ce_2Fe_{14}B$	424	Uncalc.	Uncalc.
$Pr_2Fe_{14}B$	565	1.19 ± 0.020	$566\pm0.88^*$
$Nd_2Fe_{14}B$	583	0.850 ± 0.0215	584 ± 1.635
$Sm_2Fe_{14}B$	616	1.215 ± 0.0085	614.3 ± 0.48
$Gd_2Fe_{14}B$	661	-1.57 ± 0.01	$657\pm1.27^*$
$Tb_2Fe_{14}B$	620	-1.208 ± 0.018	$620.6 \pm 1.24^*$
$Dy_2Fe_{14}B$	598	-0.63 ± 0.12 (±0.012)	599 ± 8.55 (±0.855)
$Ho_2Fe_{14}B$	573	-0.343 ± 0.21	574.4 ± 14.3
$Er_2Fe_{14}B$	554	-0.2475 ± 0.32	555.4 ± 12.1
$Tm_2Fe_{14}B$	541	-0.0554 ± 08.5	540.7 ± 6.08
$Yb_2Fe_{14}B$	524	Uncalc.	Uncalc.
$Lu_2Fe_{14}B$	535	0 ± 0.01	533 ± 0.3

Table 4.1: Rare earth transition metal exchanges, calculated using the numerical optimisation set out in section 3.8, Iron-Iron (Fe-Fe) exchange was fixed at 5.005E-21, following the optimisation of LaFeB with respect to its Curie temperature. A double rule separates the rare-earth elements traditionally grouped with Cerium and those traditionally grouped with Yttrium. Europium and Promethium are excluded due to their inability to form in the 2:14:1 type structure. [133]. Both Cerium and Ytterbium are left uncalculated using Lanthanum as the base rare earth, as they present with lower Curie temperatures than the Lanthanum base. This is a result of the additional stable electronic states that the Cerium and Ytterbium can occupy. Specifically Cerium has a +4 oxidation state, and Ytterbium has a +2 oxidation state in addition to the expected +3 state of the other metals in the lanthanide series. The Ytterbium +2 oxidation state is due to its position in the penultimate column of the lanthanide series, and similarly, Cerium's +4 oxidation state is due to its occupation of the fourth column of the periodic table. The Ytterbium compound has a much closer Curie temperature to the Lanthanum compound due to the preference for the +3 oxidation state. The difference in calculated Curie temperature for the Lutetium and Lanthanum compounds despite the same exchange constant is due to the smaller unit cell of the Lutetium compound. Error values are calculated using the range in CTMP results for a given simulation. The approximate proportional relationship between exchange and Curie temperature is calculated using a linear regression on the $T_C(XC)$ data. This proportionality is applied to the spread in CTMP values as a measure of the spread in possible exchange values. For low resolution simulations the specific heat and susceptibility measurements are fixed at multiples of the Temperature interval. To estimate the spread in CTMP results including the susceptibility method, the spread in Curie curves is estimated at double the spread excluding the susceptibility value in these low resolution simulations. These error estimates are asterisked (*). For comparison the spread in CTMP for $Nd_2Fe_{14}B$ including the susceptibility data is approximately 30% greater than without, and for $Sm_2Fe_{14}B$ the difference is close to 1%. Dysprosium had an unusually high spread of CTMP values, entirely as a result of the Tauxe method underestimating the T_C by 20K compared with the other methods. This is likely a numerical issue, as the second derivative is similar at the position the other CTMPs estimate the Curie temperature. Excluding this value yields the error estimates in brackets.



Figure 4.9: Graph form of table 4.1. The expected trend of increasing exchange corresponding to a matching increase in Curie temperature is recovered. The large decrease from Pr to Nd does not correspond to a significant change in the unit cell volume. Notably $Nd_2Fe_{14}B$ has much larger anisotropy than Pr which may account for a reduction in Curie exchange energy for a given Curie temperature.

the subsequent curve formed by the linear regression of the data generated during the optimisation (equal to $0.01781080807 \times 10^{-21} J/K$) the estimated range in exchange can be calculated via

$$\Delta T \cdot \left(\frac{\Delta E}{\delta T}\right) = \Delta E \tag{4.1}$$

$$0.96K \cdot 0.01781080807 \times 10^{-21} J/K = 0.01709837574 \times 10^{-21} J$$
(4.2)

(4.3)

with the differing digits underlined for emphasis. This places the error due to spread in methods at approximately 1.25% of the optimised exchange. This is substantially less than the error estimated due to experimental factors for the reference data, as presented in table 4.3. Taking the gradient over only the region local to the final Curie temperature further reduces this error value to 0.32%.

With respect to the difference between simulated behaviour and experiment on the Curie temperature, using the same CTMP methodology on the digitised empirical data from Hirosawa et al. [145] yields a deviance of 50K. This discrepancy is much larger than the spread in CTMPs when calculating the Curie temperature, suggesting a more fundamental separation in the definition of the Curie temperature theoretically, and the actual measurable quantity presented empirically. For comparison, using the linear regression method as above to estimate the affect a 50K discrepancy would have on the exchange constant for $Sm_2Fe_{14}B$, the gradient yields a percentage error of 65% in the calculated exchange.

With respect to simulation quality, repeating the same simulation with different random seeds and using the CTMP average to calculate Curie temperature results in a range of approximately 0.05K at a Temperature resolution of 2K for the temperature sweep. This is sufficiently small that the deviation from linearity demonstrated in the exchange-Curie temperature relationship would lead to a larger deviation in the calculated exchange and as such this error is not included in the exchange error estimate.

The range of Curie temperature's calculated by each CTMP in the final iteration of the optimisation of each rare earth is presented in table 4.4. As a measure of fitness of the linear estimation, the Curie temperatures in table 4.5 were all converted to exchange values using the straight line estimation presented above for estimating the error in exchange. Presented in table 4.5 are the ranges in optimised RE-Fe exchange constant calculated by reversing the range in calculated Curie temperature of the CTMP's selected for the optimisation average, as detailed above. The exchanges estimated differ somewhat in magnitude from the final calculated exchange used as input for each VAMPIRE simulation. This discrepancy is due to the non-linearity of the exchange-temperature

CTMP	Calculated Curie temperature estimate (K)
Moskowitz' extrapolation method3.6.3	614.96
Fitted M_s method 3.6.2	614.06
Tauxe's differential method3.6.5	614.00
Susceptibility peak3.6.6	614.00
Avg	614.25
Empirical [133]	620

Table 4.2: The four different CTMPs used to calculate the Curie Temperature estimate for $Sm_2Fe_{14}B$ in a 6nm system with periodic boundary conditions at zero field, with an Sm - Fe exchange of $1.36 \times 10^{-21}J$ per link. The Empirical Curie temperature 620K.

CTMP	Calculated Curie temperature estimate (K)
Moskowitz' extrapolation method3.6.3	668.28
Fitted M_s method 3.6.2	666.21
Tauxe's differential method3.6.5	650.10
Avg	661.53
Empirical [133][145]	620

Table 4.3: The difference in CTMPs when applied to the digitised data from Hirosawa et al. [145]. The methods all overestimate the digitised data suggesting a consistent difference in the methods for describing the Curie temperature computationally and experimentally. This discrepancy is between 1 and 2 orders of magnitude higher than the difference between CTMPs when applied to the simulated material.

behaviour, and due to the large error in estimating the intercept of the line used. This error ranges from 0.01 to $0.25 \times 10^{-21} J$. At the worst case, this could suggest a larger error in exchange than estimated above, but still substantially less than the discrepancy with experimental results presented in table 4.3. The largest source of error, and limiting factor, when examining the programmatic optimisation of exchange in these materials is related to the experimental data gathered and the reporting of methodologies at wide in the literature.

Compound	Curie temperature(K)				Temperature range (K)
	Bloch	Moskowitz's	Tauxe's	Susceptibility	
	protocol[<mark>113</mark>]	extrapolation [114]	method [115]	protocol	
$Pr_2Fe_{14}B$	570.13 ± 0.1	570.88 ± 0.1	570.0 ± 0.1	560.0 ± 1	0.75 ± 1
$Nd_2Fe_{14}B$	584.20 ± 0.1	585.26 ± 0.1	582.5 ± 0.1	582.0 ± 1	0.54 ± 1
$Sm_2Fe_{14}B$	614.05 ± 0.1	614.96 ± 0.1	614.0 ± 0.1	614.0 ± 1	0.96 ± 1
$Gd_2Fe_{14}B$	631.27 ± 0.1	631.15 ± 0.1	630.0 ± 0.1	620.0 ± 1	11.27 ± 1
$Tb_2Fe_{14}B$	621.24 ± 0.1	621.02 ± 0.1	620.0 ± 0.1	610.0 ± 1	11.24 ± 1
$Dy_2Fe_{14}B$	596.25 ± 0.1	597.17 ± 0.1	580.1 ± 0.1	584.0 ± 1	17.17 ± 1
$Ho_2Fe_{14}B$	598.60 ± 0.1	593.50 ± 0.1	570.0 ± 0.1	560.0 ± 1	38.60 ± 1
$Er_2Fe_{14}B$	574.09 ± 0.1	572.19 ± 0.1	550.0 ± 0.1	540.0 ± 1	34.09 ± 1
$Tm_2Fe_{14}B$	552.15 ± 0.1	551.90 ± 0.1	540.0 ± 0.1	530.0 ± 1	22.12 ± 1
$Lu_2Fe_{14}B$	541.65 ± 0.1	541.81 ± 0.1	530.0 ± 0.1	530.0 ± 1	11.65 ± 1

Table 4.4: The range in Curie temperatures calculated using each of the four CTMPs on the VAMPIRE simulation data from the final iteration of the optimisation process. This is used to generate the exchange error values in table 4.5. Methods from A)the Bloch protocol, section 3.6.2[113]; B) Moskowitz's extrapolation method, section 3.6.3[114]; C) Tauxe's method, section 3.6.5[115]; and D) the Susceptibility protocol, section 3.6.6). Errors in these measurements are presented based on the methods implemented resolution at a temperature sweep resolution of 2K for the susceptibility method, and the range over several different random seed iterations for the other methods.

Compound	Exchange $10^{-21}J$		
	Linear estimation ^a	Input Variable ^{b}	
$Pr_2Fe_{14}B$	1.10	1.19	
$Nd_2Fe_{14}B$	0.81	0.85	
$Sm_2Fe_{14}B$	1.15	1.215	
$Gd_2Fe_{14}B$	-1.22	-1.57	
$Tb_2Fe_{14}B$	-1.20	-1.208	
$Dy_2Fe_{14}B$	-0.55	-0.63	
$Ho_2Fe_{14}B$	-0.34	-0.343	
$Er_2Fe_{14}B$	-0.25	-0.2475	
$Tm_2Fe_{14}B$	-0.10	-0.0554	
$Lu_2Fe_{14}B$	-0.05	0	

Table 4.5: a)Exchange calculated by linear estimation of the relationship between exchange and Curie temperature from the optimisation data evaluated at the Curie temperature and b)the input variable provided to VAMPIRE at the Curie temperature. The deviation from linear behaviour is apparent, with the average exchange calculated via estimating a linear relationship between exchange and Curie temperatures calculated with each CTMP differing significantly from the variable provided to the VAMPIRE simulation.

4.1.2 Results in context

These results present first attempts to characterise the complicated microscopic magnetic exchange of the $Nd_2Fe_{14}B$ type rare earth ferromagnets using a macroscopic variable as a mathematical optimisation goal. These materials have complex non-cubic unit cell structures, but it has been demonstrated that macroscopic simulation properties such as the Curie temperature can be used to numerically optimise the microscopic exchange parameters without researcher intervention. This methodology uses relatively little computation and experimental data when compared with alternative avenues, including machine learning approaches using neural networks.

The treatment of exchange interaction as an energy dependent only on atom type and inter atomic distance has reduced the optimisation space substantially, by highly reducing dimensionality from an individual pairwise treatment of electronic or atomic magnetic moments. Chaining this reduction with the usage of a prototypical Lanthanum based compound, allowed the optimisation process to proceed linearly, first by optimising the iron-iron exchange in $La_2Fe_{14}B$ and subsequently the Rare earth-iron exchange in the other materials. This is an approach not examined elsewhere in the literature, and should spur greater examination of other weakly magnetic materials in an effort to better characterise similar systems such as the $SmCo_5$ and $NdFe_{12}$ groups.

The exchange constant results in themselves present an expected relationship with the Curie temperature of the compound and there is relatively good agreement with literature Curie temperature values with larger discrepancies present due to disagreements from Curie temperature methods.

This methodology therefore provides a framework for parameterising other ferromagnetic materials of complex structure using macroscopic optimisation targets which can be readily supplied by the literature. This further allows for much more rapid examination of these materials, without many researcher hours devoted to manual parameterisation.

CHAPTER CHAPTER

MAGNETIC ANISOTROPY IN $RE_2TM_{14}B$ alloys

Throughout this thesis the anisotropy is restricted to magnetocrystalline anisotropy energy due to a series of factors prohibiting the examination of the other subtypes of magnetic anisotropy. Shape anisotropy is dependent on the shape of the material, so requires a separate parameterisation *after* the parameterisation of the more fundamental magnetocrystalline anisotropy energy constants, forming a basis for future work in the field. Spin models are well suited to the examination of magnetocrystalline anisotropy, but fixed lattice models are incapable of examining tension in a crystal, prohibiting any examination of magnetoelastic anisotropy.

As a result, the restriction to the examination of magnetocrystalline anisotropy energy only is chosen due to the direct relation to the performance of atomistic models and the aim to generalise the results to all structures of $Nd_2Fe_{14}B$.

Numerous mathematical evaluations of this magnetocrystalline anisotropy energy exist, generally one can choose the basis which best suits the symmetry in the material. For example, for cubic anisotropy, one can treat the anisotropy as a series of multiplied polynomials [147], for uniaxial anisotropy as a series of Legendre polynomials [7] and as extended for this work for systems with in plane anisotropy, as a series of spherical harmonics in two dimensions, section 5.2. The constants which describe the strength of each element in these series are termed anisotropy constants. The importance of the symmetry of the system relates to the number of parameters required to describe the anisotropy. With careful choice of the basis for the anisotropy, fewer anisotropy constants can in theory describe the anisotropic effect. The anisotropy constants are the parameterised values in the description of the total magnetocrystalline anisotropy energy.

5.1 Empirical results and work by Cadogan et al.

Neodymium Iron Boron, $Nd_2Fe_{14}B$, has a complex magnetocrystalline anisotropy energy. The material exhibits not just easy axis anisotropy, with preference for spins to align in a single axis, but instead a complex three-dimensional anisotropy, containing easy axis terms, easy plane terms and azimuthal preferences. The anisotropy is largely based at the Neodymium sites in the material, due to the 4f electrons' large unbalanced orbitals' strong spin orbit coupling [148], but the contribution of the numerous iron atoms cannot be overlooked. Empirical results are presented in Cadogan et al. [72] [taken from 89] in comparison, but it should be noted that at 4.2 Kelvin, the experimental results agree comprehensively with Cadogan et al.'s work.

In [72], Cadogan et al. presented a novel analysis method for the estimation of the anisotropy of rare earth transition metal compounds, notably applicable to the 2:14:1 type rare earth ferromagnet $Nd_2Fe_{14}B$. Cadogan et al. replicated empirical low-temperature high magnetic field behaviour in $Nd_2Fe_{14}B$ crystals. The method employed involved the calculation of anisotropic exchange constants via calculation of the energy due to a set of n particular directions of the 3 dimensional magnetisation, and systematically altering the anisotropy constants until agreement with experiment. The method revolves around the expansion of empirically determined anisotropy constants, with comparison made to empirical magnetisation curves to create a fitting of the constants. These anisotropy constants relate the magnetocrystalline anisotropy of the material to an energy surface at each crystallographic site. This is fundamentally similar to the methodology presented in this thesis. In the VAMPIRE simulation however, each atom type is treated with a unique set of anisotropy exchange constants, whereas in the method presented by Cadogan et al. [72], each Neodymium crystallographic site is treated individually. The work presented in Cadogan et al. [72] has a much higher dimensional complexity, with 14 anisotropy constants, contrasted with only 5 constants evaluated for the single spin model presented in section 5.2.1, and 6 evaluated for the atomistic model in section 5.2.2.

5.2 Replicating empirical anisotropy with spin models

Using an atomistic basis for the anisotropy calculation should allow for the implicit calculation of temperature dependence of anisotropy constants, as opposed to the explicit scaling presented in Cadogan et al. The aim was therefore to replicate the empirical anisotropic effects, without increasing the dimensional complexity, and its associated computational cost. To achieve this, the number of anisotropy constants used to describe the Neodymium sites in $Nd_2Fe_{14}B$ need to be increased, to give sufficient degrees of freedom in the expression of the anisotropy.



Figure 5.1: Computed magnetisation curves from Cadogan et al. [72]. The x-axis is the magnetic field in Tesla, *in* the direction of the measurement. e.g. the [001] curve is measured in a magnetic field along the [001] direction. Temperatures for each graph are a)4.2K, b)100K, c)150K, d)275K. For the final graph, calculated values were reduced by 15% to agree with experiment, without a proposed physical interpretation.

Spherical harmonics, and specifically the Laplace spherical harmonics, are chosen as the basis for the anisotropy energy of each atom, detailed in table 5.2. The Laplacian spherical harmonics are chosen as they form an orthonormal basis, facilitating the separation of different anisotropic components. In addition, the spherical harmonics have symmetries which correspond to symmetries around crystallographic axes, which results in many of the possible anisotropic constants reducing to zero. This is an extension to the Legendre polynomials previously used in atomistic modelling. The extension $Y_l^m(\theta,\phi)$ is related explicitly to the Legendre polynomials, P_m^l via,

$$Y_{I}^{m}(\theta,\phi) = Ne^{im\phi}P_{I}^{m}(\cos\theta)$$
(5.1)

where $Y_l^m(\theta, \phi)$ is the Lagrange's spherical harmonic; P_l^m are the associated Legendre polynomials including the Condon-Shortley phase $(-1)^m$; θ is the polar angle; ϕ is the azimuthal angle; l is the orbital quantum number; and m is the magnetic quantum number.

The associated Legendre polynomials were the standard anisotropy basis in VAMPIRE prior to this work and additional implementation work performed by Jack Collings¹. The polynomials are defined as,

$$P_l^m(x) = (-1)^m (1 - x^2)^{m/2} \frac{d^m}{dx^m} (P_l(x)),$$
(5.2)

where P_l is the generator of Legendre Polynomials, given by,

$$P_{l}(x) = \frac{1}{2^{l} l!} \frac{d^{l}}{dx^{l}} (x^{2} - 1)^{l}.$$
(5.3)

and with other definitions as above. The absolute value of the orbital quantum number, |l|, is used in this generator. The mapping to Cartesian space treats x as the easy axis of the material, and by definition, there is no azimuthal component to the anisotropy, precluding the examination of the material $Nd_2Fe_{14}B$, which is approximately tetragonally symmetric about the easy axis. This level of symmetry was chosen to best replicate the work of Cadogan et al. [72] who also assumed a four-fold symmetry in the plane orthogonal to the easy axis. It is possible an improved approximation would assume only a two-fold symmetry in this plane and would therefore expect the addition of the A_2^2, A_4^2, A_6^2 terms to the anisotropy calculation. The first 3 even and non-zero orders of the associated Legendre polynomials are presented in table 5.1. The highlighted terms comprised the total anisotropy description available in VAMPIRE.

¹Computational Magnetism Group, University of York

Polynomial	Expansion
P_2	$3(z^2-1)$
P_4	$\frac{1}{8}(35z^4 - 30z^2 + 3)$
P_6	$\frac{1}{16}(231z^6 - 315z^4 + 105z^2 - 5)$

Table 5.1: Legendre polynomial expansion (n.b. not the associated polynomials) to 6th order in magnetic quantum number with 0th order in orbital quantum number. The first two rows (highlighted) were the only anisotropy terms available in VAMPIRE at the commencement of this thesis, with z corresponding to the easy axis of the material.

To form the anisotropic interaction, the polynomials are calculated for each spin whereas usual z is the easy axis direction. The value z can be replaced with $\cos(\theta)$ as a result of the normalisation of the magnetic spin, as shown here in the conversion from spherical to Cartesian coordinates:

Given that:

$$\theta = \arccos\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right),$$

$$x^2 + y^2 + z^2 = 1$$
(5.4)

 $\cos(\theta)$ can be related as:

$$\cos(\theta) = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$\cos(\theta) = \frac{z}{\sqrt{1}}$$

$$\cos(\theta) = z$$
(5.5)

Care must be taken in this conversion, as there are differing conventions with regard to the azimuthal and polar angles. Throughout this work, as is convention in Physics, the polar angle, θ , is the angle **from** the z-axis, and the azimuthal angle, ϕ , is the angle around the z-axis from the x-axis.

While multiple anisotropy types, such as cubic and easy-plane anisotropy, can be created using the summation of multiple sets of these polynomials along each axis, they cannot accommodate a rotational preference in the x-y plane. This necessitates the use of a more complex anisotropy Hamiltonian. The spherical harmonics made a simple choice, due to their appropriate symmetries around the axes of a crystal. The anisotropic terms used to model $Nd_2Fe_{14}B$ are given in table 5.2. Note that the highlighted rows are effectively a set of rescalings of the expansions given in table 5.1, with $x = \cos(\theta)$.

Prior to this work, in simulations performed with VAMPIRE the material's higher order anisotropic properties, the azimuthal fourth order, and higher order polar anisotropies

Anisotropy Term	Constant and spherical harmonic	Expansion
A_2^0	$k_2^0\bigl(Y_2^0\bigr)$	$k_2^0 \cdot rac{1}{4} \sqrt{rac{5}{\pi}} \cdot \left(3 \ cos^2(heta) ight)$
A_4^0	$k_4^0(Y_4^0)$	$k_4^0 \cdot \frac{3}{16} \sqrt{\frac{1}{\pi}} \cdot (35 \cos^4(\theta) - 30 \cos^2(\theta) + 3)$
A_4^4	$k_4^4 \big(Y_4^4 + Y_4^{-4}\big)$	$k_4^4 \cdot rac{3}{16} \sqrt{rac{35}{2\pi}} \cdot (2 \ cos(4\phi) \cdot sin^4(heta))$
A_6^0	$k_{6}^{0}(Y_{6}^{0})$	$k_{6}^{0} \cdot \frac{1}{32} \sqrt{\frac{13}{\pi}} \cdot (231 \cos^{6}(\theta) - 315 \cos^{4}(\theta) + 105 \cos^{2}(\theta) - 5)$
A_6^4	$k_6^4 \big(Y_6^4 + Y_6^{-4}\big)$	$k_6^4 \cdot \frac{3}{16} \sqrt{\frac{91}{2\pi}} \cdot \cos(4\phi) \cdot \sin^4(\theta) \cdot (11 \cos^2(\theta) - 1)$

Table 5.2: Spherical harmonic expansions of anisotropy terms to 6th order in magnetic quantum number with 0th and 4th order in orbital quantum number, where: θ is the polar angle; ϕ is the azimuthal angle; $Y_l^m(\theta, \phi)$ is the Lagrange's spherical harmonic; k_n^m is the magnetocrystalline anisotropy energy constant with orbital quantum number, n, and magnetic quantum number, m. Spherical harmonics not presented were treated with an exchange constant of zero, under the assumption that higher order terms would produce a sufficiently small contribution to be negligible and that the four-fold tetragonal symmetry was sufficient to characterise the azimuthal anisotropy of the system.

have been unexplored in the atomistic context. Experimental work by Cadogan et al. [72], using a Bitter electromagnet to induce a large magnetic field (up to 19T) in a single crystal of $Nd_2Fe_{14}B$, demonstrated a First Order Magnetic Phase Transition, (FOMP) at 17T that was not reproducible with anisotropy constants up to second order.

The FOMP presents as a rapid reorientation of the total magnetic moment of $Nd_2Fe_{14}B$ when a sufficiently large magnetic field is applied in the [100] direction of the crystal. This direction is equivalent to the x-direction in the xyz basis, with z the easy axis. The material presents a non-zero canting angle from the z-axis when no field is applied, and as the field strength in the [100] direction increases to 17T the spins gradually align more with the x-axis. The magnetisation in the x-direction increases from ~ 37% to ~ 60% gradually over an increase in Applied magnetic field of approximately 17T. At this critical point the spins reorient to saturation in the x-direction over as little as 0.5T. This reorientation isn't appropriately described by only fourth and second order uniaxial and easy plane anisotropy.

This reorientation is a result of a low gradient region in the energy surface at the 17T at low Temperatures. This saddle point of the critical point is rapidly overcome by a small increase in the magnetic field at this external field strength, resulting in the almost discontinuous reorientation and subsequent saturation of the material's moment in the

x-direction.

This reorientation is an empirically validated measurement of the complex anisotropy of $Nd_2Fe_{14}B$. It is important therefore to replicate this behaviour using the atomistic model, in order to accurately demonstrate larger scale anisotropic effects, such as the star shaped domains present in the material at low temperatures, on the 0.1 micrometer scale.

In order to reduce the complexity of the task, the number of anisotropy constants, when compared to the number employed by Cadogan et al., was reduced. The Neodymium sites therefore were treated as one anisotropic type, with up to sixth order in the orbital quantum number and fourth order in the magnetic quantum number. The Iron anisotropy was only considered to second order, in line with other iron based compounds, which are characterised by a single exchange constants [149]. This mirrors the methodology for examining exchange in $RE_2Fe_{14}B$ alloys, as the RE sites are treated with one exchange constant throughout.

5.2.1 Single spin model of anisotropy in $Nd_2Fe_{14}B$

Initially a single spin model with anisotropy aggregated over an entire unit cell was developed. This approximation reduces the complexity of the anisotropy Hamiltonian E_{ani} and removes the exchange Hamiltonian completely. The total energy of the single spin system was therefore only composed of magnetocrystalline anisotropy energy:

$$E = 7A_{Fe} + A_{Nd} \tag{5.6}$$

where:

$$A_{Nd} = A_2^0 + A_4^0 + A_4^4 + A_6^0 + A_6^4 \tag{5.7}$$

and the Applied magnetic field interaction energy.

$$E = \overrightarrow{h}_d \cdot \overrightarrow{S} \tag{5.8}$$

Forming a complete Hamiltonian

$$\mathcal{H} = \dot{h}_d \cdot \dot{S} + 7A_{Fe} + A_{Nd} \tag{5.9}$$

with symbols defined as above.

The anisotropic terms are formed from the multiplication of an anisotropic constant with a spherical harmonic. It was assumed for the work presented in this thesis that, due to the approximate tetragonal symmetry in the magnetocrystalline anisotropy energy corresponding to the orbital quantum number, only the terms with 4th and 0th order orbital quantum number are non-zero. The table of terms to 6th order in polar angle and 4th order in azimuthal angle is presented in table 5.2.

The single spin model is composed of a single spin whose energy is only dependent on its direction, and its relation to the externally applied magnetic field. In order to evaluate the behaviour of the model, and as an initial stage of the parameter search for the atomistic anisotropy constants, the system was subject to a 0-20T applied field in each of the directions used in Cadogan et al.'s work, [72], the x-, z- and xy-directions, see fig. 5.4. Initially, the minimum energy direction was found with a naive 2-D sweep over half of the unit sphere. This sweep consists of evaluating the energy at each direction composed of the angle pair (θ, ϕ) for $0 \deg \le \theta, \phi < 180 \deg$ with a step resolution of 0.45 deg. This was functional but computationally expensive and slow. To increase computational efficiency, simplicial homology global optimization was used to minimise the energy of the system with respect to each of the angle azimuthal angle and polar angle followed by a small sweep in the region of the SHGO result to increase the resolution. This optimisation reduced the runtime for this simulation from minutes to seconds. Simple homology global optimization is implemented in SciPy [150] and is detailed in work by Endres, Sandrock, and Focke. SHGO presents a possible improvement to the automated parameterisation detailed above (chapter 3), due to its ability to avoid local minima.

Critically the saddle point at 17*T* in the energy surface suggests that the $\frac{\partial^2 E}{\partial \phi \partial \theta} = 0$. A small increase in the applied magnetic field then results in a large change in the spin orientation, as the energy difference between the pre-FOMP direction, and post-FOMP direction is low. Given that the anisotropy is only dependent on the spin's angle in this single-spin regime, this condition is trivially calculable. The derivatives of the anisotropy with respect to θ and ϕ should simultaneously be 0 at stationary points of the anisotropy.

The derivative of the anisotropy with respect to polar angle:

$$\begin{aligned} \frac{\partial A_2}{\partial \theta} &= k_2^0 \frac{1}{4} \sqrt{\frac{5}{\pi}} \left(-6 \sin(\theta) \cos(\theta) \right) \\ \frac{\partial A_4}{\partial \theta} &= k_4^0 \frac{3}{16} \sqrt{\frac{1}{\pi}} \left(-140 \sin(\theta) \cos^3(\theta) + 60 \sin(\theta) \cos(\theta) \right) \\ \frac{\partial A_4^4}{\partial \theta} &= k_4^4 \frac{3}{16} \sqrt{\frac{35}{2\pi}} \left(8 \cos(4\phi) \sin^3(\theta) \cos(\theta) \right) \end{aligned} \tag{5.10}$$

$$\begin{aligned} \frac{\partial A_6}{\partial \theta} &= k_6^0 \frac{1}{32} \sqrt{\frac{13}{\pi}} \left(-1386 \sin^5(\theta) \cos(\theta) + 1512 \sin^3(\theta) \cos(\theta) - 336 \sin(\theta) \cos(\theta) \right) \\ \frac{\partial A_6^4}{\partial \theta} &= k_6^4 \frac{3}{16} \sqrt{\frac{91}{2\pi}} \cos(4\phi) \sin^3(\theta) \cos(\theta) (66 \cos^2(\theta) - 26) \\ \end{array} \tag{5.10}$$

Derivative with respect to azimuthal angle:

$$\frac{\partial A_4^4}{\partial \phi} = k_4^4 \frac{3}{16} \sqrt{\frac{35}{2\pi}} (-8sin(4\phi)sin^4(\theta))$$

$$\frac{\partial A_6^4}{\partial \phi} = k_6^4 \frac{3}{16} \sqrt{\frac{91}{2\pi}} (-4sin(4\phi)sin^4(\theta)(11cos^2(\theta) - 1))$$
(5.11)

Additionally, the second order derivatives can be used to confirm the stationary point in the energy surface is a minima. Second order derivatives, with respect to θ^2

$$\begin{aligned} \frac{\partial^2 A_2^0}{\partial \theta^2} &= k_2^0 \frac{1}{4} \sqrt{\frac{5}{\pi}} (6 - 12\cos^2(\theta)) \\ \frac{\partial^2 A_4^0}{\partial \theta^2} &= k_4^0 \frac{3}{16} \sqrt{\frac{1}{\pi}} (-60\sin^2(\theta) - 140\cos^4(\theta) + 60\cos^2(\theta) + 420\sin^2(\theta)\cos^2(\theta)) \\ \frac{\partial^2 A_4^4}{\partial \theta^2} &= k_4^4 \frac{3}{16} \sqrt{\frac{35}{2\pi}} (12\cos(4\phi)\sin^2(\theta)\cos^2(\theta) - 4\cos(4\phi)\sin^4(\theta)) \\ \frac{\partial^2 A_6^0}{\partial \theta^2} &= k_6^0 \frac{1}{32} \sqrt{\frac{13}{\pi}} (-8316\cos^6(\theta) + 11970\cos^4(\theta) - 4200\cos^2(\theta) + 210) \\ \frac{\partial^2 A_6^4}{\partial \theta^2} &= k_6^4 \frac{3}{16} \sqrt{\frac{91}{2\pi}} 2\cos(4\phi)\sin^2(\theta)(11\sin^4(\theta) + 2\sin^2(\theta) + 66\cos^4(\theta) - 6\cos^2(\theta) - 121\sin^2(\theta)\cos^2(\theta)) \end{aligned}$$
(5.12)

Second order derivatives with respect to ϕ^2

$$\frac{\partial^2 A_4^4}{\partial \phi^2} = k_4^4 \frac{3}{16} \sqrt{\frac{35}{(2\pi)}} (-32\cos(4\phi)\sin^4(\theta))$$

$$\frac{\partial^2 A_6^4}{\partial \phi^2} = k_6^4 \frac{3}{16} \sqrt{\frac{91}{(2\pi)}} (-16\cos(4\phi)\sin^4(\theta)(11\cos^2(\theta) - 1))$$
(5.13)

Second order derivatives with respect to $\theta\phi$

$$\frac{\partial^2 A_4^4}{\partial \theta \partial \phi} = k_4^4 \frac{3}{16} \sqrt{\frac{35}{(2\pi)}} (24\cos(4\phi)\sin^2(\theta)\cos^2(\theta) - 8\cos(4\phi)\sin^4(\theta))$$

$$\frac{\partial^2 A_6^4}{\partial \theta \partial \phi} = k_6^4 \frac{3}{16} \sqrt{\frac{91}{(2\pi)}} (-8\sin(4\phi)\sin^3(\theta)\cos(\theta)(-11\sin^2(\theta) + 22\cos^2(\theta) - 2))$$
(5.14)

In addition, the derivative of the field interaction is required. For brevity, only the x-direction field case is presented as the applied field H is directed along the x-axis to produce the FOMP in the literature [72, 89]:

$$E_{t} = \vec{H} \cdot \vec{S}$$

= $|H||S|(1,0,0) \cdot (S_{x}, S_{y}, S_{z})$
= $|H||S|S_{x}$
= $|H||S|sin(\theta)cos(\phi)$
80 of 142
(5.15)

The subsequent derivatives of the field interaction are given here:

$$\frac{\partial E_t}{\partial \theta} = |H||S|\cos(\theta)\cos(\phi) \tag{5.16}$$

$$\frac{\partial E_t}{\partial \phi} = -|H||S|sin(\theta)sin(\phi) \tag{5.17}$$

$$\frac{\partial^2 E_t}{\partial \theta^2} = -|H||S|\sin(\theta)\cos(\phi)$$
(5.18)

$$\frac{\partial^2 E_t}{\partial \phi^2} = -|H||S|\sin(\theta)\cos(\phi) \tag{5.19}$$

$$\frac{\partial^2 E_t}{\partial \theta \partial \phi} = -|H||S|\cos(\theta)\sin(\phi) \tag{5.20}$$

Evaluating these derivatives at specific spin orientations which are known to be minima allow for the creation of a conditional for the anisotropy constants (n,m)th-order anisotropy constant.

For example, the minimum energy direction for the Neodymium spins at zero field is known to be at a polar angle of 28.5 deg and an azimuthal angle of 45 deg [72]. Similarly, at high field in the x-direction, the system is magnetically saturated, meaning that the minimum energy direction is at a polar angle of 90 deg and an azimuthal angle of 0 deg. The values for evaluating these derivatives are selected from known spin orientations presented in [72].

Using a subset of these values does not reliably produce appropriate magnetisation curves, as visible in fig. 5.2. Despite appropriate canting angle (the total magnetisation has an energetic minima at zero field in the expected direction) the total behaviour of the system is not wholly similar to the empirical results.

Similarly, correct behaviour in one dimension does not result in correct behaviour in all dimensions, for example, despite appropriate location of the FOMP in the x-direction, there is an unwanted FOMP in the xy-direction in fig. 5.3.

Using Python 3.6, rapid iteration of different anisotropy constant sets k_{set} , stored as dictionaries, were trialled in the simple single spin model. The differential condition above, in addition to conditions on non-zero canting angle and FOMP position allow for forming sets from an incomplete set of anisotropy constants. Using the optimisation above, the set of angle pairs as a function of applied magnetic field is calculated, giving spin orientation.

While this methodology produces qualitatively good results, see fig. 5.4, the lack of an exchange between the Nd and Fe sites results in a moderate disagreement with the published literature [89, 72], as much as 30% just before the FOMP in the first sub-figure.



Figure 5.2: Example canting and high field behaviour for an anisotropy constant set. Individual characteristics, such as the canting angle, cannot reliably produce the required physical phenomena at high field. Here, the canting angle at zero field of the single spin model's spin is within 2 deg of the experimental result from Cadogan et al. in both θ and ϕ , but this does not reproduce the appropriate high-field behaviour.



Figure 5.3: Individual characteristics, such as the canting angle, cannot reliably produce the required physical phenomena at high field. The first order magnetic phase transition occurs both in the x-direction and the xy-direction for the given anisotropy parameters in the single spin model.



Figure 5.4: Single spin model of $Nd_2Fe_{14}B$ anisotropy. The applied field H, is applied in the direction that the magnetisation is plotted for. The FOMP demonstrated in references[72, 89] at the 17T in the x-direction is qualitatively reproduced, but the pre-FOMP region is under saturated.

5.2.2 Multi-spin model

The single spin model by definition contains no exchange coupling between spins. This removal of exchange coupling results in a reduction in the degrees of freedom of the system, due to the equivalence of the k_{Fe} and $k_2^0:Nd$, and the lack of relaxation provided by the exchange coupling. The single spin model however gave qualitatively good results, measuring a non-zero canting angle at zero field, and generating a FOMP at high field. The atomistic model obviously allows for the introduction of the exchange coupling, and the separation of the Iron and Neodymium sites. Using the k_{set} calculated for the single spin model, and adjusting the $k_{2:Nd}^0: k_{2:Fe}^0$ ratio of anisotropy constants, allowed for greater control of the FOMP's position. This increased control however necessitates a greater computational cost. The element wise Hamiltonian for the single spin case is replaced with the pairwise Hamiltonian common to all atomistic simulations eq. (2.7).

The addition of exchange coupling also renders the differential conditionals for the single spin incomplete, so the finer adjustment of the k_{set} was performed by hand, using the relationship between anisotropic energy terms at the critical field. The form of each of the anisotropy terms is presented in fig. 5.5, and was used to manually tweak anisotropy constants to encourage a first order magnetic phase transition at the required critical field 17T. For instance, allowing the change of one anisotropic term to be balanced by a change in another at several field strengths.



Figure 5.5: Forms of anisotropy curves in the spherical harmonic basis. Example graph of the form of each of the anisotropy terms, $k_2^0, k_4^0, k_4^4, k_6^0, k_6^4, k_{Fe}$, for a single spin model (i.e. 7 iron atoms worth of anisotropy per Neodymium atom in the average spin). The knowledge of form allows for the selective increasing and decreasing of anisotropy values, to create magnetisation curves with an appropriately positioned FOMP.



Figure 5.6: Example graph of the form of the energy contributions for an increasing external magnetic field applied in the xy- ([1,1,0]) direction, magnetisation strengths H = ..., for a single spin model (i.e. 7 iron atoms worth of anisotropy per Neodymium atom in the average spin). The knowledge of form allows for the selective increasing and decreasing of anisotropy values, to create magnetisation curves with an appropriately positioned FOMP.



Figure 5.7: Reproduction of Cadogan et al. using VAMPIRE. A multi-spin model of $Nd_2Fe_{14}B$ anisotropy² at 0 Kelvin, compared to 4.2 Kelvin in the experimental case. The applied field H, is applied in the x-direction. As in the single spin example, varying one constant can greatly change the macroscopic behaviour, and this can be used to tune the anisotropic behaviour to match experiment. Here, the k_6^4 constant is being varied, from 0.1 times the single spin value, to 3 times. This tuning is still predominantly a manual process, and demonstrates the possibility of a large gain in future automation.

5.2.3 Conversion between VAMPIRE and spherical harmonics

VAMPIRE was initially built only to use a normalised series of Legendre polynomials. As a result, to recover the same physical description of energy, anisotropy constants must use a factor for conversion related to the fractional part of the spherical harmonic basis. Similarly, as the single spin model was treated as an aggregate of 8 atoms (1 Nd and 7 Fe), the constants are divided the total magnetic moment over that range (18.6 μ_B , in units of μ_B). The conversions for the relevant terms for this work are presented in table 5.3, and the general equation is presented in section 5.2.3.

$$K_V = -f_{int} f_{sh} f_{leg} \frac{k}{18.6}$$
(5.21)

with

$$f_{sh} = \sqrt{\frac{2n+1}{4\pi} \frac{(n-m)!}{(n+m)!}}$$
(5.22)

and

$$f_{leg} = (-1)^m (1 - n^2)^{m/2} \frac{d^m}{dn^m}$$
(5.23)

where n and m are the polar and azimuthal degree, f_{sh} and f_{leg} are the Legendre factor and Spherical Harmonic factor presented in table 5.3 and f_{int} is the normalisation factor introduced into VAMPIRE, again listed in table 5.3.

For instance, to convert from the standard spherical harmonic constant k_2^0 to the constant that VAMPIRE uses to generate the same anisotropic energy K_{2V} for *one* atom; keeping the energy constant, and given that the VAMPIRE internal factor, the spherical harmonic factor, and the associated Legendre polynomial factor are:

$$f_{int} = 3$$

$$f_{sh} = \frac{1}{2}\sqrt{\frac{5}{\pi}}$$

$$f_{leg} = \frac{1}{2}$$
(5.24)

The relationship between constants for all anisotropic orders is therefore:

$$E = k_{2}^{0} (Y_{2}^{0}) = -K_{2V} cos^{2}(\theta)$$

$$Const = k_{2}^{0} \cdot \frac{1}{4} \sqrt{\frac{5}{\pi}} (3cos^{2}(\theta) - 1) = -K_{2V} cos^{2}(\theta)$$

$$Const = k_{2}^{0} \cdot 3\frac{1}{4} \sqrt{\frac{5}{\pi}} = -K_{2V}$$

$$Const = -k_{2}^{0} \cdot f_{int} f_{sh} f_{leg} = K_{2V}$$
(5.25)

Constant	Legendre factor f_{leg}	Spherical Harmonic Factor f_{sh}	Internal Factor f _{int}	
k_{2}^{0}	$\frac{1}{2}$	$\frac{1}{2}\sqrt{\frac{5}{\pi}}$	3	
k_4^0	$\frac{1}{8}$	$\frac{1}{2}\sqrt{\frac{9}{\pi}}$	35	
k_4^4	105	$\frac{1}{16}\sqrt{\frac{1}{70\pi}}$	$\frac{1}{2}$	
k_{6}^{0}	$\frac{1}{16}$	$\frac{1}{2}\sqrt{\frac{13}{\pi}}$	231	
k_{6}^{4}	$\frac{945}{2}$	$\frac{1}{720}\sqrt{\frac{13}{14\pi}}$	$-\frac{11}{2}$	

Table 5.3: Note that k_6^4 contains a negative internal factor, for consistency with VAMPIRE's representation in src/anisotropy/rotational_order_6_4.cpp in the VAMPIRE repository [152].

5.3 Multi-spin model of anisotropy, in comparison to Cadogan et al.

The multi-spin model detailed above was used to simulate the behaviour of the $Nd_2Fe_{14}B$ system in gradually increasing magnetic fields, in each of the x-, xy- and z-directions independently. The response of the magnet, the resultant spin direction exhibited, is displayed in fig. 5.8 The multi-spin anisotropy constants, evaluated for the use with VAMPIRE in J per spin site, which yield the curves presented in fig. 5.8 were:

- Fe- $k_2^0 = 4.505623e 23J/site$
- $k_2^0 = 5.365319e 22J/site$
- $k_4^0 = 3.669052e 22J/site$

- $k_6^0 = -3.288575e 21 J/site$
- $k_4^4 = -1.461785e 22J/site$
- $k_6^4 = 3.521930e 21 J/site$

The anisotropy constants obtained through this methodology have been selected numerically to produce atomistic simulations which have similar macroscopic properties to experimental data from and references in Cadogan et al. [72]. However, different constants are provided in the literature which produce similar macroscopic results using different methodologies. Many of these methodologies have suggested physical interpretations, but macroscopically produce similar results to the constants presented here. In order to differentiate these sets of constants therefore, an additional physical property must be examined from experiment to select the appropriate parameter set from the range of options.

Given the large number of experimental data points in the input data set (approx one order of magnitude above the number of constants fitted, considered a reasonable rule of thumb for regression modelling[153, 154]), the risk of over-fitting is lowered. Given the lack of first principles justification for these anisotropic constants, there is no explicit justification for their correctness at the nano-scale, but the macroscopic agreement with experiment has implications for the understanding of the number of parameters, and complexity of model, required to effectively model macroscopic behaviour in complex magnetic materials. Given the difficulty in experimentally measuring the nanoscale anisotropic behaviour, the only consistent comparison that can be made is to theoretical ab initio models, such as those employed by Yamada et al. [155].

No demonstration has thus far been made as to the uniqueness of these anisotropy constants, and similar, or identical results to those presented in fig. 5.8, could be achieved with a different set.

5.3.1 Yamada et. al: Crystal electric field calculations as a method to calculate anisotropy constants

Yamada et al. present anisotropy coefficients calculated using the crystal electric field (or crystalline-electric-field) approximation in $RE_2Fe_{14}B$ magnets[155]. The results are presented in units of Ka^{-n} where K is Kelvin, a_0 is the Bohr radius, and m is the magnetic quantum number.

The anisotropy coefficients are presented in comparison with this work in table 5.4. Conversion from the units used by Yamada et al. to Joules is performed using eq. (5.26) and presented in table 5.4.

$$k_{n}^{m} = X \cdot A_{n}^{m} \frac{k_{b} a_{0}^{n} < r^{n} >}{f_{sh,n}^{m}}$$
(5.26)

$$X = \begin{cases} \alpha = \frac{-7}{33 \cdot 33}, & \text{for } n = 2\\ \beta = \frac{-8 \cdot 17}{11 \cdot 11 \cdot 13 \cdot 297}, & \text{for } n = 4\\ \gamma = \frac{-17 \cdot 19 \cdot 5}{13^2 \cdot 11^3 \cdot 3^3 \cdot 7}, & \text{for } n = 6 \end{cases}$$
(5.27)

$$< r^{n} >= \begin{cases} 1.001, & \text{for } n = 2\\ 2.401 & \text{for } n = 4\\ 12.396, & \text{for } n = 6 \end{cases}$$
 (5.28)

where X is a numerical factor specified by Stevens[156] for each order of anisotropy, A is the crystal field coefficient, k_b is Boltzmann's constant, $\langle r^n \rangle$ is the expectation value of the 4f orbital, f_{sh} is the spherical harmonic coefficient.

 $< r^n >$ is taken from the literature[157], but it is stated that it is very sensitive to choice of density functional and this may cause inaccuracies in the stated value. For comparison with previous work by Yamada [155] the value is taken as presented.

The First order magnetic phase transition in $Nd_2Fe_{14}B$ is reproduced by Yamada et al. but the total number of Neodymium anisotropy constants used to generate this data is 18, split across two Neodymium crystal sites, compared with only 5 constants in the presented work. The model presented in this work produced results which show qualitatively similar characteristics with the calculations from Yamada et al. with oversaturated magnetisation at higher field strengths when compared with experiment. Quantitatively the modelling in this work presents a greater deviation across the entire external field range, with less sharp magnetic phase transitions and larger error values across the range. In principle, it is possible to increase the degrees of freedom in the anisotropy constants for our model. The two neodymium sites could be independently treated, and additional spherical harmonics can be used for the calculation of the anisotropy energy, in order to match the number of parameters presented in the work by Yamada et al. This would be result in prohibitively expensive programmatic evaluation of anisotropy constants due to the increased parameter space however, suggesting the need for a more considered approach in constant evaluation. Numerically, the anisotropy constants presented in this work are between two and four orders of magnitude larger than equivalent crystal electric field parameters (after unit conversion). This can only be reconciled with additional calculations and comparison to experiment at temperature, or with greater measurement of the directionality of individual spins, as the average spin direction would be similar while ratios remain consistent.

Similarly, Yamada et al. use $Y_2Fe_{14}B$ as a prototype to inform information about the Iron sublattice in the other rare earths, as $La_2Fe_{14}B$ is used in this work.

Anisotropy order	$CEF[155] \\ Ka^{-n} in$	VAMPIRE representation J/f_{sh}	This work J/f_{sh}
k_2^0	$2.95 imes 10^2$	4.03×10^{-23}	-1.03×10^{-21}
k_2^{-2}	$-4.54 imes 10^{-2}$	-2.62×10^{-23}	0.0*
k_4^0	-1.84×10	1.20×10^{-26}	$4.07 imes 10^{-22}$
k_4^4	0.0*	0.0*	$3.00 imes 10^{-22}$
k_6^0	-1.84×10	1.20×10^{-26}	4.07×10^{-22}
k_{6}^{-2}	9.80×10	$-6.37 imes 10^{-26}$	0.0*
k_6^4	$-1.59\times10^{+01}$	$1.03 imes 10^{-25}$	-8.15×10^{-22}

Table 5.4: Crystal electric field coefficients used for anisotropy calculations by Yamada et al. in $Nd_2Fe_{14}B$ and their equivalent values in the same unit system used by VAMPIRE (Joules per spherical harmonic coefficient).[155]. Equivalent to Herbst[133] via eq. (5.26) without the Boltzmann factor for conversion to Joules. Asterisked (*) values are not included in the basis representation for that anisotropy constant set.

The resultant high field behaviour is in some aspects very similar to the experimental work available in Cadogan et al. [72] [taken from 89]. The location of the rapid change in alignment, at 17T when the field is applied in the x-direction, is clearly visible but is overestimated, with the transition occurring at approximately 18.5 Tesla instead. The nature of the rapid alignment change is different however, with a slightly more continuous transition region, although this could be due to the resolution of the figure in the original work by Cadogan et al. There is also a consistent increase in the expected magnetisation at all field strengths, suggesting the Anisotropy constant series could be better optimised with the addition of future work. The large overestimation in the xy-direction (the right subfigure of fig. 5.8) suggests an overestimation of the planar anisotropy terms when compared with the polar uniaxial terms and this should be examined at a future date.



Figure 5.8: Reproduction of Cadogan et al. using VAMPIRE. A multi-spin model of $Nd_2Fe_{14}B$ anisotropy at 0 Kelvin, compared to 4.2 Kelvin in the experimental case. The applied field H, is applied in the direction that the magnetisation is plotted for. The FOMP demonstrated in [72, 89] at the 17T in the x-direction is only qualitatively reproduced, especially when compared to the model by Cadogan et al. and the single spin model. The multi-spin model in use is VAMPIRE, with anisotropy constants a factor of 2.66 larger than those for the single spin model. The FOMP in the x-direction graph is appropriately reproduced, although the introduction of "relaxation" of the directional nature of the anisotropy, due to the exchange between spin sites, causes the large increase required in the constants, as well as the smoothness of the phase transition when compared to the single-spin model in fig. 5.4.

Cadogan et al. presented a system that does not fully saturate in the x-direction at the highest field examined, consistent with the slight temperature increase compared to fig. 5.8.

Similar crystal electric field coefficients are presented in Herbst [158] with each presented of a similar order of magnitude. The set of constants varies however, with several sets including differing magnitudes for the two f and g Nd atoms[159, 72] further increasing the complexity of the parameterisation.

5.4 Measuring anisotropy

Experimentally, atomic scale magnetic order can be probed via inelastic neutron scattering. The scattering of a neutron from an atomic system is dependent on the strong nuclear force, but the scattering of a neutron due to the electromagnetic force is dependent on the internal magnetic structure of the material being probed.[160].

Scattering has been used to differentiate between measurements of single and 2 ion anisotropy, and can provide insight into bulk and surface magnetic ordering at high resolution[161]. In addition, $Nd_2Fe_{14}B$ is being examined using neutron scattering for larger scale samples[162] and spin reorientation of individual atomic sites has been observed in $Nd_2Fe_{14}B$ and $Er_2Fe_{14}B$ [163]. Magnetic small angle neutron scattering (Magnetic SANS) allows for examination of magnetic structures of order 1-300nm[164], however the anisotropy measured will relate to the sum of the magnetic anisotropy in a local area, rather than the components which form the spherical harmonic basis set presented in [155] and this work.

Additionally anisotropy can be inferred from measurements of the anisotropy of magnetic susceptibility of a material (AMS), anisotropy in remanence, and in hysteresis at larger scales, without sufficient resolution for nanoscale examination[165].

There is scope for additional experimental measurements of anisotropic behaviour of several of these rare earth ferromagnets, especially with respect to large single crystal measurements which are most able to be compared to the bulk simulations most addressable via the atomistic model.

5.4.1 Results in context

The anisotropic constants presented herein yield a considerable amount of fidelity to the macroscopic high field behaviour experienced empirically and through other theoretical approaches. This fidelity is despite the substantial reduction in the number of characterised constants used in the simulation. The current approach to examining anisotropic constants, first with simpler models and eventually using results from atomistic simulations, has generated a set of anisotropic constants that behave macroscopically similar to those presented in the literature, without any additional first principles calculations. This phenomenological approach will allow for an increasing number of complex materials to be simulated which are currently prohibitively expensive. The greater saturation magnetisation demonstrates that the high field behaviour of this parameterisation and model is over saturated when compared with literature requiring more examination of the parameter set at high temperature. The parameterisation allows for the atomistic model to provide temperature dependent anisotropic behaviour moving forward, instead of the manual adjustments made in prior work[72], providing an avenue for evaluating the form of the temperature dependence of the anisotropy constants.

CHAPTER 9

CONCLUSION

Curie Temperature Measurement Protocols were compared to consistently calculate the Curie temperature programmatically without researcher input. The selection of Tauxe's method, Moskowitz's extrapolation method, the Bloch protocol and the Specific Heat and Susceptibility protocols was made due to their consistency across datasets enabling repeated evaluation of the Curie Temperature. Automatic parameterisation of small bodycentered-cubic Iron (bcc-Fe) and 2:14:1 type rare earth ferromagnet alloys was demonstrated, using the Nelder-Mead and Brent-Dekker method's to perform numerical optimisation of the atomistic exchange constants required to describe the alloys. The Nelder-Mead method was used to demonstrate the viability of the approach on bcc-Fe. The single atomistic exchange constant in bcc-Fe, the iron to iron exchange, was evaluated, and the resultant Curie temperature was calculated and compared with literature values. The 2:14:1 type rare earth ferromagnet $(RE_2Fe_{14}B)$ compounds magnetic properties were parameterised for small system sizes. The atomistic exchange constant between iron atoms, and between iron and rare earth atoms in each of $La_2Fe_{14}B$, $Pr_2Fe_{14}B$, $Nd_2Fe_{14}B$, $Sm_2Fe_{14}B$, $Gd_2Fe_{14}B, Tb_2Fe_{14}B, Dy_2Fe_{14}B, Ho_2Fe_{14}B, Er_2Fe_{14}B, Tm_2Fe_{14}B, Lu_2Fe_{14}B$ was optimised using Brent's method, by minimising the absolute difference between Curie temperature calculated using the atomistic modelling software VAMPIRE, and the accepted empirical value [133]. The optimisation evaluates exchanges to within the range of Curie Temperature values produced by a range of CTMPs on the order of several Kelvin. The optimisation rate is in the order of <20 system evaluations, which is far less than the complete examination of the parameter space for this level of precision. The automatic parameterisation method is applicable to other magnetic alloys reducing the time commitment for future parameterisation and allowing for a bank of material
parameters to be more readily created. A set of anisotropy constants to replicate the high field First Order Magnetic Phase Transition in $Nd_2Fe_{14}B$ reported by Cadogan et al. was evaluated using a spherical harmonic basis, using the application of a single-spin model and cross-examination of average spin angle with the accepted experimental results. The phase transition was partially replicated using the single-spin and atomistic models, and comparisons between the models were made.

6.1 Future work

The prospective field of future research into the automatic parameterisation of atomistic models is large. As demonstrated, the parameter space for appropriate characterisation of a range of even similar alloys is a significant barrier to accurate simulation of these materials. This confirms the use case of optimisation methods for calculating atomistic parameters. Initially, specific improvements to the methodology for evaluation 2:14:1 type rare earth ferromagnets should allow for more accurate macroscopic behaviour in atomistic simulations. For example, generating systems more closely related to manufactured rare earth systems, by simulated annealing and sintering of larger system sizes, would allow for better comparison to real life magnet usage. Currently, comparisons are only made to relatively pure, well-formed rare earth crystals grown in a lab environment [89]. This could cause a large increase in the number of parameters to effectively describe a system however, as interfacial atoms can behave differently to atoms in the bulk, increasing the computational cost for appropriate characterisation. Similarly, simultaneous multidimensional optimisation of exchange constants and low temperature rescaling exponents would allow for more accurate reproduction of sub-Curie temperature behaviour, at a cost to the model's complexity. This multidimensional optimisation should make use of the entire magnetisation curve, via a regression algorithm (such as least squares), instead of just using the Curie temperature to define the direction of the optimiser. This improvement would allow for the low temperature rescaling exponents, and possibly anisotropy driven spin reorientations to be replicated during the same optimisation phase.

Using performance improvements in VAMPIRE that better take advantage of parallel computation on cluster machines, and heterogeneous Graphics Processing Unit (GPU) compute platforms, will also allow for larger systems to be sufficiently explorable to be used as optimisation systems in future. Any increase in simulation and optimisation efficiency will reduce the total computational cost for evaluating a new larger system. These systems will more closely relate to experimental data, and could contain multiple phases including grain boundaries and interstitial phases. Improving the range of systems that can be simulated increases the amount of viable comparisons for currently examined materials, and increases the number of materials that can be examined, by connecting the literature's experimental data more stringently to the simulation. Following the improvements to the method for $Nd_2Fe_{14}B$ -like rare earth alloys, other magnetic materials of interest will be explored, with a view to generating and examining novel magnetic alloys. For example, similar parameterisation work can be performed on the $NdFe_{12}$ and $SmCo_5$ families of magnetic alloys. The next major step in generating and evaluating novel structures will involve examination of combination alloys. These materials can be thought of as a traditional rare earth ferromagnet doped with another metal, often with concentration of the dopant varying in space. These alloys have the potential to improve Curie temperatures and coercivity of permanent magnets when compared to "pure" rare earth ferromagnets.

With an increase in the number of materials examined, the generated data may reach a quantity that enables the use of machine learning optimisation. For instance, an artificial neural network could be trained with a range of similar ferromagnets (using parameters estimated with numerical optimisation), and then tasked with evaluating the parameters for an unknown material or combination of materials. Finer examination of the quantity of materials evaluated versus the reliability of such a machine learning model would be required, but it would be possible to estimate a very large number of atomistic parameters for a large range of magnetic materials as a result. The separation of the training phase and the parameterisation phase could substantially reduce the computational burden for researchers to parameterise materials of interest, but would increase the computational cost for the model trainer.



APPENDIX A

A.1 VAMPIRE - input files

A.1.1 Curie temperature monte carlo simulation

```
#-----
1
2 # Creation attributes:
  #-----
3
  create:periodic-boundaries-x
4
  create:periodic-boundaries-y
\mathbf{5}
  create:periodic-boundaries-z
6
7
  #-----
8
  # System Dimensions:
9
  #-----
10
  dimensions:system-size-x = 4 !nm
11
  dimensions:system-size-y = 4 !nm
12
  dimensions:system-size-z = 4 !nm
13
14
  #-----
15
  # Material Files:
16
  #-----
17
  material:file=NdFeB.mat
18
  material:unit-cell-file=NdFeB.ucf
19
  #-----
20
```

```
# Simulation attributes:
21
   #-----
22
   sim:minimum-temperature=200.0
23
   sim:maximum-temperature=800.0
24
   #sim:equilibration-temperature=0.0
25
   sim:temperature-increment=10.0
26
   sim:equilibration-time-steps=20000
27
   sim:time-steps-increment=1
28
   #sim:total-time-steps=10000
29
   sim:loop-time-steps=20000
30
31
   #-----
32
   # Program and integrator details
33
   #-----
34
   sim:program=curie-temperature
35
   sim:integrator=monte-carlo
36
   sim:integrator-random-seed=
37
38
   # data output
39
   output:temperature
40
   output:mean-magnetisation-length
41
   output:mean-susceptibility
42
   output:mean-specific-heat
43
   output:real-time
44
   output:temperature
45
   output:material-magnetisation
46
   output:material-mean-magnetisation-length
47
   output:material-mean-susceptibility
48
49
   screen:temperature
50
   screen:mean-magnetisation-length
51
```

Listing 1: The input file for a Curie temperature Monte-Carlo simulation for use with the vampire_opt exchange optimisation program. The random number seed is intentionally left blank, as it is generated by the optimising program.

A.2 Wyckoff Positions for 2:14:1 type ferromagnets

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
16	k	1	(x,y,z) $(-x,-y,z)$ $(-y+1/2,x+1/2,z+1/2)$
			(y+1/2,-x+1/2,z+1/2) $(-x+1/2,y+1/2,-z+1/2)$
			(x+1/2,-y+1/2,-z+1/2) $(y,x,-z)$ $(-y,-x,-z)$
			(-x,-y,-z) $(x,y,-z)$ $(y+1/2,-x+1/2,-z+1/2)$
			(-y+1/2,x+1/2,-z+1/2) $(x+1/2,-y+1/2,z+1/2)$
			(-x+1/2,y+1/2,z+1/2)(-y,-x,z)(y,x,z)
8	j	m	(x,x,z) $(-x,-x,z)$ $(-x+1/2,x+1/2,z+1/2)$
			(x+1/2,-x+1/2,z+1/2) $(-x+1/2,x+1/2,-z+1/2)$
			(x+1/2,-x+1/2,-z+1/2)(x,x,-z)(-x,-x,-z)
8	i	m	(x,y,0) $(-x,-y,0)$ $(-y+1/2,x+1/2,1/2)$
			(y+1/2,-x+1/2,1/2) $(-x+1/2,y+1/2,1/2)$
			(x+1/2,-y+1/2,1/2) (y,x,0) (-y,-x,0)
8	h	2	(0,1/2,z) $(0,1/2,z+1/2)$ $(1/2,0,-z+1/2)$ $(1/2,0,-z)$
			(0,1/2,-z)(0,1/2,-z+1/2)(1/2,0,z+1/2)(1/2,0,z)
4	g	m.2 m	(x,-x,0) $(-x,x,0)$ $(x+1/2,x+1/2,1/2)$
			(-x+1/2,-x+1/2,1/2)
4	f	m.2 m	(x,x,0) $(-x,-x,0)$ $(-x+1/2,x+1/2,1/2)$
			(x+1/2,-x+1/2,1/2)
4	е	2.m m	(0,0,z) (1/2,1/2,z+1/2) (1/2,1/2,-z+1/2) (0,0,-z)
4	d	-4	(0,1/2,1/4) $(0,1/2,3/4)$ $(1/2,0,1/4)$ $(1/2,0,3/4)$
4	с	2/m	(0,1/2,0)(0,1/2,1/2)(1/2,0,1/2)(1/2,0,0)
2	b	m.m m	(0,0,1/2) (1/2,1/2,0)
2	a	m.m m	(0,0,0) (1/2,1/2,1/2)

Table A.1: The crystallographic positions of atoms in the space group of $Nd_2Fe_{14}B$, $P4_2/mnm$, No. 136. Table retrieved from https://cryst2.ehu.eus/cgi-bin/cryst/programs/nph-wp-list [91]. The Neodymium sites are at f and g, with the remaining sites Iron, the Boron would be at site f with centrosymmetry, and the sites «fixme»

```
# Calculating the Curie temperature using Moskowitz's extrapolation method
1
    #
             + Temperature Array --/
2
              / + Magnetisation array-- Both over extrapolation range
3
    #
    #
              / / + Magnetisation at T=0
4
    #
              / / / + initial guess for Curie temperature
5
              1 1 1
    #
                    1
6
    def mosk(T,M,M0,T0):
7
        # Moskowitz's approximation
8
        # calculate [J(T)/JO] 2 until flattening of M(T) curve, from TO_start -> TO
9
        J_sq = (M/MO) * * 2.0
10
        # Linear regression of this curve
11
        slope, intercept, r_value, p_value, std_err = linregress(T,J_sq)
12
        # slope = -1/(Tc-TO) -> Tc=-1/slope - TO
13
        Tc = -1/slope + T0
14
15
        return Tc
16
```

Listing 2: Python 3.6: Moskowitz' extrapolation method CTMP, implemented by Andrew Naden in [99]. The function linregress refers to the scipy.stats.linregress function [166].

A.2.1 Implementation of CTMP methods

Presented here are the Python implementations of the CTMP's referenced in sections 3.6.2 to 3.6.6 and 3.6.8. listing 2

```
# Calculating the Curie temperature using the two tangent method
1
                 + Temperature in range below curie temperature
2
    #
3
    #
                 1
                         + Magnetisation in range below curie temperature
4
    #
                                 + Temperature in range above curie temperature
    #
                         1
                                          + Magnetisation in range above curie temperature
5
6
    #
    def two_tan(T_below,M_below,T_above,M_above): # This uses too many magic numbers,
7
                                                    # they need to be defined better.
8
9
        min len = 18
        # choose midpoint of data set
10
        if len(T_below) < min_len:</pre>
11
            mid = len(T_below)//2
12
             ran = len(T_below)//2 - 1
13
14
        else:
            mid = len(T_below)-(min_len/2) # not an actual mid point,
15
                                             # is closer to the estimated curie temperature
16
            ran = min_len//4 # may need tweaking to ensure that it's always to the below
17
                               # the curie temperature, but that should probably be handled a layer up.
18
19
         # first tangent curve : central difference method
20
        slope = (M_below[mid+ran] - M_below[mid-ran])/(T_below[mid+ran] - T_below[mid-ran])
         #intercept = slope*(T_below - T_below[mid]) + M_below[mid]
21
        intercept = M_below[mid-ran] - slope*T_below[mid-ran]
22
        curve1 = [slope,intercept]
23
24
25
        # choose midpoint of data set
        if len(T_above) < 12:</pre>
26
            mid = len(T_above)//2
27
             ran = len(T above)//2 - 1
28
29
        else:
30
            mid = len(T_above)-6 \# not an actual mid point, is closer to the estimated curie
           temperature
            ran = 3
                                   # may need tweaking to ensure that it's always to the above
31
                                   # the curie temperature, but that should probably be handled a layer
32
                                   # up.
33
34
         # second tangent curve : central difference method
        slope = (M_above[mid+ran] - M_above[mid-ran])/(T_above[mid+ran] - T_above[mid-ran])
35
        intercept = M_above[mid] - slope*T_above[mid]
36
37
        curve2 = [slope,intercept]
         # linear equation solver, break into separate function?
38
39
        solution=[]
        solution.append(curve1[0]-curve2[0])
40
        solution.append(curve1[1]-curve2[1])
41
        Tc=solution[1]/-solution[0]
42
        return Tc,curve1,curve2
43
```

Listing 3: Python 3.6: Grommé's two tangent method CTMP, implemented by Andrew Naden in [99]

```
# Calculating the Curie temperature using the two line linear regression method
1
                 + Temperature in range below curie temperature
2
    #
    #
                         + Magnetisation in range below curie temperature
3
    #
                                  + Temperature in range above curie temperature
4
    #
                                          + Magnetisation in range above curie temperature
5
    #
6
7
    def two_lin(T_below,M_below,T_above,M_above):
8
         # first lienar regression curve
        slope, intercept, r_value, p_value, std_err = linregress(T_below,M_below)
9
10
        curve1 = [slope,intercept]
11
         # second linear regression curve
        slope, intercept, r_value, p_value, std_err = linregress(T_above,M_above)
12
        curve2 = [slope,intercept]
13
        # linear equation solver, break into separate function?
14
        solution=[]
15
        solution.append(curve1[0]-curve2[0])
16
        solution.append(curve1[1]-curve2[1])
17
        Tc=solution[1]/-solution[0]
18
19
        return Tc,curve1,curve2
20
```

Listing 4: Python 3.6: Linear regression CTMP, implemented by Andrew Naden in [99]

```
# Calculating the Curie temperature by fitting Ms(T)
1
                + temperature in range below Tc
    #
2
                / + magnetisation in range below Tc
3
    #
                   / + Optional initial guess for Tc
4
    #
                1
    #
                1
                   1
                              + optional initial guess for exponent
5
                      1
                1
6
    #
                   1
                      1
7
    def fit_Ms(T, M, T0=700, b0=0.5):
        # currently only for mag_calc = (1.0 - (T/Tc))**b, no internal exponent
8
9
        params,
        pcurve_fit(f=mag_calc,xdata=T,ydata=M,p0=[T0,b0],bounds=([max(T),-np.inf],[np.inf,np.inf]))
10
        return params[0],params[1]
11
```

Listing 5: Python 3.6: Fitting to Bloch's Law CTMP, implemented by Andrew Naden in [99]

105 of 142

```
# Tauxe method, maximum derivative of M wrt T
1
              + temperature in range below Curie temperature
2
    #
               / + magnetisation in range below Curie temperature
3
    #
4
    #
               / / + optional extrapolation of gradient
    #
               111
5
    def tauxe(T,M,ext=False):
6
7
        G = np.gradient(M,T)
        G = np.gradient(G,T)
8
9
        # non interpolated, can only return a T present in T
10
        Tc = T[np.where(abs(G) == max(abs(G)))[0]][0]
11
        # if extrapolation between points is required
12
        if ext:
13
             # perform 1-d interpolation of -abs(G) wrt T, allowing for minimisation in next step
14
             # this gives largest magnitude of G as the minimum
15
            f = interp1d(T,-abs(G),kind='cubic')
16
             # minimize to find T for highest gradient
17
            Tc = minimize(f,x0=Tc,bounds=((min(T),max(T)),))
18
19
             ## visualize the interpolation
20
             #x = np.linspace(T[0], T[-1], 1000)
21
             #for i in x:
22
                 print(i, f(i))
23
             #
            return float(Tc.x[0])
24
        else:
25
26
            return Tc
27
```

Listing 6: Python 3.6: Tauxe's method CTMP, implemented by Andrew Naden in [99]

The implementation of linear regression in SciPy.

1

```
2
3
    def linregress(x, y=None, alternative='two-sided'):
         .....
4
        Calculate a linear least-squares regression for two sets of measurements.
5
6
7
        Parameters
         ____
8
9
        x, y : array_like
10
             Two sets of measurements. Both arrays should have the same length.
                                                                                    If
             only `x` is given (and ``y=None``), then it must be a two-dimensional
11
             array where one dimension has length 2. The two sets of measurements
12
             are then found by splitting the array along the length-2 dimension. In
13
             the case where ``y=None`` and `x` is a 2x^2 array, ``linregress(x)`` is
14
             equivalent to ``linregress(x[0], x[1])``.
15
        alternative : {'two-sided', 'less', 'greater'}, optional
16
             Defines the alternative hypothesis. Default is 'two-sided'.
17
             The following options are available:
18
19
             * 'two-sided': the slope of the regression line is nonzero
20
             * 'less': the slope of the regression line is less than zero
21
             * 'greater': the slope of the regression line is greater than zero
22
23
             .. versionadded:: 1.7.0
\mathbf{24}
25
        Returns
26
         ____
27
        result : ``LinregressResult`` instance
28
             The return value is an object with the following attributes:
29
30
             slope : float
31
                 Slope of the regression line.
32
             intercept : float
33
                 Intercept of the regression line.
34
35
             rvalue : float
                 The Pearson correlation coefficient. The square of ``rvalue``
36
37
                 is equal to the coefficient of determination.
             pvalue : float
38
```

107 of 142

```
The p-value for a hypothesis test whose null hypothesis is
39
                 that the slope is zero, using Wald Test with t-distribution of
40
                 the test statistic. See `alternative` above for alternative
41
                 hypotheses.
42
             stderr : float
43
                 Standard error of the estimated slope (gradient), under the
44
                 assumption of residual normality.
45
             intercept_stderr : float
46
                 Standard error of the estimated intercept, under the assumption
47
                 of residual normality.
48
49
        See Also
50
         ____
51
52
         scipy.optimize.curve_fit :
             Use non-linear least squares to fit a function to data.
53
         scipy.optimize.leastsq :
54
             Minimize the sum of squares of a set of equations.
55
56
        Notes
57
         ____
58
        Missing values are considered pair-wise: if a value is missing in `x`,
59
         the corresponding value in `y` is masked.
60
61
        For compatibility with older versions of SciPy, the return value acts
62
         like a ``namedtuple`` of length 5, with fields ``slope``, ``intercept``,
63
         ``rvalue``, ``pvalue`` and ``stderr``, so one can continue to write::
64
65
             slope, intercept, r, p, se = linregress(x, y)
66
67
         With that style, however, the standard error of the intercept is not
68
         available. To have access to all the computed values, including the
69
         standard error of the intercept, use the return value as an object
70
        with attributes, e.g.::
71
72
73
             result = linregress(x, y)
74
             print(result.intercept, result.intercept_stderr)
75
         Examples
76
```

77

```
>> import numpy as np
78
         >> import matplotlib.pyplot as plt
79
         >> from scipy import stats
80
         >> rng = np.random.default_rng()
81
82
         Generate some data:
83
84
         \gg x = rng.random(10)
85
         \gg y = 1.6 * x + rng.random(10)
86
87
88
         Perform the linear regression:
89
         >> res = stats.linregress(x, y)
90
91
92
         Coefficient of determination (R-squared):
93
         >> print(f"R-squared: {res.rvalue**2:.6f}")
94
         R-squared: 0.717533
95
96
         Plot the data along with the fitted line:
97
98
         >> plt.plot(x, y, 'o', label='original data')
99
         >> plt.plot(x, res.intercept + res.slope*x, 'r', label='fitted line')
100
         >> plt.legend()
101
         >> plt.show()
102
103
104
         Calculate 95% confidence interval on slope and intercept:
105
         >> # Two-sided inverse Students t-distribution
106
         >> # p - probability, df - degrees of freedom
107
         >> from scipy.stats import t
108
         \gg tinv = lambda p, df: abs(t.ppf(p/2, df))
109
110
         \gg ts = tinv(0.05, len(x)-2)
111
         >> print(f"slope (95%): {res.slope:.6f} +/- {ts*res.stderr:.6f}")
112
         slope (95%): 1.453392 +/- 0.743465
113
         >> print(f"intercept (95%): {res.intercept:.6f}"
114
                    f" +/- {ts*res.intercept_stderr:.6f}")
115
          . . .
          intercept (95%): 0.616950 +/- 0.544475
116
```

109 of 142

```
117
          .....
118
         TINY = 1.0e-20
119
         if y is None: # x is a (2, N) or (N, 2) shaped array_like
120
              x = np.asarray(x)
121
              if x.shape[0] == 2:
122
123
                  x, y = x
124
              elif x.shape[1] == 2:
                  x, y = x.T
125
126
              else:
                  raise ValueError("If only `x` is given as input, it has to "
127
128
                                    "be of shape (2, N) or (N, 2); provided shape "
129
                                    f"was {x.shape}.")
130
         else:
131
             x = np.asarray(x)
              y = np.asarray(y)
132
133
         if x.size == 0 or y.size == 0:
134
              raise ValueError("Inputs must not be empty.")
135
136
137
         if np.amax(x) == np.amin(x) and len(x) > 1:
              raise ValueError("Cannot calculate a linear regression "
138
                                "if all x values are identical")
139
140
         n = len(x)
141
         xmean = np.mean(x, None)
142
143
         ymean = np.mean(y, None)
144
          # Average sums of square differences from the mean
145
             ssxm = mean((x-mean(x))^2)
          #
146
              ssxym = mean((x-mean(x)) * (y-mean(y)))
147
          #
         ssxm, ssxym, _, ssym = np.cov(x, y, bias=1).flat
148
149
          # R-value
150
          # r = ssxym / sqrt( ssxm * ssym )
151
         if ssxm == 0.0 or ssym == 0.0:
152
              # If the denominator was going to be O
153
154
             r = 0.0
         else:
155
```

110 of 142

```
r = ssxym / np.sqrt(ssxm * ssym)
156
              # Test for numerical error propagation (make sure -1 < r < 1)
157
              if r > 1.0:
158
                  r = 1.0
159
              elif r < -1.0:
160
                  r = -1.0
161
162
163
         slope = ssxym / ssxm
         intercept = ymean - slope*xmean
164
         if n == 2:
165
166
              # handle case when only two points are passed in
              if y[0] == y[1]:
167
168
                  prob = 1.0
169
              else:
                  prob = 0.0
170
              slope_stderr = 0.0
171
              intercept_stderr = 0.0
172
         else:
173
              df = n - 2 # Number of degrees of freedom
174
              # n-2 degrees of freedom because 2 has been used up
175
              # to estimate the mean and standard deviation
176
              t = r * np.sqrt(df / ((1.0 - r + TINY)*(1.0 + r + TINY)))
177
              t, prob = scipy.stats._stats_py._ttest_finish(df, t, alternative)
178
179
              slope_stderr = np.sqrt((1 - r**2) * ssym / ssxm / df)
180
181
              # Also calculate the standard error of the intercept
182
              # The following relationship is used:
183
                  ssxm = mean((x-mean(x))^2)
              #
184
                       = ssx - sx*sx
              #
185
                       = mean(x^2) - mean(x)<sup>2</sup>
186
              #
              intercept_stderr = slope_stderr * np.sqrt(ssxm + xmean**2)
187
188
         return LinregressResult(slope=slope, intercept=intercept, rvalue=r,
189
                                   pvalue=prob, stderr=slope_stderr,
190
191
                                   intercept_stderr=intercept_stderr)
192
193
194
```

111 of 142

195	
196	
197	
198	
199	
200	
201	

Listing 7: Python 3.6: The function scipy.stats.linregress [166]

 $112 \ {\rm of} \ 142$

A.3 VAMPIRE

A.3.1 Implementation of VAMPIRE statistics methods

Presented here are the C++ implementations of the statistics VAMPIRE calculates referenced in sections 3.6.1 and 3.6.6.

```
//-----
1
    // Function to calculate magnetisation of spins given a mask and place result in a magnetization
2
    array
<u>ے</u>
    //-----
3
    void magnetization_statistic_t::calculate_magnetization(const std::vector<double>& sx, // spin
4
    unit vector
                                                           const std::vector<double>& sy,
5
                                                           const std::vector<double>& sz,
6
                                                           const std::vector<double>& mm){
7
8
       // initialise magnetization to zero [.end() seems to be optimised away by the compiler...]
9
       std::fill(magnetization.begin(),magnetization.end(),0.0);
10
11
       // calculate contributions of spins to each magetization category
12
       for(int atom=0; atom<num_atoms; ++atom){</pre>
13
          const int mask_id = mask[atom]; // get mask id
14
          magnetization[4*mask_id + 0] += sx[atom]*mm[atom];
15
          magnetization[4*mask_id + 1] += sy[atom]*mm[atom];
16
          magnetization[4*mask id + 2] += sz[atom]*mm[atom];
17
          magnetization[4*mask_id + 3] += mm[atom];
18
       }
19
20
21
       // Reduce on all CPUS
       #ifdef MPICF
22
          MPI_Allreduce(MPI_IN_PLACE, &magnetization[0], 4*mask_size, MPI_DOUBLE, MPI_SUM,
23
    MPI_COMM_WORLD);
       #endif
24
25
       // Calculate magnetisation length and normalize
26
       for(int mask_id=0; mask_id<mask_size; ++mask_id){</pre>
27
          double msat = magnetization[4*mask_id + 3];
28
          double magm = sqrt(magnetization[4*mask_id + 0]*magnetization[4*mask_id + 0] +
29
                            magnetization[4*mask_id + 1]*magnetization[4*mask_id + 1] +
30
```

```
magnetization[4*mask_id + 2]*magnetization[4*mask_id + 2]);
31
32
           // normalize to msat // this is what we want std_dev of in time - AJN
33
          magnetization[3*mask_id + 0] = magnetization[4*mask_id + 0]/magm; // unit vector // x - AJN
34
          magnetization[4*mask_id + 1] = magnetization[4*mask_id + 1]/magm;
                                                                                                // y
35
          magnetization[4*mask_id + 2] = magnetization[4*mask_id + 2]/magm;
                                                                                                11 z
36
          magnetization[4*mask_id + 3] = magm/msat; // m/m_s
                                                                                                // m
37
       }
38
39
40
       // Zero empty mask id's
       for(unsigned int id=0; id<zero_list.size(); ++id) magnetization[zero_list[id]]=0.0;
41
42
43
       // Add magnetisation to mean
       const int msize = magnetization.size();
44
       for(int idx=0; idx<msize; ++idx) mean_magnetization[idx] += magnetization[idx];</pre>
45
       mean_counter+=1.0;
46
47
48
       return;
49
    }
50
```

Listing 8: C++: Implementation of the calculation of the magnetisation of a system in cpp in VAM-PIRE[152] by Richard Evans, Oscar Arbeláez-Echeverri, and Andrew Naden

```
// determine inverse temperature mu_B/(kB T) (flushing to zero for very low temperatures)
1
2
          const double itemp = temperature < 1.e-300 ? 0.0 : 9.274e-24/(1.3806503e-23*temperature);
3
          // determine inverse mean counter and its square
4
          const double imean_counter = 1.0/mean_counter;
5
          const double imean_counter_sq = 1.0/(mean_counter*mean_counter);
6
7
          // loop over all elements
8
          for(int id=0; id< num_elements - 1; ++id){ // ignore last element as always contains
9
    non-magnetic atoms
 \rightarrow 
10
             const double prefactor = itemp*saturation[id]; // in mu_B
11
             const double sus_x = prefactor*(mean_susceptibility_squared[4*id +
12
    0]*imean_counter-mean_susceptibility[4*id + 0]*mean_susceptibility[4*id + 0]*imean_counter_sq);
```

```
const double sus_y = prefactor*(mean_susceptibility_squared[4*id +
13
     1]*imean_counter-mean_susceptibility[4*id + 1]*mean_susceptibility[4*id + 1]*imean_counter_sq);
\hookrightarrow
              const double sus_z = prefactor*(mean_susceptibility_squared[4*id +
14
    2]*imean_counter-mean_susceptibility[4*id + 2]*mean_susceptibility[4*id + 2]*imean_counter_sq);
_
              const double sus_m = prefactor*(mean_susceptibility_squared[4*id +
15
    3]*imean_counter-mean_susceptibility[4*id + 3]*mean_susceptibility[4*id + 3]*imean_counter_sq);
\hookrightarrow
16
17
              result « sus_x « sus_y « sus_z « sus_m;
18
```

Listing 9: C++: Implementation of the calculation of the magnetic susceptibility of a system in cpp in VAMPIRE[152] by Richard Evans and Andrew Naden

```
//-----
1
    // Function to calculate specific heat of the system and retain the mean value
\mathbf{2}
    11
3
             C_v = ( \langle E^2 \rangle - \langle E \rangle^2 )
    11
4
    11
                      _____
\mathbf{5}
                          k B T^2
6
    11
    11
7
    //-
                   _____
8
    void specific_heat_statistic_t::calculate(const std::vector<double>& energy){
9
10
       // loop over all elements
11
       for(int id=0; id< num elements; ++id){</pre>
12
13
          // copy energy
14
15
          const double E = energy[id];
16
          mean_specific_heat[id] += E;
17
          mean_specific_heat_squared[id] += E*E;
18
19
       }
20
21
22
       mean_counter += 1.0;
23
\mathbf{24}
       return;
25
    }
26
```

 $115 \ \mathrm{of} \ 142$

Listing 10: C++: Implementation of the calculation of the specific heat capacity of a system in cpp in VAMPIRE[152] by Richard Evans and Andrew Naden

GLOSSARY OF TERMS

Term	Symbol	Description
(n,m)th-order anisotropy constant	k_n^m	magnetocrystalline anisotropy energy constant with orbital quantum number n and magnetic quantum number m, the constant that multiplies the spherical harmonic $Y_{1}^{m=m}$
2:14:1 type rare earth ferromag- net	Nd ₂ Fe ₁₄ B	rare earth ferromagnet with the same structure as the prototypical Neodymium Iron Boron.
anti-ferromagnet		A material with characteristic magnetic ordering. Each spin has an energetic preference to align along the opposite direction as neighbouring spins. Negative exchange constant. Contrast with ferromagnet.
Applied mag- netic field	\overrightarrow{h}_d	Applied magnetic field vector, with direction j
applied mag- netic field strength	Н	the applied magnetic field strength, in Tesla unless otherwise stated.
atomistic spin model		An approximation used for magnetic materials mod- elling. Instead of treating individual electrons' spins as interacting, the estimated total magnetic moment is localised to a fixed atomic site. This total moment interacts with other atomic sites via an exchange in- teraction, and with applied magnetic fields. The mag- netocrystalline anisotropy energy experienced by each magnetic site is formed by a sum of spherical harmon- ics.
azimuthal angle	φ	The azimuthal angle, angle from the x- axis anticlock- wise around the z-/easy axis

Term	Symbol	Description
Bohr magneton	μ_B	The natural unit for the magnetic moment of an electron caused by it's spin. $\mu_B = \frac{e\hbar}{2m_e} = 9.2740100783(28) \times 10^{-24} JT^{-1}$ see elementary charge of an electron, reduced Planck constant, mass of an electron
Bohr magneton	μ	the natural unit of magnetic moment of an electron, caused by it's spin and orbital momentum. In SI, it is defined as $\mu = \frac{e\hbar}{2m_e}$ where e is the elementary charge, \hbar is the reduced Planck constant, and m_e is the mass of an electron.
Boltzmann con- stant	k_B	Boltzmann constant, relating energy and temperature, in SI units $1.380649 \times 10^{-23} J K^{-1}$
Brent's method	Brent	A numerical method for the optimisation of an objec- tive function
C++ canting angle	C++ θ	The C++ programming language. The angle from the z-axis. Especially relevant for zero field simulations, equivalent to the polar angle.
СТМР		Curie Temperature Measurement Protocol, a method for estimating the Curie temperature of a material from empirical or simulated data.
Curie tempera- ture	T_C	The temperature of a ferromagnetic material at which the thermal fluctuations of the spin are greater than the exchange energy, resulting in a complete loss of magnetic ordering. Above the Curie Temperature the material behaves as a paramagnet.
elementary charge of an electron	е	The elementary charge of an electron in SI units, $-1.602176634 \times 10^{-19}C$
energy	E	The magnetic and thermal energy of the system, ig- nores strain in the crystal etc
exchange	E_{xc}	The energy associated with a preference for adjacent spins to align. A positive exchange constant corre- sponds to ferromagnets, while a negative echange constant corresponds to preference to anti-align, an anti-ferromagnet.

Term	Symbol	Description
exchange con- stant tensor	J_{ij}	The tensor of constant energies associated with a pref- erence for adjacent spins to align. A positive exchange constant corresponds to ferromagnets, while a nega- tive exchange constant corresponds to preference to anti-align, an anti-ferromagnet.
ferromagnet		A material with characteristic magnetic ordering. Each spin has an energetic preference to align along the same direction as neighbouring spins. Positive exchange constant. Contrast with paramagnet.
figure of merit		The parameter that an optimisation problem is using as a performance metric. Often this parameter is max- imised, minimised, or optimised towards an expected empirical value. see objective function
FOMP		A First Order Magnetic Phase transition, a magnetic phase transition where the first derivative wrt the Free energy of the system is discontinuous.
Hamiltonian	${\mathcal H}$	The quantum mechanical operator that corresponds to the total energy of the system, can be decomposed into different energy sources such as Hamiltonian of applied magnetic field and Hamiltonian of the spin exchange
Hamiltonian of applied mag- netic field	H_{app}	Applied magnetic field Hamiltonian
Hamiltonian of the spin exchange	H_{exch}	Exchange component of Hamiltonian, corresponds to the energy of the spin exchange between atomic sites
Landé's g-factor	g	A dimensionless factor relating the electron's quantum numbers to its magnetic moment.
Laplace's set of spherical harmonics magnetic mo- ment of spin	μ_i	The set of spherical harmonics that solve Laplace's equation. The magnetic moment of the spin i
i		

Term	Symbol	Description
magnetic quan- tum number	m	<i>l</i> is the quantum number of an atomic orbital separat- ing individual orbitals within one subshell. Defined as the integers between $-l$ and $+l$ including zero, or l < m < l. Integer.
magnetisation	\overrightarrow{M}	The magnetisation of the of a system, normalised to between ± 1 .
magnetisation length	m_l	The length of the magnetisation vector
magne- tocrystalline anisotropy energy	${E}_{ani}$	Energy due to the relationshop between a spin and it's neighbouring crystal environment. This anisotropy causes directional preferences for spins to align along that are related to the magnet's crystal struc- ture. There are several orders of magnetocrystalline anisotropy energy constants used throughout this work, (n,m)th-order anisotropy constant are defined via a spherical harmonic basis set.
mass of an elec- tron	m_e	The mass of an electron in SI units, $9.1093837015(28) \times 10^{-31} kg$
normalised atomic spin vector	\vec{S}	a single spin's magnetisation as a spin vector,A single atomic sites spin, the subscript (i) denotes the spin
objective func- tion	obj	The function that an optimisation method aims to minimise or maximise. see figure of merit
orbital quantum number	l	Also known as the azimuthal quantum number, l is the quantum number of an atomic orbital describing it's total angular momentum and subsequent shape. Integer.
orthonormal ba- sis set		A basis set through which the basis vectors inner prod- ucts is zero, and the basis vectors magnitudes is equal
Pairs of neigh- bouring spins	$\langle i,j angle$	to one. Set of pairs of neighbouring spins, i and j
paramagnet		A material without long range magnetic ordering, where the thermal fluctuations in the spins randomise their direction without na externally applied magnetic field. Contrast with ferromagnet.

Term	Symbol	Description
polar angle	θ	The polar angle, angle from the z-/easy axis.
Python 3.6	Python 3.6	The Python Programming language, version 3.6
rare earth	RE	A rare earth metal is one of 17 elements including the
		lanthanide series of the periodic table, and often in-
		cluding yttrium and scandium due to similar chemical
		and physical properties.
reduced Planck constant	ħ	The reduce Planck constant in SI units 6.582119569 × $10^{-16} eV \cdot s$
saturation mag- netisation	$\overrightarrow{M_s}$	The magnetisation of a material at 0 Kelvin
SciPy	SciPy	Open source scientific computing library for python
specific heat ca-	С	The specific heat capacity of the system is the amount
pacity		of heat energy applied required to raise the system by
		one unit temperature, per unit mass. The specific heat
		the exchange interaction and enjectropy
spherical har-	$\mathbf{Y}^{m}(\boldsymbol{\theta},\boldsymbol{\phi})$	Special functions defined on the surface of a sphere
monic	- [(0,φ)	The functions form an orthonormal basis set. The spe-
		cific set of Laplace's set of spherical harmonicss is used
		throughout this work for defining the estimated mag-
		netocrystalline anisotropy energy. The harmonics are
		defined in terms of the orbital quantum number, mag-
		netic quantum number, polar angle and azimuthal
		angle.
spin exchange	J_{ij}	The constant energies associated with a preference
constant		for adjacent spins to align. A positive exchange con-
		stant corresponds to ferromagnets, while a negative
		exchange constant corresponds to preference to anti-
		align, an anti-ferromagnet.
susceptibility	X	The magnetic susceptibility of the system, the mea-
		sure of ease with which a material magnetises. Re-
		lated to Applied magnetic field and magnetisation and M
		given by the ratio $\frac{m}{\vec{H}}$
temperature	T	Temperature of the system in Kelvin

Term	Symbol	Description
VAMPIRE	VAMPIRE	Atomistic spin modellling software developed at the Computational magnetism group in York.

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