

First-order Phase Transition Dynamics: Magnetization and Atomic Structure

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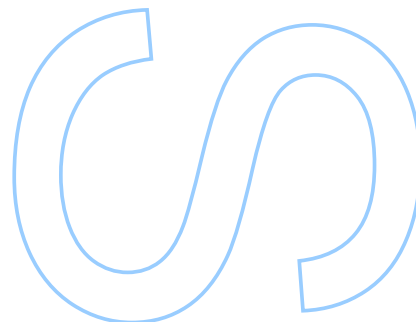
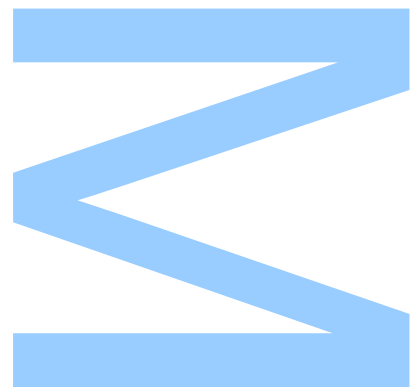
Mestrado em Engenharia Física
Departamento de Física e Astronomia
2023

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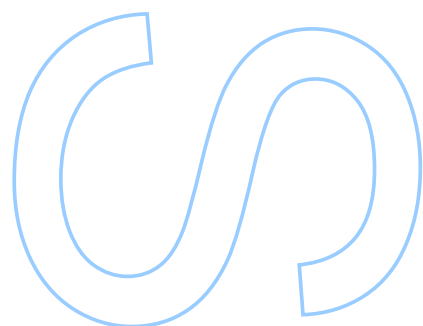
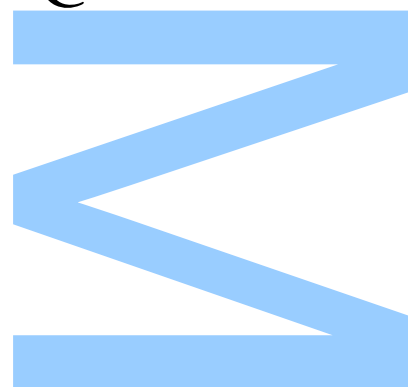
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Acknowledgements

With immense appreciation, I thank the contributions of my supervisor, Dr. João Horta Belo, whose invaluable guidance and feedback have been of utmost importance in shaping not only this thesis, but also many other related manuscripts. I further extend my gratitude to my co-supervisor, Prof. João Pedro Araújo for his constant availability and unending endorsement. A special mention goes to IFIMUP, for the unlimited access to its facilities, which has been paramount to the work developed.

My warmest thanks go to Prof. João Amaral from the Department of Physics and CICECO at University of Aveiro for his readiness in providing a computational model of the free energy landscape of $\text{LaFe}_{11.6}\text{Si}_{1.4}$, as well as his exceptional insights into its phase transition.

A distinguished acknowledgement goes to B. Beckmann, K. Skokov and O. Gutfleisch at the Technical University of Darmstadt for the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample provided, without which the presented work would not have been possible.

I am immensely grateful to J. L. Sánchez Llamazares at the Institute for Scientific and Technological Research of San Luis Potosi for the $\text{Fe}_{49}\text{Rh}_{51}$ and $\text{Fe}_{50}\text{Rh}_{50}$ samples provided, allowing further investigation into this set of materials, as well as to P. Álvarez-Alonso at the University of Oviedo for his notable insights.

The PDF beamline and its members at the Brookhaven National Laboratory's National Synchrotron Light Source II have been an indispensable partner, playing a vital role in the success achieved in performing the structural characterization presented in this work.

Thank you to all the professors and university staff which allowed for an enriching experience during my studies at FCUP and FEUP.

Lastly, I wish to express my heartfelt thanks to all my colleagues, friends, and family for their unwavering support and encouragement throughout this journey.

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Abstract

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Departamento de Física e Astronomia

MSc. Engineering Physics

First-order Phase Transition Dynamics: Magnetization and Atomic Structure

by André BELEZA

As a consequence of climate change and economic growth, a rise in need for cooling technologies is expected in the upcoming years. This surge in demand is accompanied by a growing urgency to replace traditional vapour compression devices with more environmentally friendly and energy-efficient alternatives. Material optimisation for environmentally friendly caloric applications, such as magnetic refrigeration, may be brought about by the use of magnetocaloric materials presenting magnetostructural first-order phase transitions, FOPTs. While these materials exhibit large entropy and adiabatic temperature changes linked to their magnetically induced FOPT, their hysteretic losses and phase transition dynamics have been the two main factors hindering their widespread use. Through the application of a magnetic field at intensities around that of the critical field needed to onset the FOPT, a detailed characterization of the magnetic and structural phase transition dynamics was performed in two alloys belonging to the most prominent giant magnetocaloric material families: $\text{LaFe}_{11.6}\text{Si}_{1.4}$ and $\text{Fe}_{49}\text{Rh}_{51}$. The two alloys are shown to present similar magnetic and structural time-dependent responses when magnetically driven to the vicinity of their FM-PM and AFM-FM phase transitions, respectively, and allowed to reach equilibrium thereafter. The dynamics of magnetic field removal are also explored, establishing its symmetric resemblance with those observed upon magnetic field application when the magnetic field is partially removed. Lastly, the (de)coupled nature of the magnetic and structural phase transitions is evaluated in both alloys, providing a pathway for material optimization and smarter design of magnetic field cycling in real-life devices.

Keywords: Magnetocaloric Materials, Phase Transition Kinetics, Magnetometry, X-ray Diffraction, Free Energy Landscape, Magnetic Relaxation, Lattice Relaxation, Magneto-volume Coupling

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Resumo

Faculdade de Ciências da Universidade do Porto

Departamento de Física e Astronomia

Mestrado em Engenharia Física

Cinética das Transições de Fase de Primeira-ordem: Magnetização e Estrutura Atômica

por André BELEZA

Como consequência das mudanças climáticas e do crescimento económico, é esperado um aumento da necessidade de tecnologias de arrefecimento nos próximos anos. Este aumento de procura é acompanhado por uma crescente urgência em substituir os dispositivos tradicionais de compressão de vapor por alternativas mais ecológicas e de baixo consumo energético. A otimização de materiais para aplicações calóricas amigas do ambiente, como para refrigeração magnética, pode ser alcançada pelo uso de materiais magnetocalóricos que apresentem transições de fase magnetoestruturais de primeira ordem, FOPTs. Embora estes materiais exibam grandes variações de entropia e de temperatura adiabática associadas à sua FOPT magneticamente induzida, as perdas histeréticas e as dinâmicas de transição de fase são os dois principais fatores que impedem a sua ampla utilização. Através da aplicação de um campo magnético até intensidades em torno do campo crítico necessário para iniciar a FOPT, a caracterização detalhada das dinâmicas de transição de fase magnética e estrutural foi realizada em duas ligas pertencentes às famílias mais proeminentes de materiais magnetocalóricos gigantes: $\text{LaFe}_{11.6}\text{Si}_{1.4}$ e $\text{Fe}_{49}\text{Rh}_{51}$. Ambas as ligas apresentam respostas magnéticas e estruturais dependentes do tempo semelhantes quando magneticamente induzidas em torno das suas transições de fase FM-PM e AFM-FM, respetivamente, e daí deixadas atingir equilíbrio. A dinâmica de remoção do campo magnético também é explorada, estabelecendo a semelhança simétrica da remoção parcial do campo magnético com aquela observada na aplicação do campo magnético. Por fim, a natureza (des)acoplada das transições de fase magnética e estrutural é avaliada em ambas as ligas, estabelecendo um caminho para a otimização do material e para um melhor design da ciclagem do campo magnético em dispositivos reais.

Palavras-chave: Materiais Magnetocalóricos, Cinética de Transição de Fase, Magnetometria, Difração Raio-X, Perfil de Energia Livre, Relaxação Magnética, Relaxação Estrutural, Acoplamento Magnetovolumico

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Chapter 1

Underlying Theoretical Concepts

In this first chapter an introduction to the overarching theme of the thesis is provided together with a brief theoretical description of key concepts drawn upon throughout the thesis. Lastly, in bridging the gap to the current state-of-the-art research within the field of magnetocaloric materials, the application of a magnetocaloric material in a thermodynamic cycle is broadly described.

1.1 Motivation

As climate change progressively makes the Earth's climate more extreme and a rise in economic growth leads to better access to cooling technologies, the projected demand for residential heating is expected to reduce, while the demand for cooling is expected to increase [1, 2]. With Refrigeration, Air-Conditioning and Heat-Pumping (RACHP) equipment having accounted for 40% of global energy-related CO₂ emissions [3] and the cooling sector alone responsible for over 10% of global greenhouse gas emissions, of which 30% arise from direct emissions pertaining to refrigerant leakages and the remaining from electricity consumption [4], decarbonising this industry is increasingly more important.

Conventional cooling technologies are based in vapour compression of hazardous gases, which is why, in line with the current EU goals of achieving carbon neutrality by 2050, the Kigali Amendment proposes a gradual phase down of the now commonly used hydrofluorocarbons (HFCs), whose global warming potential (GWP) can be of tens to thousands [5, 6], and whose reduction comes at the cost of flammability or performance [7]. As such, there is a high demand for alternative cooling technologies capable of not

only decreasing direct greenhouse gas emissions, but also presenting improved energy efficiency.

1.1.1 Caloric Effects

Taking advantage of caloric effects for cooling and heat transfer stands out as a solid-state environmentally friendly alternative to vapour compression [8], whereby caloric materials show reversible thermal changes when an external driving field is applied [9].

In accordance to the nature of the driving field used in observing the caloric effect, be it a magnetic, electric or stress field, the effect is accordingly coined, as shown in Figure 1.1. Additionally, when a material exhibits a thermal response that is a consequence of the application of more than one of such driving fields, it may then be referred to as a multicaloric material, and hence exhibiting the multicaloric effect.

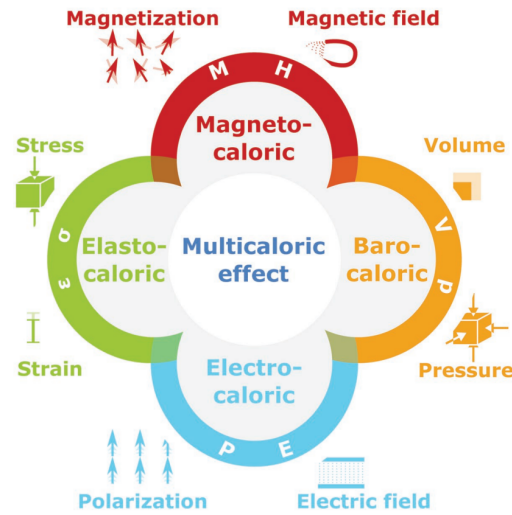


FIGURE 1.1: Classification of caloric effects according to their driving field. Image taken from reference [10].

1.2 The Magnetocaloric Effect

Succeeding the discovery of the giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ associated to a magnetic field induced ferromagnetic to paramagnetic phase transition at 276K [11], magnetic refrigeration at room temperature gained traction as a potential future competitor to vapour compression [9], as it promises to operate with a higher energy efficiency [12] and lower total environmental warming impact, whose working material has no global

warming or ozone depletion potential [13], thus moving closer to achieving zero carbon heating and cooling.

1.2.1 Thermodynamic Characterization

In describing a magnetocaloric material's thermal response two figures are to be considered [14, 15], the adiabatic temperature change upon magnetic field change, ΔT_{ad} , given by Equation 1.1, which is often measured directly through the use of a thermocouple, and the total entropy change, ΔS , which may arise from lattice, electronic or magnetic contributions [16, 17]. The magnetic entropy change ΔS_m , given by Equation 1.2, is the magnetic component of the total entropy change, and is often calculated through magnetization data [14]. Further insight into their derivation can be had in Appendix A.

$$\Delta T_{ad} = -\mu_0 \int_{H_i}^{H_f} \frac{T}{C_{p,H}} \left(\frac{\partial m}{\partial T} \right)_{p,H} dH \quad (1.1)$$

$$\Delta S_m = \mu_0 \int_{H_i}^{H_f} \left(\frac{\partial m}{\partial T} \right)_{p,H} dH \quad (1.2)$$

Although thermodynamic equilibrium is assumed with the use of the Maxwell relation used to derive these, such is only strictly the case for second-order phase transitions. For first-order phase transitions, additional care must be taken to counteract magnetic hysteresis and ensure the initial and final thermodynamic states are the same, which in practice can be achieved by increasing or decreasing the sample's temperature outside of the hysteretic region[18].

1.2.2 Maximizing Magnetocaloric Effects

As observed in Equation 1.2 and 1.1, ΔT_{ad} and ΔS_m are maximized with sudden and substantial magnetization changes with respect to temperature, which are characteristic of magnetic phase transitions in compounds also exhibiting large magnetic moments and available magnetic entropy [14, 15].

1.2.2.1 Theoretical Moment and Entropy Predictions

As derived in Appendix B, the magnetic moment of a group of N 4f atoms occupying a given volume, V, may be estimated by the following equation:

$$M = \frac{N}{V} g_J \mu_B J B_J \left[\frac{g_J \mu_B B}{k_B T} \right] \quad (1.3)$$

Which, in combination with the theoretical magnetic contribution to the entropy, estimated in Equation 1.4, and those conclusions derived from Equation 1.2 and 1.1, is indicative that maximal ΔT_{ad} and ΔS_m are achieved in atoms whose total angular momentum, J , is mostly maximized.

$$S = N k_B T \ln(2J + 1) \quad (1.4)$$

1.2.2.2 Phase Transitions

Put simply, phase transitions occur when there is a change in thermodynamic phase resulting from a change of the external conditions. The Ehrenfest's classification proposes these to be classified by the order of the lowest differential of the Gibbs energy, G , with respect to a state variable, such as temperature or magnetic field, which exhibits a discontinuity [19].

By this definition, it is clear that first-order phase transitions are characterized by a discontinuity of the first derivative of the Gibbs energy, G , while second-order phase transitions and beyond, commonly referred to as continuous phase transitions, exhibit smoother Gibbs energy functions, as observed in Figure 1.2. As a result of this, first-order phase transitions are associated with latent heat, $L = \Delta Q_{rev} = T_c \Delta S$, due to the discontinuity of the entropy, S , of these systems, given by $S = - \left(\frac{\partial G}{\partial T} \right)_p$, at a given critical temperature, T_c .

Further distinctions are observed when comparing second differentials of the Gibbs energy, G , such as heat capacity, C . In these, a sharp lambda-like shaped peak associated to their discontinuity is observed in first-order phase transitions, which contrasts with its absence in second-order phase transitions, as schematically pictured in Figure 1.2.

Additionally, as some phase transitions are crossed, the system's symmetry may be altered in such a way its symmetry is considered to be broken. Such is the case of a paramagnetic to ferromagnetic phase transition, where the paramagnetic state has perhaps unintuitively high-symmetry, and inducing the phase transition to the ferromagnetic state breaks the rotational symmetry of the system, therefore making it the low symmetry state [19, 20]. In this example, it is this spontaneous breaking of symmetry which brings about an order parameter, in this case the magnetization, M , of the system.

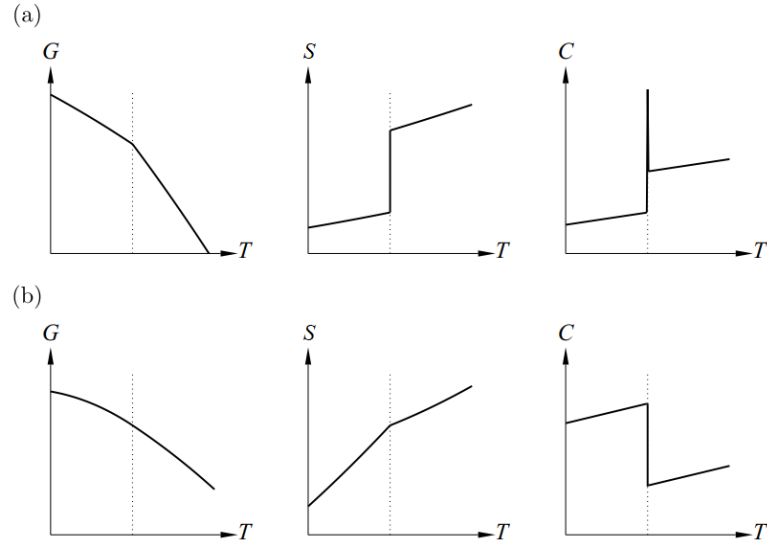


FIGURE 1.2: Profile of the Gibbs energy and its derivatives as a function of temperature for (a) first and (b) second-order phase transitions. Image adapted from reference [19].

1.2.3 Landau Theory

With the intention of better characterizing these phase transitions, Landau theory approximates the Helmholtz energy, $F = G - PV$, of a system near its critical temperature, T_c , through a power series of a small order parameter η with only even powers akin to the system's symmetry at zero conjugate field, h , for a second-order phase transition [21, 22]:

$$F(\eta) = F_0 + a(T)\eta^2 + b\eta^4 \quad (1.5)$$

Here F_0 and b are constants, b is assumed positive and $a(T) = a_0(T - T_c)$, thus changing its sign as the critical temperature, T_c , of the system is crossed. Depending on the system in question the order parameter η may be the system's density, polarization density, phase of the wave function or magnetization [22].

In determining the system's equilibrium ground states, the partial derivative $\partial F / \partial \eta$ may be taken to equal zero, and thus the following solutions are obtained:

$$\eta_{eq} = 0 \quad \vee \quad \eta_{eq} = \pm \sqrt{\frac{a_0}{2b}}(T_c - T) \quad (1.6)$$

For temperatures above T_c there are no real solutions for the second result, and, for those below T_c , according to the second derivative of F with respect to η , the first solution is an unstable equilibrium. As a result, the temperature dependence of the equilibrium order parameter η of the system, for temperatures close to T_c , may be given by:

$$\eta_{eq} = \begin{cases} \pm \sqrt{\frac{a_0}{2b}(T_c - T)} ; & T < T_c \\ 0 ; & T > T_c \end{cases} \quad (1.7)$$

Which may be visualised in Figure 1.3 as the singular energetic minimum of the Helmholtz energy, F , present above the critical temperature T_c being superseded by two opposite energetic minima as the temperature is decreased to be below T_c .

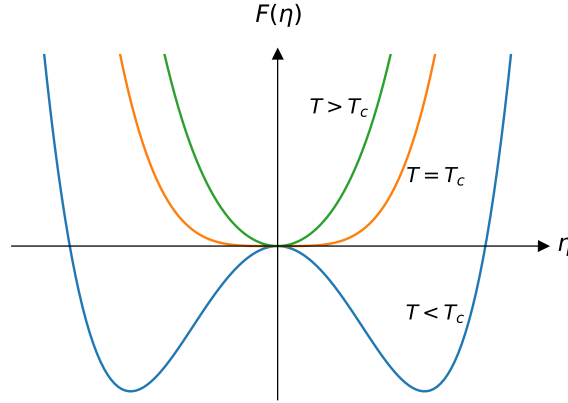


FIGURE 1.3: Helmholtz energy, F , as a function of the order parameter, η , for an illustrative set of temperatures around T_c .

Adding a conjugate field h to the expression of the Helmholtz energy yields the following equation:

$$F(\eta) = F_0 + a(T)\eta^2 + b\eta^4 - h\eta \quad (1.8)$$

Whose equilibrium ground states are given by :

$$h = 2a_0(T - T_c)\eta + 4b\eta^3 \quad (1.9)$$

Here it can be concluded that, regardless of temperature, a non-zero applied field, h , results in η taking on values strictly different from zero.

1.2.4 First-Order Phase Transitions

While Landau theory for ferromagnetism correctly predicts that the magnetization, M , below the critical temperature, T_c , is proportional to $(T_c - T)^\beta$, experimentally the critical exponent β , is found to vary [22]. Nevertheless, the many successes from this theory have warranted its adaptation to allow the additional modelling of first-order phase transitions.

Although the addition of an odd-order term to the Helmholtz energy would suffice in turning the phase transition into a first-order kind [23], as previously alluded to, attending to the system's symmetry, namely the invariance to the transformation $\eta \rightarrow -\eta$, all odd-order terms must be zero [22].

The solution to respecting the system's symmetry while ensuring it exhibits a first-order phase transition is to extend the energy expansion beyond the 4th order [24, 25] such as in:

$$F(\eta) = F_0 + a(T)\eta^2 - |b|\eta^4 + c\eta^6 - h\eta \quad (1.10)$$

Here, and as represented in Figure 1.4a, as long as the highest ordered term is positive, ensuring an adequate description of the system as $\eta \rightarrow \pm\infty$, having a negative quadratic term adds the necessary discontinuity in the first derivatives of F and creates an energetic barrier responsible for a metastable state which leads to the observed hysteresis [24], such as the one observed in Figure 1.4b.

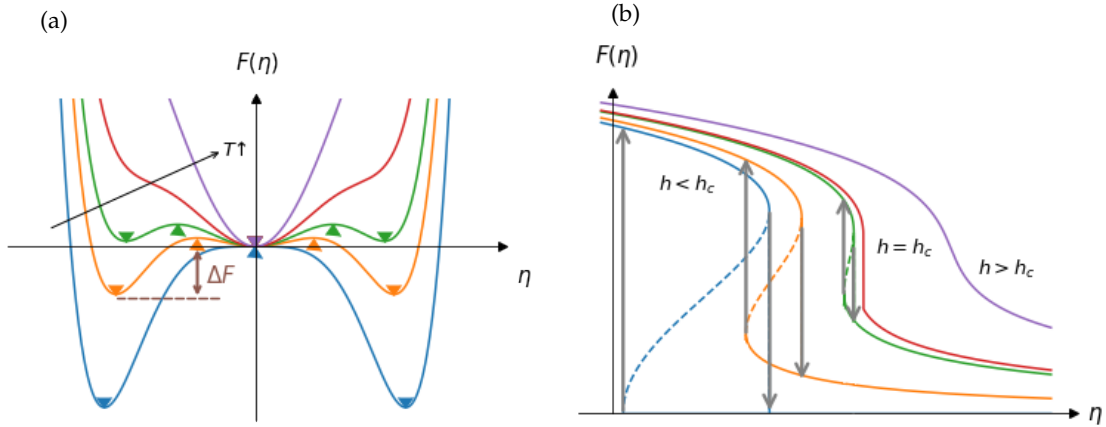


FIGURE 1.4: a) Profile of the Helmholtz energy, F , as a function of the order parameter, η , presented for an illustrative set of temperatures around T_c and b) the temperature, T , dependence of the order parameter, η , for an illustrative set of external applied fields, h . The energetic extrema are represented by up and down triangles and an example of an energetic barrier is represented.

1.2.4.1 Phase Diagram of a Caloric Material

All in all, a material's free energy landscape dictates most aspects of its phase transition. At a glance, the presence of a discontinuity in the derivatives of the free energy allows for the determination of the order of the phase transition, which may be verified through latent heat calculations. However, a good and detailed understanding of the free energy

landscape allows for the calculation of important and diverse figures [17], such as the order parameter, the energy barriers, the entropy of the system and its hysteresis, together with their dependence on external factors, such as temperature and external field, while also playing a key role in uncovering the phenomena underlying the origin of the phase transition.

When it comes to caloric materials, there are three variables which help condense the information gathered from the free energy landscape and help build and navigate the material's phase diagram [8, 26]. These variables are the material's order parameter, η , its temperature, T , and the externally applied field, which according to the type of caloric material to be characterized may be the magnetic field, for magnetocaloric materials, the electric field, for electrocaloric materials, uniaxial stress, for elastocaloric material, or pressure, for barocaloric materials.

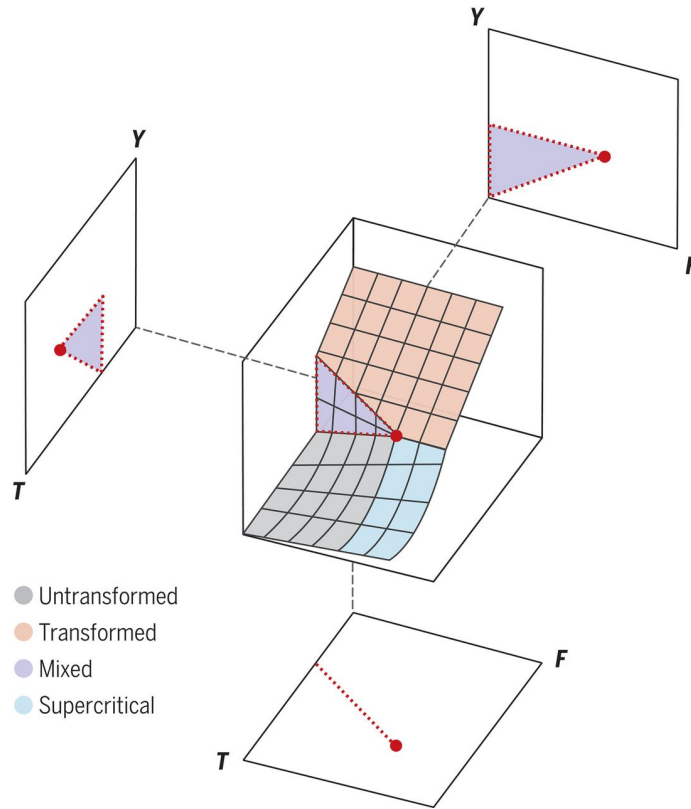


FIGURE 1.5: Phase diagram of a caloric material which undergoes a phase transition. The three projections of the diagram are shown for each of the axis: temperature, T , external field, F , and order parameter, here presented as Y . Image taken from reference [8].

In Figure 1.5 a generalised phase diagram is shown for a first-order phase transition caloric material which, for simplicity, has a sharp transition and does not show hysteresis.

Here, the half-line presented in the temperature, T , against external field, F , plot represents the phase boundary and delimits the conditions in which the transformed and the untransformed phases occur. The end point of this half-line is called a critical point and represents the point after which the transformed and untransformed phases coexist.

In the order parameter against temperature plot, for a given external field and below the critical point, as the temperature is increased a high η transformed phase is sharply converted into a low η untransformed phase by crossing the phase boundary, to which is associated a latent heat. Similarly, for a given temperature and below the critical point, an untransformed phase may be sharply transformed upon application of an external field. Additionally, the phase of the material may be altered without a formal phase transition occurring by circumventing the critical point through a supercritical state.

1.2.5 Thermodynamic Cycles for Magnetic Refrigeration

By navigating the phase diagram of a magnetic material through changes to its external conditions, such as temperature and external field, a cycle of thermodynamic processes may be constructed in such a way it allows for a continuous and cyclic conversion of heat into work and vice versa [19]. According to the thermodynamic processes utilised in a thermodynamic cycle, ranging from, but not limited to, adiabatic, isothermal and isofield magnetization, these cycles have different designations.

The most notable example of which is the Carnot cycle, known to be the most efficient cycle operating between two thermal sources [14], and is constituted by alternating isothermal and adiabatic magnetization and demagnetization processes of the working material, as presented in Figure 1.6.

Here, as the magnetic field is applied from a low field, H_0 , to a high one, H_1 , two processes occur. At first, the magnetic refrigerant is partially magnetized under adiabatic conditions, $dQ = 0$, from (1) to (2), increasing its temperature from T_{cold} to T_h . Then, as the remainder of the magnetic field is applied isothermally, up to H_1 , from (2) to (3), the excess heat generated is exchanged with the high temperature sink, $Q_h = T_h \Delta S_m(T_h)$. As the magnetic field decreases under adiabatic conditions, from (3) to (4), the temperature of the magnetic refrigerant decreases from T_h to T_{cold} . Lastly, the cycle is completed with the isothermal removal of the magnetic field, allowing for heat exchange with the low temperature sink to happen, $Q_c = T_{cold} \Delta S_m(T_{cold})$, therefore enabling the system to be used as a cyclic heat pump [14, 27].

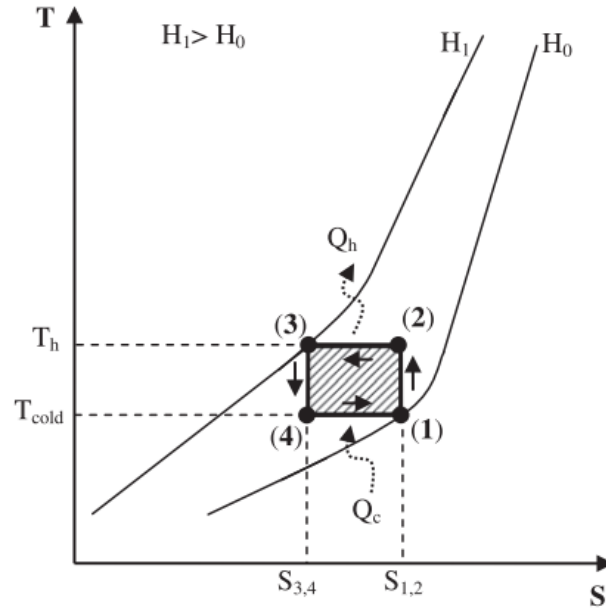


FIGURE 1.6: T-S, temperature versus entropy, diagram of a magnetic refrigeration Carnot cycle, showing low, H_0 , and high, H_1 , isofield curves, as well as the heat exchanged with the temperature sinks, Q_c and Q_h . Image taken from reference [27].

While most efficient, refrigeration based on the Carnot cycle is only utilised for cryogenic applications as it has proven to not be a cost-effective solution when employed at room temperature [27]. As such, multiple other thermodynamic cycles have been explored with the goal of achieving cost-effective magnetic refrigeration at room temperature, namely the Ericsson and Brayton cycles, however the AMR, active magnetic regenerator, cycle has proven to be the best performing and efficient, second to the Carnot cycle, which is why it has been used in most prototypes [27, 28].

Traditionally magnetic refrigeration employs the use of a regenerator, to allow for the transfer of heat to and from the heat transfer fluid at different stages of the thermodynamic cycle, however, in an AMR cycle, the magnetocaloric material serves as both the refrigerant and the regenerator [14]. Despite the cycle being characterized by alternating adiabatic and isofield processes, in which heat regeneration takes place, it's representation can not be achieved through a simple T-S diagram [27].

Chapter 2

Literature Review

Succeeding the introductory chapter, this next chapter goes one step ahead in presenting the theme of the thesis by narrowing its focus down to the key research topics surrounding the time dependent phase transition dynamics in magnetocaloric materials which continue to motivate its in-depth study. It is also in this chapter that the selected materials, $\text{LaFe}_{11.6}\text{Si}_{1.4}$ and $\text{Fe}_{49}\text{Rh}_{51}$, are presented, together with relevant knowledge of their phase transitions.

2.1 Benefit of First-Order Phase Transitions

As presented in Chapter 1, materials presenting first-order phase transitions, FOPTs, are of special interest in the field of magnetocaloric materials as the discontinuity of their order parameter, namely the magnetization, results in higher figures of merit, and hence an increase in performance when operated in a thermodynamic cycle working across the phase transition [15].

Figure 2.1 showcases the isothermal entropy change, ΔS , found across the phase transition of prominent magnetocaloric materials. Here, the high entropy change over a small temperature span of $\text{La}(\text{Fe},\text{Si})_{13}$, and the high entropy change of equiatomic FeRh over a wide temperature range, is compared to that observed in a Gd sample.

The temperature dependence of the entropy change of Gd is found to be extremely wide with a low maximum ΔS around its transition temperature. This is due to the fact that Gd exhibits a second-order magnetic phase transition, in contrast to the first-order phase transition experienced by the other presented materials.

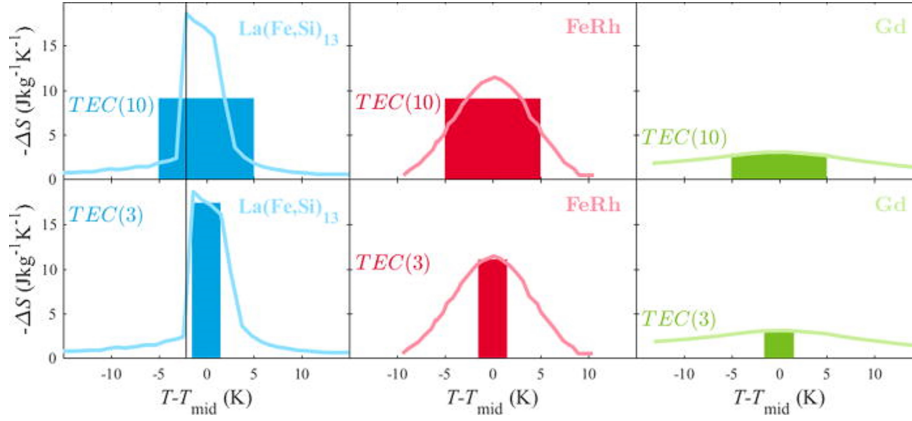


FIGURE 2.1: Entropy change found in different materials exhibiting the giant magnetocaloric effect. $TEC(i)$ stands for the temperature averaged entropy change over the temperature span of i for a field change of 1 T. Image taken from reference [29].

In practical terms, this equates to FOPT magnetocaloric materials being a better fit to operate in devices employing layered regenerators in AMR cycles [29], as the quick decay of ΔS when the temperature is brought further away from T_c may be counteracted by the use of several layers consisting of the same material with slight critical temperature variations, therefore increasing the device's temperature operation range while taking advantage of the larger ΔS peak [30, 31].

Additionally, FOPT magnetocaloric materials allow for the use of smaller driving magnetic fields to perform the cyclic switching between its PM and FM states, while still allowing the device to make use of most of the large entropy changes which arise from driving the sharp phase transition in full [32].

2.1.1 Giant Magnetocaloric Effects

Materials exhibiting giant magnetocaloric effects have their properties arising from coupling between the magnetic and structural lattices [33, 34]. $Gd_5(Si,Ge)_4$ is an example of a material whose magnetic phase transitions have been reported to be closely related to its structural phase transitions [35] and, as a result, its entropy change, characterizing its magnetocaloric effect, having significant contributions from both the magnetic and lattice components.

However, the nature of the coupling of these transitions, magnetic and structural, in giant magnetocaloric materials may vary. While the giant effects found in $Gd_5(Si,Ge)_4$

stem from simultaneous phase transitions [36], other materials exhibiting giant magnetocaloric effects, such as $\text{LaFe}_{11.4}\text{Si}_{1.6}$, see these giant effects arising from an itinerant electron metamagnetic transition [37, 38].

2.2 Phase Transitions Hysteresis

In spite of their advantages, FOPT magnetocaloric materials bring forth a new set of challenges pertaining to magnetic and thermal hysteresis, phase transition asymmetries, cyclability, as well as phase transition dynamics, the former being the focus of this section.

As a direct consequence of the FOPT, the directional irreversibility of the phase transition between the PM and FM states leads to energetic losses which inevitably lower the energy efficiency of magnetic cooling devices, and hence their competitiveness [14]. This hysteresis may have either of two origins [32, 39], those linked to intrinsic characteristics of the material, such as its magnetism and phase transition [40], or those linked to extrinsic characteristics, such as geometry and grain size [41].

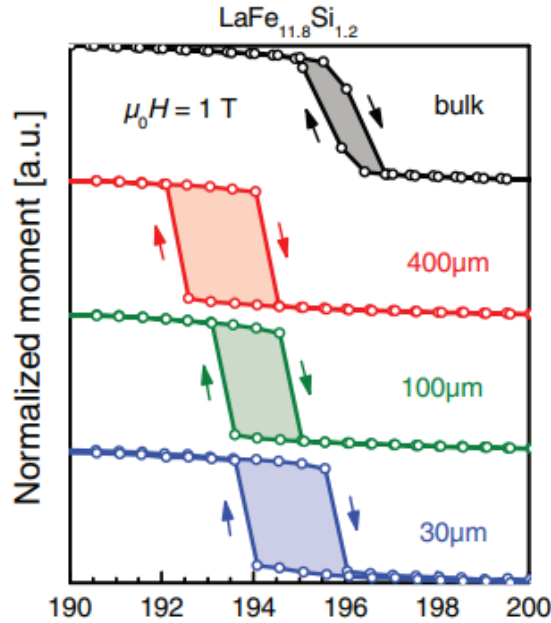


FIGURE 2.2: M-T loops of single particles of $\text{La}(\text{Fe}_{11.8}\text{Si}_{1.2})$ with different sizes compared to that found in a bulk sample. Image taken from reference [10].

As shown in Figure 2.2, differently sized single particles of the alloy $\text{La}(\text{Fe}_{11.8}\text{Si}_{1.2})$ show a distribution of transition temperatures and thermal hysteresis widths. In spite of their sharp transitions, the large distribution of transition temperatures found across the tested single particles, which commonly arise due to chemical inhomogeneity, would

be expected to result in a bulk alloy whose hysteresis is slanted. However, as observed, the hysteresis of the bulk sample retains a rather sharp appearance which is due to the high volumetric changes and the high sensitivity of the transition temperature to stress, resulting in an increase of the sharpness of the transition as the material's grain size is brought closer to a bulk state [10, 42]. In fact, as the volume of a bulk sample increases due to a phase transition, be it during cooling or heating, its surrounding outer constituents get to exert pressure, thereby increasing the sample's stress, in turn shifting the transition temperature of its inner constituents towards higher temperatures, ultimately observed as an asymmetrically sharp transition occurring at a slightly higher temperature than that observed in a singular particle [10, 43]. On the other hand, as loose powder lacks this stress-inducing character, a cluster of powdered particles would simply see their phase transition be slanted, highlighting its chemical inhomogeneities.

2.3 First-Order Phase Transition Dynamics

As it pertains to phase transition dynamics, the time evolution of the magnetization of several giant magnetocaloric materials, namely $\text{Gd}_5(\text{Si,Ge})_4$ [44], $\text{La}(\text{Fe,Si})_{13}$ [45, 46] and near-equiatomic FeRh [47, 48], has been reported to extend well beyond the time of field application.

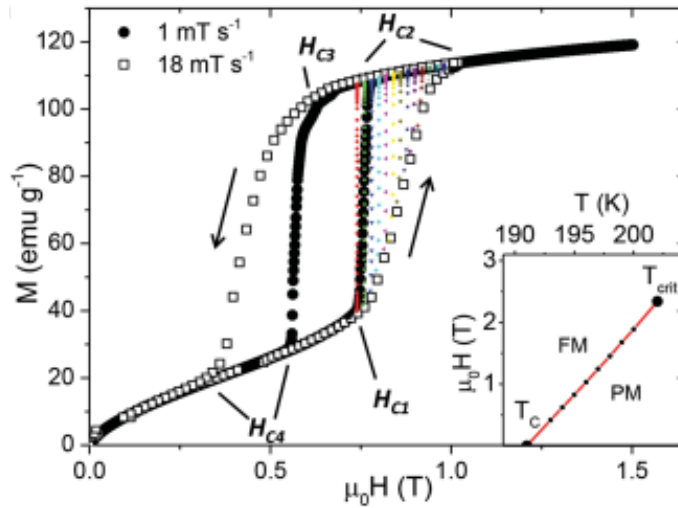


FIGURE 2.3: Magnetization as a function of applied magnetic field loop at different field sweep rates for a $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample. The inset shows the phase diagram of the sample. Image taken from reference [46].

In observing this effect, a magnetic field must be applied at the onset of the magnetic field induced phase transition. Attending to the slanted nature of its hysteretic loop, different critical field landmarks may be denoted [46, 49], namely H_{c_i} , where $i = 1; 2; 3; 4$, as shown in Figure 2.3. Their formal characterization in a material undergoing a PM to FM phase transition is as follows, during isothermal magnetic field application: H_{c1} is the minimum applied magnetic field necessary to onset the magnetically-induced phase transition from a PM to a FM state; H_{c2} is the minimum applied magnetic field which completely induces the PM to FM transition; during magnetic field removal: H_{c3} is the maximum applied magnetic field necessary to onset the FM to PM transition; H_{c4} is the maximum applied magnetic field which completely induces the FM to PM transition.

From a practical point of view, and attending to possible experimental factors that may not be accounted for, the presented critical fields H_{c_i} may also be defined a posteriori as the minimum/maximum fields at which, beyond field-driven changes, relaxation effects are/are not observed.

Experimentally this disparity between field application time and order parameter response can be systematically described through the isothermal application of a magnetic field. And, by continuing to measure the magnetization beyond the point of pausing the magnetic field, these relaxation effects appear as striking vertical lines in a M-H loop, as observed in Figure 2.3 or simply as a further variation of the magnetization in a magnetization as a function of time plot, as presented in Figure 2.4, where $t = 0$ s represents the time in which the magnetic field was paused at a given intensity.

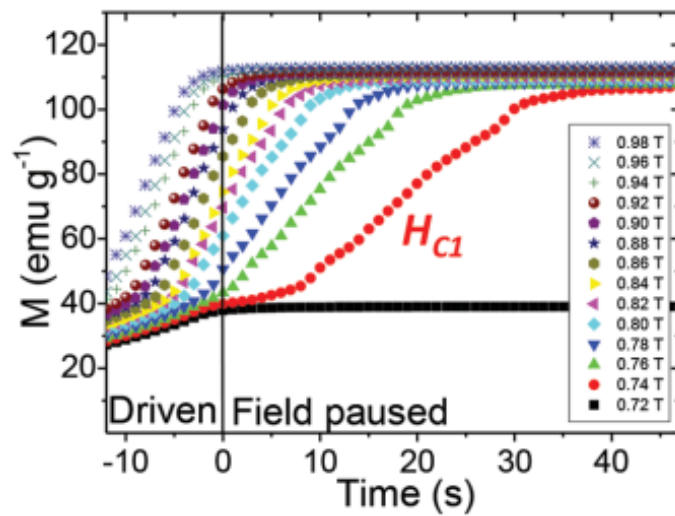


FIGURE 2.4: Relaxation of the magnetization after the applied magnetic field is paused between H_{c1} and H_{c2} for a $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample. Image taken from reference [46].

In analysing the presented relaxation effects, it is observed that, as the field is driven up to the desired intensity, H_{pause} , the magnetization follows a similar path irrespective of the final value set for the magnetic field, which is to be expected. Then, as the field is paused between H_{c1} and H_{c2} , the magnetization gradually increases up to the saturation value given by the upper bound of the M-H loop obtained at the same field sweep rate used to drive the field up to H_{pause} .

The same way hysteresis plays a key role in determining the fit of a material to being used in an energy efficient cyclic device, the presented magnetization dynamics must also be taken into account. Ultimately, the kinetics of the phase transition play a critical role in determining the rate at which a material may be cycled for optimal performance [48, 50–53], as an incomplete phase transition is inherently associated to a suppressed thermal response, therefore demanding a lower operation frequency to ensure adequate saturation of the phase transition.

2.3.1 Dynamics Origin

Although current research is limited, several attempts at pinning the origin of these relaxation effects have been made. The following is a summary of some of the leading hypothesis and examples.

2.3.1.1 $\text{Gd}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_4$

When the temperature of a $\text{Gd}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ sample is held close to, but above, its PM to FM transition temperature, an applied magnetic field is capable of transforming its high temperature monoclinic PM phase into its low temperature orthorhombic FM phase [44].

Upon pausing the driving the magnetic field, the observed relaxation of the magnetization in $\text{Gd}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ followed an exponential increase of the kind shown in equation 2.1, as shown in Figure 2.5, which led to the conclusion that the process behind it is a nucleation and growth process by thermal activation over an energy barrier [44].

$$M(t) = M_0 + M_1 \left(1 - e^{-\frac{t}{\tau}}\right) \quad (2.1)$$

In equation 2.1, M_0 is the magnetization of the alloy at time zero, when the magnetic field reaches the H_{pause} value, $M_0 + M_1$ is the asymptotic value of the magnetization and τ is the relaxation time constant. As the relaxation time constant, τ , is inversely related to the rate constant, k , through the Arrhenius equation [54], equation 2.2, the process is then

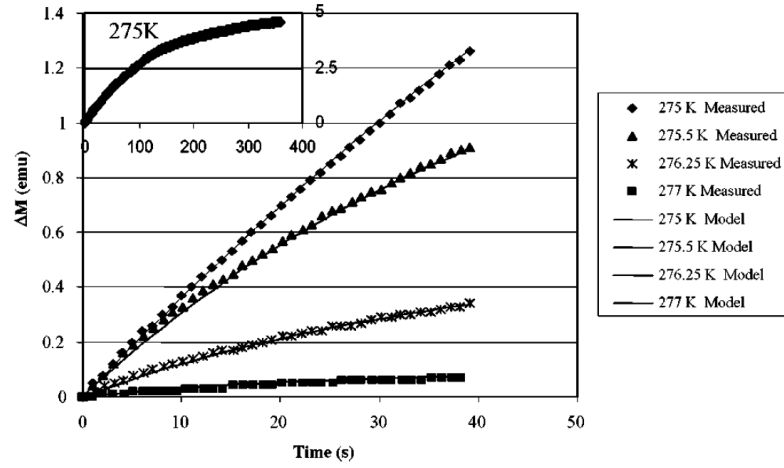


FIGURE 2.5: Magnetization as a function of time after the same applied magnetic field is paused ($t=0s$) at different temperatures. The fitted curves are calculated using equation 2.1. Image taken from reference [44].

concluded to be driven by an activation energy required to overcome an energy barrier, E_A , and, through its temperature dependence, it was concluded the growth mechanism is activation by thermal energy, $k_B T$.

$$k = Ae^{-\frac{E_A}{k_B T}} \quad (2.2)$$

Considering that the magnetic coupling in the alloy is observed through the movement of itinerant conduction electrons across (Si,Ge)-(Si,Ge) covalent bonds, it becomes apparent that the breaking and reforming of these bonds during the magneto-structural phase transition, induced by temperature and/or magnetic field variations, establishes a connection between the magnetic properties of the electronic band structure and the associated energy barrier [44, 55].

2.3.1.2 FeRh Alloys

An equivalent expression to equation 2.1 was used in analysing the relaxation observed for the magnetization of an $\text{Fe}_{50}\text{Rh}_{50}$ sample during a magnetic field driven isostructural AFM to FM transition [47, 48], also linking these relaxation effects to a nucleation and growth process thermally activated over an energy barrier. Here, similarly to what has been described for $\text{Gd}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ [56], the additional presence of secondary phases, proposed to act as nucleation sites, lowered the height of the energy barrier and decreased the field needed to onset the AFM to FM transition [48], thus lowering the observed relaxation and improving cyclability.

Similar to the relaxation effects observed during an isothermal phase transition driven by a magnetic field, the temperature-driven phase transition also demonstrates a time-dependent evolution of the order parameter, as seen in Figure 2.6. Specifically, when the material's temperature is raised and brought to a halt in close proximity to the critical temperature, changes in the order parameter continue to occur over time.

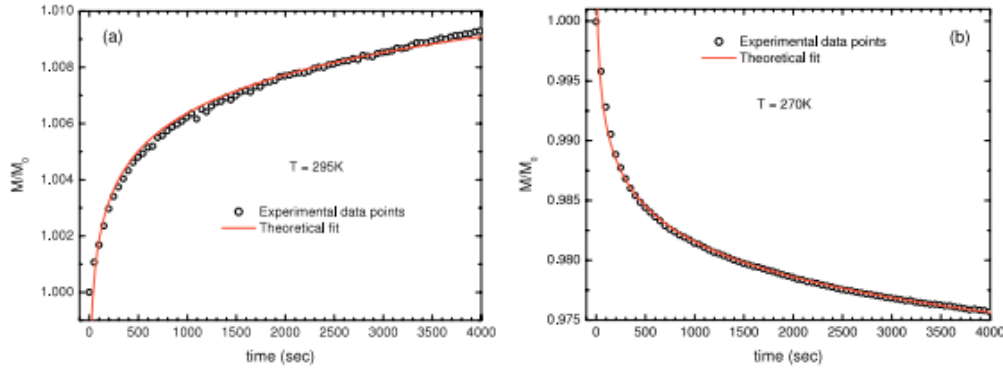


FIGURE 2.6: Magnetization as a function of time after the temperature is a) raised or b) lowered and then stopped ($t=0$ s) at the specified value. Fits are performed using the Kolmogorov-Johnson-Mehl-Avrami relation. Image taken from reference [57].

As such, the magnetization of a $(\text{Fe}_{0.975}\text{Ni}_{0.025})_{50}\text{Rh}_{50}$ sample, when driven thermally or by a magnetic field, was observed to exhibit a time-dependent behavior that adheres to a power law described by the Kolmogorov-Johnson-Mehl-Avrami relation [57], equation 2.3, where the time-evolution of the fraction of a new phase, f , is related to the rate constant, k , and the Avrami index, η , which depends on geometric factors [58, 59].

$$f = 1 - e^{-kt^\eta} \quad (2.3)$$

This time dependence is believed to originate from the strong long-range dipolar interactions between ferromagnetic clusters, providing evidence of a nucleation and growth behavior [57].

2.3.1.3 $\text{La}(\text{Fe,Si})_{13}$ Alloys

The relaxation of the magnetization in the $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ family can be understood through a nucleation and growth process, or by considering the heating effect resulting from its magnetocaloric properties. In the first case, the nucleation and growth process is attributed to either thermal activation over an energy barrier [60], or alternatively, explained by local heating and cooling at the phase boundary and the magnetic dipole interaction [61, 62].

Additionally, some also suggest these effects could stem from the heating of the material caused by its magnetocaloric properties. Specifically, as the FM phase grows, it generates and disperses heat to its surroundings, thereby increasing the magnetic field required for the phase transition to occur in the surrounding grains [45, 49].

This phenomenon could explain the flaring of the M-H loop when the magnetic field sweep rate is increased, shown in Figure 2.7. As the rapid application of the field causes the transformed phase to generate heat more quickly, intensifying the effects caused by inadequate thermal linkage to the thermal bath. Consequently, the temperature of the untransformed surroundings rises, together with its critical field, leading to the observed flaring.

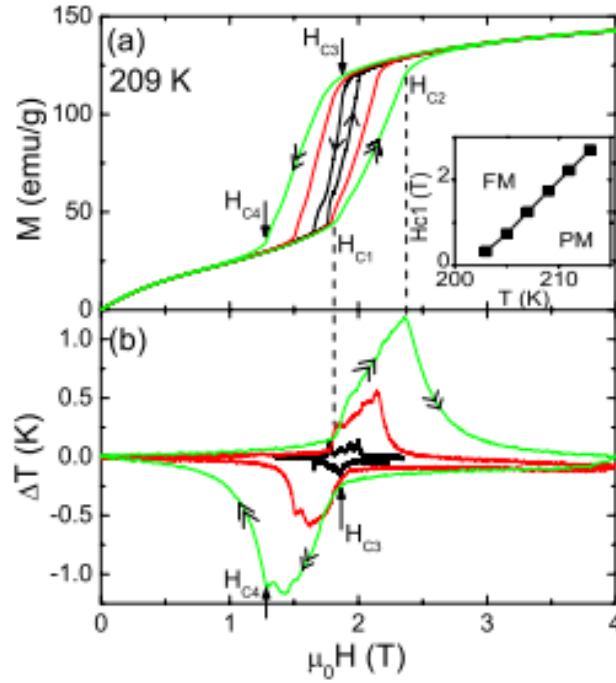


FIGURE 2.7: a) M-H loop of a $\text{LaFe}_{11.71}\text{Co}_{0.19}\text{Si}_{1.11}$ sample obtained at different magnetic field sweep rates, inner loop at 0.02T/min, middle loop at 0.2T/min and outer loop at 0.7T/min. b) Temperature difference, ΔT , of the sample relative to the bath. Image taken from reference [49].

2.4 $\text{La}(\text{Fe},\text{Si})_{13}$ Magnetic and Structural Properties

As already discussed, $\text{La}(\text{Fe},\text{Si})_{13}$ -based materials are known to present the giant magnetocaloric effect, GME, near room temperature associated to their magneto-structural itinerant electron FM to PM FOPT [46, 63], turning these into a very promising subset

of materials for thermomagnetic energy harvesting [64–66] and magnetic refrigeration [67, 68].

In addition to being constituted by relatively abundant materials, La being the most abundant rare earth element and only used in a small fraction, their Curie temperature can be adjusted by varying Si content, as shown in Figure 2.8, its increase leading to an increase in T_c . As the silicon content decreases from $x=0.18$, the material undergoes a notable change in its phase transition behavior, shifting from a second-order transition to a more abrupt first-order transition [69]. As a result, hysteresis emerges and grows in magnitude.

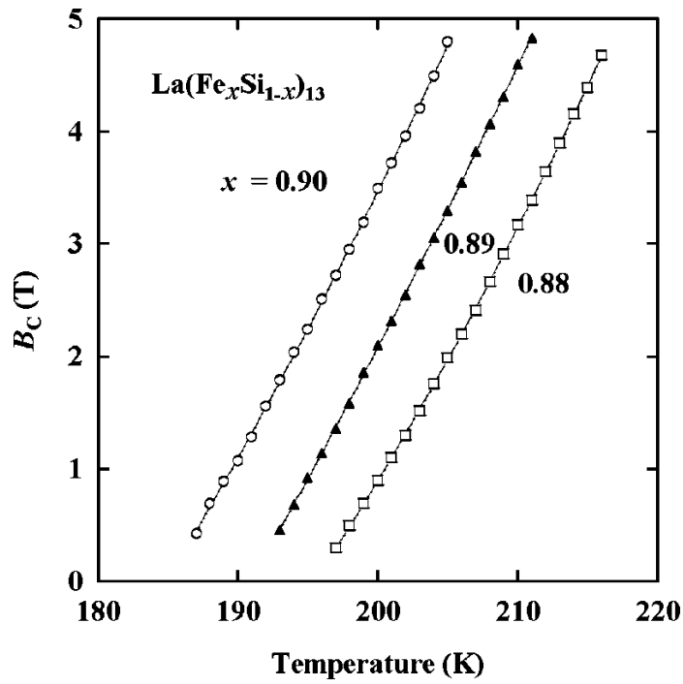


FIGURE 2.8: Phase diagram of $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ as a function of silicon content, $1 - x$. Note the opposite convention of x used. Image taken from reference [70].

Additionally, their transition temperature has been reported to be highly tunable by partial substitution of Fe with Mn atoms, resulting in a decrease in T_c , and Co atoms, which lead to an increase in T_c [67, 71–75]. Additionally, hydrogenation of the material brings its T_c closer to room temperature, while also increasing the stability of its magnetic properties [70, 76].

Such $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ compounds with $1.4 < x < 2.6$ crystallize in a cubic NaZn_{13} -type structure (space group Fm-3c) [77, 78], with the La, 8a and Fe1, 8b sites fixed at the fractional coordinates $(1/4, 1/4, 1/4)$ and $(0, 0, 0)$, and further Fe2 and Si atoms occupying the 96i sites at $(0, y, z)$ randomly [63, 79, 80]. Parallel to the formation of these alloys, α -Fe

is a commonly found secondary phase induced by the presence of a La-Si phase, typically representing 5-8 wt% of the sample. [79, 81, 82].

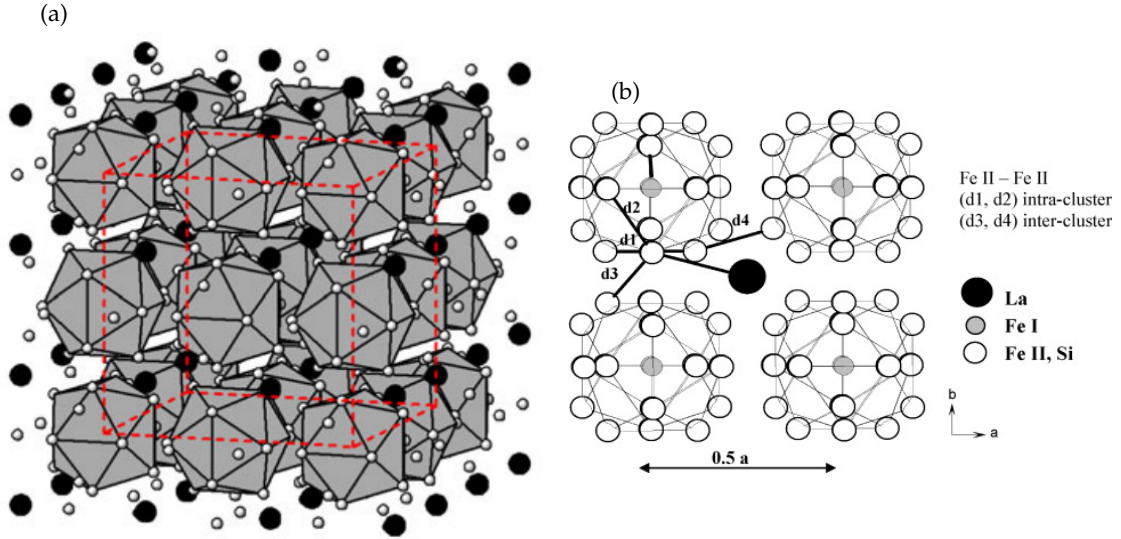


FIGURE 2.9: a) Unit cell $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ alloys delimited in red. Large spheres represent La atoms, while smaller spheres represent Fe atoms. Fe atoms belonging to each Fe cluster are connected in a icosahedron. b) Detail of the most relevant interatomic distances. Images taken from reference [63] and [83] respectively.

As the material is heated above its Curie temperature, T_C , the FM to PM transition occurs, and these alloys undergo a large discontinuous isostructural volumetric change, of about 1% [46], that is characterized by its negative thermal expansion [81, 84]. The lattice parameter is strongly correlated with the magnetic moment of Fe atoms. Consequently, the magnetovolume coupling in this first-order phase transition arises from the itinerant electron metamagnetic transition stemming from the itinerant Fe 3d electrons [37, 63, 83, 85]. Furthermore, the increase in the materials T_C by the addition of hydrogen and chemical substitution of Fe with other transition materials has been linked to the lengthening of the Fe1-Fe2 inter-atomic distances which is thought to promote stronger FM exchange interactions [63, 79].

2.5 Near-equiatomic FeRh Magnetic and Structural Properties

Although FeRh was the first intermetallic alloy discovered to exhibit the giant magnetocaloric effect near room temperature [14, 86, 87], due to its large adiabatic temperature changes, it continues to serve as a point of reference in comparing FOPT magnetocaloric materials [9, 88, 89].

Such $\text{Fe}_{100-x}\text{Rh}_x$ alloys with $48 \leq x \leq 54$ crystallize in a cubic CsCl-type structure (space group Pm-3m) and undergo two distinct isostructural phase transitions [88, 90–92], as observed in Figure 2.10. One, close to room temperature, where the magnetic ordering changes from AFM to FM as the temperature is increased and is associated with the inverse magnetocaloric effect, in which the material cools down upon magnetic field application. During this transition, the alloy's magnetization increases from near-zero up to its saturated value as a result of the exchange inversion arising from the thermal expansion of the unit cell volume [93]. In contrast, in the second phase transition, occurring at higher temperatures, the PM state takes over the FM state of the alloy, giving rise to the "direct" magnetocaloric effect and bringing its magnetization to zero [88, 91].

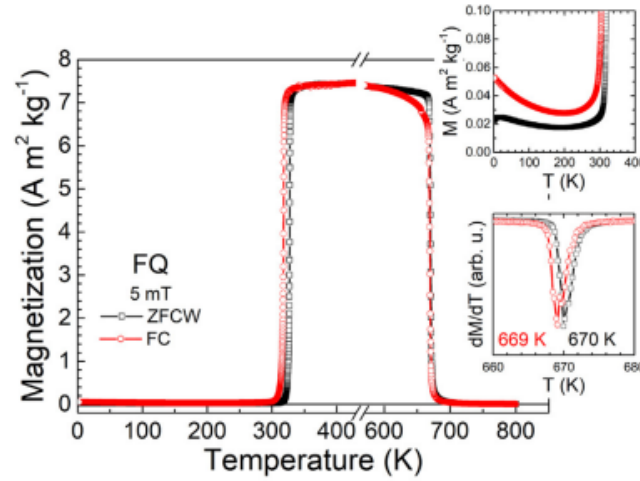


FIGURE 2.10: Magnetization of $\text{Fe}_{49}\text{Rh}_{51}$ as a function of temperature during warming after zero-field cooling, ZFCW, and during field cooling, FC. The insets show the low, AFM-FM, and high, FM-PM, temperature phase transitions in higher detail. Image adapted from reference [93].

When near-equiatomic FeRh is in its AFM state, its magnetic properties have their origin exclusively from the magnetic moment of the Fe atoms, which are aligned in an alternating fashion along the (1 1 1) plane, as shown in Figure 2.11a, while in its FM state, the Rh atoms gain a magnetic moment which is aligned with the rest of the Fe magnetic moments [92, 94], as shown in Figure 2.11b.

However, the impressive adiabatic temperature changes linked to the AFM to FM transitions of the FeRh family, have been observed to deteriorate upon magnetic field cycling [95–97]. This degradation has been attributed to a gradual reduction in the size of FM domains, and subsequent increased role of the domain walls, caused by the alloy's giant magnetostriction [95], representing a volumetric change of close to 1% [88, 94, 98].

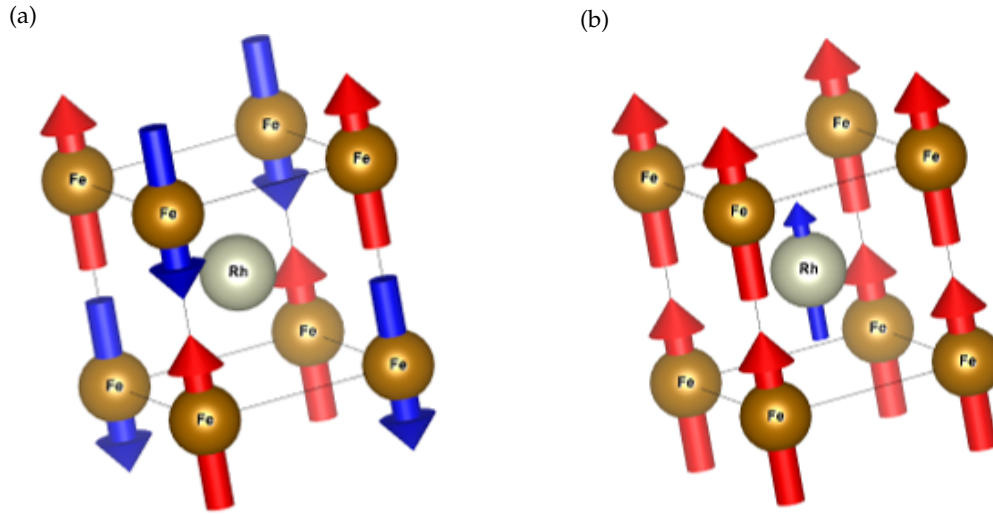


FIGURE 2.11: Atomic structure and atomic moments of equiatomic FeRh in an a) AFM state and in a b) FM state.

Conversely, the cyclability of these alloys has been reported to improve with the addition of secondary phases which, by creating nucleation sites, lower the critical field of the phase transition, thereby improving the fraction of the transformed phase [48].

Despite the unlikelihood of being implemented as the working material in a high-volume application, considering its extremely high cost [88, 96], in part due to the rarity of Rh, alloys of the FeRh family are of great research interest, not only due to its inverse magnetocaloric properties at room temperature, but also due to its baro and elastocaloric properties which, by allowing an additional tailoring of the critical temperature through the application of a non-magnetic field, such as hydrostatic pressure and stress [97–101], make this a useful material in studying multicaloric materials and applications [102, 103].

The properties of $\text{Fe}_{100-x}\text{Rh}_x$ alloys with identical stoichiometry vary greatly based on the fabrication protocol followed [88, 93], with their critical temperature generally decreasing with increasing Rh content [90]. In addition, these alloys may be doped, adding in further complexity, as the critical temperature of the transition, as well as its sharpness [94], may be tuned by chemical substitution of Rh with other transition metals such as Pt, Ir and Au, all of which increase the critical temperature of the phase transition [104–107], while doping with Pd, Cr, Co, Ni and Cu moves the transition temperature to lower temperatures [104–109].

Chapter 3

Experimental Methods

This chapter introduces the techniques used to characterize the magnetic and structural phase transitions in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ and $\text{Fe}_{49}\text{Rh}_{51}$, allowing for the measurement of the relaxation effects associated with these.

A description of the preparation process of these previously fabricated samples is given in Appendix C.

3.1 X-ray Diffraction

X-ray radiation is used as a probe of the atomic lattice due to the similarity between its wavelength and size of the interatomic distances commonly found in most materials, of the order of the Ångström, 10^{-10} m.

By aiming a beam of X-ray radiation at an evenly spaced stack of atomic layers, whose interlayer distance is d , a sharp peak in the intensity of the scattered radiation is observed when this radiation is specularly reflected, and so the incidence and reflected angles, θ , are equal, and it constructively interferes with that reflected from surrounding atomic planes, as shown in Figure 3.1. Bragg's law rewrites these conditions as the path difference between x-rays reflected off of successive planes equalling an integer, n , of the wavelength, λ , also referred to as the order of the reflection [110], as shown in the following equation.

$$n\lambda = 2d \sin \theta \quad (3.1)$$

A diffractogram can then be constructed by sweeping the desired θ range, which can be achieved by moving the x-ray source and detector in tandem, and registering the intensity of scattered radiation, I , effectively constructing a unique fingerprint of the material

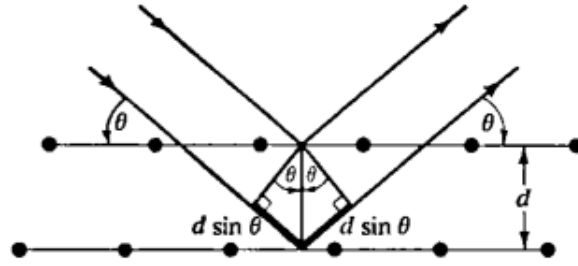


FIGURE 3.1: Bragg reflection in parallel lattice planes highlighting the geometry of the system. Image adapted from reference [110].

to be analysed. These diffractograms, usually plotted as I as a function of 2θ , may be analysed in different ways to determine a range of characteristics of the material's crystal structure such as the atomic positions and interatomic distances of its atoms, its crystallinity, grain size, strain and preferred orientation.

3.1.1 Rietveld Refinements

As a material's structure becomes more complex and of lower symmetry, X-ray diffraction diffractograms become harder to analyse and, consequently, there is an increased need for computational help.

By taking into account different aspects of each diffractogram, from experimental factors like the wavelength used, to crystallographic factors such as the position and shape of the observed peaks, a Rietveld refinement is the minimization process of a generic quantity, S , as shown in the following equation, which fits the whole pattern with a structural model by means of different individually refinable parameters acting on a preconceived model until a convergence criterion is reached [111].

$$S = \sum_i w_i (y_i^{obs} - y_i^{calc})^2 \quad (3.2)$$

Here, y_i^{obs} is the observed intensity and y_i^{calc} is that obtained from the model at each given refinement. The sum over all data points, i , is taken by attributing a weight, w_i , to each.

Due to the complexity arising from the number of parameters to be fitted during a Rietveld refinement, care must be taken to avoid fitting errors and divergences. As certain fitting parameters are correlated with each other, a commonly employed strategy involves performing iterative refinements using a different set of parameters at each iteration.

In general these refinable parameters are subdivided into three categories, those pertaining to profile parameters, which include the peak fitting function and its half width parameters u, v and w ; those related to the unit cell, such as the lattice constants a, b and c , and the preferred orientation; and lastly the structural parameters, which include the scale factor, the fractional coordinates of each atom and the isotropic Debye-Waller factors.

And so, on top of the atomic positions and lattice parameters, these refinements also allow for the determination of a variety of characteristics such as the amorphous fraction through the analyses of the background, and strain and particle size through the evolution of the FWHM of the peaks.

In the scope of this work the software used in performing and analysing Rietveld refinements was FullProf's Suite [112], and the evaluation of each model was made based on that discussed in Appendix D. Batch processing of X-ray patterns and analysis of interatomic distances was also made possible through this software.

3.1.2 Synchrotron

While conventional X-ray diffraction apparatus allows for good angular resolution, it often lacks in the ability to track quick changes of a material's lattice structure over time due to an insufficient number of scattering events. To add to that, specialized equipment is often necessary to allow for the simultaneous application of an external field.

As such, a specialized large-facility, the Brookhaven National Laboratory's National Synchrotron Light Source II in this case [113], had to be resorted to for the simultaneous application of a variable magnetic field and tracking of the subsequent structural changes as a function of time, achieved through the high frequency of pattern acquisition.

At the Pair Distribution Function (PDF) beamline [114] the incident beam's energy can be adjusted to 75 keV or 117 keV, with a flux of $500 \cdot 10^9$ photons s^{-1} and $1 \cdot 10^9$ photons s^{-1} , respectively, allowing for the acquisition of a good quality diffraction pattern every 2 seconds. The spot size at the beamline may be varied, with its width ranging from 0.1 mm to 1.0 mm and its length ranging from 0.25 mm to 2.00 mm.

Outside of their limited availability, the compromise in these facilities is often a limited probing range of the diffraction angle. While materials exhibiting lower degrees of symmetry should not be a cause for concern, as they intrinsically show a higher number

of diffraction peaks, the position of some of the peaks in those characterized by highly symmetric structural lattices should be confirmed to lie inside the probing range.

Although, ideally, the coupling of the magnetic and structural lattices should be studied simultaneously, allowing for a direct correlation of the observed behaviours of the structure and magnetic lattices, attending to the complexity of achieving such an experimental setup, these lattices may be studied separately under similar conditions, and correlations can then be inferred.

3.2 SQUID Magnetometer

Superconductive quantum interference devices are very sensitive magnetic flux detectors and, as such, are a very common type of magnetometer. Their operation relies on the flux quantization of a closed superconducting loop and the Josephson effect, which is a manifestation of the long-range quantum coherence found in superconductors [115, 116].

Closed superconducting circuits cooled under a magnetic field trap discrete magnetic flux quanta [115, 117], known as fluxons, $\Phi = h/2e$, where h and e are the Planck's constant and the charge of an electron, respectively. If this magnetic field is small enough, then a single quanta will be circulating this ring and, when the magnetic field is removed, Faraday's law of induction induces a current which opposes the change of the magnetic field by generating a magnetic field itself. In a resistive circuit, the induced current would eventually decay, and so would the flux contained in it. However, in a superconducting loop, as quantities lower than a singular fluxon are not allowed, a discontinuous change of states spanning the entire system would need to occur. As these are characterized by the long-range coherence of the superconducting state, the probability of such a discontinuous change is extremely low, thus enabling the current to circulate with no resistance.

When the gap between a superconducting junction is small enough, its superconducting states will be related to one another, through the Josephson's effect, therefore enabling the conduction of a current with no resistance across the junction. From a practical point of view, dc SQUID magnetometers function as a magnetic flux to voltage transducer built upon two Josephson's junctions enclosed in a superconducting loop in which flux quantization occurs, as shown in Figure 3.2. As a result, when a magnetic field is varied a current, which faces no resistance, is induced and, due to the quantization of the magnetic flux, enables its highly accurate measurements.

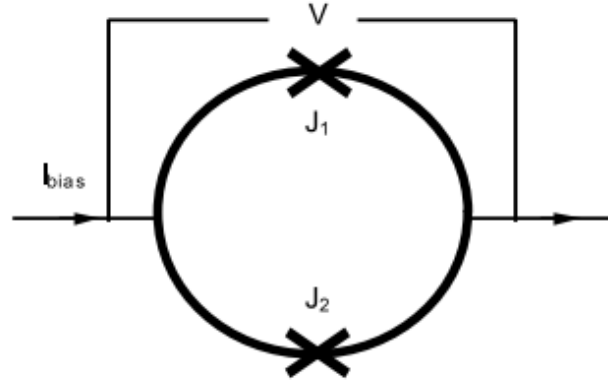


FIGURE 3.2: Schematic representation of the basic configuration of a DC SQUID. Two Josephson's junctions forming a closed circuit are represented, as well as the bias current and voltmeter used to measure the magnetic flux going through the device. Image adapted from reference [115].

The Quantum Design's MPMS 3 [118], Magnetic Property Measurement System 3, was the SQUID magnetometer used and it allowed for the measurement of the magnetization of different materials with respect to time, temperature and magnetic field. To capture time-dependent phenomena, it was operated under its VSM, Vibrating Sample Magnetometer, mode, which is capable of achieving high sensitivities [117] while maintaining a good time resolution for the scale of the relaxation processes to be measured.

VSM measurements are also based on Faraday's law of induction in which the magnetic sample is vibrated in a sinusoid fashion with-in a perpendicularly arranged set of pick-up coils, therefore inducing an electromotive force, ϵ , in the coils through changes of the magnetic flux, ϕ . So long as the exact motion, $\frac{dz}{dt}$, of the sample is known, the generated electromotive force may then be related to the sample's magnetic moment through a calibration on:

$$\epsilon = -\frac{d\phi}{dt} = -\frac{d\phi}{dz} \frac{dz}{dt} \quad (3.3)$$

Induction caused by variations in the applied magnetic field can be removed geometrically through the use of a set of pick-up coils which are wound in opposite directions to one another.

Quantum Design's MPMS 3 is capable of reaching temperatures of 1.8K to 400 K at sweep rates of 0.01 to 50 K/min and magnetic fields ranging from -7 to 7 T at sweep rates ranging from 1.58 to 700 Oe/s. These were important figures to keep in mind in designing the experiments, so as to cover as much of the accessible parameter space as possible.

3.3 Kinetics Measurement Protocols

Inspired by the work of E. Lovell and co-authors [46], a measurement protocol was followed throughout to determine the relaxation of the magnetic and structural phases upon magnetic field application, ensuring the reproducibility of the results.

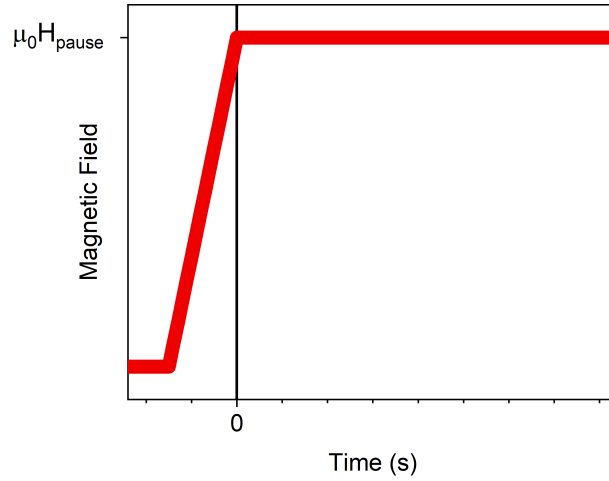


FIGURE 3.3: Profile of the applied magnetic field when a field is paused at $t = 0$ at a designated value, labelled $\mu_0 H_{\text{pause}}$.

First, the sample, weighing a few tens of grams, is cooled to the measurement temperature, usually a few Kelvin above or below T_c , ensuring the sample is in its low magnetization state, and allowed to reach thermal equilibrium for 5 to 15 minutes. Then, to magnetically induce the phase transition, a magnetic field is increased at a fixed sweep rate up to a given intensity, H_{pause} , and kept constant thereafter, allowing for the detection of non-field driven relaxation effects, as shown in Figure 3.3. Subsequently, the evolution of the magnetization or lattice parameter is measured as the magnetic field is removed, therefore allowing for the examination of the magnetization or structural dynamics during complete magnetic field cycles. In between measurements, a paramagnetic thermal reset was performed by heating or cooling the samples up to $T = T_c \pm 40$ K, effectively erasing the magnetic memory of the sample.

The time at which the magnetic field reaches the desired intensity of H_{pause} is taken to equal zero, be it upon magnetic field application, from a low magnetic field to H_{pause} , or magnetic field removal, from a high magnetic field to H_{pause} . In this way, a straightforward observation of non-field driven relaxation effects for each of the different experiments performed may be accomplished with ease.

An additional variation of this protocol was employed to probe the kinetics of magnetic field removal in more detail. In this variation, upon halting the magnetic field at H_{pause} for the intended duration, the magnetic field is increased up to a high magnetic field, ensuring saturation of the phase, usually up to 2T. After waiting for 5 minutes, the reverse of the above protocol is carried out. First, the magnetic field is decreased up to the desired H_{pause} and paused there, allowing for the detection of non-field driven effects. Then, the magnetic field is removed completely and the thermal reset performed, allowing for another measurement to take place.

Chapter 4

LaFeSi Dynamics

In this chapter the complete characterization of the magnetic and structural phase transitions of the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ alloy will be described and analysed. First these are discussed separately and then, in the last subsection, the interplay between the structural and magnetic lattices is explored.

4.1 Magnetic Phase Transition

A complementary characterization of the magnetic phase transition to that presented in reference [46] was performed to not only establish potential sample variability but also to further analyse the relaxation of the magnetization upon magnetic field removal and hence study the (a)symmetry of the transition dynamics.

In performing the magnetic characterization of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ different samples were used, two of which are powdered samples, sample 1 and 2 weighing 28.80 mg and 5.85 mg, respectively, and a third bulk sample, sample 3, which was thermally isolated and weighed 15.14 mg.

4.1.1 Equilibrium Measurements

The first step in characterizing the phase transition of the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample is to determine its Curie temperature as accurately as possible. This may be achieved by measuring the magnetization of the sample as a function of temperature, as presented in Figure 4.1. Here, the temperature range was swept at 1 K min^{-1} , ensuring as close to equilibrium conditions as possible, at the low applied magnetic field of 0.01T.

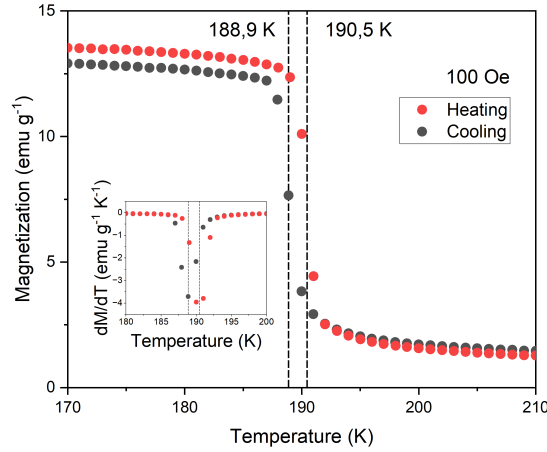


FIGURE 4.1: Temperature dependence of the magnetization measured at the low magnetic field of 100 Oe across the PM to FM phase transition of the alloy at 1 K min^{-1} for sample 2. A slight asymmetric behaviour is found, turning the phase transition upon cooling less sharp, as evidenced by the derivative of the magnetization with respect to temperature presented in the inset.

By calculating the derivative of the obtained data, a Gaussian fit may be performed to enable the determination of the temperature at which the slope is maximal, as such, this temperature is taken to equal T_c . An extremely narrow thermal hysteresis of 1.6 K is observed, with both values of T_c , during heating and cooling, in good agreement to those reported for this alloy [46, 70]. The slight asymmetry of the magnetization observed upon cooling has been described as originating from internal pressure arising from neighbouring particles competing for space due to its volume expansion [43].

Secondly, the determination of the critical fields at which magnetic relaxation occurs may be performed by measuring different magnetization as a function of magnetic field curves for the desired set of temperatures. Knowing that magnetic relaxation is bound to occur, the manner in which these curves are obtained is of extreme importance.

With the purpose of determining critical fields H_{c1} and H_{c3} with utmost precision, stable equilibrium measurements obtained at a low magnetic field sweep rate are best, shown in Figure 4.2a. This is due to the fact that these stable equilibrium measurements allow the magnetization to saturate between each measurement, in turn making the transition appear sharper and the mentioned critical fields of easier identification.

On the other hand, M-H loops obtained in a continuous fashion, as shown by the dashed line in Figure 4.2b, where the magnetic field is varied at the constant sweep rate of 5.4 mT s^{-1} between predefined bounds while measurements are taken continuously,

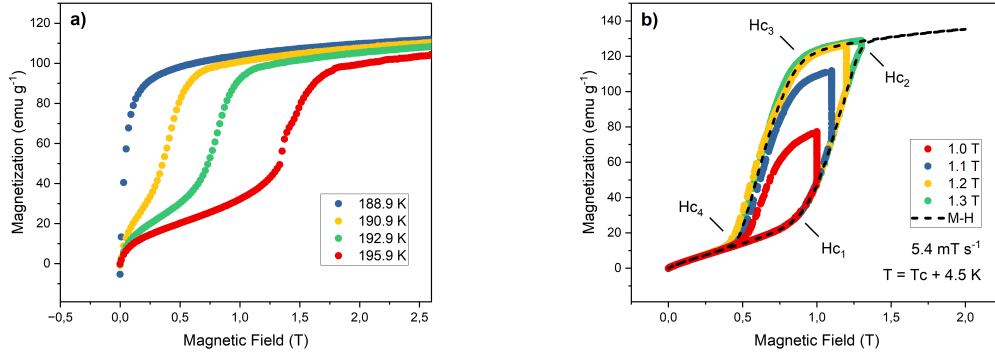


FIGURE 4.2: a) Magnetization as a function of applied magnetic field for a set of temperatures at and above T_c . These measurements were obtained in a step-like stable equilibrium with a magnetic field sweep rate of 1 mT s^{-1} using sample 2. b) Magnetization as a function of magnetic field obtained by varying the magnetic field at a constant sweep rate of 5.4 mT/s and continuously measuring the magnetization using sample 1. The relaxation of the magnetization upon pausing the magnetic field at different stages across the phase transition is observed as vertical lines.

show flaring, which, as previously described in Chapter 2.3.1.3, arises from the increased impact of poor thermal linkage to the bath [49].

However, as these continuous measurements mimic the magnetic field profile during real-world magnetic field cycling, critical fields H_{c2} and H_{c4} obtained in this manner, exhibiting flaring, may be of higher interest as these effectively allow the determination of the magnetic field after which relaxation is no longer observed in cyclic devices operating at the measured magnetic field sweep rate [45, 46].

From Figure 4.2a, the temperature dependence of H_{c1} may be calculated to be the inverse of $4.74 \pm 0.08 \text{ K/T}$, which is in excellent agreement with what has previously been found for this alloy composition, between 4.92 K/T [119] and 4.66 K/T [46], which accounts for a 1.7% and 3.7% relative difference, respectively. These differences are primarily caused by slight variations in the chemical composition of each sample.

4.1.2 Hpause Measurements

Following the protocol described in Chapter 3.3, the kinetics of the phase transition upon magnetic field application and removal were evaluated. As shown in Figure 4.3, the application of a magnetic field between H_{c1} and H_{c2} results in the time evolution of the magnetization after the driving magnetic field is paused at $t = 0 \text{ s}$. Conversely, when removing this magnetic field, from H_{pause} down to 0 T , the magnetization is shown to decrease quickly, thus not exhibiting any non-field driven effects.

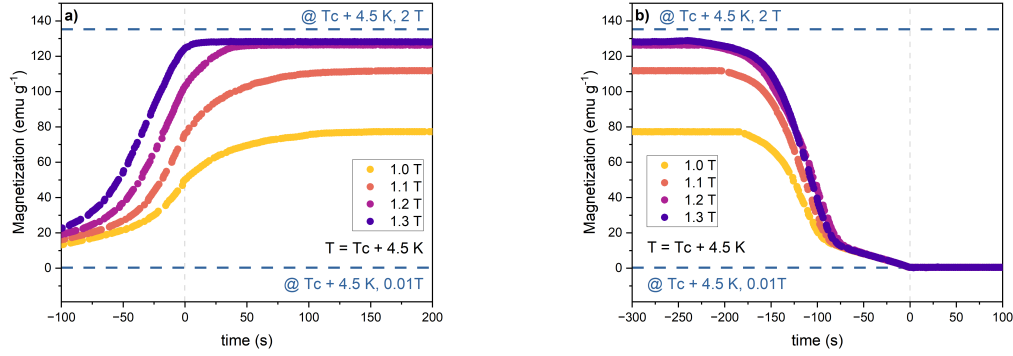


FIGURE 4.3: Relaxation profiles of the magnetization of sample 1 as a function of time as the magnetic field is paused a) after application, up to the presented values of $\mu_0 H_p$, and b) after its complete removal, from these same values until 0 T, where $t = 0$ s represents the point in time the magnetic field reaches 0 T.

Figure 4.2b showcases an alternative perspective on the relaxation of the magnetization. In this figure, the application of the magnetic field up to H_{pause} is shown to follow its dynamically measured M-H loop, obtained at the same sweep rate of 5.4 mT/s. Accordingly, if the magnetic field is paused between H_{c1} and H_{c2} , the magnetization is shown to relax up to a given saturated state, describing a vertical line on the graph.

Conversely to what has been described in reference [46], the saturated magnetization of a specific H_{pause} is shown to not be that of the other tail of the M-H loop, but rather that shown in Figure 4.4.

Here, the obtained magnetization's relaxation profiles upon magnetic field application, shown in Figure 4.3, were fitted with the simple exponential fit, $M(t) = M_{\text{sat}} - M_{\text{rel}}e^{-t/\tau}$, where τ is the system's relaxation constant, M_{sat} is the saturated value of the magnetization, at approximately $t = 200$ s, and M_{rel} is the relaxation's contribution to M_{sat} .

The unsaturated magnetization, defined as that measured when the magnetic field is paused, i.e. $t=0$ s in Figure 4.3a, is shown to be that of the M-H loop, as previously described in Figure 4.2b. Meanwhile, the saturated magnetization, measured at 200 seconds in Figure 4.3a, is shown to only reach the upper tail of the M-H loop if the magnetic field H_{pause} is high enough. Additionally, the time taken to reach saturation, proportional to the value of τ , is observed to decrease as H_{pause} is brought closer to H_{c2} .

The discrepancy between this sample, which does not reach the other tail of the M-H loop upon full magnetic relaxation, and the sample measured in reference [46], which does so, could be attributed to the fact that the sample measured here is a powder, as opposed to bulk. In obtaining a powdered sample, a bulk sample is milled for a duration

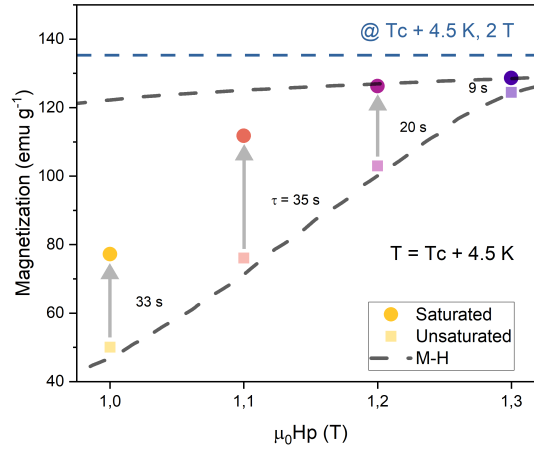


FIGURE 4.4: The observed unsaturated ($t = 0$ s) and saturated values of the magnetization of sample 1 as a function of the pausing magnetic field for the relaxation profiles presented in Figure 4.3 upon field application, together with the time constant separating the two states. The M-H loop obtained dynamically at 5.4 mT/s is used to show how far along the phase transition is induced by relaxation of the magnetization. The horizontal dashed line delimits the magnetic field bound of the transition at 2T.

of time until the desired grain size is reached. This milling process has been shown to induce additional strain and widen the phase transition of the sample [84]. This may be thought as the critical temperature of the individual particles contained in the powdered sample being described by a wider distribution around T_c , but also as the critical fields H_{c1} possessing a similar type of distribution. As a result, applying a magnetic field up to the critical field H_{c1} observed in Figure 4.2b would effectively allow for only a fraction of these particles to undergo the magnetically-induced phase transition. Leaving the remaining particles whose critical field is characterized by $H_{c1} + \delta H_{c1}$ untransformed upon full magnetic relaxation.

4.1.2.1 Relaxation Upon Field Removal

Attending to the striking asymmetry of the magnetization between magnetic field application and magnetic field removal, observed in Figure 4.3, a variation of the described measurement protocol was followed to study in detail the phase transition upon magnetic field removal. Here, as shown in Figure 4.5b, a magnetic field was removed from 2T down to intensities around H_{c3} in a bulk $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample which was thermally isolated, resulting in the magnetization profiles observed in Figure 4.5a.

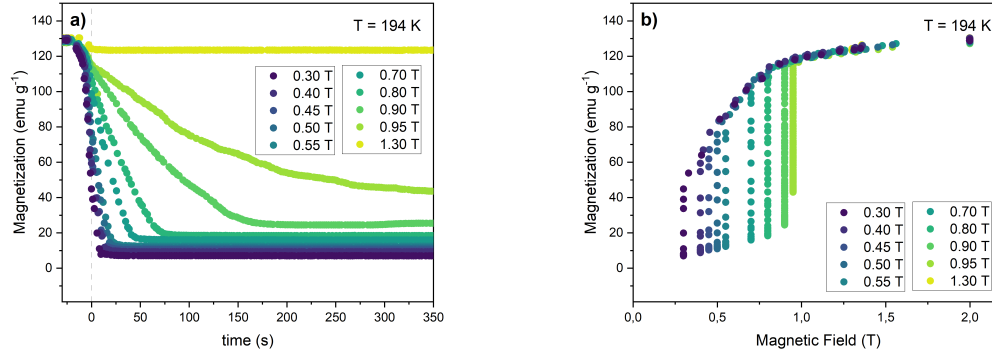


FIGURE 4.5: Relaxation of the magnetization of sample 3 as a function of a) time and b) magnetic field, after an applied magnetic field of 2 T is removed at a constant sweep rate of 70 mT s^{-1} down to the described Hpause value in a thermally isolated bulk sample whose critical field H_{c3} is of 1T. The decreased linkage to the thermal bath is thought to increase the observed relaxation.

The previously described connection of the relaxation with H_{c3} may be observed, as only Hpause values beyond this field result in the relaxation of the magnetization, similarly to how H_{c1} determines the first magnetic field at which relaxation occurs during magnetic field application. Additionally, the observed value of H_{c4} at this magnetic field sweep rate is determined to lie outside of the tested region, as all shown Hpause measurements have some degree of relaxation.

While the asymmetry observed in Figure 4.3 may be explained as the pausing magnetic field of 0.01 T not lying within the range of H_{c3} to H_{c4} , and so no relaxation is observed in magnetic field removal, additional care must be taken to interpret what H_{c4} would mean in this unsaturated magnetic field cycle.

As observed in Figure 4.2b, when the fully saturated FM state is not reached, because the value of Hpause is close to, but higher than, H_{c1} , upon field removal, the trajectory of the magnetization on the M-H graph is not the same. What then arises is an additional degree of complexity in determining the exact values of H_{c3} and H_{c4} , as these now also largely depend on how far along the transition was induced by the first magnetic field application. Note however that, during an incomplete magnetic field cycle, if the magnetization reaches its fully saturated state, as would be the case in bulk samples with sharp phase transitions, there should be no change in value of H_{c4} .

Additionally, similarly to what occurs during fast magnetic field application, the role of thermal linkage to the bath through thermal isolation of the sample is thought to have played an important role in the relaxation profiles observed. In Figure 4.5a, the increase in

adiabaticity from thermally isolating the sample is thought to result in an increase of the magnetization relaxation time, observed to take as long as approximately 300 seconds. Although no relaxation profiles were obtained at this sweep rate upon magnetic field application, a degree of relaxation time asymmetry would be expected between magnetic field application and removal, as the phase transition and its magnetic phases have been reported to be highly asymmetric [43, 120].

4.1.3 Evaluation of the Magnetic Relaxation

4.1.3.1 Magnetic Field Application

In quantifying the evolution of the magnetization past magnetic field application, the relaxation rate, dM/dt , of the phase transition may be derived from the obtained measurements, in addition to the described relaxation time constant, τ .

The magnetization's relaxation rate characterizes the asymptotic behaviour of the magnetization as the magnetic field is paused, at time $t=0$ s. This slope may be calculated numerically through a linear fit to the beginning of the exponential-like relaxation of the magnetization, and denotes the speed at which the magnetization progresses towards saturation at that point in time.

As shown in Figure 4.6a, as H_{pause} is increased past critical field H_{c1} , the relaxation rate is observed to also increase up to a plateau, the beginning of which is given by the value of H_{c2} [46]. Accompanied by the decrease in the observed relaxation time constant, when H_{pause} is increased past H_{c1} , shown in Figure 4.6b, these findings are in line with the previously described reduction in the relaxation time of the magnetization as H_{pause} is brought closer to H_{c2} .

Additionally, the effects of temperature are described and shown to have a smaller impact in the phase transition dynamics at the measured scale. A 3K increase in the sample's temperature, shifting the system deeper into the PM state, was shown to reduce the relaxation rate, dM/dt , resulting in a 8% decrease in the value of its plateau, in turn increasing the time taken to reach the saturated value of the magnetization, evidenced by an increase of the relaxation time constant.

Interestingly, the relaxational effects are shown to not be as sharp as previously described in reference [46], with some degree of relaxation occurring just below H_{c1} . This is thought to arise from strain inhomogeneities of the sample caused by ball milling leading to a broader critical field H_{c1} distribution [84].

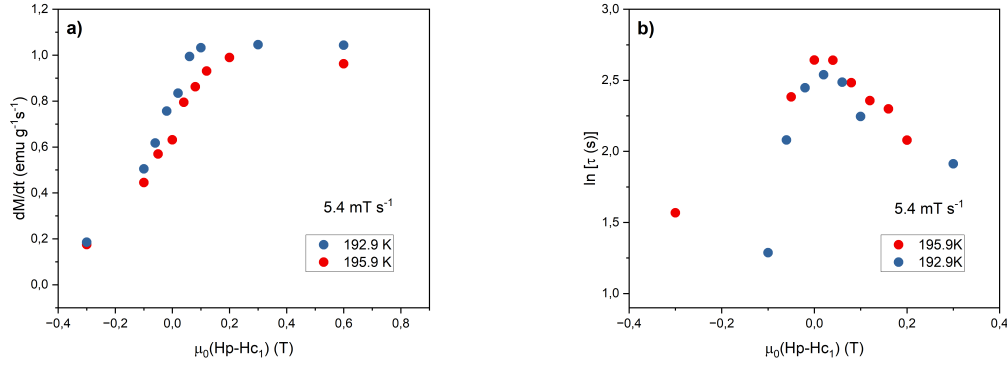


FIGURE 4.6: a) Magnetization's relaxation rate, dM/dt , and b) natural logarithm of the magnetization's relaxation time constant, $\ln \tau$, as a function of how far away from H_{c1} the value of H_{pause} is for a set of temperatures below T_c for sample 2. The relaxation rate was derived from the linear slope of the magnetization's relaxation during magnetic field application, while the relaxation time constant was derived from an exponential fit of the kind $M(t) = M_{\text{sat}} - M_{\text{rel}}e^{-t/\tau}$ to the magnetization's relaxation found in each H_{pause} measurement. Chemical inhomogeneities are believed to have a greater impact in the results shown here, as these were obtained from the small powdered sample 2, ultimately leading to a decrease in the observed relaxation time.

4.1.3.2 Magnetic Field Removal

Similar effects to those observed during magnetic field application were found upon partial magnetic field removal, as the overall shape of the relaxation rate and relaxation time constants plots during magnetic field application and removal are found to be quite similar, although in latter case surrounding critical field H_{c3} , as opposed to critical field H_{c1} .

As shown in Figure 4.7a, the relaxation rate is shown to decrease as the magnetic field is decreased closer to 0T, a special emphasis must be placed on the negative sign of the relaxation rate shown here.

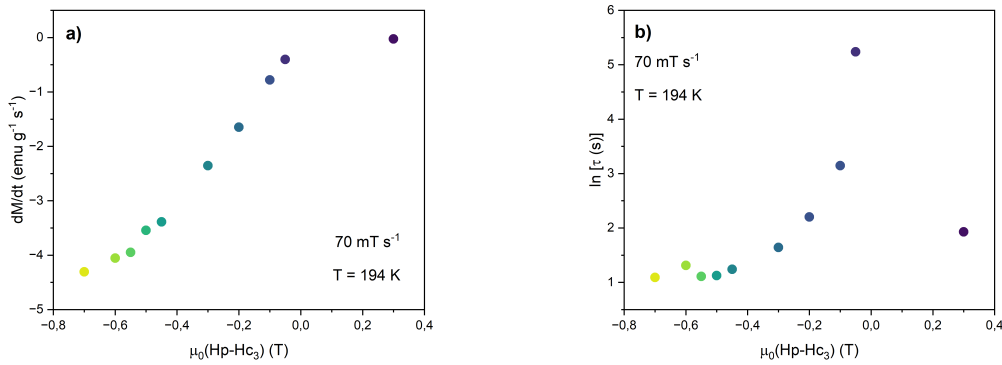


FIGURE 4.7: a) Magnetization's relaxation rate, dM/dt , and b) natural logarithm of the magnetization's relaxation time constant, $\ln \tau$, as a function of how far away from H_{c3} the value of H_{pause} is upon magnetic field removal for the bulk sample 3.

Although no plateau is strictly observed at low H_{pause} , as previously mentioned and observed in Figure 4.5b, the tested conditions do not allow probing of H_{c4} . Otherwise, the symmetry of the system, together with the fast decay of the relaxation time constant as the pausing magnetic field is made smaller, found in Figure 4.7b, could be an indication that such a plateau would exist.

A direct comparison of the saturated values of the relaxation rate found in Figure 4.6a and 4.7a showcases how striking the difference can be between magnetic field application and removal at different sweep rates in a powder sample and a thermally isolated bulk sample, respectively. Although not a straight forward comparison, around a threefold increase in the absolute value of the relaxation rate is observed upon field removal, showcasing the importance of these factors in determining the rate at which the magnetization progresses towards saturation.

Similarly, in comparing the relaxation time constants shown in Figure 4.6b and 4.7b the following is observed. While in Figure 4.6b the logarithm of the relaxation time constant is found to be roughly linear with the value of H_{pause} , when H_{pause} is higher than H_{c1} , the sharper distribution of the critical fields H_{c3} in the bulk sample is thought to cause the remarkable peak in relaxation time observed when the magnetic field is paused at H_{c3} , which is followed by its quick decay as H_{pause} is further decreased, shown in Figure 4.7b.

4.2 Structural Phase Transition

Prior to this work, there was a lack of fundamental understanding of the time dynamics of the structural phase transition, and, since these are coupled, its interplay with the magnetic transition. In the following section, the asymmetry and the kinetics of the isostructural phase transition is investigated through time-dependent X-ray diffraction at one of the most brilliant X-ray sources currently available, the National Synchrotron Light Source II at Brookhaven National Laboratory [113] in the Pair Distribution Function (PDF) beamline.

In performing the structural characterization of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ a powdered sample with tens of milligrams was used.

4.2.1 Equilibrium Measurements

Although the magnetic characterization of the alloy has already allowed for the determination of the Curie temperature and critical fields, differences in experimental apparatus, such as heat conductivity and the sample's distance to the thermocouple, may result in significantly different absolute values for these parameters. As such, X-ray diffraction patterns were obtained as a function of temperature and magnetic field, with the end goal of being able to compare the registered structural relaxation directly to the the previously measured magnetic relaxation through referencing all measurement temperatures back to T_c , $T = T_c + T_0$.

Rietveld refinements were performed to the obtained diffractograms to allow the extraction of the temperature dependence of the lattice parameter, as shown in Figure 4.8. Additionally, a Gaussian fit to its derivative with respect to temperature allowed for the determination of T_c during heating and cooling, as presented in the inset of Figure 4.8.

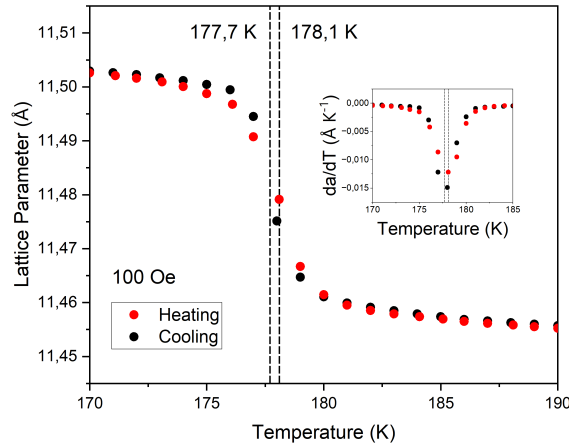


FIGURE 4.8: Temperature dependence of the lattice parameter measured across the PM-FM phase transition of the alloy at 1 K min^{-1} . Its derivative, shown in the inset, was used in calculating the Curie temperature upon heating and cooling through a Gaussian fit.

Here, the negative thermal expansion of the alloy is observed and its relative volumetric change calculated to be of approximately 0.5% in the short temperature span measured. The observed lattice parameter thermal hysteresis is determined to not only be extremely small, of only 0.4 K, but also smaller than that observed for the thermal hysteresis of the magnetization, determined to be of 1.6 K. Further comparison with magnetic

measurements showcases a difference of 11.2 K and 12.4 K in T_c during cooling and heating, respectively, which, besides apparatus variability, is indicative of the difference in thermal hysteresis width.

Although a tentative lattice parameter as a function of magnetic field measurement was performed, from which the critical field H_{c1} could be extrapolated, using its previously calculated temperature dependence presented in the section 4.1.1, it ended up only being used to guide the measurements performed due to the inherent slight deviations of these calculated values.

As such, keeping in mind what has been discussed in the same section 4.1.1, and attending to the limited time available at the synchrotron, the critical field H_{c1} was ultimately determined through the dynamic measurements of H_{pause} , as shown in Figure 4.9.

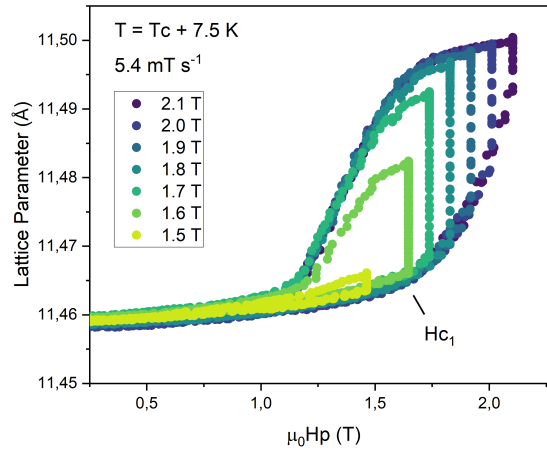


FIGURE 4.9: Lattice parameter as a function of magnetic field obtained by varying the magnetic field at a constant sweep rate of 5.4 mT/s. Upon pausing the magnetic field at different stages across the phase transition, the relaxation of the lattice parameter is observed as vertical lines.

The lattice parameter is shown to always follow a set path until the magnetic field is paused. Here, the first magnetic field observed to onset the magnetically-induced phase transition was taken to equal H_{c1} .

4.2.2 Structural Time-evolution of the Lattice Parameter

The measurement protocol described in Chapter 3.3, with magnetic field application up to H_{pause} , as seen in Figure 4.10a, followed by field removal down to 0T, was followed to characterize the relaxation of the structural lattice when subjected to a magnetic field.

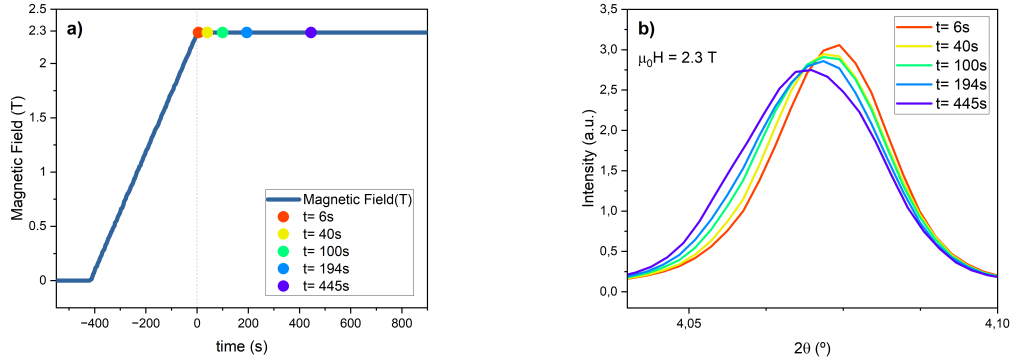


FIGURE 4.10: a) Profile of the applied magnetic field as a function of time describing its application at a constant sweep rate of 5.4mTs^{-1} up to its saturated value of $\mu_0 H_{\text{pause}} = 2.3\text{ T}$, at which point the time is taken to equal zero. b) Time evolution of the diffraction pattern's most intense peak (4 2 2) for the set of points identified as coloured dots in a) after the applied field is paused at $\mu_0 H_{\text{pause}} = 2.3\text{ T}$, 10.5 K above the PM to FM transition.

The resulting time evolution of the sample's structure is clearly observed for the set of diffracted peaks shown in Figure 4.10b, where the presented diffraction patterns were obtained at the same temperature, $T = T_c + 9.3\text{K}$, and at different times after the magnetic field had been stopped at $\mu_0 H = 2.3\text{T}$. Here, the diffraction peak's positions are shown to shift to lower 2θ values after the magnetic field had been paused, corresponding to an increase of the lattice parameter, according to Bragg's law, which is consistent with the sample's field-driven isostructural phase transition, from a low-volume paramagnetic state towards a high-volume ferromagnetic state [37, 70].

Upon analysis of these diffraction patterns through Rietveld refinements the exact time dependence of the lattice parameter is made clear, as the high pattern acquisition frequency and their Rietveld refinements provide an accurate time-dependent evolution of the crystal lattice, including, although not limited to, its lattice parameter. In Figure 4.11 an example of a Rietveld refinement is shown, together with its respective raw data, showing good agreement between the two.

As observed, the lattice exhibits further relaxation extending beyond the point in time at which the magnetic field is paused.

In establishing the effects of thermal fluctuations and other experimental factors that might have not been accounted for, the time evolution of a zero-field equilibrium measurement was performed and compared to that of a $H_{\text{pause}} = 1.1\text{T}$ measurement, as also shown in Figure 4.12. Attending to the time-invariant nature of the zero-field data and

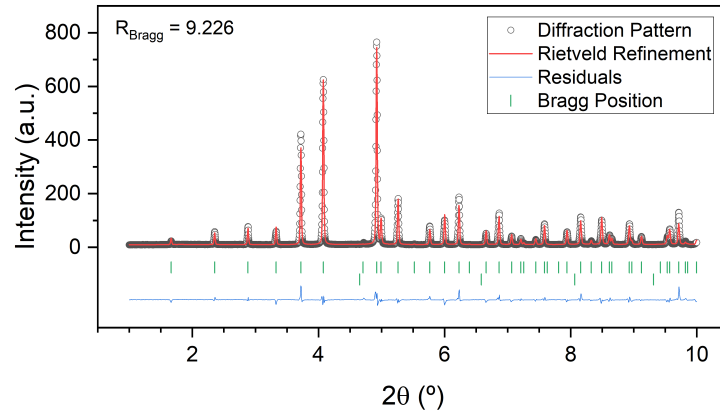


FIGURE 4.11: Complete diffraction pattern of the sample (in circles) at $t = 6$ s, according to Figure 4.10, obtained with a wavelength of $0.1665 \text{ \AA}$, together with the performed Rietveld refinement (in red) and difference between the two (in blue). The reflection angle of the miller planes (in green) lying within the measured range are also shown.

the starting value of the presented curves, the observed relaxation of the lattice parameter can be safely attributed to the kinetics of the magnetic-field induced phase transition.

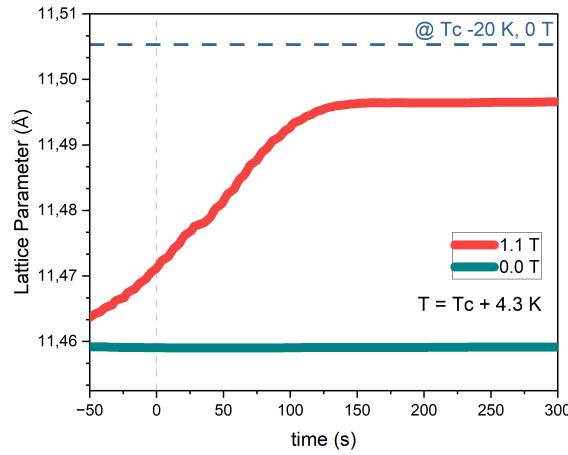


FIGURE 4.12: Time evolution of the lattice parameter obtained from Rietveld's refinements, 4.3 K above T_c , showcasing the role of the magnetic field on triggering the material's isostructural phase transition (in red) in comparison with a zero-field equilibrium measurement (in green).

4.2.3 Magnetic Field Dependence of the Structural Relaxation

A detailed study of the effects of pausing the magnetic field at different intensities, H_{pause} , on the observed structural relaxation was conducted at magnetic fields around and above a critical field, labelled H_{c1} [46] and defined in Figure 4.9.

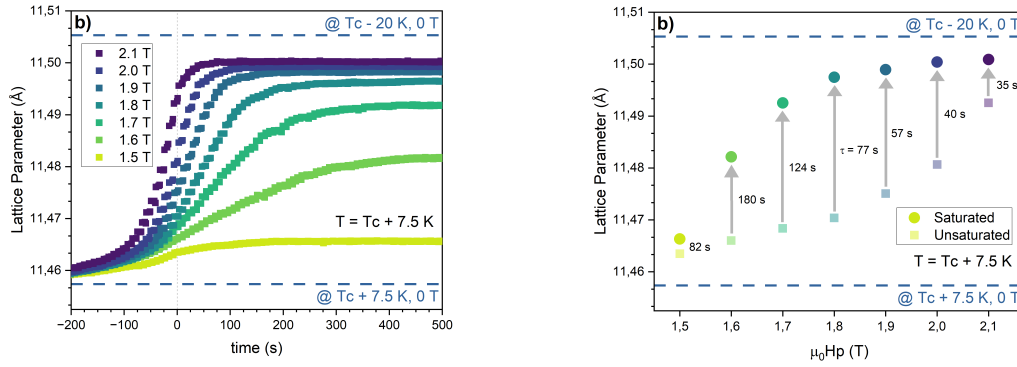


FIGURE 4.13: a) Relaxation of the lattice parameter as a function of time after the applied magnetic field is driven at 5.4 mT s^{-1} and paused at varying intensities across the phase transition, identified in the caption, 7.5 K above T_c . b) The observed unsaturated ($t = 0$ s) and saturated values of the lattice parameter as a function of applied magnetic field for the relaxation profiles presented in a), together with the time constant separating the two states. The horizontal dashed lines delimit the temperature bounds of the structural transition at zero-field, the lattice parameter of the FM state being characterized by its value at $T_c - 20$ K and its PM boundary defined by its value at $T_c + 7.5$ K.

In Figure 4.13a, a sudden increase in the relaxation time of the lattice parameter is observed when the paused magnetic field intensity is equal to that of $\mu_0 H_{c1} = 1.6 \text{ T}$, which is followed by its gradual decrease with increasing intensity of each paused magnetic field, as observed in the presented relaxation time constants, τ shown in Figure 4.13b. Similarly, it is also around this magnetic field that an abrupt increase of the saturated lattice parameter is observed, with only marginal increases when $\mu_0 H_{\text{pause}}$ surpasses 1.8 T , as shown in Figure 4.13b. The displayed dependence of the lattice parameter with magnetic field intensity and time is analogous to that reported by E. Lovell's and co-authors previous work [46] for the magnetization of this alloy following the same H_{pause} protocol. However, the observed structural kinetics seem to suggest these occur at a much larger time scale (hundreds of seconds as opposed to tens of seconds), evidenced when comparing the lattice relaxation times here presented to those exhibited by the magnetization, which in the cited work peaked at around 25 seconds at similar experimental conditions.

4.2.3.1 Evaluation of the Structural Relaxation

The lattice parameter's relaxation in time may be further characterized by its asymptotic slope, as presented in Figure 4.15a, denoting the speed at which the lattice parameter progresses towards saturation as the magnetic field is paused at a given value. As shown in Figure 4.14a, as the pausing magnetic field is pushed past the value of the critical field

Hc1 this relaxation rate takes on values different from zero and, as the pausing field intensity is further increased, the relaxation rate also increases in a linear fashion. These results reaffirm what can be qualitatively seen in Figure 4.13a, as the higher the pausing magnetic field intensity, beyond Hc1, the quicker the material reaches the saturated value of the lattice parameter after the field is paused. Additionally, the material's temperature is shown to have only a minimal effect on the lattice parameter's relaxation rate as it is brought closer to Tc, with no differences being observed for the higher magnetic fields tested.

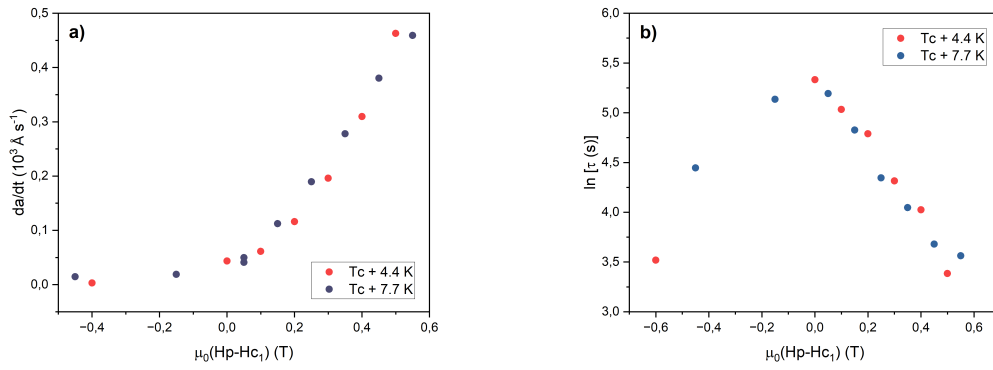


FIGURE 4.14: a) Lattice parameter relaxation rate, da/dt , and b) natural logarithm of the relaxation time constant, $\ln(\tau)$, of the lattice parameter as a function of $\mu_0(H_p - H_{c1})$.

On the one hand, these results are in excellent agreement with what has been reported for the magnetic field dependence of the relaxation rate of the magnetization for this alloy by E. Lovell and co-authors [46], aside from the unobserved plateau of the relaxation rate at high magnetic fields, which could be attributed to the set of magnetic fields tested not having been of high enough intensity. On the other hand, the temperature dependence of the magnetization's relaxation rate was reported to be of an increase as the temperature of the alloy is brought closer to Tc, which is in stark contrast with the presented insignificant changes observed for the lattice parameter's relaxation rate.

Upon fitting the obtained lattice parameter's relaxation profiles with the simple exponential fit, $a(t) = a_{sat} - a_{rel}e^{-t/\tau}$, as shown in Figure 4.15a and similarly to that performed for the magnetization, where τ is the system's relaxation constant, a_{sat} is the saturated value of the lattice parameter and a_{rel} is the relaxation's contribution to a_{sat} , the following Figure 4.14b was constructed.

Here a peak in τ , which is proportional to the relaxation time of the lattice parameter, is observed when the pausing magnetic field is equal to that of the critical field Hc1.

Furthermore, the exponential decay of τ observed with increasing values of the paused magnetic field, together with its unchanging temperature dependence, is consistent with the presented increase of the lattice parameter's relaxation rate. While these findings further highlight the importance of phase transition dynamics in overcoming the structural relaxation observed, and hence maximizing cyclability, they also suggest that temperature has a negligible effect in these dynamics outside of determining the critical field, H_{c1} , at which the phase transition is triggered. Once again, this is unexpected considering the magnetostructural nature of the phase transition and what has been reported in reference [46] for the magnetization of $\text{La}(\text{Fe}_{11.6}\text{Si}_{1.4})$.

4.2.3.2 Transition Direction Asymmetry

The atomic structure was investigated for the span of a full magnetic field cycle, field application and halt followed by complete field removal, enabling the assessment of the (a)symmetry of the phase transition. As evidenced by Figure 4.15a and 4.15b, there is a striking contrast between the atomic structure time-dependent evolution on ramping the field up, forward transition, versus ramping the field down, backwards transition. In the latter, there is no observable time-dependent structural relaxation as the isostructural transition is completed while the field is still ramping down, i.e., at a non-zero magnetic field. As such, after the field reaches zero, there is no time-evolution of the lattice parameter as the transition was already completed whilst the field was ramping down.

Interestingly, this time-dependent asymmetry between the forward and backward directions was also observed for its magnetization counterpart, as can be seen in Figure 4.3. Additionally, the larger time-span necessary to achieve the phase transition during magnetic field application is akin to the observed slopped temperature dependence of the phase fractions during cooling, while its quick time progression towards its PM baseline upon magnetic field removal is similar to that observed for the phase fractions upon heating [43]. Therefore, suggesting a similarity between magnetic field application/removal and cooling/heating of the sample, respectively [121]. Although the latter has been explained to arise from neighboring particles competing for space as they increase in volume, as will be demonstrated below, the time-dependent asymmetry of the phase transition can be explained on the grounds of the different energy landscapes and corresponding energy barriers a state must overcome in the forwards and backwards directions.

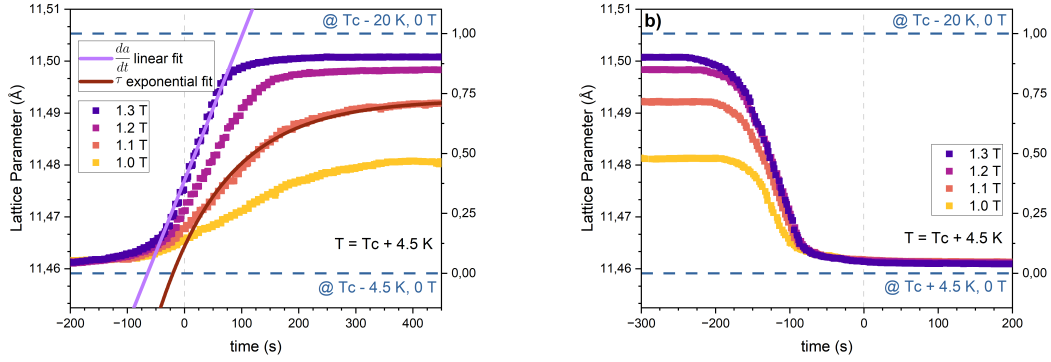


FIGURE 4.15: Relaxation profiles of the lattice parameter as a function of time as the magnetic field is paused a) after application, up to the presented values of $\mu_0 H_p$, and b) after its complete removal, from these same values until 0 T, where $t = 0 \text{ s}$ represents the point in time the magnetic field reaches 0 T. In a) an example of a linear and b) exponential fit employed to extract the relaxation rate, da/dt , and relaxation time constant, τ , is shown.

This striking asymmetry reinforces the role that the magnetic field has on triggering the structural transition and further suggests the idea that the structural and magnetic transitions are linked, given that, when the magnetic field is removed and the magnetization of the material quickly goes to zero, the structure follows suit. Similarly, when the magnetic field is applied and the magnetization slowly relaxes to its saturated state [46], the structure exhibits equally impressive relaxation times.

The effect of varying the magnetic field sweep rate can be observed in 4.16, where, despite the small sweep rate range examined, a clear increase in the lattice parameter's relaxation time constant, τ , is observed with increasing sweep rate, going from 97 and 109 seconds, at 1.8 mT/s and 3.6 mT/s respectively, to 120 seconds at 5.4 mT/s. In spite of this, the total time taken for the material to undergo the magnetic field induced transition, including the magnetic field application time, decreases as the magnetic field sweep rate is increased, which comes in agreement to what had previously been reported for the magnetic phase transition of the alloy [46].

4.2.3.3 Interatomic Distances

As the magnetic properties in this family of alloys are strongly correlated with the interatomic distances between Fe atoms [63, 79], the nearest neighbour interatomic distances were extracted from the Rietveld refinements and plotted as a function of time in Figure 4.17, corresponding to the distances d_1 and d_3 shown in Figure 2.9 in Chapter 2.4.

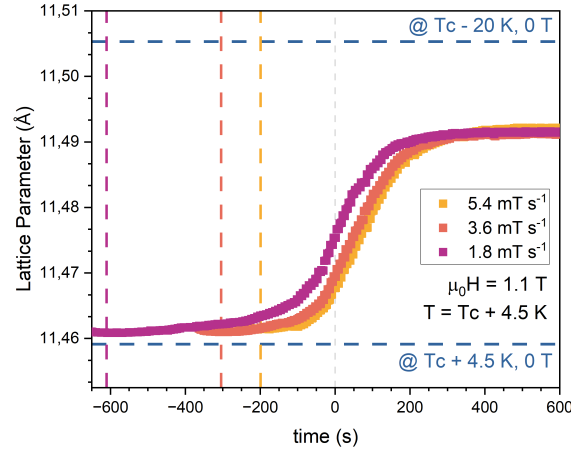


FIGURE 4.16: Relaxation profiles of the lattice parameter as a function of time when the magnetic field is driven at different magnetic field sweep rates up to the same value of H_{pause} .

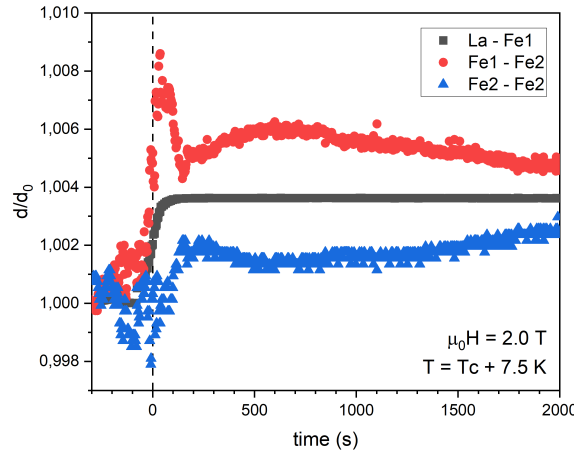


FIGURE 4.17: Time dependence of the relaxation of the interatomic distances normalized to their value before magnetic field application. The interatomic distance La-Fe1 is equal to half of the lattice parameter.

Here each set of distances was normalized to its length at zero magnetic field, and so the time evolution of these can be compared relative to one another. Additionally, the distance La-Fe1 is effectively half of the lattice parameter and so they may be used interchangeably.

As observed, already accounting for the increase in unit cell volume related to the magnetic field driven isostructural phase transition, delimited by the distance La-Fe1, a further change in the Fe1-Fe2 and Fe2-Fe2 nearest neighbour interatomic distances is observed. The disproportionate increase of approximately 0.25% in distance between the

nearest neighbours Fe1-Fe2, equivalent to the radius of each Fe2 icosahedron centered around each Fe1 atom, together with a decrease of approximately 0.2% in the nearest neighbour Fe2-Fe2 interatomic distance, which corresponds to the distance between the edges of these Fe2 clusters, is indicative of the Fe2 cluster getting disproportionately bigger when compared to the expected expansion due to the unit cell volume increase of the isostructural phase transition, which, by lengthening the bonds between Fe atoms, is expected to account for the onset of ferromagnetism of the phase transition.

Interestingly however, there are two peaks in the time evolution of the Fe1-Fe2 distance, one which quickly vanishes, at approximately 200 seconds, and another one, which is broader, reaching its highest 600 seconds after the magnetic field is paused, slowly decaying closer to the baseline of the unit cell volume thereafter. While comparison with the relaxation of the lattice parameter could suggest the former is responsible for the relaxation of the magnetization, case in which the relaxation of the lattice parameter would cease simultaneously with that of the magnetization, this could also indicate that the material is still undergoing its magnetic phase transition, long after its lattice parameter has stabilized.

4.3 Magnetostructural Coupling

With the aim of shedding light at the relationship between the magnetic and structural phase transitions, and to assess how the two are (de)coupled, the observed time dependence and asymmetries of the phase transition are evaluated through direct comparison with the magnetization and volume dependent free energy landscape of a compressible 3D Ising lattice. First however, the magnetic and structural relaxation profiles are compared directly in the following Figure 4.18.

In comparing these relaxations the temperature distance to T_c and the intensity of each H_{pause} was kept the same, ensuring as close of a comparison as possible without actually measuring both quantities, lattice parameter and magnetization, simultaneously.

As observed in Figure 4.18a, for the same H_{pause} , the magnetization saturates more quickly than the lattice parameter. This could indicate that the extremely long relaxation time of the Fe1-Fe2 distances observed in Figure 4.17 does not have an impact on the magnetization of the alloy, and its the shorter peak observed which is responsible for the onset of ferromagnetism. Meanwhile on magnetic field removal, Figure 4.18b, both

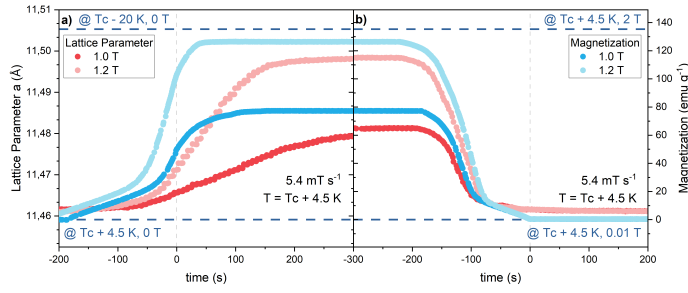


FIGURE 4.18: Relaxation of the lattice parameter, a , and of the magnetization (of sample 1), M , after a) the magnetic field is driven and paused at the specified value of H_{pause} , and b) the magnetic field is removed from H_{pause} to 0T. The horizontal lines depict the temperature and magnetic field bounds of the phase transition used to delimit the structural and magnetic phase transitions, respectively.

the magnetization and lattice parameter seem to decay extremely quickly and reach their respective saturated states 100 seconds before the magnetic field reaches 0T.

The relaxation rate of the magnetization and lattice parameter are compared in Figure 4.19 by normalizing their values to the bounds of the phase transition presented in Figure 4.18. In achieving this comparison a degree of subjectiveness is added in describing how far along the phase transition is considered to be saturated, as a magnetic field of 2 T, for the magnetization, is implicitly made to be equivalent to lowering the temperature of the sample 20 K below its T_c , for the lattice parameter.

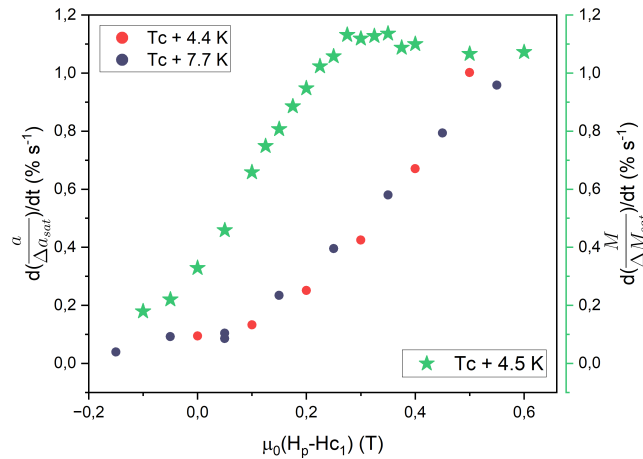


FIGURE 4.19: Relaxation rates of the lattice parameter, a , in circles, and of the magnetization (of sample 1), M , in stars, as a function of the distance of H_{pause} to critical field H_{c1} . These were compared by normalizing their respective values to the temperature and magnetic field bounds of the phase transition, shown in Figure 4.18.

Nevertheless, the relaxation rate of the magnetization is observed to be faster than that of the lattice parameter. However, as the relaxation rate of the magnetization is observed

to saturate at a lower magnetic field than that of the lattice parameter, which is not shown to saturate in the tested range, the critical fields H_{c2} of the lattice and of the magnetization are inferred to not be the same. This difference in H_{c2} could arise from the saturation of the exchange interaction.

4.3.1 Modelling of the Magnetovolume Phase Transition

To gain further insight on the experimentally observed structural and magnetic kinetics of $\text{LaFe}_{11.6}\text{Si}_{1.4}$, a comparable magnetic system was kindly modelled by Prof. Dr. João Amaral from the Department of Physics and CICECO at University of Aveiro. The system comprises of a compressible 3D lattice, where the interaction energy includes magneto-volume coupling [122]:

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} \left[J(v) S_i \cdot S_j \right] + \frac{1}{2} K v^2 - M H \quad (4.1)$$

In Equation 4.1, J is the magnetic exchange parameter between S_i and S_j nearest neighbor spins, v is the volume and K the compressibility. The dependence of J on volume is given by $J(v) = J_0 + J'(v - v_0)/v_0$, where v_0 is the volume at the paramagnetic limit, with corresponding J_0 . J' is an adjustable parameter which drives the first-order transition. The simulated lattice is of a cubic array of Ising spins, each representing an (Fe,Si) icosahedron of the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ unit cell. An agreeable comparison between experimental isothermal magnetization data and simulation, particularly for the critical field dependence on temperature and applied field, is reach considering a spin value of $7/2$ for each (Fe,Si) icosahedron, as shown in Figure 4.20.

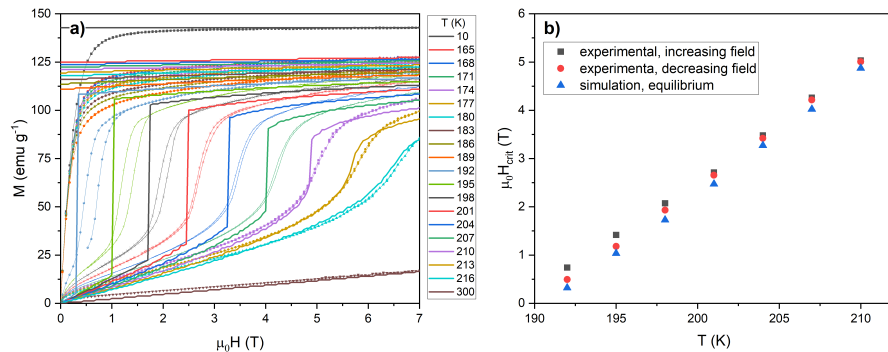


FIGURE 4.20: a) Experimental (solid symbols) and simulated (solid lines) isothermal magnetization data and b) corresponding critical field dependence on field and temperature. Image obtained from Prof. Dr. João Amaral from the Department of Physics and CICECO at University of Aveiro.

After its validation by direct comparison with the experimental lattice parameter and magnetization data, measured as a function of temperature and magnetic field under equilibrium conditions, as observed in Figure 4.18, the Gibbs energy was simulated for a wide range of temperatures, magnetic fields, magnetization and lattice parameters. As presented in Figure 4.21a and 4.21b, these were then grouped together to form the energy landscape of the system for a given temperature and magnetic field, where isoenergy levels are represented as closed loops.

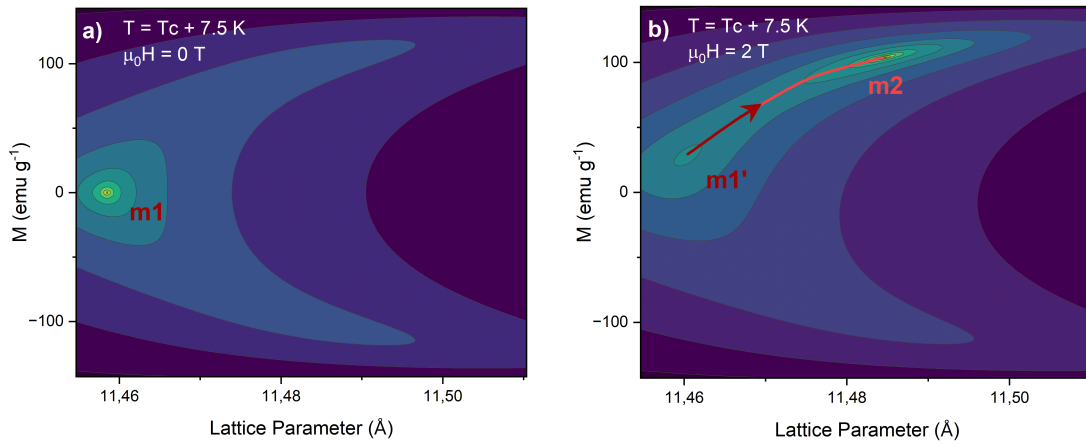


FIGURE 4.21: Contour plots of the simulated free Gibbs energy landscapes of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ as a function of the lattice parameter and the magnetization, 7.5 K above T_c , at a) 0 T and b) 2 T. These contour plots, from low, in white, to high, in yellow, energy values, show a single minimum at 0 T, denoted as m1, which is replaced by two minima at 2 T, denoted as m1' and m2, as highlighted in each plot.

As observed in Figure 4.21a, the energy landscape at zero magnetic field predicts a single minimum of the Gibbs energy at zero magnetization and just below 11.46 Å, denoted by m1. This minimum is then replaced by two local minima when a magnetic field of 2 T is simulated, one minimum in the vicinity of the 0 T minimum, with slightly higher magnetization and lattice parameter values, denoted as m1', and another which occurs at high magnetization and high lattice parameter, denoted as m2. However, when taking a closer look at the energy profile as a function of lattice parameter alone, shown in Figure 4.22a, the high lattice parameter minimum m2 is revealed to have a slightly lower energy value than m1', hence turning it into the global minimum, corresponding to a stable state, while the other local minimum m1' corresponds to a metastable state.

As such, during the transition from the local minimum m1' (metastable state) to the absolute minimum m2 (stable state), the system must first traverse an upward energetic slope to reach the local maximum (path section in dark red) and then descend towards

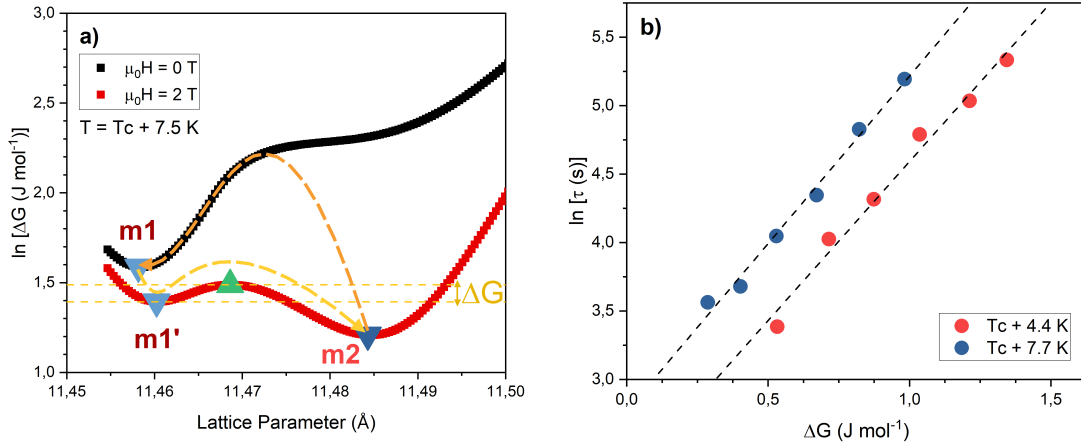


FIGURE 4.22: a) The Gibbs energy landscape of the lattice parameter shown for 0 T and 2 T, where the route taken by the equilibrium value of the lattice parameter is denoted by a yellow arrow, for magnetic field application, and an orange dashed arrow, for magnetic field removal. The local maximum and minima are represented by up and down triangles. The energy barrier, ΔG , associated with surpassing the local maximum is represented by the horizontal yellow dashed lines. b) The natural logarithm of the relaxation time constant, $\ln(\tau)$, as a function of the energy barrier, ΔG . A representative line of best fit to each temperature is presented, displaying these as parallel.

the absolute minimum (path section in light red in Figure 4.21b). The local maximum which separates these minima is indicative of an energy barrier which must be overcome for the system to reach its lowest energy state from its initial metastable state. For a given temperature and magnetic field combination, the height of this barrier, ΔG , represented in Figure 4.22a, was calculated and plotted in Figure 4.22b as a function of the relaxation time constant previously presented in Figure 4.14b. The m1 and m2 states above described are the equivalent to the experimentally measured lattice parameter (and magnetization) states observed at 0 T and 2 T, respectively.

As shown, an increase in the energy barrier can be linearly correlated with an increase in the natural logarithm of the lattice parameter relaxation time for magnetic fields above H_{c1} . The linearity of the logarithm of the relaxation time constant with the simulated energy barrier is indicative of a nucleation and growth process by activation over an energy barrier. In contrast to the previously reported thermally activated growth process observed in the magnetically induced FOPT of $Gd_5(Si_{0.5}Ge_{0.5})_4$ [44], the parallel slopes found in Figure 4.22b provide additional evidence that the growth process is not thermally activated [46].

By the same token, the absence of an energy barrier in the energy landscape when no magnetic field is applied, meaning only one minimum is observed, suggests no relaxation should be observed on full magnetic field removal, which coincides precisely with what

is observed in Figure 4.15a and 4.15b, and hence explains the asymmetric behaviour of the lattice parameter's and magnetization's relaxations.

A similar situation can be argued for the magnetization, as observed in Figure 4.23.

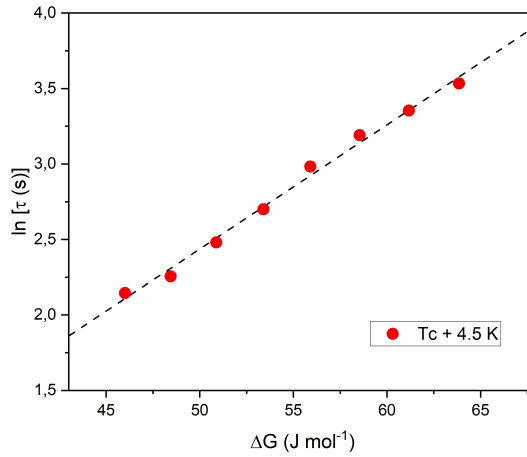


FIGURE 4.23: The natural logarithm of the relaxation time constant of the magnetization of sample 1, $\ln(\tau)$, as a function of the energy barrier, ΔG . A representative line-of-best-fit is presented.

Here, the logarithm of the relaxation of the magnetization is shown to linearly increase as the height of the energetic barrier is increased for Hpauses between H_{c1} and H_{c2} , providing additional evidence of a nucleation and growth process by activation over an energy barrier. In distinguishing the nature of the activation process, the similarity between the magnetic and lattice energy landscapes, previously shown in Figure 4.21, could also favour the interpretation that it is not a thermally activated process.

Similarly to that discussed for the lattice, the absence of an energy barrier upon full magnetic field removal also suggests no relaxation should be observed, which aligns with experimental observation. However, at magnetic fields higher than H_{c4} , the presence of an energy barrier in the reverse direction is observed, corresponding that observed in the trajectory from the m_2 to m_1' in Figure 4.21b. Here, when m_1' becomes a global minimum, as the magnetic field is decreased from 2 T, the energy state m_2 would become metastable and relaxation would ensue, corresponding to critical field H_{c3} , as experimentally observed.

4.4 Two-Phase Approach

When peaks of higher scattering angles were analyzed in the diffraction pattern, as shown in Figure 4.24, the application of a magnetic field was revealed to split each of the zero-field peaks, signaling the coexistence of the PM (low-volume) and the FM (high-volume) phases, consistent with a first order transition.

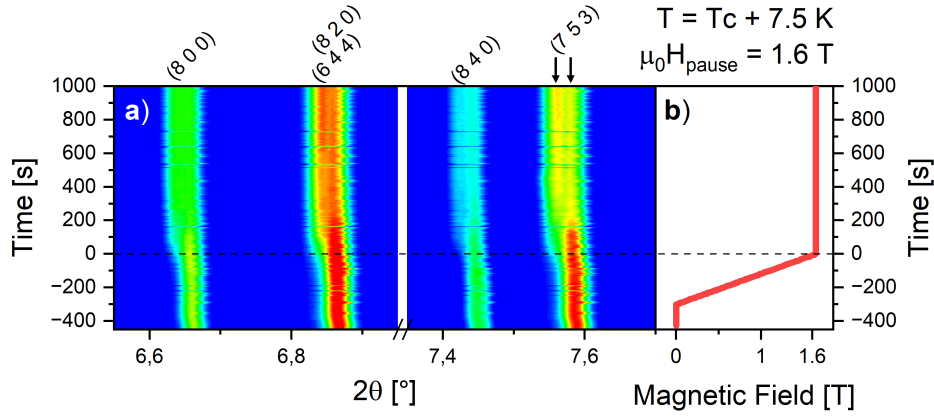


FIGURE 4.24: a) Time evolution of a selected region of the diffraction pattern where the coexistence of the PM and FM phases is clearly observed. b) Profile of the magnetic field applied in a) as a function of time describing its application at a constant sweep rate of 5.4 mT s^{-1} up to $\mu_0 H_{\text{pause}} = 1.6 \text{ T}$ at 7.5 K above T_C , at which point the time is set to zero.

As such, a two-phase model for the Rietveld fitting of the X-ray diffraction data was employed with the help of John S.O. Evans from Durham University with software TOPAS.[123, 124] In Figure 4.25 an example of such a Rietveld refinement is shown, showing good agreement between the measured and the calculated patterns.

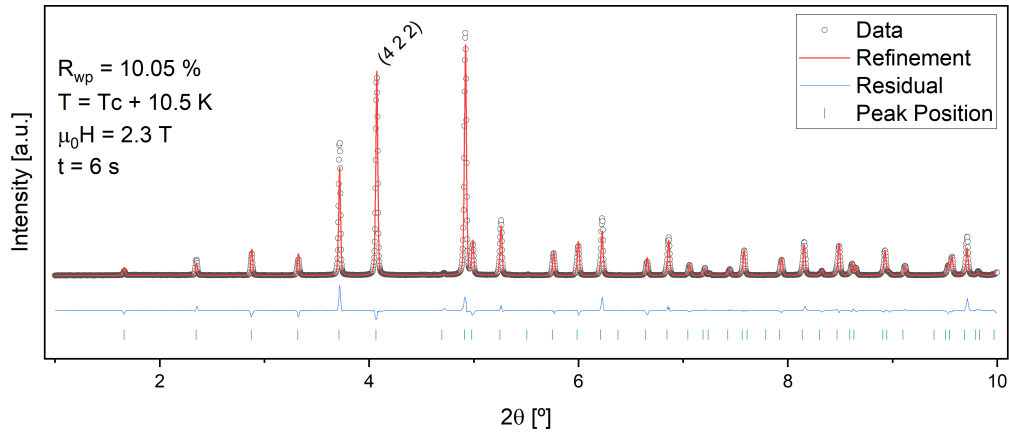


FIGURE 4.25: Illustrative diffraction pattern of the sample at $t = 6 \text{ s}$ (black open circles), together with the Rietveld fit (red line) and the difference between the two (blue line). The Bragg reflection angles (vertical green bars) for the PM phase are also shown.

With this model, the simultaneous tracking of the individual cell parameter (a) of each phase and their phase fraction (f) as a function of time was possible, as observed in Figure 4.26 in the Supporting Information. By combining each of these fractions with its corresponding cell parameter, the time evolution of the weighted cell parameter was calculated as follows in Equation 4.2.

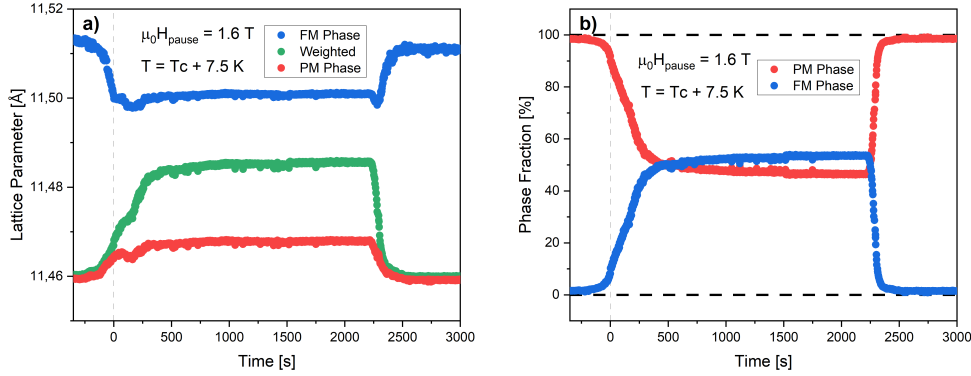


FIGURE 4.26: Relaxation of the a) lattice parameter and b) phase fraction of the PM (red) and FM (blue) phases as the field is driven up to $\mu_0 H_{\text{pause}} = 1.6 \text{ T}$ at 7.5 K above T_C . A complete magnetic field cycle is presented, where $t = 0 \text{ s}$ denotes the time at which magnetic field application was stopped. The weighted lattice parameter (green) was then calculated attending to the fraction and lattice parameter of each phase, as shown in a).

$$\langle a \rangle = a_{PM} f_{PM} + a_{FM} f_{FM} \quad (4.2)$$

As shown in Figure 4.27a) and Figure 4.27b) for a given temperature and set of values of H_{pause} , the FM phase fraction (f_{FM}) and the weighted cell parameter ($\langle a \rangle$) exhibit relaxation beyond the point in time at which the magnetic field is paused (set as $t = 0$, for easy reference), allowing for the determination and comparison of the relaxation times observed for each of the different experiments performed.

Inspection of the relaxation profiles presented in Figure 4.26, in particular the relaxation measurement with $\mu_0 H_{\text{pause}} = 1.6 \text{ T}$ at 7.5 K above T_C , reveals the profile of the weighted lattice parameter to be a result of the increase of the FM phase fraction after the magnetic field is paused, and subsequent decrease of the complementary PM phase fraction, coupled with an increase of the PM lattice parameter and decrease of the FM lattice parameter, as had previously been reported.[43] In turn, this may be quantified as 7% of the FM phase having been induced while driving the external field, and an additional fraction of 46% arising after the magnetic field had been halted (when $t > 0 \text{ s}$). Simultaneously, during the application of the magnetic field, the lattice parameter of the FM

phase decreased by approximately 0.1% and stayed constant thereafter. In contrast, the PM lattice parameter increased by almost 0.05% due to magnetic field application and an additional 0.03% during relaxation.

To establish the effects of thermal fluctuations and other experimental factors that might influence these conclusions, the time evolution of a zero-field measurement series was inspected and compared to that of a $\mu_0 H_{\text{pause}} = 1.1$ T measurement series, as shown in Figure 4.27c). Given the time-invariant nature of the zero-field data and the starting value of the presented curves, the observed evolution of the lattice parameter can be safely attributed to the kinetics of the magnetic-field induced phase transition.

4.4.1 Magnetic field dependence of the structural relaxation

A detailed study of the effects of pausing the magnetic field at different field strengths, H_{pause} , on the observed structural relaxation was conducted at magnetic fields around and above a critical field, H_{c1} .

In Figure 4.27b), an increase in the relaxation time of the weighted lattice parameter is observed when $\mu_0 H_{\text{pause}} = \mu_0 H_{c1} = 1.6$ T. This increase is followed by a gradual decrease as H_{pause} further increases, as observed in the corresponding relaxation time constants (τ), shown in Figure 4.27d). These time constants were calculated from k and η through a fit of the kind $f_{FM}(t) = f_{\text{sat}} - f_{\text{rel}} \exp(-kt^\eta)$, as illustrated in Figure 4.27 and discussed in the next section. Similarly, it is also around this magnetic field that a large increase of the saturated weighted lattice parameter and FM phase fraction is observed, with progressively smaller increases as $\mu_0 H_{\text{pause}}$ further increases, as shown in Figure 4.27d). The dependence of the lattice parameter with magnetic field strength and time is similar to that reported for the magnetization of this alloy by Lovell and co-authors' previous work following the same H_{pause} protocol.[46] However, the observed structural kinetics occur on a much longer time scale than those reported for the magnetization, which, in the cited work, peaked at around 25 seconds under similar experimental conditions.

Due to the presence of small plateaus in certain relaxation profiles of the phase fraction, along with disturbances in the time evolution of the lattice parameter of each individual phase, some plateaus occur in the time evolution of the weighted lattice parameter, as shown in Figure 4.26 and in Figure 4.27a) and Figure 4.27b). These resemble the plateaus observed in the relaxation of magnetization, and those observed in the magnetization and phase fraction upon heating/cooling in previous reports.[43, 46] This effect

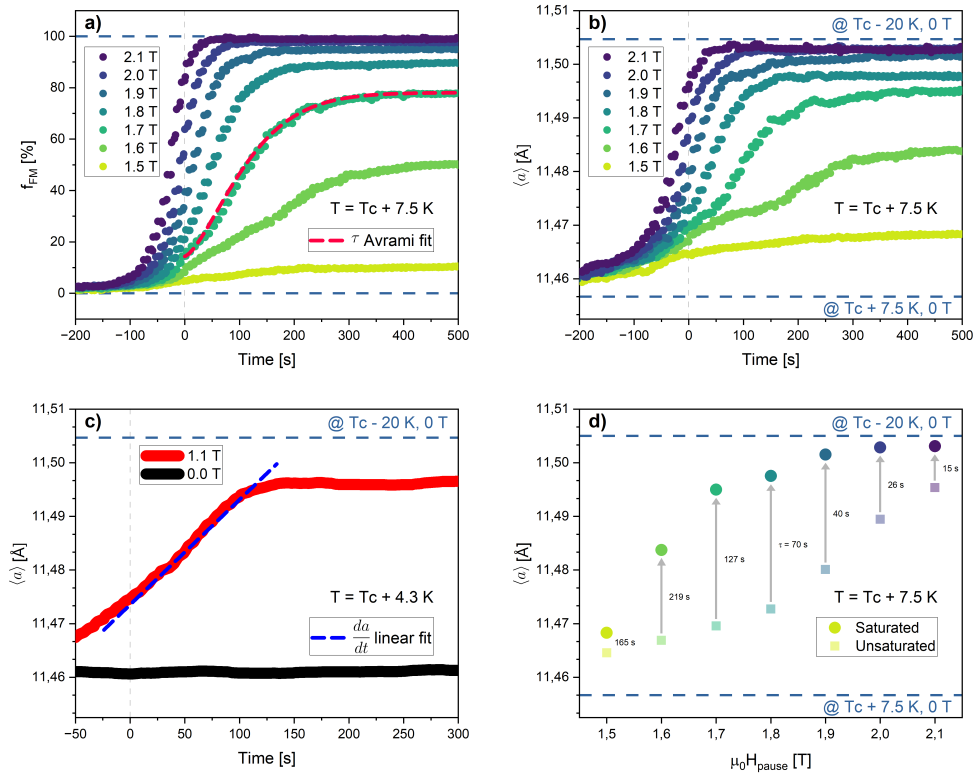


FIGURE 4.27: Relaxation of the a) FM phase fraction and b) weighted lattice parameter as a function of time after the applied magnetic field is driven at 5.4 mT s⁻¹ and paused at varying field strengths at 7.5 K above T_C. c) Time evolution of the weighted lattice parameter, 4.3 K above T_C, showcasing the role of the magnetic field on triggering the material's isostructural phase transition (red) in comparison with a zero-field equilibrium measurement series (black). The a) Avrami and c) linear fits (dashed lines) are shown as employed to extract the relaxation rate (da/dt) and relaxation time constant (τ), as presented in Figure 4.28. d) The observed unsaturated ($t = 0$ s) and saturated ($t = 500$ s) values of the lattice parameter as a function of applied magnetic field for the relaxation profiles presented in b), together with the time constant separating the two states, as presented in Figure 4.28b). The horizontal dashed lines delimit the temperature and phase fraction bounds of the structural transition at the specified conditions.

is most pronounced at magnetic field values of 1.6 T, 1.7 T, and 1.8 T and occurs around the same phase fraction, where structural relaxation consistently displays a two-step behavior. These plateaus are not observed when those fractions are surpassed by driving to a higher magnetic field. Given the powdered nature of the sample and its caloric properties, these plateaus highlight the significant role played by thermal linkage within the sample in influencing the relaxation profiles.

4.4.1.1 Evaluation of the structural relaxation

To facilitate the comparison of our results with those reported by Lovell and co-authors for the magnetization,[46] the lattice parameter's relaxation in time was characterized by

its slope, achieved through a linear fit to the beginning of the relaxation of the lattice parameter, as presented in Figure 4.27c), which quantifies how fast the lattice parameter expands towards saturation as the magnetic field is paused at a given value. As shown in Figure 4.28a), when the pausing magnetic field is increased past the value of the critical field H_{c1} , the relaxation rate increases in a linear fashion. These results are consistent with what is observed in Figure 4.27b), where higher H_{pause} values are shown to reach their respective saturation lattice parameter sooner. Additionally, Figure 4.28a) demonstrates that temperature does not influence the lattice parameter's relaxation rate, with no differences being observed for the magnetic fields tested, suggestive of a phenomenon that is not thermally activated. When plateaus were observed in a relaxation profile, only the major relaxation process was considered, as it exhibited identical characteristics to the others.

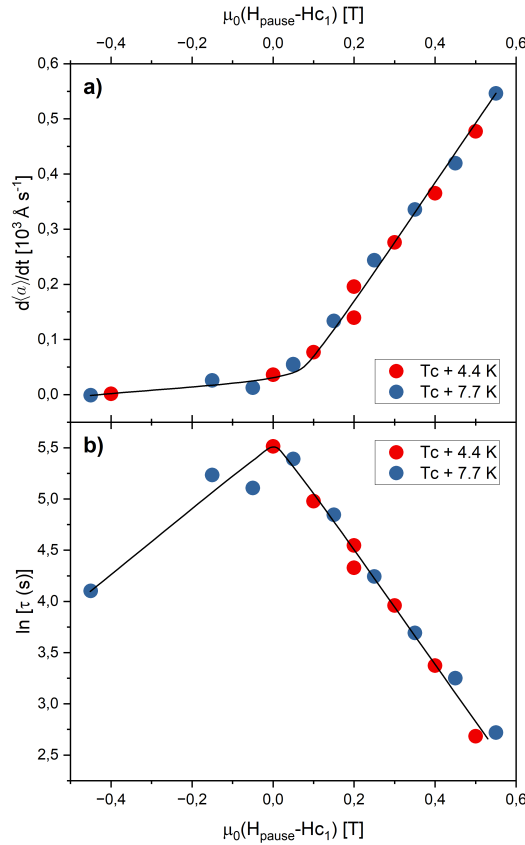


FIGURE 4.28: a) Lattice parameter relaxation rate (da/dt) and b) natural logarithm of the relaxation time constant (τ) of the FM phase fraction as a function of $\mu_0(H_{pause} - H_{c1})$. The relaxation rate (da/dt) was derived from linear fits to the weighted lattice parameter's relaxation, presented in Figure 4.27c), as the magnetic field is paused. The relaxation time constant (τ) was obtained from fitting the phase fraction's relaxation to the Kolmogorov-Johnson-Mehl-Avrami relation and calculated as $\tau = k^{-1/\eta}$.

The lattice parameter relaxation rate results are in excellent agreement with what has been reported for the magnetic field dependence of the magnetization relaxation rate by Lovell and co-authors,[46] aside from the unobserved plateau of the relaxation rate at high magnetic fields, which is attributed to the set of magnetic fields tested not having been of high enough intensity to saturate the phase transition during field application. However, in the cited work, the magnetization's relaxation rate was reported to decrease and subsequently vanish as the temperature of the alloy was raised up to 13.5K above T_C , which is in contrast with the insignificant temperature related changes observed for the lattice parameter's relaxation rate described here. Comparing the relaxation rates of the lattice parameter and the magnetization, measured from the same sample, as shown in Figure 4.29, demonstrated that they exhibit slightly different behavior. Notably, the magnetization exhibits higher relaxation rates compared to the lattice parameter and reaches its saturated value at a magnetic field closer to H_{c1} .

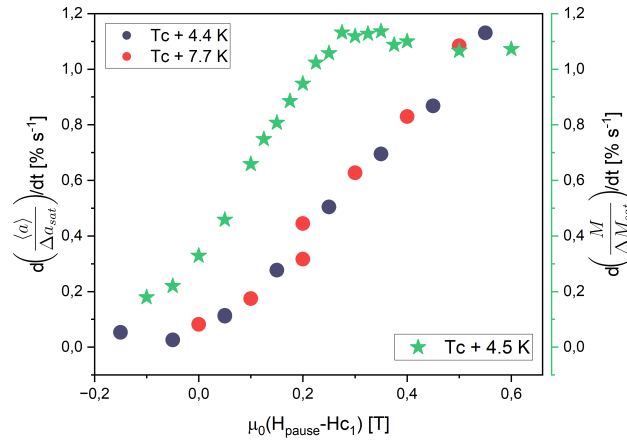


FIGURE 4.29: Relaxation rates of the weighted lattice parameter (circles) and of the magnetization (stars) as a function of the distance of H_{pause} to critical field H_{c1} . These were compared by normalizing their respective values to the temperature and magnetic field bounds of the phase transition.

The experimental phase fraction's relaxation profiles were fitted with the adapted Kolmogorov-Johnson-Mehl-Avrami relation, $f_{FM}(t) = f_{sat} - f_{rel} \exp(-kt^\eta)$, as shown in Figure 4.27a) and Figure 4.30. Here, k is related to the activation energy, η is the Avrami exponent, f_{sat} is the saturated value of the FM phase fraction and f_{rel} is the relaxation's contribution to f_{sat} . This yielded the outcomes presented in Figure 4.28b).

Here a peak in relaxation time constant (τ), calculated as $k^{(-1/\eta)}$, is observed when the pausing magnetic field is equal to that of the critical field H_{c1} . Furthermore, the exponential decrease of τ observed with increasing values of H_{pause} , together with its

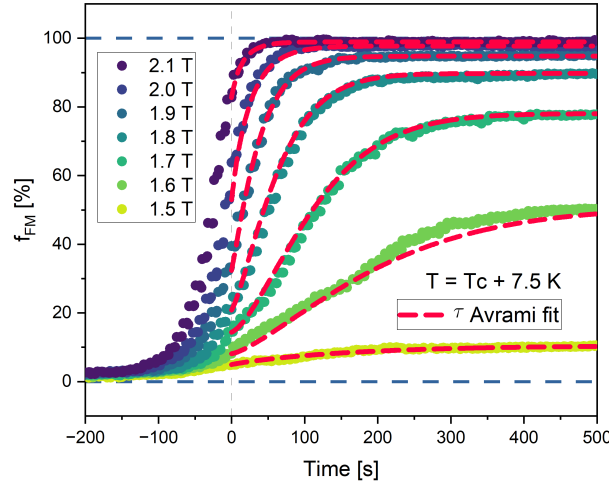


FIGURE 4.30: Relaxation of the FM phase fraction as a function of time after the applied magnetic field is driven at 5.4 mT s^{-1} and paused at varying field strengths at 7.5 K above T_C . The Avrami fits (dashed lines) employed to extract the relaxation time constant (τ) are presented.

invariant temperature dependence, is consistent with the above presented increase of the lattice parameter's relaxation rate. While these findings further highlight the importance of phase transition dynamics in overcoming the structural relaxation observed, and hence maximizing cyclability, they also suggest that temperature has a negligible effect on these dynamics (for the temperature range tested), outside of determining the critical field (H_{c1}) at which the phase transition is triggered. Once again, this is an unexpected feature, given the magnetovolume nature of the phase transition and the reported relaxation process for the magnetization of $\text{LaFe}_{11.6}\text{Si}_{1.4}$, which was found to be neither thermally activated nor athermal.[46]

4.4.1.2 Transition Direction Asymmetry

The phase evolution was investigated for the span of a full magnetic field cycle (field application and halt followed by field removal), enabling the assessment of the (a)symmetry of the phase transition kinetics. As evidenced by Figure 4.31a) and 4.31b), there is a striking contrast between the time-dependent phase evolution on ramping the field up (forward transition) versus ramping the field down (backwards transition). In the latter, there is no observable time-dependent structural relaxation, as the isostructural transition is completed while the field is still ramping down. This was consistent across all tested

temperatures, ranging from $T_C + 4.4$ K up to $T_C + 10.5$ K, during field removal at 5.4 mT s^{-1} .

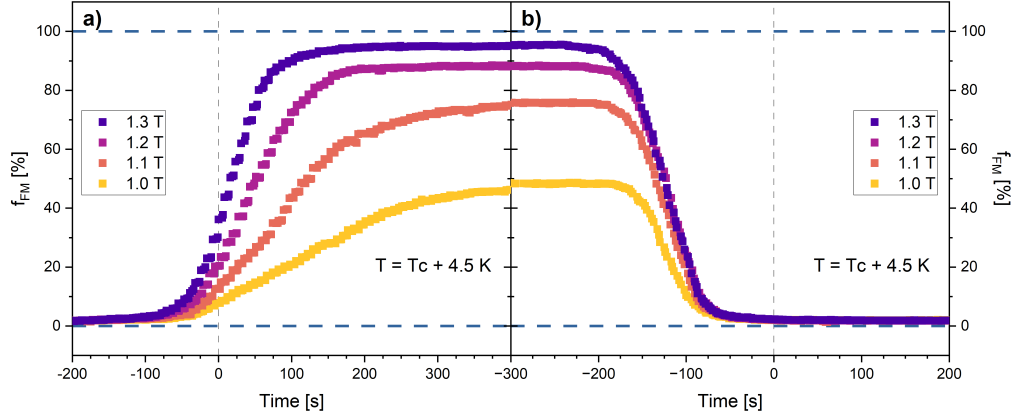


FIGURE 4.31: Relaxation profiles of the FM phase fraction as a function of time as the magnetic field is paused a) after application, up to the presented values of $\mu_0 H_{pause}$, and b) after its removal, from these same values until 0 T, where $t = 0$ s corresponds to the time when the magnetic field reaches 0 T.

Interestingly, this time-dependent asymmetry between the forward and backward directions of the structural phase transition was also observed for its magnetization counterpart under identical conditions (temperature, H_{pause} and field sweep rate), as can be seen in Figure 4.32. Additionally, this temporal asymmetry mimics what is observed during temperature cycling, where the phase transition is sharper upon heating into the PM state, as compared to cooling into the FM state.[43] Therefore, the similarity between the transition asymmetry upon magnetic field application/removal and the transition asymmetry upon sample cooling/heating is reinforced.[121] In bulk materials, this has been postulated to arise from neighboring crystals competing for space as they increase in volume.[10, 43] However, as will be demonstrated below, the time-dependent asymmetry of the magnetovolume phase transition here presented can be explained on the grounds of the different energy landscapes and their corresponding energy barriers.

The effect of varying the magnetic field sweep rate can be observed in Figure 4.33, where a clear increase in the lattice parameter's relaxation time constant (τ) is observed with increasing sweep rate, going from 94 to 107 to 123 seconds, at 1.8 mT s^{-1} , 3.6 mT s^{-1} and 5.4 mT s^{-1} , respectively. Despite this, the total time taken for the material to undergo the magnetic field induced transition, including the magnetic field application time, decreases as the magnetic field sweep rate is increased, which is in agreement to what has previously been reported for the magnetic phase transition of the alloy.[46]

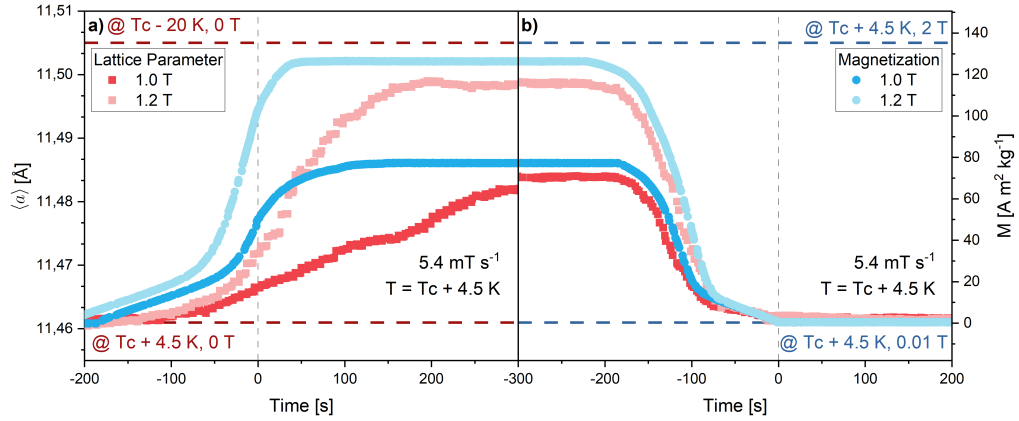


FIGURE 4.32: Relaxation of the weighted lattice parameter (shades of red) and of the magnetization (shades of blue) after a) the magnetic field is driven and paused at the specified value of H_{pause} , and b) the magnetic field is removed from H_{pause} to 0 T. The vertical lines, $t = 0$ s, show the time at which the magnetic field was paused, either a) at H_{pause} or b) at 0 T. The horizontal lines depict the bounds used to delimit the structural (red) and magnetic (blue) phase transitions.

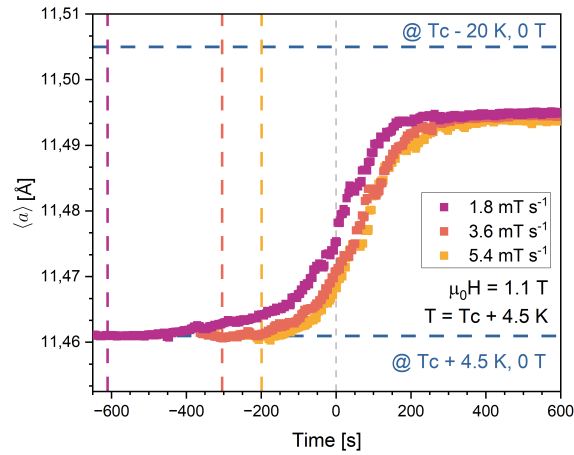


FIGURE 4.33: Relaxation profiles of the weighted lattice parameter as a function of time when the magnetic field is driven at different magnetic field sweep rates up to the same value of H_{pause} . The colored vertical dashed lines show the beginning of the magnetic field ramp for each of the field sweep rates.

4.4.2 Modelling of the magnetovolume phase transition

To gain further insight on the experimentally observed structural and magnetic kinetics of $\text{LaFe}_{11.6}\text{Si}_{1.4}$, the same Hamiltonian model was employed as that presented in Figure 4.21.

As shown in Figure 4.34, an increase in the energy barrier can be linearly correlated with an increase in the natural logarithm of the relaxation time for magnetic fields above

Hc1. The linearity of the logarithm of the relaxation time constant with the simulated energy barrier is indicative of a nucleation and growth process by activation over an energy barrier. In contrast to the previously reported thermally activated growth process observed in the magnetically induced FOPT of $\text{Gd}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_4$, [44] the parallel slopes found in Figure 4.34) provide additional evidence that the growth process is not thermally driven, but instead reflect the material's free energy landscape. [46]

Accordingly, the absence of a second minimum in the energy landscape when no magnetic field is applied, and thus the absence of an energy barrier, suggests that no relaxation should be observed upon complete removal of the magnetic field. This coincides precisely with what is observed experimentally and shown in Figure 4.31a) and 4.31b), and hence explains the asymmetric behavior of the lattice parameter and magnetization's relaxations.

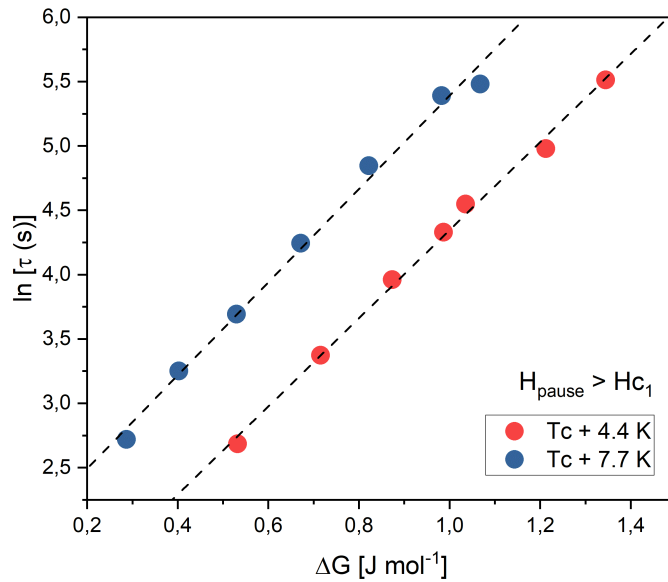


FIGURE 4.34: The natural logarithm of the relaxation time constant (τ) as a function of the energy barrier (ΔG) for magnetic fields above H_{c1} . Linear regressions with slopes $(3.4 \pm 0.2) \text{ mol J}^{-1}$ and $(3.6 \pm 0.3) \text{ mol J}^{-1}$ are presented, corresponding to low and high temperature respectively; demonstrating these are near parallel and hence temperature invariant.

Chapter 5

FeRh Dynamics

In this chapter a similar characterization to that presented for $\text{LaFe}_{11.6}\text{Si}_{1.4}$ will be performed for an $\text{Fe}_{49}\text{Rh}_{51}$ alloy. As highlighted in the Chapter 2.5, the distinctive features of this alloy being its AFM to FM transition with its associated inverse giant magnetocaloric effect and positive thermal expansion of its isostructural phase transition.

5.1 Magnetic Phase Transition

While the magnetic relaxation in this alloy has been the focus of previous studies, as highlighted in Chapter 2.3.1.2, none have yet to perform a comprehensive and methodical characterization of this phenomenon. In addition to the magnetization relaxation upon magnetic field application, an equally strong emphasis will be placed on magnetic field removal.

In performing the magnetic characterization of $\text{Fe}_{49}\text{Rh}_{51}$ a rectangular bulk sample of 34.76 mg was used. This sample originated from a fragment of one of the slices characterized in referenced [88].

5.1.1 Equilibrium Measurements

Determining the critical temperature of the alloy was performed by spanning a wide range of temperatures, in cooling and heating, and measuring the changes in magnetization, as presented in Figure 5.1. Unfortunately, due to the temperature limits specified for the used SQUID magnetometer of 400 K, the FM to PM phase transition of the alloy was not characterized.

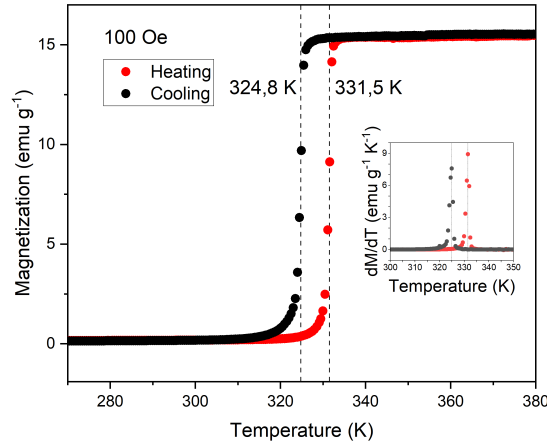


FIGURE 5.1: Magnetization as a function of temperature measured at the low magnetic field of 100 Oe at 1 K min^{-1} . According to its derivative, presented in the inset, the heating and cooling critical temperatures of the AFM to FM phase transition are of 331.5K and 324.8K, respectively.

Here a low temperature phase with low magnetization, the AFM phase, is shown to be overtaken by a high magnetization phase, the FM phase, as the temperature is increased. The critical temperature at which this transition occurs was calculated through a Gaussian fit to the derivative of the measured magnetization with respect to temperature, dM/dT , and found to be of 331.5 K (around 58°C) during heating.

Additionally, thermal hysteresis is found to be of 6.7K, which, although not as impressive as that of $\text{LaFe}_{11.6}\text{Si}_{1.4}$, comes in good agreement to that previously reported for this alloy [93].

Equilibrium magnetization as a function of magnetic field measurements acquired at a low sweep rate were obtained for a set of temperatures, as shown in Figure 5.2a. Here, an increase in temperature is shown to decrease the critical field H_{c1} needed to onset the AFM to FM phase transition, while critical field H_{c3} is shown to disappear when the temperature is above that of the critical temperature during cooling.

Additionally, in Figure 5.2b, magnetization as a function of magnetic field loops obtained in a cyclic manner show flaring as the sweep rate of magnetic field cycling is increased, evidence by the increase in hysteresis width, ΔH . As the magnetic field is applied, the sample undergoes its AFM to FM phase transition and cools down as a result of its inverse magnetocaloric effect. Cooling of the neighbouring particles while the transition is ongoing effectively increases the critical field needed to onset their phase transition,

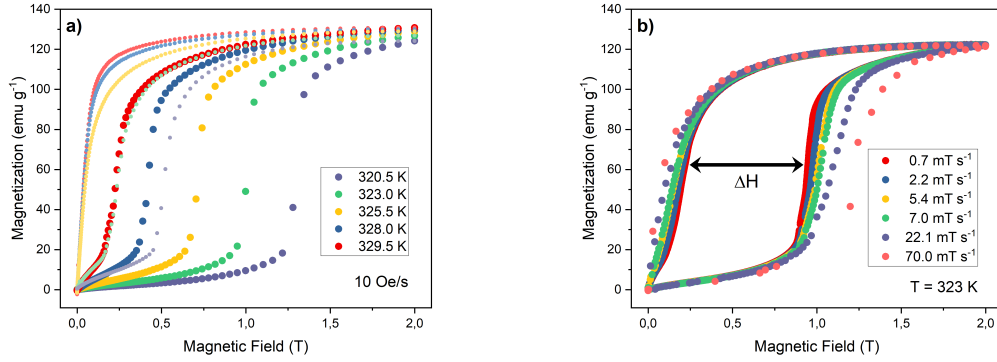


FIGURE 5.2: a) Equilibrium magnetization during application (big circles) and removal (small circles) of a magnetic field for varying temperatures below T_c , obtained at a magnetic field sweep rate of 10 Oe s^{-1} . b) Dynamic magnetization as a function of applied magnetic field curves obtain at 323K, 8.5K below T_c , for a range of magnetic field sweep rates.

resulting in the flaring previously described for a PM to FM phase transition in alloys exhibiting the direct magnetocaloric effect [49].

The exact temperature dependence of the critical fields H_{c1} and H_{c3} is laid out in Figure 5.3 from that observed in Figure 5.2a. The temperature dependence of H_{c1} , $\mu_0 \frac{dH_{c1}}{dT}$, may be calculated to be the inverse of $-8.20 \pm -0.06 \text{ K/T}$, which is found to be in excellent agreement to that previously reported of 8.3 K/T [93] and accounts for a 1.2% relative difference. While the temperature dependence of H_{c3} can be observed to be similar to that of H_{c1} , as only two of the presented points are not saturated due to temperature, the latter could not be precisely calculated.

5.1.2 Hpause Measurements

The protocol described in Chapter 3.3 was followed with the additional probing of magnetic field removal. As such, the magnetic field was firstly applied up to the desired magnetic field, H_{pause} , and kept constant. Then, to probe magnetic field removal, the magnetic field was increased up to 2T, kept there for 5 minutes, and decreased up to the desired magnetic field value, H_{pause} , after which the evolution of the magnetization was measured.

The resulting relaxation of the magnetization measured upon magnetic field application, presented in Figure 5.4a, shows the onset of relaxation to be sharper than that of the previously presented $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample. This is attributed to the fact that the $\text{Fe}_{49}\text{Rh}_{51}$ sample is a bulk sample which exhibits a very sharp phase transition, as evidenced by

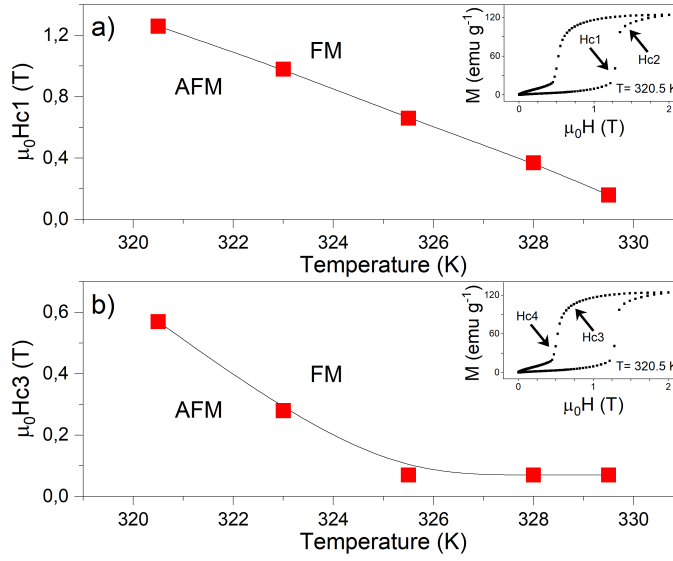


FIGURE 5.3: Temperature dependence of the critical magnetic fields a) H_{c1} and b) H_{c3} , extracted from Figure 5.2. The insets illustrate these during a) field application, H_{c1} and H_{c2} , and b) field removal, H_{c3} and H_{c4} .

Figure 5.1 and 5.2. As a result, the variability in critical fields arising from chemical inhomogeneities in the sample is expected to be low.

Due to the sharpness of the phase transition interesting effects around H_{c1} are observed. Between 0.92T and 0.94T, the magnetization is shown to only exhibit relaxation after around 50 seconds, after which the saturated value of the magnetization is increased. Additionally, while a small fraction of the sample undergoes its phase transition at 0.98T, the longest relaxation time is observed to occur at 1T, the latter coinciding with the critical field H_{c1} determined previously.

Applying increasingly higher magnetic fields yields lower relaxation times, eventually leading to only field driven magnetization changes being measured when H_{pause} is higher than H_{c2} .

The dynamics on magnetic field removal were observed to be similar to those reported for the magnetization of $\text{LaFe}_{11.6}\text{Si}_{1.4}$. Decreasing the magnetic field from 2T down to some value between H_{c3} and H_{c4} results in changes to the magnetization after the driving magnetic field is stopped, as shown in Figure 5.4b.

Contrasting that observed upon magnetic field application, the relaxation effects registered upon magnetic field removal show a less abrupt dependence of the magnetization of the saturated state with the value of H_{pause} .

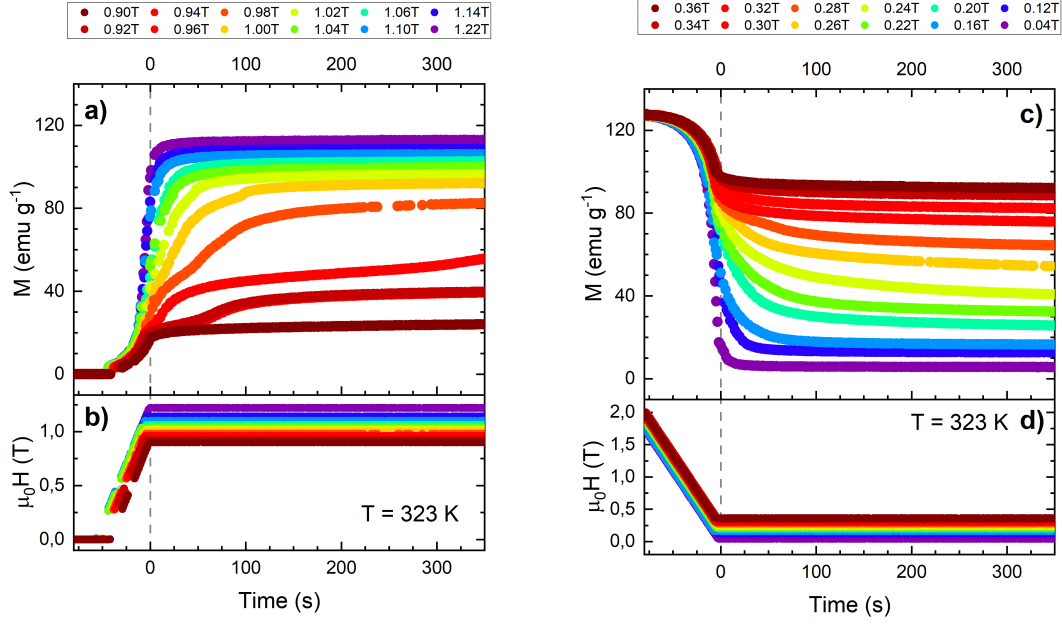


FIGURE 5.4: Profile of the driving magnetic field isothermally b) applied from 0 T and d) removed from 2T at 22.1 mT/s up to different magnetic field intensities, resulting in the relaxation of magnetization over time as shown in a) and c), respectively. When the intensity of the applied magnetic field is around that of the critical field a) H_{c1} and c) H_{c3} , the relaxation time is observed to reach its maximum.

At the magnetic field sweep rate used to obtain this plot, 22.1 mT s^{-1} , the critical field of H_{c4} could not be probed due to the flaring described, as evidence in the M-H loop presented in Figure 5.2b for 22.1 mT/s .

An alternative perspective of these Hpause measurements is shown in Figure 5.5. Here the relaxation of the magnetization is evidenced by a vertical line.

Similarly to what occurred in the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample, and in contrast to what has been reported in [46], the magnetization of $\text{Fe}_{49}\text{Rh}_{51}$ does not quite reach the upper and lower tails of the M-H loop upon magnetic field application and removal, although values of Hpause closer to H_{c2} come extremely close to it.

Comparison of the equilibrium M-H loop from reference [46] to those shown in Figure 5.2a, demonstrate the difference in sharpness of the phase transitions. While the $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample used in that study had an extremely sharp phase transition, leading to relaxation across the entirety of the phase transition starting at H_{c1} , the $\text{Fe}_{49}\text{Rh}_{51}$ sample here used has a slightly less sharp phase transition, leaving an untransformed fraction when the magnetic field is paused close to H_{c1} .

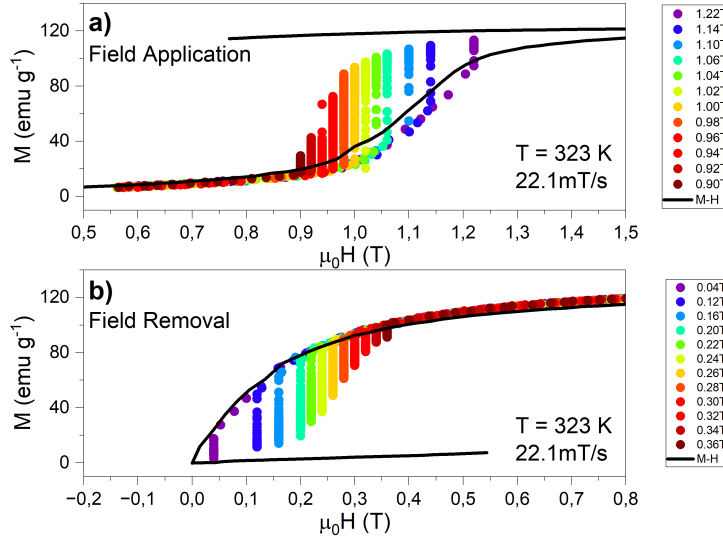


FIGURE 5.5: a) Magnetization as a function of applied magnetic field for the data presented in Figure 5.4a and b) for the data presented in Figure 5.4b. Comparison of these to the corresponding dynamic M-H curve reveals the magnetization follows its set path during the field-driven segment.

5.1.2.1 Temperature Dependence of the Relaxation

The temperature dependence of the relaxation upon magnetic field application and removal was also evaluated for a given H_{pause} whose values were those of H_{c1} and H_{c3} at 323K. As a result, 323K is expected to exhibit the highest relaxation time.

Considering the temperature dependence of the critical field H_{c1} and H_{c3} , shown in Figure 5.3, as well as the dependence of the relaxation with these, measured in the previous section, the following results should come at no surprise. In Figure 5.6a, increasing the temperature past 323K is found to decrease the relaxation time, which is a direct consequence of the decrease in critical fields H_{c1} and H_{c2} . When the temperature is increased sufficiently, the H_{pause} used surpasses H_{c2} , hence relaxation of the magnetization is no longer observed.

Decreasing the temperature from 323K has the opposite effect of the described above. The expected increase of critical field H_{c1} results in any H_{pause} measurement at that magnetic field to not exhibit any relaxation upon halting the magnetic field.

A similar situation occurs on magnetic field removal, as shown in Figure 5.6c. While increasing the temperature leads to lower values of H_{c3} , which results in no relaxation of the magnetization being observed. Decreasing the temperature increases the value of H_{c3} and H_{c4} , therefore enabling the phase transition to occur. Once the temperature is lower

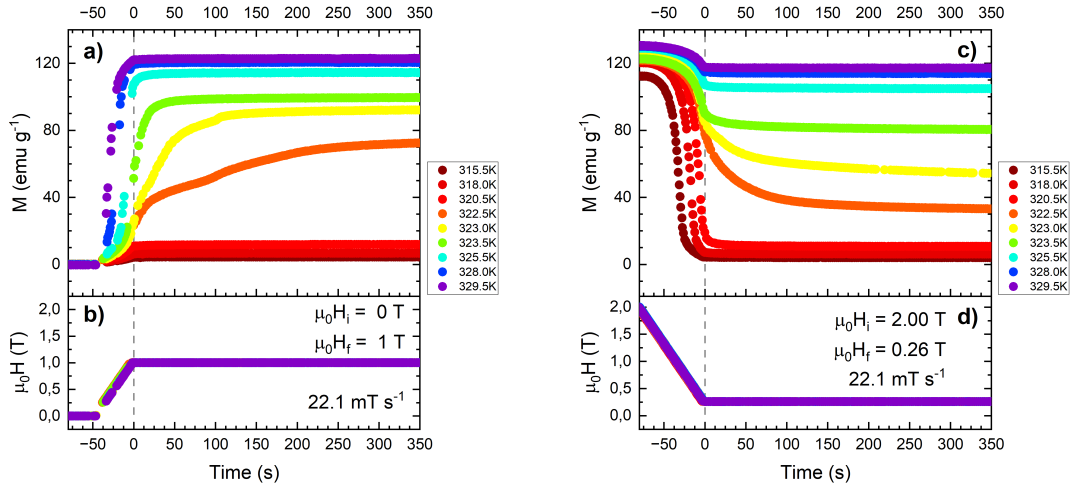


FIGURE 5.6: Profile of the driving magnetic field isothermally b) applied up 1 T and d) removed from 2T down to 0.26T at 22.1 mT/s for a set of temperatures across the phase transition, resulting in the relaxation of magnetization over time as shown in a) and c), respectively. The closer the intensity of H_{pause} is to that of the corresponding critical field a) H_{c1} and c) H_{c3} , for that given temperature, the longer the relaxation time observed.

enough, the magnetic field becomes lower than that of H_{c4} , and so no relaxation of the magnetization is observed.

5.1.3 Temperature Pause

As described in Chapter 2.3.1.2, a similar protocol to pausing magnetic fields, H_{pause} , may be followed for temperature, T_{pause} . In this case, at a very small magnetic field of 0.01 T, the temperature is increased steadily at a sweep rate of 1 K min^{-1} and paused at various stages across the temperature-induced phase transition. The magnetization is then recorded as a function of time, and its observed time evolution presented in Figure 5.7.

The presented graph showcases two T_{pause} measurements during cooling and heating, both paused 1K before the respective critical temperature. The timescale at which these temperature-driven relaxation effects occur is found to be higher than that observed in magnetic field driven relaxations.

A low and high temperature thermal reset was performed in obtaining the heating and cooling measurements, respectively. In spite of this, a clear asymmetry is observed between these measurements, suggesting the phase transition upon cooling is much sharper than that in heating, which coincides with that observed in Figure 5.1.

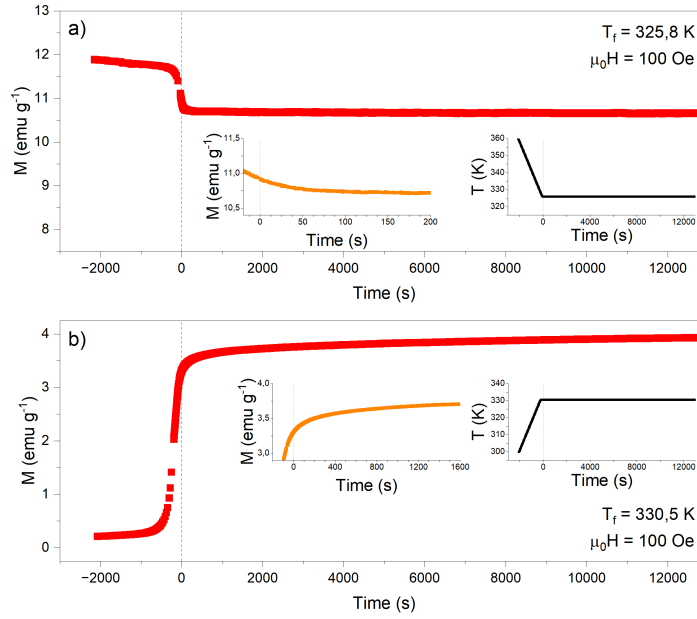


FIGURE 5.7: The resulting isofield relaxation of magnetization over time when the sample is a) cooled to 325.8K and b) heated to 330.5K at a rate of 1K min^{-1} , following the temperature profile shown in each inset. Although most of the magnetization change is driven by the changing temperature, further variations are observed after the temperature is paused, as highlighted in the inset.

While the relaxation effects have mostly ceased after 100 seconds and 1600 seconds for cooling and heating, as observed in the insets presented, some degree of relaxation is observed beyond this point in time. Most notably during heating, as the phase transition is less sharp, the magnetization is observed to have increased slightly 12000 seconds after the temperature has been paused. As a result of its shape, these relaxations may be better described by the power law of the Kolmogorov-Johnson-Mehl-Avrami relation [57–59], which has been discussed in Chapter 2.3.1.2.

5.1.4 Evaluation of the Magnetic Relaxation

From Figure 5.2b the hysteresis of each magnetic field cycle was evaluated and presented in Figure 5.8a. Similarly to that reported for $\text{La}(\text{Fe,Si})_{13}$ [46, 49], an increasingly higher hysteresis is observed as the magnetic field sweep rate is increased, providing concrete evidence that flaring of the M-H loops also occurs with this alloy.

Attending to the high magnetic field sweep rates used in achieving devices with high operation frequency, the practical implication of this flaring is an increase in critical field H_{c2} , effectively increasing the span in which the presented relaxation effects occur.

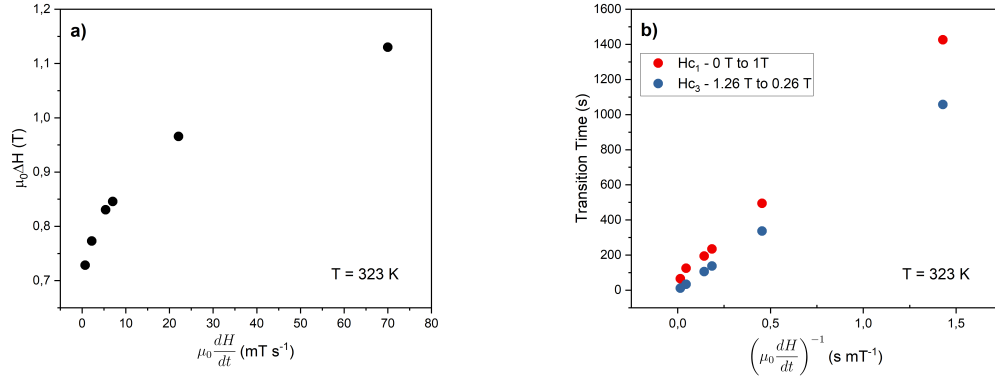


FIGURE 5.8: a) The hysteresis width of the dynamically obtained M-H loops shown in Figure 5.2 as a function of magnetic field sweep rate. b) The total transition time of the phase transition, upon magnetic field application, in red, and removal, in blue, as a function of the inverse of the magnetic field sweep rate. Although the Hpause measurements performed on magnetic field removal were obtained from 2T down to H_{c3} , the contribution of magnetic field removal to the total transition time was only considered starting at 1.26T, ensuring an adequate comparison between transition directions.

Figure 5.8b presents the complementary view in this discussion, as the total transition time, pertaining to magnetic field application and saturation of the magnetization, is found to increase linearly with the inverse of the magnetic field sweep rate. As a result, the higher the magnetic field sweep rate, the faster a magnetic field cycle may be restarted.

5.1.4.1 Magnetization Relaxation Rate

The relaxation rate of the magnetization describes the speed at which the phase transition progresses towards saturation when the magnetic field is paused.

Similarly to what has been described in reference [46] for $\text{LaFe}_{11.6}\text{Si}_{1.4}$, the relaxation rate of the magnetization of $\text{Fe}_{49}\text{Rh}_{51}$ linearly increases with H_{pause} starting at H_{c1} and up to H_{c2} , after which a plateau is observed, as shown in Figure 5.9a. As the magnetic field at which this plateau occurs is given by H_{c2} , it is inherently magnetic field sweep rate dependent, with the value of the relaxation rate plateau increasing with increasing field sweep rate.

Upon magnetic field removal, a similar behaviour is observed, as shown in Figure 5.9b. As the value of H_{pause} is decreased below H_{c3} , the relaxation rate is found to also decrease up to a sweep rate dependent plateau. Although this decrease does not occur in the linear fashion presented upon field application, it still follows a set path. The value at which the plateau occurs is found to be that of H_{c4} , which explains why the higher

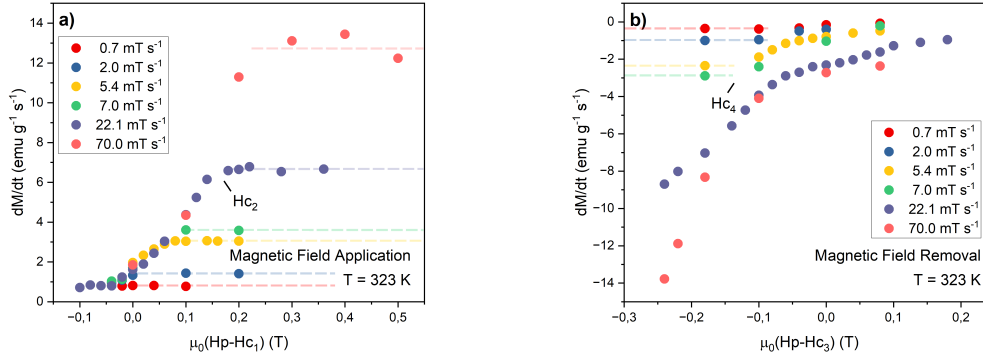


FIGURE 5.9: Magnetization relaxation rate, dM/dt , as a function of how far away from a) H_{c1} or b) H_{c3} the value of H_{pause} is for a set of magnetic field sweep rates. The relaxation rate was derived from the linear slope of the magnetization's relaxation during magnetic field a) application and b) removal at 323K.

magnetic field sweep rates tested do not show one even at 0T, as the flaring observed in the M-H loops effectively means no critical field H_{c4} can be detected.

As the magnetic phase transition is less sharp upon magnetic field removal, Figure 5.9b exhibits a small slope for magnetic field values higher than H_{c3} , which interestingly is also found to be affected by flaring of the M-H loop.

On magnetic field application up to the critical field H_{c1} of each temperature, the relaxation rate of the magnetization is found to increase as the temperature is brought closer to the critical temperature, as shown in Figure 5.10a. Similarly, on magnetic field removal from 2T down to each of the temperature's H_{c3} , shown in Figure 5.10b, the opposite occurs, where the relaxation rate of the magnetization is shown to decrease as the temperature is brought closer to the critical temperature. Naturally, both of these findings are in line with faster phase transitions being found when the sample is operated closer to its FM state. Additionally, faster relaxation rates are consistently observed throughout the temperature range probed during field removal, with a factor of about 4 differentiating the two.

5.1.4.2 Magnetization Time Constant

Similarly to what has been previously found for $\text{LaFe}_{11.6}\text{Si}_{1.4}$, the logarithm of the relaxation time constant of the magnetization peaks at critical fields H_{c1} and H_{c3} during magnetic field application and removal, as shown in Figure 5.11.

During magnetic field application, despite a large variability across the tested magnetic field sweep rates, the logarithm of the relaxation time constant is found to be roughly

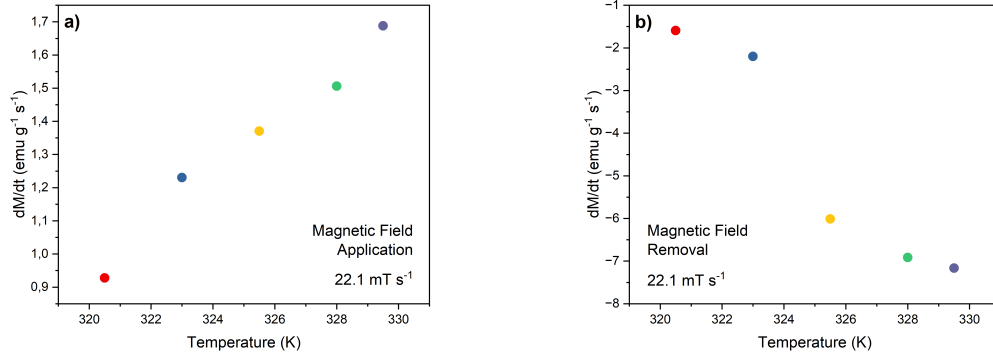


FIGURE 5.10: Magnetization relaxation rate, dM/dt , as a function of temperature obtained by following the Hpause protocol during a) magnetic field application up to H_{c1} and b) magnetic field removal down to H_{c3} . The pausing magnetic fields were those found in Figure 5.2 for each of the measured temperatures.

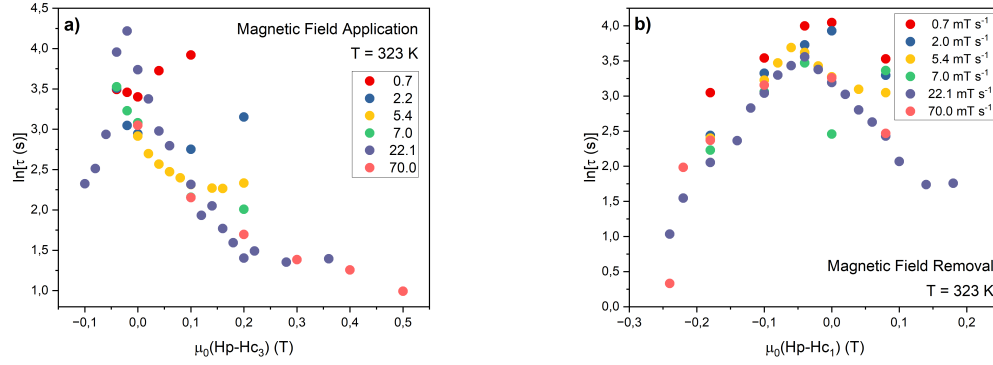


FIGURE 5.11: The natural logarithm of the magnetization's relaxation time constant, $\ln \tau$, as a function of how far away from a) H_{c1} or b) H_{c3} the value of H_{pause} is for a set of magnetic field sweep rates. The relaxation time constant was derived from an exponential fit of the kind $M(t) = M_{\text{sat}} - M_{\text{rel}}e^{-t/\tau}$ to the magnetization's relaxation found in each Hpause measurement.

linear with the value of H_{pause} , as observed in Figure 5.11a. Similarly, during magnetic field removal the logarithm of the relaxation time constant is found to be linear with the value of H_{pause} , shown in Figure 5.11b. As a result, the growth process is determined to be of activation over an energy barrier, which corroborates what has been reported for this alloy [48].

5.2 Structural Phase Transition

Attending to the magnetostructural nature of the phase transition of $\text{Fe}_{49}\text{Rh}_{51}$, similar relaxation of the lattice parameter in time is expected to be observed. With the goal of characterizing the lattice parameter relaxation in this alloy, time-dependent X-ray diffraction at one of the most brilliant X-ray sources currently available, the National Synchrotron Light Source II at Brookhaven National Laboratory [113], was employed.

In performing the structural characterization of $\text{Fe}_{49}\text{Rh}_{51}$ a rectangular bulk sample with tens of milligrams was used. This sample was the remaining fragment of the divided slice used for the magnetic characterization.

Due to experimental constraints, the magnetic field was applied along the short-axis of the bulk sample, and, as a result, the role of the demagnetizing field in the sample is expected to impact its magnetization.

5.2.1 Equilibrium Measurements

Attending to the differences in experimental apparatus, the critical temperature of the alloy was measured once again by obtaining X-ray patterns as a function of temperature across the phase transition at a low magnetic field of 0.01 T. These were later analysed through Rietveld refinements and the temperature dependence of the lattice parameter made clear, as shown in Figure 5.12a.

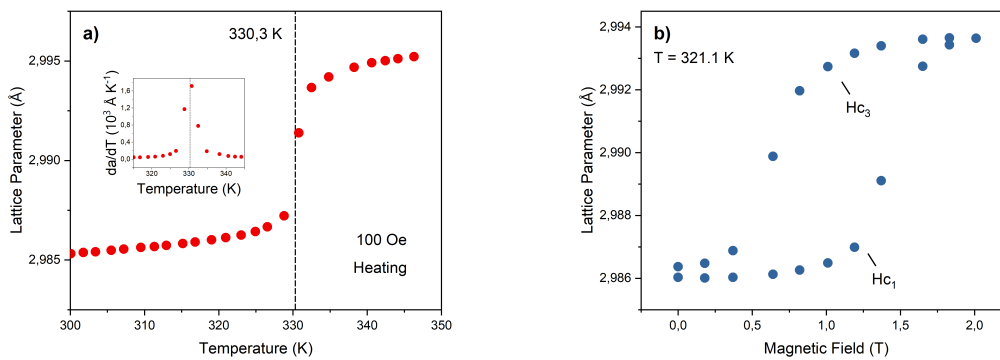


FIGURE 5.12: a) Temperature dependence of the lattice parameter measured across the AFM to FM phase transition of the alloy at 1 K min^{-1} . Its derivative, shown in the inset, was used in calculating the critical temperature upon heating through a Gaussian fit. b) Lattice parameter as a function of magnetic field obtained by varying the magnetic field in a step-like manner from 0 T to 2 T and back. The critical fields H_{c1} and H_{c3} are represented.

As observed, the critical temperature of the alloy, obtained through a Gaussian fit to the derivative of the lattice parameter with respect to temperature, is similar to that obtained experimentally from magnetic measurements, accounting for 1.2K difference. Across the observed temperature range, a volumetric increase of close to 0.35% is measured. Additionally, the structural transition is found to be slightly less sharp than its magnetic counterpart.

The magnetically-induced phase transition was then studied by measuring the lattice parameter as a function of applied magnetic field in near-equilibrium, shown in Figure 5.12b. Here the lattice parameter is observed to exhibit the same critical field landmarks as the magnetization, with special emphasis on critical field H_{c1} , which had to be determined at the presented temperature, in the AFM state, so as to allow for the extrapolation of H_{c1} across the range of temperatures to be measured at the time of carrying out the experiment.

During analysis of the data however, these extrapolated critical fields were ultimately not used, as those determined from the dynamics measurements of H_{pause} are generally more desirable, as they more closely resemble the cyclic lattice parameter as a function of magnetic field loop.

5.2.2 Structural Time-evolution of the Lattice Parameter

The measurement protocol described in Chapter 3.3 was followed with complete magnetic field cycles from 0T to H_{pause} and back. Although magnetic field removal was measured, technical issues have yet to allow the gathering of that data.

Nevertheless, the following Figure 5.13a demonstrates the magnetic field application profile, and, in Figure 5.13b, the corresponding lattice evolution with time for a measurement of H_{pause} at 1.5T and at 321K. The shown X-ray diffraction peak is observed to move towards lower 2θ values after the magnetic field has been paused, corresponding to an increase of the lattice parameter, which is consistent with the sample undergoing its isostructural phase transition, from a low-volume anti-ferromagnetic phase to a high-volume ferromagnetic phase [88].

Analysis of these diffraction patterns through Rietveld refinements enables the extraction of the lattice parameter as a function time, made possible due to the high pattern acquisition frequency. Figure 5.14 shows an example of an obtained diffraction pattern

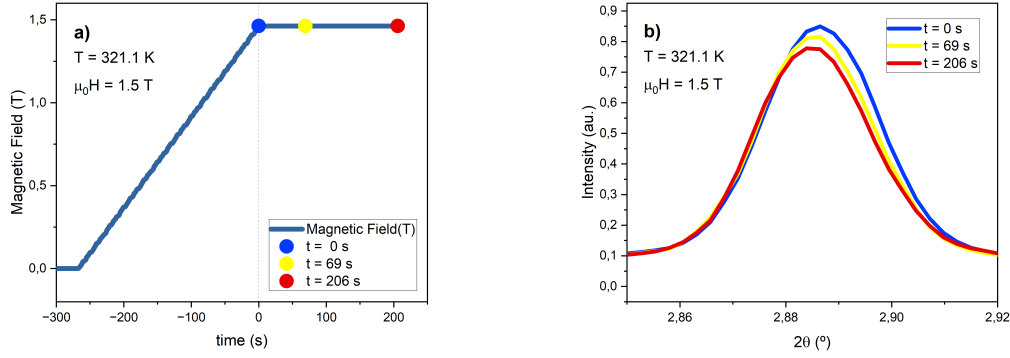


FIGURE 5.13: a) Profile of the applied magnetic field as a function of time describing its application at a constant sweep rate of 5.4 mTs^{-1} up to its saturated value of $\mu_0 H_{\text{pause}} = 1.5 \text{ T}$, at which point the time is taken to equal zero. b) Time evolution of the diffraction pattern's most intense peak (1 1 0) for the set of points identified as coloured dots in a) after the applied field is paused at $\mu_0 H_{\text{pause}} = 1.5 \text{ T}$, 9.2 K below the AFM to FM transition.

of $\text{Fe}_{49}\text{Rh}_{51}$, together with its respective Rietveld refinement, showing good agreement between the two.

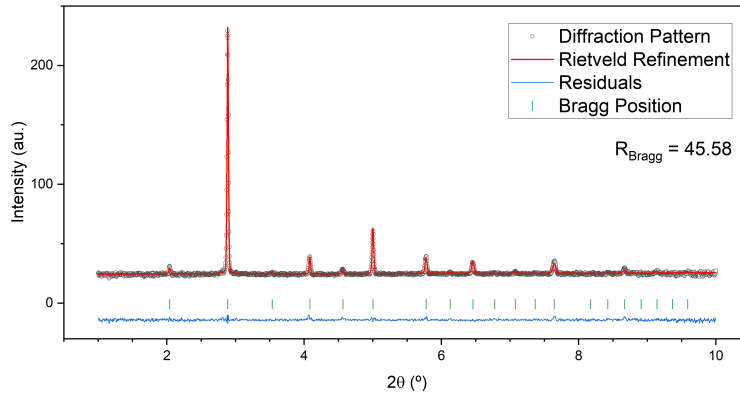


FIGURE 5.14: Complete diffraction pattern of the sample at $t = 0 \text{ s}$, according to Figure 5.13, obtained with a wavelength of $0.1065 \text{ \AA}$, together with the performed Rietveld refinement, allowing for a detailed characterization of the sample's structure at any given point in time.

5.2.3 Magnetic field Dependence of the Structural Relaxation

In the following Figure 5.15a a set of H_{pause} measurements are shown for a range of magnetic fields across the phase transition. The relaxation of the lattice parameter is shown to extend beyond the point in time at which the magnetic field is paused, when the value of H_{pause} is higher than that of H_{c1} . Additionally, a magnetic field of 1.9 T is shown to exhibit almost no relaxation and hence be extremely close to H_{c2} , which is in line with that

found in the corresponding lattice parameter as a function of magnetic field loop from Figure 5.12b.

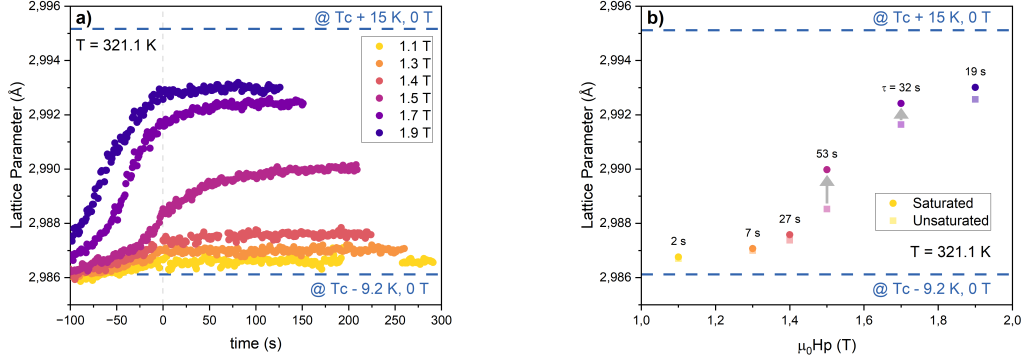


FIGURE 5.15: a) Relaxation of the lattice parameter as a function of time after the applied magnetic field is driven at 5.4 mT s^{-1} and paused at varying intensities across the phase transition, identified in the caption, 9.2 K below the critical temperature. b) The observed unsaturated ($t = 0$ s) and saturated values of the lattice parameter as a function of applied magnetic field for the relaxation profiles presented in a), together with the time constant separating the two states. The horizontal dashed lines delimit the temperature bounds of the structural transition at zero-field, the lattice parameter of the FM state being characterized by its value at $T_c + 15$ K and its AFM boundary defined by its value at $T_c - 9.2$ K.

A very narrow dependence of the saturated and unsaturated lattice parameter as a function of H_{pause} is found in Figure 5.15b, and is indicative that the relaxations of lattice parameter observed have not transformed a significant fraction of the sample, which is in contrast to that found for both $\text{LaFe}_{11.6}\text{Si}_{1.4}$'s magnetization and lattice parameter, but also of the significant relaxations observed for the magnetic phase transition of $\text{Fe}_{49}\text{Rh}_{51}$.

5.2.3.1 Evaluation of the Structural Relaxation

Analyses of the relaxation rate at which the lattice parameter moves to saturation, shown in Figure 5.16a, shows similarities to those observed for the magnetization of the alloy. A linear region is superseded by a plateau which, in this case, is found to be temperature dependent.

Attending to the fact that the value of H_{c2} , the H_{pause} at which the relaxation rate is expected to plateau, is temperature dependent, changes in the value of the saturated relaxation rate are expected. However, as observed, the saturation of the relaxation rate for 310.8K is close to that of 315.8K, while that of 321.1K is lower.

Although the higher temperature of 321.1K is expected to result in a lower H_{c2} value, ultimately leading to a lower saturation relaxation rate, the similarity of the saturation relaxation rate of the remaining temperatures could indicate a sharper transition is observed as the temperature is reduced.

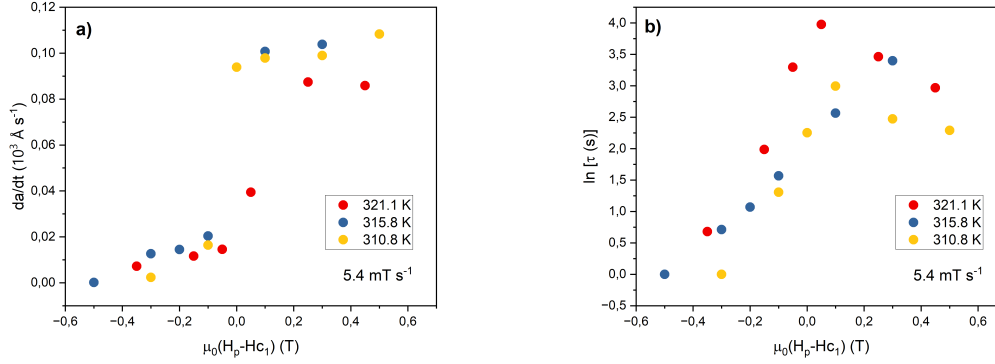


FIGURE 5.16: a) Lattice parameter relaxation rate, da/dt , and b) natural logarithm of the relaxation time constant, $\ln \tau$, of the lattice parameter as a function of $\mu_0(H_p - H_{c1})$ for a set of temperatures below the AFM to FM phase transition of the alloy.

The logarithm of the relaxation rate of the alloy is shown to peak at values of H_{pause} close to critical field H_{c1} , as presented in Figure 5.16b. Its decay is then observed as the magnetic field is paused further away from critical field H_{c1} , be it at slightly higher magnetic fields, closer to H_{c2} , or at slightly lower magnetic fields.

Unlike what has been found for $\text{LaFe}_{11.6}\text{Si}_{1.4}$, the relaxation time constant is found to be temperature dependent. Although higher temperatures seem to lead to higher relaxation time constants, a higher data sample size would be needed to ascertain such findings.

5.3 Magnetostructural Coupling

In establishing how the magnetic and structural phase transitions are coupled in $\text{Fe}_{49}\text{Rh}_{51}$, H_{pause} measurements for the lattice parameter and magnetization are compared in Figure 5.17a under similar conditions.

Here, the magnetization and lattice parameter are shown to exhibit a further increase beyond magnetic field application. Although near critical field H_{c1} both relaxations occur at a similar time scale, when the value of H_{pause} is increased, the magnetization is observed to reach saturation at a lower driving magnetic field, indicative of the slightly

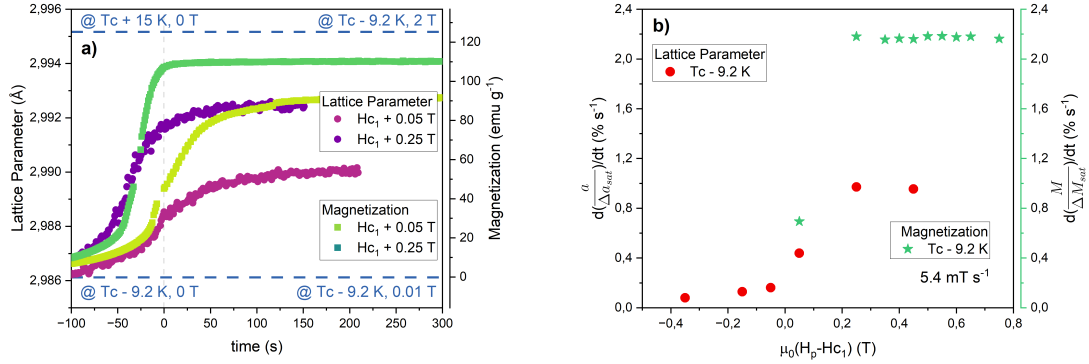


FIGURE 5.17: a) Relaxation of the lattice parameter, a , and of the magnetization, M , as a function of time after the magnetic field is driven and paused at the specified value of H_{pause} . b) Relaxation rates of the lattice parameter, a , in circles, and of the magnetization, M , in stars, as a function of the distance of H_{pause} to critical field H_{c1} . The horizontal lines in a) depict the temperature and magnetic field bounds of the phase transition used to delimit the structural and magnetic phase transitions, respectively, which were then used in b) to normalize the presented relaxation rates.

sharper magnetically-induced phase transition of the magnetization in comparison to that of the lattice parameter.

In comparing the relaxation rate of both the magnetic and structural phase transitions these were normalized to their temperature, in the case of the lattice parameter, and magnetic field bounds, for the magnetization, as shown in Figure 5.17b.

Both relaxation rates are shown to increase with applied magnetic field up to a plateau. In better correlating the onset of this plateau, occurring at the value of critical field H_{c2} for each of the phase transitions, a more detailed study is required, as only a single H_{pause} has been registered to lie within the range of H_{c1} and H_{c2} .

Although the normalized relaxation rates here presented must be compared with care, as these are highly dependent on the previously defined bounds, the saturated relaxation rate of the magnetization is shown to be a factor of 2 higher than that of the structural transition. As a result, the structural phase transition is expected to required more time before its saturated value is achieved, therefore accounting for the slightly longer relaxation times previously observed in Figure 5.17a.

5.4 Fe₅₀Rh₅₀

The characterization of the magnetic phase transition of equiatomic FeRh, Fe₅₀Rh₅₀, was performed to highlight how small changes in the stoichiometry of an alloy may drastically

affect its phase transition. To this end, a rectangular bulk sample of 32.95 mg was used.

5.4.1 Equilibrium Measurements

The critical Temperature of the AFM to FM phase transition of equiatomic FeRh, Fe₅₀Rh₅₀, was determined by measuring the magnetization of the alloy as a function of temperature.

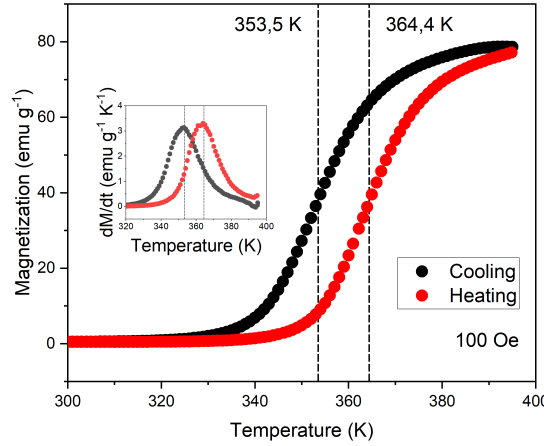


FIGURE 5.18: Temperature dependence of the magnetization measured at the low magnetic field of 100 Oe across the AFM to FM phase transition of the alloy at 1 K min⁻¹. The heating and cooling critical temperatures of the phase transition were calculated through a Gaussian fit to its derivative, presented in the inset.

As shown in Figure 5.18, this alloy exhibits a second order-like phase transition that is characterized by a broad transition whose critical temperatures are of 364.4 K and 353.5 K upon heating and cooling, respectively, resulting in a thermal hysteresis of 10.9 K. Although the equipment does not allow probing of temperatures higher than 400 K, these findings are in excellent agreement to what has been described in reference [88], in which the authors face the same issue.

Comparison of the equivalent measurement performed on the Fe₄₉Rh₅₁ sample, shown in Figure 5.1, highlights the role the stoichiometry of the alloy has on achieving a sharper transition whose thermal hysteresis is lower, as well as establishing the order of the phase transition.

5.4.2 Magnetic Relaxation

Following the protocol described in Chapter 3.3, the kinetics of the phase transition were assessed when a magnetic field was applied, up to the value of H_{pause} , and, upon saturation of the magnetization, removed. In Figure 5.19a the resulting time evolution of the magnetization is shown upon magnetic field application.

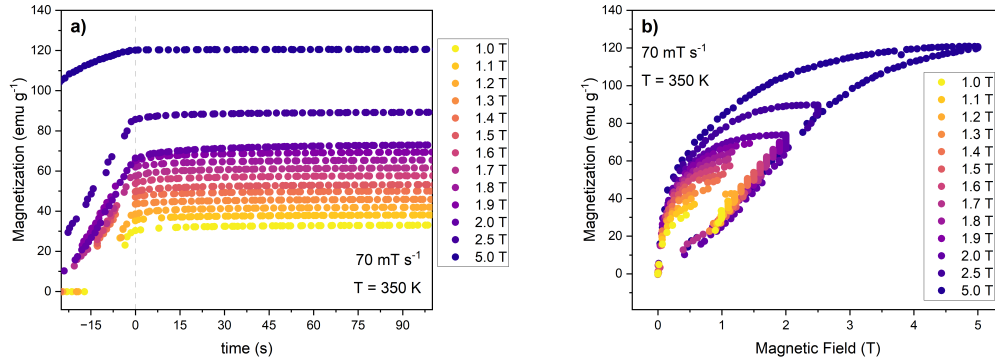


FIGURE 5.19: Relaxation of the magnetization as a function of a) time and b) field after the applied magnetic field is driven at 70 mT s^{-1} and paused at varying intensities across the phase transition, identified in the caption, 14.4 K below the critical temperature. In b) the relaxation of the lattice parameter is observed as vertical lines and, upon magnetic field removal, no further relaxation of the magnetization is observed after the magnetic field is paused.

As a result of the second order-like phase transition which $\text{Fe}_{50}\text{Rh}_{50}$ exhibits, the observed magnetic relaxation occurs at a time scale lower than 10 seconds with minimal increases in magnetization for all tested values of H_{pause} except that of 2 T , in which the magnetization is observed to increase by 11% over the span of 400 seconds.

The relaxation of the magnetization as a function of magnetic field can be analysed from Figure 5.19b. Here, the smoother magnetically-induced phase transition is observed to contrast that of $\text{Fe}_{49}\text{Rh}_{51}$.

The interval in which a magnetic field can be paused resulting in some degree of relaxation is observed to be extensive, ranging from 1 T to 2.5 T , although, only when the pausing magnetic field is of 2 T does the relaxation observed amount to a significant amount. Magnetic field removal may be also analysed through this figure. Decreasing the magnetic field from H_{pause} down to 0.01 T reveals the AFM to FM phase transition to not have been saturated at 5 T and no relaxation is detected when the magnetic field is removed.

Chapter 6

Conclusions

In this work, the kinetics of the magnetic and structural components of the magnetostructural phase transition in $\text{LaFe}_{11.6}\text{Si}_{1.4}$ and $\text{Fe}_{49}\text{Rh}_{51}$ are analysed, further building upon prior knowledge mainly derived from magnetic measurements. In both alloys, a strong influence on the profile of the applied magnetic field, intensity, sweep rate and direction, as well as temperature was observed in the time evolution of the magnetovolume coupled phase transition.

At temperatures close to their critical temperatures, the application of a magnetic field was capable of inducing their respective isostructural phase transitions. However, if the magnetic field is paused beyond critical field H_{c1} , both the magnetization and lattice parameter show further relaxation in time until they reach a given saturated state, wherein the lattice parameter relaxation time is observed to exceed that of the magnetization. As the magnetic field is paused increasingly closer to critical field H_{c2} , higher relaxation rates and lower relaxation times are observed, and after which relaxation effects cease to occur.

The rate at which the magnetic field is applied was also observed to strongly influence this relaxation time. Although faster applications resulted in longer relaxation times, the shorter field application time inherently associated to higher sweep rates was observed to offset this increase, leading to an overall decrease in transition time.

Additionally, the sample's temperature played a key role in determining the magnetization and lattice parameter at zero magnetic field, as well as the critical field at which the phase transition is initiated. While the characteristics of the relaxation profiles of the lattice parameter of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ were found to be largely independent from temperature, those found for its magnetization show an increase in the magnetization's relaxation rate as the temperature is decreased. Conversely, due to its AFM to FM phase transition, the

relaxation rate of $\text{Fe}_{49}\text{Rh}_{51}$'s magnetization is shown to increase as the temperature is increased. Definitive conclusions regarding the lattice parameter's relaxation rate dependence with temperature remain elusive, warranting additional investigation.

Magnetic field cycling upon saturation of the phase transition following field application between critical fields H_{c1} and H_{c2} showcased the phase transition asymmetry, as the magnetization and lattice parameter were found to return to its zero magnetic field values while the magnetic field had not yet been completely removed. Contrastingly, pausing the magnetic field between critical fields H_{c3} and H_{c4} during its removal and after driving the phase transition in full reveals similar relaxation effects to those described upon magnetic field application.

For $\text{LaFe}_{11.6}\text{Si}_{1.4}$, this asymmetry of the phase transition dynamics during field cycling was explained with the aid of a model which simulated the Gibbs energy landscape of the magnetization and lattice parameter for a wide range of temperatures and magnetic fields across the phase transition of a compressible 3D Ising lattice. On magnetic field application, the appearance of an energetic local maximum gives rise to a metastable energy state which is shown to be responsible for the phase transition dynamics observed through correlation of the associated energy barriers and the observed relaxation times. As the magnetic field is removed completely, the absence of an energy barrier justifies the lack of transition dynamics in the backwards direction. While not this study's focus, the observed existence of an energetic barrier during partial removal of the magnetic field makes a compelling argument to justify the relaxations observed in these conditions. Additionally, the temperature dependence of the relaxation time in respect to the energetic barrier is indicative of a growth process that is not thermally activated.

These findings prompt the necessity to not neglect the structural, as well as the magnetic, dynamics of the phase transition in device engineering of magnetic refrigerators and thermomagnetic energy harvesters operating FOPT magnetocaloric materials, as these ought to reflect the phase transition asymmetry, characterized by long relaxation times upon magnetic field application and their absence, or presence, upon complete, or partial, magnetic field removal, respectively. Furthermore, these highlight the importance of a study aiming at comparing the magnetic and structural dynamics simultaneously, while providing opportunities for exploring innovative methodologies in the study of diverse phase transitions.

6.1 Future Work

While conducting this thesis, several other questions which remain unexplored have surfaced. The following is a brief summary on ideas which continue this line of work.

The most straightforward continuation of the presented analysis is the completion of the structural characterization of $\text{Fe}_{49}\text{Rh}_{51}$, not only adding onto the number of tested temperatures but also increasing the number of tested H_{pause} measurements performed above critical field H_{c1} . Simultaneously, replication of the partial field removal studies performed for the magnetization of the alloy would allow probing of field application and removal, while also optimizing the time used at the synchrotron beamline by spending less time ramping the magnetic field, versus doing the experiments separately. Additional beam time is foreseen to be available in the upcoming months for this purpose.

A similar approach could also be employed to study the structural phase transition of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ on partial field removal. A comparison with the modelled energetic barrier could then provide further insight into the kinetics of the phase transition.

A model taking into account the structure of $\text{Fe}_{49}\text{Rh}_{51}$ could also be implemented to allow a similar analysis to that performed for $\text{LaFe}_{11.6}\text{Si}_{1.4}$, although the added complexity introduced by the discontinuous temperature dependence of the magnetic moment of the Rh atoms could be a barrier to its conception.

Additional studies establishing the impact of sample geometry, such as using diverse bulk, powdered, thin films or even nanostructured samples, and the orientation of the sample with respect to the magnetic field axis in the kinetics of the phase transition would be useful in determining its influence to the observed effect.

Further insights into these phase transitions may be obtained if these were to also be studied through a temperature-based approach, by performing T_{pause} measurements in both samples. Despite the time-intensive nature of these measurements, they could help to ascertain the distinct contributions of temperature and external field in driving the phase transition, as well as any shared characteristics between them.

Lastly, an attempt at performing the simultaneous characterization of the structural and magnetic lattices could be performed at the beamline ID12 of the European Synchrotron Radiation Facility, ESRF, allowing this characterization to take place under ideal circumstances, while also enabling probing of the electrical properties of the sample.

Appendix A

Deduction of ΔS_m and ΔT_{ad} in Magnetocaloric Materials

The magnetocaloric effect can be described in thermodynamic systems through the work performed by an applied magnetic field [14, 15], here described for a system undergoing a second-order phase transition. According to the first law of thermodynamics, the internal energy of an isolated system, U , may be related to its heat flux, Q and the work performed by the system on its surroundings, W , through the following expression:

$$dU = \delta Q - \delta W = TdS - pdV + \mu_0 H dm \quad (\text{A.1})$$

Here the work component was divided into its mechanical, pdV , and magnetic, $-\mu_0 H dm$, components for a quasistatic process, where T , S , V and m are the material's temperature, entropy, volume and magnetic moment, respectively, H is the applied magnetic field and μ_0 is the vacuum magnetic permeability.

In writing the differential form of the Gibbs energy, $dG = Vdp - SdT - m\mu_0 dH$, the following Maxwell relation between entropy, S , and magnetic moment, m , may be derived:

$$\left(\frac{\partial S}{\partial H}\right)_{p,T} = \mu_0 \left(\frac{\partial m}{\partial T}\right)_{p,H} \quad (\text{A.2})$$

This equation may then be rearranged in its integral form to describe the total isothermal, $dT = 0$, magnetic entropy change, ΔS_m , due to a magnetic field change:

$$\Delta S_m = \mu_0 \int_{H_i}^{H_f} \left(\frac{\partial m}{\partial T}\right)_{p,H} dH \quad (\text{A.3})$$

From this point deriving the adiabatic temperature change simply involves writing the entropy as a function of magnetic field and temperature:

$$dS = \left(\frac{\partial S}{\partial T} \right)_{p,H} dT + \left(\frac{\partial S}{\partial H} \right)_{p,T} dH \quad (\text{A.4})$$

Then, for an adiabatic process, using $dS = 0$ to highlight dT , combined with the equation of the heat capacity, C :

$$C_{p,H} = T \left(\frac{dS}{dT} \right)_{p,H} \quad (\text{A.5})$$

Yields the total adiabatic temperature change, ΔT_{ad} :

$$\Delta T_{ad} = -\mu_0 \int_{H_i}^{H_f} \frac{T}{C_{p,H}} \left(\frac{\partial m}{\partial T} \right)_{p,H} dH \quad (\text{A.6})$$

Appendix B

Theoretical Moment and Entropy Derivation

The Helmholtz free energy, F , of a system with N non-interacting spins may be obtained through the partition function of a single spin, Z_1 , as:

$$F = -Nk_B T \ln Z_1 \quad (\text{B.1})$$

Where k_B is the Boltzmann constant. Attending to the fact that the average magnetic moment of the system can be calculated through the derivative of the Helmholtz energy in respect to an applied magnetic field, B , [17, 22] the following is obtained:

$$M = -\frac{1}{V} \left(\frac{\partial F}{\partial B} \right)_T = \frac{N}{V} k_B T \frac{d \ln Z_1}{dB} = \frac{N}{V} g_J \mu_B J B_J \left[\frac{g_J \mu_B B}{k_B T} \right] \quad (\text{B.2})$$

Where V represents the volume of the system, μ_B is the Bohr magnetron, J is the total angular momentum of the atom, $B_J(y)$ is the Brillouin function, and g_J is the called the Landé g-value given by:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (\text{B.3})$$

Here the total angular momentum of an atom, J , can be defined as the sum of the orbital angular momentum, L , and the spin angular momentum S , of an atom.

Considering the limit of the field $B \rightarrow 0$, the Brillouin function present in equation B.2 may be approximated as:

$$B_J(y) \xrightarrow{y \rightarrow 0} \frac{y(J+1)}{3} \quad (\text{B.4})$$

The susceptibility, χ , of the system can then be derived from the dependence of the magnetization with the applied field:

$$\frac{dM}{dH} = \chi = \frac{N}{V} (g\mu_B)^2 \mu_0 \frac{J(J+1)}{3k_B T} \quad (\text{B.5})$$

Which yields the equivalent to the classical Curie law, $\chi = C_{\text{Curie}}/T$. An effective paramagnetic moment, μ_{eff} , can then be interpreted as the following:

$$\mu_{\text{eff}} = g_J \mu_B \sqrt{J(J+1)} \quad (\text{B.6})$$

Similarly, the magnetic entropy of a system, S , may be obtained from the Helmholtz energy [17, 22] as:

$$S = - \left(\frac{\partial F}{\partial T} \right)_B = Nk_B \frac{d}{dT} (T \ln Z_1) \quad (\text{B.7})$$

Which, in the case of a field $B \rightarrow 0$ results in the following expression:

$$S = Nk_B T \ln (2J + 1) \quad (\text{B.8})$$

Given the importance of 3d and 4f ions in magnetic compounds such as magnetocaloric materials, and since 4f ions have some of the largest magnetic moments [15], it is imperative to have a model which correctly predicts their magnetic moment and entropy. Through comparison with experimental data [22], the theoretical predictions presented above are shown to be in excellent agreement with those observed experimentally in the case of 4f ions. For 3d ions however, the fact the crystal field interaction is much stronger than the spin-orbit interaction gives rise to what is known as orbital quenching and hence Hund's third rule should not be applied, and so taking $J = S$ in equation B.6 yields more accurate results [22].

Appendix C

Sample Preparation

The samples characterized in this work had already been prepared with the appropriate protocols to ensure good quality of the sample and its properties.

The bulk $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample, provided by researchers at the Technical University of Darmstadt, was prepared by induction melting and subjected to a heat treatment at 1373 K for 1 week. In transforming it into a powder, milling was performed. A representative particle size distribution of the powdered sample is shown and characterized in Figure C.1.

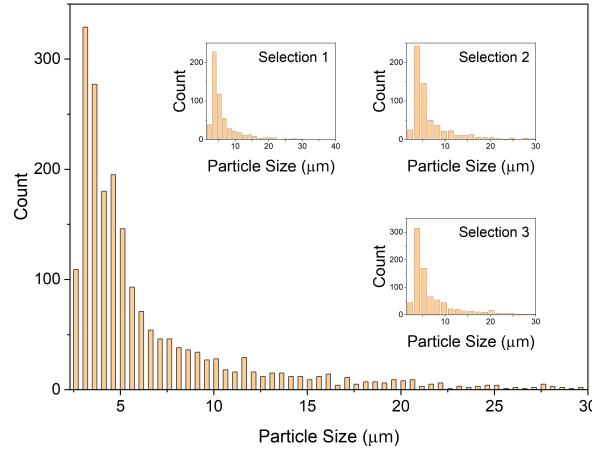


FIGURE C.1: Particle size distribution of the powder $\text{LaFe}_{11.6}\text{Si}_{1.4}$ sample used to perform the structural characterization of the alloy, displaying an average radius of 7.7 μm , a median of 4.5 μm and a standard deviation of 9.5 μm . The histogram was obtained by combining those measured from different SEM images of the sample, shown as insets.

The $\text{Fe}_{49}\text{Rh}_{51}$ and $\text{Fe}_{50}\text{Rh}_{50}$ samples, provided by researchers at the Institute for Scientific and Technological Research of San Luis Potosi, were prepared by forming pre-alloyed

buttons with their respective stoichiometry through arc melting under an Ar atmosphere. Subsequently, these were subjected to induction melting 3 times, also under an Ar atmosphere, until a temperature of 1973 K, 58 K above their melting point, was reached, 30 seconds after which the power was turned off and the sample allowed to reach room temperature. The sample was annealed under vacuum at 1273 K for 48 hours and quenched in iced-water.

Appendix D

Rietveld Refinement Evaluation

In evaluating the quality of a refinement several figures may be taken into account [125], ranging from the weighted profile R-factor, R_{wp} , which is simply the square-root of the scaled quantity previously defined as S , and so it follows:

$$R_{wp}^2 = S \cdot \left(\sum_i w_i (y_i^{obs})^2 \right)^{-1} \quad (D.1)$$

Another figure to be considered is the expected R factor, R_{exp} , when the model is assumed to be ideal. In this case, if, on average, the squared difference between the calculated and observed intensities is given by a statistical variance, σ^2 , then, if the weighing scheme also follows this purely statistical nature, $w_i = (\sigma^2[y_i^{obs}])^{-1}$, it follows that:

$$R_{exp}^2 = N \cdot \left(\sum_i w_i (y_i^{obs})^2 \right)^{-1} \quad (D.2)$$

Where N is the number of degrees of freedom, i.e. number of data points minus the number of varied parameters.

The ratio between these two figures can then be used to establish the χ^2 of the refinement simply as:

$$\chi^2 = \left(\frac{R_{wp}}{R_{exp}} \right)^2 \quad (D.3)$$

Lastly, the structure factor of each given peak, F_{hkl} , which corresponds to a different set of miller indices, can be used to estimate the quantity R_F^2 and may also be referred to as R_{Bragg} .

$$R_F^2 = \sum_{hkl} (F_{hkl}^{obs})^2 - (y_{hkl}^{calc})^2 \cdot \left(\sum_{hkl} (F_{hkl}^{obs})^2 \right)^{-1} \quad (D.4)$$

However convenient these figure may be in analysing the quality of a fit at a glance, the best indicator of a good quality Rietveld refinement remains to be good visual agreement between the observed and calculated patterns [125].

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