Thermodynamics of Magnetic Multilayers

Tathagata Mukherjee

University of Nebraska-Lincoln, tatha.muk@gmail.com

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THERMODYNAMICS OF MAGNETIC MULTILAYERS

by

Tathagata Mukherjee

A DISSERTATION

Presented to the Faculty of

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Our interest in thermodynamics of magnetic thin film heterostructure began by exploring the possibility to use magnetic nanostructures in the search for optimized magnetocaloric materials for potential room temperature refrigeration. In the present thesis magnetic thin film heterostructures are experimentally realized by Molecular Beam Epitaxy (MBE) and Pulsed Laser Deposition (PLD). Co/Cr and Fe/Cr superlattices were fabricated using mean-field theoretical concepts as guiding principles. The potential of artificial antiferromagnets for near room-temperature refrigeration is explored. Magnetocaloric properties are deduced from measurements of the temperature and field dependence of the magnetization of our samples. The effects of intra-plane and inter-plane exchange interactions on the magnetic phase diagram in Ising-type model systems are revisited in mean-field considerations with special emphasis on tailoring magnetocaloric properties. The experimental results are discussed in light of our theoretical findings, and extrapolations for future improved nanostructures are provided.

Further, magnetization relaxation is investigated in a structurally ordered magnetic Co/Cr superlattice. Magnetization transients are measured after exposing the heterostructure to a magnetic set-field for various waiting times. Scaling analysis reveals an asymptotic power-law behavior in accordance with a full aging scenario. The temperature dependence of the relaxation exponent shows pronounced anomalies at the equilibrium phase transitions of the antiferromagnetic superstructure and the ferromagnetic to paramagnetic transition of the Co layers. The latter leaves only weak fingerprints in the
equilibrium magnetic behavior but gives rise to a prominent change in non-equilibrium properties. Our findings suggest scaling analysis of non-equilibrium data as a probe for weak equilibrium phase transitions.

In addition some misleading interpretations concerning the rigorousness of phenomenological thermodynamics are clarified. Specifically, it is shown that the Maxwell relation incorporates contributions from the spin degrees of freedom and potential lattice degrees of freedom into the isothermal entropy change. A minimalist model involving pairs of exchange coupled, mobile Ising spins is investigated. It is explicitly shown that lattice degrees of freedom can be activated via applied magnetic fields and the integrated Maxwell relation contains this lattice contribution. A simple and intuitive analytic expression for the isothermal entropy change in the presence of field-activated lattice degrees of freedom is provided. We quantify the impact of quantum corrections in the low-temperature limit. To this end, we compare calculations which include elastic interaction with the rigid exchange model in the high-temperature limit. We find that quantum effects provide quantitative corrections in the low-temperature limit. In addition we show that the elastic contributions to the isothermal entropy change can be additive but, remarkably, it can also give rise to reduced isothermal entropy change in certain temperature regions.
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Dedicated to my Mother
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Chapter 1

Introduction

Thin film magnetism and in particular the thermodynamic properties of thin-film heterostructures are archetypal examples of the broad class of interacting many body systems which challenge our basic understanding to this day. From a fundamental point of view, understanding the behavior of an ensemble of interacting and confined spins remains one of the outstanding problems of thermal and statistical physics. The subject of bulk magnetic order obtains additional complexity through surface phenomena and emerging interface effects. Their understanding on a phenomenological and microscopic level plays a major role for advances in various modern technological applications. Thermodynamics sets the periphery for technology and thereby rules the margins of its derivatives. Among the various technologies, energy harvesting is mandatory to mankind and its demands are continuously increasing on a global scale. Thus an efficient use of nature’s energy reserves becomes obligatory. One important aspect of this thesis is laying out how basic principles of magnetic thin-film heterostructures can help to understand and improve magnetocaloric material properties and thereby advance the efficiency of cooling devices.

In addition to their role as model systems in magnetism [1] magnetic thin-film heterostructures play a key role in modern information technology ranging from magnetic
data storage to data processing. The current interest in magnetic recording extends from magnetic recording media to read heads, magnetic random access memories (MRAM), and field sensors to name just a few. These phenomena have moved to the forefront of current materials research.

Almost all of those applications have to function at increasing speeds regarding writing, reading and processing of information. Hence dynamics rather than equilibrium thermodynamics has ever-increasing importance for basic science and its applications. This thesis studies one limit of the dynamic range which is the long-time response of magnetic heterostructures to external stimuli which bring systems out of thermal equilibrium. This temporal relaxation from a state far from equilibrium towards thermal equilibrium is known as magnetic aging. The prominent property of interaction tunability allows one to tailor the time scales on which the magnetic after-effects appear.

The advancement of these crucial technologies to the benefit of human needs not only improves the understanding of scientific know-how but also creates new avenues and reason to study basic science which still remain unexplored to some extent. The search points to a domain which hitherto has not been traversed by equilibrium structures offered in abundance by nature. In the realm of Physics, Magnetism grants this flexibility where synthetic structures can foster properties not offered by equilibrium physics. This conceptual design points to a artificially tailored multilayer heterostructures in which equilibrium phase diagrams don’t narrow sample fabrication. Thus spin interaction can be intelligently matched to suit the purpose of technological applications.

Modern society relies heavily on cooling technology for food safety, comfort and medical applications. For example, in the US about 34% of the electricity is consumed by cooling, air conditioning and ventilation [2] and 15% of the total worldwide energy consumption involves the use of refrigeration (conditioning, refrigeration, freezing, chilling, etc.) [3]. Most of today’s cooling devices are based on the gas-compression
technology, which has been developed in the 19th century. This technique uses strong greenhouse gases and the energy efficiency has reached its limit, raising international concerns about global warming due to an ever increasing energy consumption calls for a change. Recently, several solid-sate cooling technologies, such as optical refrigeration [4], thermoelectric refrigeration [5, 6], electric refrigeration [7, 8] and magnetic refrigeration [9, 10], are considered as viable alternative techniques because they are becoming increasingly efficient and affordable. However, for a technique to become a fully grown alternative, a more detailed study on the fundamental physical properties and clever engineering are needed.

Out of various cooling technologies investigated magnetic refrigeration is expected to play a key role in the quest for energy-efficient and environmentally friendly technologies of the near future [11, 12, 13, 14]. The magnetocaloric effect (MCE) of modern magnetocaloric materials provides the physical basis of magnetic refrigeration technology having the potential to replace today’s common gas compression refrigerators. A major advantage is the increased cooling efficiency of magnetic refrigeration technology which can reach a significant fraction of the ideal coefficient of performance in comparison to about 10% only reached by conventional gas-compression refrigeration. To put this potential of energy-efficiency into perspective one has to remember the importance of refrigeration for modern society. In fact, improvement in energy-efficiency of refrigeration technology can significantly contribute to the global challenge of energy conservation. Since magnetic refrigeration does not use ozone-depleting chemicals like chlorofluorocarbon compounds it can be realized environmentally friendly and also noise and maintenance free both very timely additional demands for advanced technologies.

The magnetocaloric effect (MCE) is defined as magnetic field induced entropy variation due to the coupling of a spin system. Magnetic refrigeration is based on the magnetocaloric effect (MCE), which was discovered by Warburg in 1881 [15]. Originating
from coupling of a magnetic field with magnetic moments and quantified in terms of temperature and/or entropy changes, the MCE reflects the field-induced, reversible variations of internal energy of a magnetic system.

Historically, the MCE in paramagnets was measurable at temperatures close to absolute zero, where the enhanced, but still limited change of magnetization with respect to temperature is offset by the negligible lattice heat capacity of a solid. Early research on the magnetocaloric effect in paramagnets was carried out because of the drive to reach ultra-low temperature by adiabatic demagnetization cooling. The low thermal conductivity of paramagnetic salts is detrimental for adiabatic demagnetization applications, and therefore, paramagnetic intermetallic compounds have attracted some attention with respect to their magnetocaloric properties at low temperatures. It is worth noting that the pioneering work of Giauque and MacDougall, who studied low-temperature magnetocaloric properties of paramagnetic Gd$_2$(SO$_4$)$_3$. 8H$_2$O, showed that a temperature of less than 1 K could be reached [16]. This work and other important contributions to the low-temperature behavior of solids resulted in Giaugue winning the 1949 Nobel Prize in chemistry.

To achieve an appreciable MCE with moderate applied magnetic fields at room temperature new magnetic materials with tailored magnetocaloric properties must be synthesized. This quest pushes the technological frontiers and is cutting-edge materials science [17, 18, 19, 20]. Only significant advances in materials science allow systematic progress in magnetic cooling technology and therefore a world-wide search for magnetocaloric materials with high relative cooling power is taking place. These significant efforts are triggered to a large extent by the potential applications such as household refrigerators, cooled infra-red CCD-cameras, air-conditioning in all-electric cars, and portable refrigerators. However, the challenges for the materials scientists are complex. First one must find cost-effective, stable, and environmentally friendly materials that
maximize the MCE in the vicinity of room-temperature while the temperature of peak performance should be tunable in a wide range between the high and low temperature baths to optimize cyclic operating cooling devices. Second, one must tailor the dynamic properties involved in the magnetization relaxation process for applications in refrigeration technology. In fact, the capability of fast demagnetization of a magnetocaloric material is essential when high operation frequency is envisioned which in turn is crucial to take advantage of the proportionality between operation frequency and cooling power.

Despite some serious challenges originating from the above sources, most of today’s research activities focus on the giant MCE in bulk materials like Gd$_5$Ge$_2$Si$_2$ or related rare-earth metal alloys. Gd$_5$Ge$_2$Si$_2$ was the class of materials which started the worldwide revival of the MCE in conventionally grown bulk alloys. Recently, materials undergoing metamagnetic transitions generated interest as potential materials with appreciable MCE [21, 22, 23]. This includes low-spin to high-spin transitions, transitions from antiferromagnetic (AF) to ferromagnetic (FM) order, and field-induced magnetization states. The AF to FM transition has the advantage over FM to paramagnetic (PM) transitions that the applied magnetic fields necessary for magnetic entropy changes do not destroy and, hence, smear out the criticality of the phase transition. Steepness of the temperature dependence of the magnetization in a large magnetic field range is the key for large entropy changes and adiabatic temperature changes. Some bulk materials which involve metamagnetic transitions of interest are Ho$_5$Pd$_2$, Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and Fe$_{0.8}$Mn$_{1.5}$As to name just a few exotic examples [23, 24, 25].

Virtually unexplored scientific terrain is the nanotechnological approach in magnetocaloric materials design. This thesis outlines our efforts towards new nanostructured materials with a tailored MCE. In order to avoid any misconception about the approach it is not proposed here to replace magnetocaloric bulk systems by simple superparamagnetic nanoparticles. In the former the entropy changes are realized via spin rearrangements on
the atomic scale while the majority of the spin degrees of freedom in the superparamag-
netic nanoparticles are frozen out and do not contribute to the entropy change, although
this might be compensated by increase of adiabatic temperature change. For this reason,
simple non-interacting superparamagnetic nanoparticles are very unlikely to be of any
advantage for an increase of the figure of merit of magnetocaloric refrigeration. Our aim
is to widen the range of materials suitable for magnetic cooling by tailoring interactions in
and between ultra-thin-films. Using simple magnetic materials and realizing the design of
the macroscopic properties via nanostructuring, provides a huge opportunity to harness
the full potential of the MCE.

Nanotechnology allows overcoming some of the limitations of the traditional bulk
processing approaches where the flexibility of tailoring microscopic parameters is widely
constrained for instance by equilibrium thermodynamics of compositional phase diagrams.
Hence, tailoring of macroscopic magnetic properties is limited. Controlled growth of
magnetic multilayer structures of ultra-thin constituents opens the possibility to exploit the
microscopic parameter space in a systematic manner. Here we demonstrate the tailoring
of magnetic properties such as the critical temperature of ferromagnetic constituent films
by geometrical confinement and interaction between the FM films via nonmagnetic spacer
layers of controlled thickness. In multilayers of ultra-thin-films, it is possible to exploit
individual microscopic spin degrees of freedom, because spin fluctuations at magnetic
phase transitions in reduced dimensions yield a pronounced entropy change. In this
sense it is possible to harness the advantages of the bulk and the nanomagnetic world
where large spin fluctuations are thermally activated using coupled two-dimensional
subsystems with controlled strength and sign of the magnetic interactions.

Conceptually we suggest the following means to achieve a high MCE in nanostructured
multilayers in the vicinity of room-temperature:
(i) Growth of ultra-thin FM films such that finite-size scaling effects allow one to tailor the Curie temperature of the films and the crossover to reduced spatial dimension enhances spin fluctuations.

(ii) AF interlayer coupling of the FM constituent films allowing one to tailor a metamagnetic transition with pronounced temperature dependence of the transition line and a prominent magnetic discontinuity at the transition.

(iii) Adjusting the FM to PM transitions of the FM constituent films with the global metamagnetic transition for maximum entropy change.

Metamagnetic phase transitions, specially those induced by a magnetic field, have an extended history of investigation in long range ordered antiferromagnets [26]. These systems are generally distinguished by the property that on the application of magnetic field at low temperature, they undergo a first-order phase transition from a state with a low magnetization and low susceptibility, to a state with a relatively high magnetization and low susceptibility. Their unique characteristic of magnetization jumps with magnetic field from antiferromagnetic (AF) to a saturated paramagnetic (PM) state points to the opportunity of using this system in application such as magnetocaloric effect where one of the criteria is the change in entropy is determined by change in magnetization. Recent research has also focused on a wide range of other material systems including clean metals, magnetic cluster compounds and geometrically frustrated magnets, all of which display transitions induced by a magnetic field [27, 28, 29, 30]. Most of these efforts are directed at studying these transitions at low temperatures, far below room temperature ($\approx 300$ K). Tuning of spin-spin interaction in bulk systems to optimize metamagnetic transitions at room temperature is severely restricted. Artificial heterostructures allows overcoming some of the limitations of the traditional bulk approaches where the flexibility
of tailoring microscopic parameters is widely constrained by equilibrium thermodynamics of compositional phase diagrams.

In general, interlayer exchange coupling (IEC) has given rise to interesting physics in the realm of static magnetism. Mapping of the spin structure of a metamagnet to a magnetic multilayer heterostructure dictates that the nearest neighbor interaction should be ferromagnetic while the next nearest neighbor interaction should be AF. In the above scenario if FM layer is thin enough such that finite scaling effects can be observed then we have a scheme where we have competing FM and AF interaction. Such a system can serve as our experimental playground for metamagnetism in multilayered structure with tailored interaction for studying its thermodynamics.

The aim of the present study is to design a multilayer structure that mimics the behavior of metamagnets such as FeCl$_2$ [31], utilizing the great flexibility offered by magnetic multilayers to tune all relevant magnetic properties for MCE. The basic idea is to use simple 3d transitional ferromagnetic metal layers with high Curie temperatures $T_c$ reduced to room temperature by finite size scaling. The FM layers are separated by a layer providing AF interlayer coupling, in the range of the desired AF-FM transition temperature. The final approach is that at room temperature, this system behaves as antiferromagnetically coupled layers with a low net magnetic moment in remanence. As the temperature is raised to approach $T_c$, the magnetization of the ferromagnetic constituents is gradually reduced to zero, and consequently the coupling strength provided adjacent AF coupling layer is reduced. Eventually, the coupling between the FM layers becomes dominated by their Zeeman energy. As a result, parallel alignment of their moments and a net magnetic moment equal to the sum of the moments with the applied magnetic field of the layers evolves. When the temperature is raised further it leads to a second order FM to paramagnetic (PM) phase transition of the individual FM layers. This is a non-equilibrium nano-structure effect which would not appear in atomic systems.
such as FeCl$_2$. This kind of superlattices will be used to study the MCE. It is also found that the FM to PM phase transition is not easily detectable at all when we measure the equilibrium properties such as the temperature dependent magnetization or susceptibility of the FM-subsystem. A method is also provided which helps to deduce equilibrium properties from non-equilibrium methods of measurement.

This thesis is organized as follows: Chapter 2 serves as basic theoretical background that guides my work encompassed in this thesis. Chapter 3 describes the experimental methods used to study these effects, including sample preparation and characterization. Finally, Chapters 3-6 describe the various studies performed and predominately originates from published or submitted journal articles.
Chapter 2

Basic Theoretical Aspects

In this chapter I discuss the basic theoretical background that guides my work encompassed in this thesis. The following sections contain a brief summary of Metamagnetism, Interlayer Exchange Coupling in Magnetic Heterostructures, Finite Size Scaling for tuning of Curie Temperature, Magnetocaloric Effect and Aging phenomena far from Equilibrium.

2.1 Metamagnetism

Metamagnetism is a term, generally used to describe a sudden increase in the magnetization of a material with a small change in an externally applied magnetic field. The metamagnetic behavior may have quite different physical causes for different types of metamagnets.

Magnetic materials which exhibit field induced transitions can generally be divided into two classes [26]

1. Those which are highly magnetically anisotropic, and

2. Those which are magnetically isotropic or weakly magnetically anisotropic.
The phase transition in magnetically anisotropic materials is generally characterized by simple reversals of the local spin directions (spin-flip) whereas in case of magnetically isotropic materials there is a rotation of spin direction (spin-flop). Well-known examples of class (1) are FeCl$_2$ and DyPO$_4$. The phase diagrams of these two systems are shown in Fig. 2.1(a). As the crystals are cooled in zero field, they undergo a second-order phase transition at their respective Néel temperature ($T_N$). Below $T_N$, they are ordered antiferromagnetically with a two sublattice structure, in which the large anisotropy constrains the spins to point parallel or anti-parallel to the easy axis. On application of a magnetic field at high temperature but below $T_N$, there is a second order phase transition from antiferromagnetic to the paramagnetic phase. This behavior persists for a range of temperature below $T_N$, and hence there a is line of second-order transitions (or critical points) in low fields. On the application of a field at low temperature the behavior is strikingly different. There is still a phase transition from the antiferromagnetic phase directly to the paramagnetic phase, but now this transition is first order. This behavior persists over a range of temperatures, down to $T = 0$, and thus there is a line of first order transition in high fields (shown dashed in Fig.2.1(a)). The line of critical points at high temperature and the line of first order transition at low temperature meet at a point which is known as a tricritical point. Note that both in the antiferromagnetic and paramagnetic phase the spins are constrained by anisotropy to lie along the easy axis.

Other systems belonging to the class (1) are CoCl$_2.2$H$_2$O and FeCl$_2.2$H$_2$O. Fig. 2.1(b) shows the phase diagram of these systems. At low temperature both order antiferromagnetically with a six sub-lattice structure in which the spins lie parallel or antiparallel to the easy axis. At high temperatures, there is a line of critical points which separates the antiferromagnetic and paramagnetic phases while at low temperatures upon application of a field there is initially a first order transition from the antiferromagnetic phase to a ferrimagnetic phase in which four of the sublattice are parallel and two antiparallel
Figure 2.1: Schematic phase diagram of FeCl₂ and DyPO₄. $H_i$ is the internal magnetic field and $T$ is the temperature. The solid and dashed lines denote the second and first-order transitions respectively. (b)Schematic phase diagram of CoCl₂.2H₂O and FeCl₂.2H₂O. One probable result is shown out of various possible ones. (c)Schematic phase diagram of MnF₂ and GdAlO₃ (Taken from [26]).
to the easy axis. At higher field strengths there is another first order phase transition from ferrimagnetic to the paramagnetic phase. The two phase boundaries meet at a triple point where the antiferromagnetic-paramagnetic boundary begins. MnF$_2$ and GdAlO$_3$ are systems which belong to class (2). Fig 2.1(b) shows the phase diagram for such weakly anisotropic systems. Both order antiferromagnetically in zero field, and display a line of critical points in low fields. When a magnetic field is applied at low temperature there is first order transition to the spin-flop phase in which the spins are canted away from the easy axis. This is shown in Fig 2.1(c). At higher fields, there is a second order transition to the paramagnetic phase as the angle between the spins goes continuously to zero.

In the metamagnets considered here, belonging to class (1), the magnetic moments (or spins) can only point in two possible directions (up or down due to the large single ion anisotropy), so that a spin Ising model can be used as a model for such a system. In this section we shall study this model, assuming antiferromagnetic nearest neighbor (nn) interactions and either ferro- or antiferromagnetic next nearest neighbor (nnn) interactions, in the mean field approximation. It will be shown that for sufficiently strong ferromagnetic nnn interactions a phase diagram much like that for FeCl$_2$, including a tricritical point, will be found. For other choices of the interaction strengths other types of phase diagrams are obtained which may also be found in nature.

Next we consider a model, where the magnetic moments or spins are arranged on a regular lattice of $N$ sites that consists of two equivalent inter-penetrating sublattices, denoted by 1 and 2, each having a total of $N/2$ sites. The $z$ nearest-neighbors (nn) of every spin on a particular sublattice are all on the other sublattice, while $z'$ the next-nearest neighbors (nnn) of every spin are all on the same sublattice (see Fig. 2.2). The particular type of lattice structure (e.g. simple cubic, stacked ferromagnetic planes coupled antiferromagnetically will have a significant effect on the properties of the model. However in the mean field approximation the only relevant properties of the lattice
Figure 2.2: The lattice for the metamagnet can be decomposed into two interpenetrating sublattices (○, ●). Nearest neighbors (nn) are on different sublattices, next-nearest neighbors (nnn) are on the same sublattice. The plane square lattice (i) has \( z = 4, z' = 4 \). The simple cubic lattice (ii) has \( z = 6 \) and \( z' = 12 \) (Taken from [31]).
structure that enter are $z$ and $z'$.

We restrict ourself to a classical Hamiltonian, $\mathcal{H}$, of the system as

$$
\mathcal{H} = J \sum_{nn} \sigma_i \sigma_j - J' \sum_{nnn} \sigma_i \sigma_j - \mu_B \mu_0 H \sum_{i=1}^{N} \sigma_i
$$

(2.1)

where $J$ is the nn spin exchange constant; $\mu$ is magnetic moment of a spin; $\sigma_i = \pm 1$ depending on whether the spin at the ith site is up or down, respectively; $J'$ is nnn spin exchange constant; $\mu_0 H$ is the strength of the external magnetic field; $\sum_{nn}$ represents sum over all pairs of nn spins; $\sum_{nnn}$ represents sum over all pairs of nnn spins.

It is assumed that $J > 0$, i.e. the nn interaction is antiferromagnetic, tending to align nn spins antiparallel, while we leave open for the moment the sign of $J'$ so that it can be either antiferromagnetic ($J' < 0$) or ferromagnetic ($J' > 0$). Note that this convention is opposite to regular usage AF exchange coupling constant where $J < 0$ and vice versa for FM coupling constant. The external magnetic field is assumed to be in the up direction, so that the spin can align either parallel or antiparallel to the field.

The thermodynamic properties and in particular the phase diagram of a system described by the Hamiltonian can be found from the partition function $Z_N(T, H)$ since the Gibb’s free energy $G(T, H, N)$ is given by:

$$
G(T, H, N) = -k_B T \ln[Z_N(T, H)]
$$

(2.2)

where

$$
Z_N(T, H) = \sum_{\sigma_i} \exp(-\mathcal{H}/kT)
$$

(2.3)

Here $\sum_{\sigma_i}$ denotes a sum over all possible spin configurations; $k_B$ is Boltzmann’s constant.

Since an exact evaluation of Eq. 2.3 for the Hamiltonian of Eq.2.1 is not possible at present, we will later compute $Z_N(T, H)$ in the mean field approximation.
2.2 Interlayer Exchange Coupling in Magnetic Heterostructures

In the history of science, the development of new technical skills and equipment has been playing a crucial role in discovering new physical phenomena and disclosing new fields of research. This is exemplified by the development in the vacuum deposition technology during recent decades which allows the growth of samples with control down to a few atomic layers. This has led to the manifestation of phenomena like interlayer exchange coupling (IEC). The investigation of the coupling of ferromagnetic films across non-ferromagnetic spacers has resulted in a spectrum of scientific discoveries as well as technologically useful devices.

The IEC is observed between two thin magnetic metallic layers that are separated by a very thin (a few atomic layers) nonmagnetic layer. Depending on the thickness of the spacer layer, the two magnetic layers are found to have their magnetization direction either parallel or anti-parallel. It was first discovered as the antiferromagnetic coupling in a Fe/Cr/Fe multilayer structure by Grünberg in 1988 [33]. Later, by Parkin [34], the coupling was shown to oscillate between parallel and anti-parallel orientation as a function of thickness of the non-magnetic metallic interlayer with a periodicity of typically 1 nm and decreases very rapidly in strength as the spacer becomes thicker. Fig.2.3 illustrates the variation of antiferromagnetic coupling strength of $J_{AF}$ vs thickness of Cr layer ($d_{Cr}$) for (211) and (100) oriented Fe(14Å)/Cr($d_{Cr}$) superlattices measured at room temperature.

The IEC originates from the so-called Ruderman-Kittel-Yosida (RKKY) coupling that was used decades before to explain the coupling between magnetic impurities in a non-magnetic matrix [35, 36, 37]. In the case of coupling across a non-magnetic spacer, the RKKY-coupling experienced by a specific interface atom in the magnetic layer is sum of
the contributions of interface atoms. The interference of these coupling contributions is strongest when the interface is smooth and as a consequence the coupling is detrimentally affected by the mixing of interfaces.

Since the change in sign of the coupling by a difference in the spacer thickness of typically 0.5 nm only, it is obvious that the coupling is very sensitive to corrugations of the interlayer, in particular when the interlayer is not uniform. This in our studies is not a disadvantage because we are here concerned about weak antiferromagnetic coupling. The interface and thereby the reduced coupling strength is strongly influenced by growth methods. It is well-known that Fe/Cr superlattices grown by Molecular Beam Epitaxy (MBE) have the smoothest interface compared to those grown by DC-magnetron sputtering [38].
A series of theoretical models have been proposed to explain the interlayer exchange coupling across both metallic and insulating spacer layers.

For metallic layers:

1. the RKKY model [35, 36, 37], in which the FM layers are represented by arrays of localized spins interacting with electrons through a contact exchange potential;

2. the tightbinding model or hole confinement model [42, 43], which considers spin-dependent potential steps;

3. the sd-mixing model [44, 45, 46]; and

4. the quantum interference model [47], in which multiple reflection of electron waves at the ferromagnetic/spacer interfaces and their interference are considered.

All these models have related the oscillatory period of interlayer exchange coupling in metals to the Fermi surface of the bulk spacer material in the limit of large spacer thickness.

RKKY-based models do not use an appropriate description of the magnetism in transition metals but they do point out some important general features of models for the interlayer exchange coupling. They point out that the periods of the oscillatory coupling are determined by critical spanning vectors of the Fermi surface of the material that makes up the spacer layer [42, 48]. Critical spanning vectors, are vectors in the direction of the interface normal, that connect two sheets of the Fermi surface that are parallel to each other at the endpoints of the vector. Critical spanning vectors determine the coupling periods in all models of interlayer exchange coupling.

While models based on the RKKY interaction capture much of the essential physics and correctly predict possible coupling periods, they do not correctly predict the strength of the coupling because they do not adequately describe magnetism in transition metals.
An alternate approach, which is also not quantitative but captures much of the essential physics, is to make a free-electron approximation in each layer with exchange split bands in the ferromagnetic material. The two simple models, RKKY and spin-split free-electron bands, represent two extremes in the description of magnetism, local-moment models and itinerant models respectively.

One feature of free-electron models is that the strength of the interlayer coupling depends on the spin difference of the reflection amplitudes for electrons in the spacer layer reflecting from the interfaces with the magnetic material. This dependence transfers to models with general band structures \([47]\). Spin-dependent reflection from the interfaces gives quantum confinement in the spacer layer \([42]\), setting up spin-dependent quantum-well states, both true bound states and resonances, due to the interference resulting from multiple reflection from the interfaces. As mentioned above, these quantum-well states have been seen experimentally in photoemission and inverse photoemission \([49]\). The filled quantum-well states give rise to the oscillatory polarization. As the thickness of the spacer layer is changed, the quantum-well states move up or down in energy depending on the details of the spacer-layer band structure. The oscillatory interlayer exchange coupling is determined by the energy changes associated with filling and emptying these states as they cross the Fermi energy when the thickness of the spacer layer is varied. The stronger the spin-dependent reflection, the stronger the confinement and the stronger the oscillatory coupling.

All these models, RKKY, quantum-confinement, and interface-reflection predict that for large spacer-layer thicknesses, \(d\), the coupling should be given by a sum of terms of the form

\[
J(d) = \sum_{\alpha} \frac{J_{\alpha}}{d^2} \sin(q_{\perp}^\alpha + \phi^\alpha) 
\]  

(2.4)

There is a contribution from each critical point, labeled by \(\alpha\), with critical spanning vector
coupling strength, $J^\alpha$, and phase $\phi^\alpha$. For large thicknesses, this form is independent of the model used to describe the interlayer coupling. For small thicknesses, other terms, called pre-asymptotic corrections, become important. In all models, the periods are determined by the critical spanning vectors of the spacer-layer Fermi surface, $L^\alpha = \frac{2\pi}{q^\perp}$. Thus, the best way to compare measured coupling periods with theory is to use the critical spanning vectors found from analyzing experimental measurements of the Fermi surfaces [48].

Model-independent comparisons are not possible for comparing coupling strengths. Two main approaches have been used for computing coupling strengths. The first approach is to calculate the total energy of the multilayer by computing and filling all the electron states below the Fermi energy. These calculations can be self-consistent, allowing the potential to vary in response to variations in the densities, or not. Even if not done self-consistently, these calculations are computationally very demanding. They have been implemented using different approximations for the band structure. The two most common approximations are tight-binding (TB) approximations or the local-density approximation (LDA).

The second approach is to calculate the coupling strength, $J^\alpha$, in the asymptotic expansion for each contribution to the sum. These calculations are much less demanding computationally and give insight into what aspects of the band structures, Fermi surfaces, and electronic wave functions are important. The asymptotic form results from an approximation that ignores the energy and parallel wave-vector dependence of the reflection amplitudes and assumes that the Fermi surface is strictly quadratic near the critical points of the Fermi surface.

A final theoretical issue is related to self-consistency in the electronic structure calculations. All of the asymptotic calculations and many of the total-energy calculations ignore the effect of the electron-electron interaction in the spacer layer on the spin-density
wave that gets set up there. Ignoring the electron-electron interaction is analogous to using the bare susceptibility, $\chi_0$, as opposed to the Stoner enhanced susceptibility, $\chi = \chi_0/(1 - J\chi_0)$. For noble metal spacer layers, this approximation appears to be good. In Fe/Cr multilayers, the coupling is found to be a superposition of a short period and a long period. Ignoring the electron-electron interaction is not a good approximation for the short-period component of the coupling. On the other hand, it may be a good approximation for the long-period contribution. It is difficult to determine the importance of the electron-electron interactions in other systems.

2.3 Finite Size Scaling for tuning of Curie Temperature

The question of what happens to the bulk thermodynamic properties of a system when one or more of its dimensions are reduced to atomic size is one of fundamental importance. Statistical mechanical calculations of second-order phase transitions suggest that the position and nature of a critical singularity will be affected in a precise defined way by scaling of thickness of ferromagnetic films.

To obtain a comprehensive understanding of the correlation between the magnetism and structure of materials has been a research goal of scientists for a long time. Early in the 1930s, Bethe and Slater found a phenomenological relationship between the direct exchange interaction and the atomic separation [50, 51] (Fig. 2.4). Recently, the correlation between the structure and the magnetism for 3d metals has been investigated with advanced self-consistent energy-band calculations [52, 53, 54]. These calculations show that the magnetic properties of a 3d metal are closely related to the atomic volume. Normally magnetic transition metals will lose their magnetic moment at a compressed volume and, on the other hand, nonmagnetic transition metals will become ferromagnetic at an expanded volume. Thus a transition from the nonmagnetic to a magnetic state is
Figure 2.4: The Bethe-Slater curve relates the exchange constant $J$ to the ratio of the atomic separation $R$ to the radius of the d shell $R_d$ (Taken from [55]).

expected for all 3d transition metals when the atomic volume is increased. In the limit of large volume, the magnetic moment approaches the value determined by Hunds rule for the free-atom configuration.

Finite-size scaling theory predicts that the Curie temperatures of magnetic thin-films will decrease from the bulk value as the film thickness is reduced because of the sensitivity of the long ranged correlation length near the critical point to the system boundaries. The physical boundaries effectively act as a cut-off length to the correlation length. One expects, therefore a strong dependence of the critical phase transition as one, or more, of its dimensions is reduced, one important example of which is the large change in the critical temperature with varying film thickness observed in the systems.

This has been observed in a variety of thin-film systems. For example, the thickness($n$) dependent Curie temperatures $T_c(n)$ in ferromagnetic thin-films and the spin-freezing temperature $T_g$ in spin-glass multilayers have been observed to be significantly lower than their bulk values.

The finite-size scaling of Curie temperature can be best expressed in the form of a power law as [56]

$$\frac{T_c(\infty) - T_c(n)}{T_c(n)} = \left( \frac{n - n'}{n_0} \right)^{-\lambda}$$

(2.5)

is established and experimentally, well confirmed in diverse systems ranging from
ferromagnetic metallic thin-films such as Co [66, 108] to insulating antiferromagnetic oxides such as CoO [57]. Here, $n$ is the thickness of the film where discreteness of the growth via individual monolayers has to be taken into account in the limit of ultrathin-films, $n'$ is the critical thickness above which long-range order sets in, $n_0$ is the extrapolated $T = 0$ correlation length, and $\lambda$ is the shift-exponent. The latter has been related to the critical exponent, $\nu$, of the correlation length according to $\lambda = 1/\nu$ [58, 59], indicating the physical origin of Eq. 2.5 as the geometrically limited growth of the correlation length. The latter tends to diverge with a power-law and critical exponent when approaching the critical temperature in the thermodynamic limit of bulk systems. Measurements of the Curie temperatures of Co, Ni, and Co$_1$Ni$_9$, [66] alloy films show the film thickness dependent Curie temperature in $T_c(n)$ is best described in the ultrathin-film limit by a finite-size scaling relation of this form [Eq. 2.5].

When the thickness of a magnetic film decreases to monolayer range, a dimensionality crossover from three-dimensional (3D) to two-dimensional (2D) behavior is expected. Statistical mechanics predicts different critical exponents for systems of different dimensionality. The critical exponent $\beta$ for example, describes how the magnetization $M$ of a ferromagnet vanishes near $T_c$

$$M \propto (1 - \frac{T}{T_c})^\beta, T \to T_c$$ (2.6)

Different $\beta$ values are predicted when different models representing different universality classes are used, but they are independent of the specific details of the chosen system. In the Heisenberg model, the orientation of the spins is not restricted by anisotropy. In this model, long-range magnetic ordering is expected only for three dimensional systems. The predicted $\beta$ value is about 0.365. If the spin orientation is confined in a plane, one obtains the $xy$ model. In this case, $\beta \approx 0.34$ for 3D system and $\beta \approx 0.23$ for finite 2D
In the Ising model, a preferred spin orientation exists so that there are only two choices for the spins, parallel or opposite to the given direction. In this case, the critical exponents are 0.325 for a 3D system and 0.125 for a 2D system.

The critical exponents have been measured for a number of ultrathin films. These data, compiled by Himpsel et al. [60], are listed in Table 2.2. The measured exponents fall into two groups, which correspond to the 2D Ising model and the finite xy model.

<table>
<thead>
<tr>
<th>System</th>
<th>β</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Pd(100)</td>
<td>0.127</td>
<td>[61]</td>
</tr>
<tr>
<td>Fe(110)/Ag(111)</td>
<td>0.137</td>
<td>[62]</td>
</tr>
<tr>
<td>Fe/W(110)</td>
<td>0.123</td>
<td>[63]</td>
</tr>
<tr>
<td>Fe/Au(100)</td>
<td>0.22</td>
<td>[64]</td>
</tr>
<tr>
<td>Ni/Cu(111)</td>
<td>0.24</td>
<td>[65]</td>
</tr>
<tr>
<td>Ni/Cu(111)</td>
<td>0.28</td>
<td>[66]</td>
</tr>
<tr>
<td>Ni/Cu(100)</td>
<td>0.24</td>
<td>[66]</td>
</tr>
<tr>
<td>Fe/W(100)</td>
<td>0.22</td>
<td>[67]</td>
</tr>
</tbody>
</table>

Table 2.1: Experimentally measured critical exponents β for ultrathin metal films. Values close to 0.125 are characteristic of Ising-like systems, while values around 0.23 are indicative of 2D xy models.

Early investigations of the magnetic properties of iron films on Cu(100) concentrated on the characterization of the magnetic ground state and the determination of the magnetic anisotropy. Little attention was given to measurement of the magnetic moment for fcc Fe, and a direct correlation between the structure and magnetism of the films had not yet been established. Moreover, even the results that describe the magnetic ground state and the magnetic anisotropy showed surprising discrepancies. Table 2.2 summarizes some early experimental observations. Since a pronounced dependence of the magnetic properties upon film thickness and growth temperature was found, these parameters are specified. Some researchers found that the ground state of the fcc iron films was antiferromagnetic, others claimed that it was ferromagnetic or even found the absence of ferromagnetism. Similarly contradictory findings were also reported for the magnetic anisotropy. There
is general consensus, however, that for ultrathin iron films the magnetization is initially aligned perpendicular to the surface. Above a certain critical thickness, the magnetic anisotropy changes from perpendicular to in-plane.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Measuring technique</th>
<th>Film thickness, growth temperature</th>
<th>Magnetic ground state Curie or Néel temperature</th>
<th>Magnetic anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>[68]</td>
<td>Mossbauer spectroscopy</td>
<td>4 ML, 300 K</td>
<td>Antiferromagnetic (40 K)</td>
<td>-</td>
</tr>
<tr>
<td>[69]</td>
<td>Mossbauer spectroscopy</td>
<td>4 ML, 420 K</td>
<td>Antiferromagnetic (65 K)</td>
<td>-</td>
</tr>
<tr>
<td>[70]</td>
<td>Spin-polarized photoemission, SMOKE</td>
<td>Up to 20 ML, 420-460 K</td>
<td>Ferromagnetic (&gt; 420K)</td>
<td></td>
</tr>
<tr>
<td>[71]</td>
<td>Spin-polarized photoemission</td>
<td>1, 3, 5 ML, 300 K</td>
<td>Ferromagnetic (300 K)</td>
<td>1 ML, 3, 5 ML, ⊥ (for T &lt; 30K)</td>
</tr>
<tr>
<td>[72]</td>
<td>Spin-polarized secondary-electron emission</td>
<td>5-7ML, 125 K (annealed at 300 K)</td>
<td>Ferromagnetic (350K)</td>
<td>5 ML,</td>
</tr>
<tr>
<td>[73]</td>
<td>SMOKE</td>
<td>1-8 ML, 110-350K</td>
<td>Ferromagnetic</td>
<td>d &lt; 6ML, ⊥</td>
</tr>
<tr>
<td>[74]</td>
<td>Spin-polarized photoemission</td>
<td>Up to 20 ML, 300 K</td>
<td>Ferromagnetic</td>
<td>d &lt; 14ML, ⊥</td>
</tr>
<tr>
<td>[75]</td>
<td>Brillouin scattering</td>
<td>Up to 20 ML, 300 K</td>
<td>Ferromagnetic</td>
<td>d &lt; 6ML, ⊥</td>
</tr>
</tbody>
</table>

Table 2.2: Summary of various experimental investigations of the magnetic properties of Fe on Cu(100). || and ⊥ denote a magnetization parallel or perpendicular, respectively, to the surface.
2.4 The Magnetocaloric effect

The magnetocaloric effect (MCE) is defined as the heating or cooling (i.e., the temperature change) of a magnetic material due to the application of a magnetic field. For years this effect has been exploited in low temperature physics in the framework of adiabatic demagnetization. For excellent reviews on the MCE, see [77, 78, 79, 80, 81]. The magnetocaloric effect was discovered in 1881, when Warburg observed it in iron [15]. The origin of the MCE was explained independently by Debye [82] and Giauque [16]. They also suggested the first practical use of the MCE: the adiabatic demagnetization, used to reach temperatures lower than that of liquid helium, which had been the lowest achievable experimental temperature. There is a great deal of revived interest in using the MCE as an alternative technology for refrigeration, from room temperature to the temperatures of hydrogen and helium liquefaction (20-4.2 K). The magnetic refrigeration offers the prospect of an energy-efficient and environment friendly alternative to the common vapour-cycle refrigeration technology in use today.

The magnetic work done on a magnetic substance with the magnetization ($M$) in an external magnetic field ($H$) is given by

$$dW = -V\mu_0 H dM$$

(2.7)

First law of thermodynamics for a system involving magnetic work yields

$$dU = dQ - dW = TdS + V\mu_0 H dM$$

(2.8)

where $U$ is the internal energy, $T$ is the absolute temperature, $S$ is the entropy, and $V$ is the volume.

From Eq. 2.8 one obtains via two-fold Legendre transformation of Gibbs free energy,
which reads as [83]

\[ G = U - TS - \mu_0 VMH \]  \hspace{1cm} (2.9)

and

\[ dG = -SdT - \mu_0 VMdH \]  \hspace{1cm} (2.10)

The determination of entropy \( S \) and Magnetization \( M \) is given by:

\[
S(T, H) = -\frac{1}{\mu_0 V} \left( \frac{\delta G}{\delta T} \right)_H
\]

\[
M(T, H) = -\frac{1}{\mu_0 V} \left( \frac{\delta G}{\delta H} \right)_T
\]  \hspace{1cm} (2.11)

One can represent the specific heat of a system via the second derivative of Gibbs free energy with respect to temperature as

\[
C_H = -\frac{T}{\mu_0 V} \left( \frac{\delta^2 G}{\delta^2 T} \right)_H
\]  \hspace{1cm} (2.12)

By definition if the first order derivative of the Gibb’s free energy is discontinuous at the phase transition, then the phase transition is of first order. Therefore, the magnetization and entropy of the magnetic material are discontinuous at a first-order phase transition. If the first derivative of the Gibb’s free energy is continuous at the phase transition but the second derivative is discontinuous, then the phase transition is of second order.

An external magnetic field can strongly affect the magnetic order of a material, and also its temperature if phonon and magnetic excitations are well coupled via spin-lattice coupling. Considering the absolute temperature \( T \) and magnetic field \( H \) as independent thermodynamic variables, the total entropy \( S(T, H) \) of a magnetic solid with localized magnetic moments is the sum of the electronic \( (S_E) \), lattice \( (S_L) \), and magnetic \( (S_{spin}) \) entropies. In a solid with magnetic moments carried by itinerant electrons, the separation of the \( S_E \) and \( S_{Spin} \) may not be straightforward. However, all three contributions to the
total entropy can be considered as functions of both $T$ and external magnetic field $H$. While $S_{\text{spin}}$ strongly depends on $H$, $S_E$ and $S_L$ are usually magnetic field independent. If the magnetic and crystalline lattices are strongly coupled, both $S_E$ and $S_L$ may also become functions of $H$. The total entropy can be expressed as

$$S(T, H) = S_E(T, H) + S_L(T, H) + S_{\text{spin}}(T, H)$$  \hspace{1cm} (2.13)

Since entropy is state function, the complete differential of the total entropy is given by

$$dS(T, H) = \left( \frac{\partial S}{\partial T} \right)_H dT + \left( \frac{\partial S}{\partial H} \right)_T dH$$  \hspace{1cm} (2.14)

Under isothermal conditions ($dT = 0$), the differential of the total entropy becomes

$$dS(T, H) = \left( \frac{\partial S}{\partial H} \right)_T dH$$  \hspace{1cm} (2.15)

For a field change $\Delta H = H_i - H_f$, the total entropy change can be obtained by numerically integrating eq: 2.15 as

$$\Delta S(T, H) = \int_{H_i}^{H_f} \left( \frac{\partial S}{\partial H} \right)_T dH$$  \hspace{1cm} (2.16)

As long as the magnetic equation of state is known, the magnetic entropy change can be calculated.

The entropy change is related to the bulk Magnetization $M(H, T)$, the magnetic field and the temperature through Maxwell’s relation

$$\left( \frac{\partial S(T, H)}{\partial H} \right)_T = \mu_0 V \left( \frac{\partial M(T, H)}{\partial T} \right)_H$$  \hspace{1cm} (2.17)
Integrating Maxwell’s relation [Eq. 2.17] the isothermal entropy change is given by

\[
\Delta S_{iso} = \mu_0 V \int_{H_i}^{H_f} \left( \frac{\partial M}{\partial T} \right)_H dH
\]

(2.18)

for the isothermal entropy change induced by a field increase from the initial value, \( H_i \), to the final value, \( H_f \).

The adiabatic temperature change can be estimated by

\[
\Delta T_{ad} = -\mu_0 TV \int_{H_i}^{H_f} \frac{1}{C_H} \left( \frac{\partial M}{\partial T} \right)_H dH
\]

(2.19)

This expression describes the drop in temperature of a sample with positive MCE (see below) when removing the applied magnetic field while heat exchange with the surrounding is suppressed.

A sum rule can be derived from Eq. 2.18 concerning the area under the curve under a plot of \( \Delta S \) vs. \( T \) for a given applied field, \( H \) [14]

\[
\int_0^\infty \Delta S(T') dT' = -\mu_0 VH M_s
\]

(2.20)

This integral is defined as of what is called Relative cooling Power (RCP). This sum rule implies that for materials with same saturation moment, \( M_s \), materials with high entropy change at a given temperature will have low entropy changes at other temperatures, and those materials which do not have a large entropy change at any particular temperature can undergo a moderate entropy change over a broader temperature range.

A final word about classification of positive and negative MCE. A majority of published reports on MCE focused on compounds that undergo paramagnetic(PM) to ferromagnetic (PM \( \rightarrow \) FM) transition, in which \( \Delta S \) is negative and hence they exhibit normal or positive
MCE. In contrast to ferromagnets which cool upon demagnetization, antiferromagnets cools upon adiabatic magnetization, i.e., they show inverse or negative MCE in which $\Delta S$ is positive. Materials demonstrating both positive MCE and negative MCE can be used to enhance refrigerant capacity (RC) as they are cooled by both adiabatic magnetization and demagnetization.

### 2.5 Aging phenomena far from Equilibrium

Non-equilibrium thermodynamics is one of today’s active frontiers in fundamental science [84]. Particularly appealing are some of the unifying aspects of systems far from equilibrium when considered against the background of the evermore specializing fields of the physical, chemical and biological sciences. Spin glass physics and its relation to concepts of memory and pattern recognition in biological neural networks is one example for transdisciplinarity of non-equilibrium statistical mechanics [85, 86]. Progress in experiment and theory of statistical mechanics is needed to push the boundaries of the understanding of non-equilibrium properties of complex systems even further.

The concept of aging phenomena refers to evolution of material property over time, even without any apparent forces acting on them. Aging arises when the relaxation processes of a system, brought out of equilibrium by a sufficiently rapid change of its thermodynamic state variables, are governed by large fluctuation effects which prevent a rapid return to the stationary state. This may happen quite independently on whether the equilibrium state of the system is itself at an equilibrium critical point or not.

**Definition:** A physical many-body system is said to undergo aging if the relaxation process towards its stationary state(s) obeys the properties [84]:

1. slow dynamics (i.e. non-exponential relaxation)
2. breaking of time-translation-invariance

3. dynamical scaling

Magnetic model systems serve traditionally as workhorses in equilibrium statistical mechanics [1, 87]. They maintain their importance in the challenging field of non-equilibrium thermodynamics. Magnetic aging phenomena are conceptually simple with well-defined experimental protocols. At the same time, even macroscopically complex magnetic behavior can be described by simple model Hamiltonians. Similarly to the celebrated concept of universality in equilibrium statistical mechanics where symmetry of the interactions and dimensionality unify otherwise microscopically different systems into classes with common critical behavior, there are magnetic control parameters grouping microscopically distinct model systems into classes with universal aspects of non-equilibrium thermodynamics.

Magnetization relaxation in weakly correlated spin systems is typically a fast process on a laboratory time scale since it depends on the microscopic spin-flip time of about $10^{-8}$ s. From an experimental point of view it is convenient to study magnetic relaxation phenomena on a time scale from seconds to hours. However, this requires the presence of non-exponentially decaying spin-spin correlation. Our novel approach to study magnetic relaxation in ordered magnetic systems builds on the increase of the characteristic spin-spin correlation length in comparison to atomic bulk systems when taking advantage of magnetic nanostructuring. We use magnetic superlattices, structured on the nanoscale, to increase relaxation times when replacing atomic spins through mesoscopically correlated regions.

It is well-known that spin glasses are characterized by the shared effects of disorder and frustration [88, 89]. Experiments to this date might suggest to presume that aging would only occur for glassy systems. However, simple, non-disordered and non-frustrated
ferromagnets show aging as well. This is very fortunate, since presumably the dynamics of simple magnets should be much easier to understand than the one of complex glassy systems. The differences in the aging behavior of glassy systems and simple magnets have recently been discussed in [90, 91] through the study of spatial-temporal fluctuations out of equilibrium. It has been argued that the observed difference in fluctuation pattern in ferromagnets and in glassy systems is due to more restricted dynamical symmetries in the former as compared to the latter.

The basic experimental set-up is as follows:

1. Prepare the system in a high-temperature state ($T \gg T_c$).

2. Lower the temperature (quench) to a value low enough such that several equilibrium states exist and perform the quench rapidly enough such that the system is forced out of equilibrium.

3. Fix the temperature and observe the evolution of the system, e.g. in case of magnetic system evolution of magnetization in response to a magnetic field.

In order to understand what we are really measuring when we prepare the system in a state with a scheme described above, we need to understand the basics of Correlation and Response Functions. We consider ferromagnetic systems with neither disorder nor frustrations which should be more simple to understand than glass-forming systems. Let the value of the order-parameter (magnetization) at time $t$ and at the space point $r$ denoted by $\phi(t, r)$. The breaking of time-translation invariance suggests that the definition of two-time quantities might be appropriate for the study of aging. Consider the two-time correlation function

$$C(t, s; r) := \langle \phi(t, r)\phi(s, 0) \rangle - \langle \phi(t, r) \rangle \langle \phi(s, 0) \rangle$$  \hspace{1cm} (2.21)
of the order-parameter $\phi(t,r)$ at time $t$ and position $r$, where $t, s$ with $t \geq s$ are two times, both measured since the quench. Since we shall rapidly restrict to simple ferromagnets without disorder or frustrations, we have already assumed here spatial translation-invariance. For a fully disordered initial state, one expect $\langle \phi(t,r) \rangle = \langle \phi(0,r) \rangle = 0$. We also define the (linear) two-time spatio-temporal response function

$$R(t,s;r) := \delta \langle \phi(t,r) \rangle \bigg|_{h=0}$$

where $h$ is the external (magnetic) field canonically conjugated to the order-parameter $\phi$. Causality requires that $R(t,s;r) = 0$ for $t < s$. We point out immediately that, since the system is far away from equilibrium, $C$ and $R$ be studied independently from each other.

In aging systems, two-time quantities such as $C(t,s;r)$ or $R(t,s;r)$ generically depend on both times $t$ and $s$. Usually, $s$ is called the waiting time while $t$ is called the observation time. It is convenient to work with the autocorrelator (or autocorrelation function) and the autoresponse defined through

$$C(t,s) := C(t,s;0), R(t,s) := R(t,s;0)$$

In this thesis the thermo-remanent protocol (TRM) is used in which a small field $h$ is turned on right at the moment $t = 0$ of the quench and kept until the waiting time $s$ has elapsed. Then the field is turned off in a time scale $t' \ll s$ and at a later time $t$ the so called thermoremanent magnetization $M_{TRM}(t,s)$ is measured.

The measured time-dependent magnetization ($M$) are related to the autoresponse as follows

$$M_{TRM}(t,s) = h \int_0^s du R(t,u)$$

With this background we will next discuss the aging behavior in simple magnets.
Figure 2.5: Schematic equilibrium free energies $F(M)$ of an uniaxial magnet for (a) $T > T_c$ and (b) $T < T_c$. The ball indicates the state of the system Taken from [92].

We consider the Ising model to describe the aging behavior of simple magnets. Similar to glassy systems, we initially prepare the system in a fully disordered state (infinite initial temperature) and then quench it to a final temperature $T$ far below the critical temperature $T_c$. In figure 2.5 we illustrate the systems behavior through the equilibrium free energy before and immediately after the quench. Initially, there is a single equilibrium state and the system has had enough time to relax to it, hence it is at the global minimum of the free energy as indicated by the ball in figure 2.5(a). Directly after the quench, the state of the system has not yet evolved, but it is now at a local maximum of the free energy [see figure 2.5(b)] and should in principle relax towards one of the several
stable and equivalent equilibrium states. In the absence of a magnetic field, the distinct equilibrium states are competing with each other. Locally, however, each spin is subject to the magnetic fields of its neighbors, which will induce a preferential relaxation towards one of the equilibrium states. Hence the spins will order, but only locally and the system should decompose into distinct ordered domains. In the interior of these domains, the state of the system does not change, but the domain walls move slowly in such a way that the linear size $L(t)$ increases as a function of time. This slow motion creates the slow evolution of the state of the system.

These qualitative ideas are illustrated for the 2D Ising model quenched to a temperature $T = 1.5 \ll T_c$ in Fig. 2.6. Two snapshots of the local state of the system, at two different times $t$ after the quench is shown. It can be seen that already shortly after the quench, ordered domains have formed, the size of which is slowly increasing with time. In figure 2.6(a) we show the magnetic autocorrelator $C(t,s) = \sum_{r \in \mathbb{Z}^2} \langle M(t,r)M(s,r) \rangle$, where $M(t,r)$ is the time-dependent magnetization of the cell at location $r$. Clearly, $C(t,s)$
Figure 2.7: Aging in the 2D Ising model quenched to $T = 1.5 < T_c$. In (a) the magnetic autocorrelator $C(t, s)$ is shown as a function of $t - s$ for several waiting times $s$ and in (b) the collapse of these same data is shown when re-plotted as a function of $t/s$ (Taken from [84]).

shows a slow evolution and does not relax within some finite time to a stationary value. Furthermore, it does not merely depend on the time difference $\tau = t - s$, see figure 2.7. In addition, when the same data are replotted as a function of $t/s$, a clear collapse results, provided the waiting times are sufficiently large. This is shown in figure 2.7b. Hence the three defining conditions for aging are satisfied.

In summary,

1. Aging may arise when a many-body system is rapidly brought out of its equilibrium state and into a coexistence region of its equilibrium phase diagram, such that there are at least two stable, equivalent and competing equilibrium states where it can relax to. For simple magnets, the conceptually most simple way of doing this might be to quench the temperature from a very large initial value $T_{ini} \gg T_c > 0$ to a value $T < T_c$.

2. Aging may also arise when a many-body system is quenched onto its critical point, i.e. by rapidly changing its temperature to $T = T_c > 0$. In contrast to the case $T < T_c$,
here the slow dynamics of a many-body system at its critical point generates the aging behavior.

3. Time-translation-invariance is broken: at least one multi-time observable does not only depend on the time differences.

4. There is slow, non-exponential dynamics. Independent of the properties of the individual stationary states, one observes dynamical scaling.

5. The formation of ordered (or correlated) domains with a time-dependent length-scale $L(t)$ occurs.
Chapter 3

Sample Preparation and Characterization Techniques

This chapter outlines the sample fabrication and characterization techniques used in the work of this thesis. Thin film samples were deposited by Molecular Beam Epitaxy (MBE) with thermal evaporation and with Pulsed laser deposition (PLD). The latter is a method of depositing both thin metal films and insulators onto a substrate with Laser ablation. Throughout this study the characterization techniques fall into two categories: structural characterization and magnetic characterization. Structural characterization was accomplished with x-ray diffraction and x-ray reflectivity, which give access to the crystalline structure, thickness and local/long-range roughness of the various constituent layers. Magnetic properties of the studied films were characterized using Superconducting Quantum Interference Device (SQUID), Magneto-optical Kerr effect (MOKE) and Alternating Gradient force Magnetometry (AGFM).
3.1 Preparation Methodologies

3.1.1 Molecular beam Epitaxy

Molecular beam epitaxy (MBE) is a potential layer by layer deposition technique for growing high quality thin-films. This technique was invented in 1960s at Bell laboratories by J. R. Arthur and Alfred Y. Cho [93, 94]. Molecular Beam Epitaxy (MBE) is a well established technique to grow heterostructures under very clean and controlled conditions. The term epitaxy is derived from the Greek words epi (meaning “on”) and taxis (meaning “arrangement”) and describes the potential crystalline growth of one material on the same (homoepitaxy) or on a different material (heteroepitaxy).

The principle underlying MBE growth is simple. It utilizes essentially atoms or clusters of atoms, which are produced by heating up a solid source. They, then migrate in an ultra-high vacuum (UHV) environment and impinge with kinetic energies low in comparison to other deposition techniques on a substrate, where they can diffuse and eventually incorporate into the growing film. Despite the conceptual simplicity, a great technological effort is required to produce systems that yield the desired quality in terms of material purity, uniformity and interface control and, also achieving the epitaxial growth of the film is a gigantic challenge. MBE is a proper technique when some particular requirements are needed such as abruptness of the film surfaces, control over the interfaces and doping profiles. Typically, MBE deposition takes place in UHV (< 10^-8 mbar) and at slower deposition rates (typically less than 0.1 Å/sec for my superlattice growth) which may allow the possibility of epitaxial growth of film. Finally, the UHV environment in MBE may also provide the use of electron diffraction probes such as Reflecting High Energy Electron Diffraction (RHEED) without any differential pumping system attached RHEED gun.

Figure 3.1 is the photograph of our present MBE apparatus. Our MBE System SY050
Figure 3.1: A photograph of our present Molecular Beam Epitaxy apparatus. Two backing pumps (at the bottom), two turbo molecular pumps (not visible), an ion pump (on the left hand side) and the titanium flash (not visible) are used in pumping down the pressure of the growth chamber. A transfer rod (on the right) transfers the sample from the load-lock chamber to the manipulator of the growth chamber. A differential pumping rotational stage is helpful in mounting the sample and also in aligning sample for getting RHEED pattern. Pressure gauges (not visible) are connected to both growth and load-lock chamber separately. Four effusion cells and one e-beam evaporator are located at the bottom of the growth chamber are utilized in evaporating Co, Pd, Cr, Fe and Ni, respectively. A wobble stick is located on the other side of the growth chamber (not visible) to cover the sample before deposition. In addition to a quartz crystal monitor (not visible) and a RHEED gun is also assembled to growth chamber for monitoring layer-by-layer growth of thin-films during the deposition. Additionally this system has baking unit (not shown) to bakeout the whole chamber and further reduces the pressure. A mass spectrometer is also connected to growth chamber to monitor the gasses present inside the growth chamber during all the time. Soon we are planning connect sputtering ion gun to clean the substrates thoroughly before we evaporate thin-films on to it.
is a custom-designed machine used for growing of epitaxial layers on custom-designed sample holders of 1 inch in size. The system is fully bakeable, to achieve lowest base pressure of typical value $5 \times 10^{-11}$ mbar for crystal growth. The detailed block diagram of our MBE shown in figure 3.2 reveals the connections between different existing components in MBE. Here, I am going to discuss these different components in detail.

3.1.1.1 The Growth Chamber

A 16-inch UHV chamber that is equipped with 4 effusion cells (Createc), an electron-beam evaporator (Oxford Scientific), a manipulator (Createc), two gate valves (VAT, Inc), Reflection High Energy Electron Diffraction (RHEED) gun, an infrared heat-coil and windows for observing transfer, a cryoshroud for the chamber wall, water cooling
units for the effusion cells and a Bayard Alpert (BA) ionization gauges (Varian) for vacuum measurement. A water-cooled Quartz crystal microbalance (McVac) monitors the in-situ growth rate. A quadrupole mass spectrometer (Stanford Research systems) monitors the residual gases present in the growth chamber. The growth chamber is pumped down by an ion pump (Varian) with the help of integrated Ti sublimation (Varian) pump. The growth chamber is isolated from a load-lock chamber by means of a manual gate valve (VAT, Inc). All the components of the growth chamber are able to resist bake-out temperatures of up to 200 °C for extended periods of time, which are necessary to minimize out-gassing from the internal walls [95]. A home-built Labview code was developed to capture the image from the CCD camera, plot and measure RHEED oscillations [See Appendix B].

3.1.1.2 The Load-Lock Chamber

The Load-Lock Chamber allows loading a 1-inch wafer holder. It is connected directly to the growth chamber through a gate valve. The load-lock chamber is pumped down with a water-cooled turbo molecular pump (Varian) and a dry scroll pre-pump (Varian) to achieve very fast high vacuum (~ $10^{-9}$ mbar). One infrared heating lamp allows removing the water from mounted wafer holders just after pump down. A Bayard Alpert type gauge (Atmion) monitors UHV conditions of the chamber. The transfer rod helps in transferring samples from load-lock into growth chamber and back. A Residual Gas Analyzer (RGA) is connected to load-lock chamber which provides the information on constituents present inside the growth chamber.

3.1.1.3 The Pumping System

It is the combination of pre-pumps, turbo molecular pumps, ion pump and Ti-sublimation. The growth chamber is connected to a turbo molecular pump (~ $10^{-9}$ mbar) via RHEED
gun (Specs). Two oil free pre-pump ($1.3 \times 10^{-3}$ mbar) serves the purpose of backing pump to a turbo pump, respectively. Once the vacuum in the growth chamber reaches $\sim 10^{-9}$ mbar, then ion-pump starts working and brings down the pressure to $\sim 10^{-10}$ mbar. Later on Ti-sublimation pump sublimes once in 4-8 hours for one minute and lowers the pressure down to $5 \times 10^{-11}$ mbar. The whole process of reaching $10^{-10}$ mbar from atmospheric pressure takes usually 1.5 days and reaching $10^{-11}$ mbar takes few more days. The load-lock chamber is separately connected to a turbo molecular pump with backing oil-free pump and is isolated from growth chamber by a gate valve. Both load-lock and growth chambers are separately connected with pressure gauges. Effusion cells: These are the key components of an MBE system, because they provide an excellent flux stability and uniformity in thin-film growth. Furthermore, they should withstand the highest temperatures for the longest periods. Therefore a careful choice of elements, materials and geometry must be taken. Our chamber has four effusion cells and one electron beam gun for depositing Cobalt, Palladium, Iron, Chromium and Nickel, respectively. Cobalt and Palladium are placed in high temperature effusion cell crucible made of Beryllium Oxide, BeO ($T_{max} = 1800^\circ$C). Iron placed in single filament effusion cells and the crucibles are made of Alumina (Al$_2$O$_3$). Chromium is also placed in single filament effusion cells and the crucible is made of Vitreous Carbon (VC) ($T_{max} = 1400^\circ$C). All effusion cells are equipped with thermocouples and which are connected to proportional integral derivative (PID) controllers to readout the temperatures of effusion cells. Nickel is placed in electron beam gun. All effusion cells including the electron-beam evaporator are water cooled during all the time.

3.1.1.4 The Manipulator

It is designed for heating and cooling the sample substrate. A Tungsten wire is used as a filament to heat the wafer holder while a cryostat is used to cool the substrate
wafer. A two-stage differential pumping system is included to provide rotational freedom and limited translational freedom for the manipulator. X-, Y- and Z-adjustments of the manipulator helps in mounting the sample holder and most importantly plays crucial role on getting RHEED pattern on screen.

### 3.1.2 Pulsed Laser Deposition

With the pulsed laser deposition (PLD) method, thin-films are prepared by the ablation of one or more targets illuminated by a focused pulsed-laser beam. This technique was first used by Smith and Turner [96] in 1965 for the preparation of semiconductors and dielectric thin-films and was established due to the work of Dijkkamp and coworkers [97] on high-temperature superconductors in 1987. Their work already showed main characteristics of PLD, namely the stoichiometry transfer between target and deposited film, high deposition rates of about 0.1 nm per pulse and the typically unintended but hard to avoid occurrence of droplets on the substrate surface (see [98]). Since the work of Dijkkamp et al., this deposition technique has been intensively used for all kinds of oxides, nitrides, or carbides, and also for preparing metallic systems and even polymers or fullerenes.

#### 3.1.2.1 Experimental Setup

The set-up for PLD is schematically shown in Fig.3.3. In an ultrahigh vacuum (UHV) chamber, elementary or alloy targets are struck at an angle of 45° by a pulsed and focused laser beam. The atoms and ions ablated from the target(s) are deposited on substrates. The substrates are attached with the surface parallel to the target surface at a target-to-substrate distance of typically 6-11 cm.

In our case, an UHV base pressure of about $5 \times 10^{-9}$ mbar, an excimer laser COMPex
Figure 3.3: Schematic setup of PLD/MBE-2000 Deposition System from PVD products

*Pro* (Coherent) with KrF radiation (wavelength 248 nm, pulse duration 20 ns), Si or MgO substrates, and a target-to-substrate distance of 6-11 cm are used. In order to obtain a steady ablation rate from the target, the laser beam is scanned (in our case by rastering the focusing lens and by additionally rotating the target under the laser beam) over a sufficiently large target area (at least 1 cm²). By adjusting the number of laser pulses on each target, multilayers with desired single layer and bilayer thicknesses can be created.

The Excimer laser functions by energizing the Excimer premix gas (KrF with an inert buffer) with a high voltage which creates a short lived dimer species from the premix gas. When the dimer decomposes, the characteristic wavelength light is released. The
laser light is then directed through a focusing lens with adjustable position and onto an ablation target inside of a vacuum chamber. During ablation, the target can be rastered and rotated for even ablation. Ablation creates a plume of plasma and vapor which is released orthogonally from the surface of the target. This plume is directed onto a substrate, which is typically heated and crystalline. Gasses can be added to the vacuum chamber to control growth characteristics and serve as reactants with the plume. A schematic of the PLD apparatus is provided in Figure 3.3.

3.1.2.2 The Growth Chamber

An electro polished 304L Stainless Steel cylindrical UHV chamber (∼ 18” diameter by ∼ 22” internal height) with all conflat (CF) style flanges. Conflat flange ports includes two RHEED ports, RGA, Load-Lock, emission spectroscopy, four 4.5” CF ports for effusion cells, one 6” CF port for an ion gun or magnetron sputter source, target and substrate view ports. The effusion cell ports are set at an angle of 40° with respect to the substrate normal. The chamber includes a top flange that seal via a pair of differentially pumped Viton O-rings. A heavy duty electric hoist to lift the flange from the chamber. This allows the user to remove a set of stainless steel internal shields for cleaning. The UHV chamber is supported by the frame that includes a black anodized table top surface to support the optical train that guides the laser into the chamber.

3.1.2.3 Pumping Package, Vacuum Gauges and Gas Distribution

The system comes with an all-pneumatic valve package, a water-cooled Pfeiffer Vacuum 700 l/s Turbo drag pump, and splinter screen, followed by an Edwards XDS 10 dry scroll pump. A UHV VAT Series 64 stepper motor controlled gate valve with metal sealed bonnet and differentially pumped stepper motor feed-through is provided along with a VAT PM-5 pressure control unit. Coupled with a MKS heated 1 Torr (1.33 mbar)
full scale capacitance manometer this system provides full closed-loop pressure control from 1 to 500 mTorr (0.665 mbar). A set of internal IR heat lamps will be connected to standoffs and hung from the top flange. A second Eurotherm control unit and SCR pack is provided along with a feed-through with power. This unit allows bake out of the chamber to achieve base pressures below $5 \times 10^{-9}$ Torr ($6.65 \times 10^{-9}$ mbar). An optional cryo pumping is provided. With this a base pressure below $2 \times 10^{-9}$ Torr ($2.66 \times 10^{-9}$ mbar) can be reached with a goal of below $1 \times 10^{-9}$ Torr ($1.33 \times 10^{-9}$ mbar). Vacuum gauges include one InstruTech Mini-Convectron Gauge (measures pressure from
1 mTorr to 1 atmosphere), and one InstruTech Hornet Ion Bayard Alpert ion gauge. Two programmable MKS Mass Flow Controllers (50 sccm) calibrated for oxygen and argon each with a pneumatic shut-off valve are included for process gas. The gas handling system also includes the ability to quickly vent the chamber (coarse flow) with oxygen to pressures above 300 Torr with a by-pass valve.

3.1.2.4 Programmable Optical Train

A programmable optical train for 248-nm (KrF) operation with an aluminum breadboard and all necessary hardware is included. The optical assembly includes sets of HR coated 2" diameter mirrors mounted on kinematic mirror-mounts providing for fine positioning of the laser beam on the target surface along with a 2" diameter focus lens. A programmable actuator is mounted to one kinematic mirror mount to provide the user the ability to raster the beam across the target in a well-defined fashion. Programmable laser beam rastering enhances film thickness uniformity for single layer or multilayer films thin-films. The programmable actuator mounted on one of the kinematic mirror mount provides the ability to raster the laser completely across the ablation target. The complete optics assembly is housed within a laser-safe enclosure with a large access door. All view-ports above the target plane are enclosed by UV safe Plexiglas covers.

3.1.2.5 Ultra High Vacuum PLD Intelligent Window

The PLD-5000 Intelligent Window provides a clean optical beam path for extended period of time (over an order of magnitude longer than a standard window). It incorporates an internal fused silica disc with manual rotary feedthrough. A beam splitter mounted on an electropneumatic linear actuator and joule meter is used to monitor the energy that has passed through the complete optical train.
3.1.2.6 Programmable 6-position Target Manipulator

A UHV manipulator for six (6) user-supplied targets, each 2-inch in diameter and 6 mm thick max is integrated into the deposition chamber. A dual-axis, magnetically coupled rotary feedthrough allows for computerized selection and rastering of the active ablation target as well as continuous target rotation about its own axis at rotation speeds up to 50 RPM. A large water-cooled plate sits above the entire target assembly. The plate includes a slot located above the active target for the incident laser beam. This water-cooled plate protects all the targets, gears, and bearings from substrate radiation and minimizes cross-contamination between targets. A quick access door with cutout in the water-cooled plate will provide easy target changes through a CF port located on the side of the deposition chamber.

3.1.2.7 SiC Oxygen-Resistant Rotating Substrate Heater

A SiC Heater assembly is provided for achieving high substrate temperatures. This heater has an open architecture and is ideal for systems that utilize RHEED or magnetron sputtering along with the PLD process. Substrate temperatures of 950°C for silicon and other non-transparent substrates, and 850°C for transparent substrates such as sapphire are achievable. The SiC heating element can readily achieve temperatures in excess of 1,400°C in an oxygen environment. The heater is fully oxygen compatible. The SiC resistive element is held within a gold-coated water-cooled copper block. This cooled block absorbs a large amount of radiation and thus minimizes out gassing of water vapor from chamber walls. A substrate spinner assembly is provided and is compatible with all MBE/PLD substrate holders. This spinner is connected to a long-life Ferro Fluidic rotary feedthrough mounted on a motorized Z-stage with 2-inch stroke. The rotary feedthrough includes a programmable motor drive and encoder unit to provide substrate
rotation speeds up to 40-RPM with very accurate position stability and minimal backlash. Furthermore, with the motor drive unit the spinner can easily return to any desired angular value.

The Z-stage allows the spinner to be lowered out of the water-cooled housing for easy substrate transfers via the chamber side door or via optional loadlock transfer arm and wobble stick. The stage provides variable target-to-substrate distances ranging from 6-11 cm. The heater includes a RHEED compatible DC power supply, rack mounted Eurotherm closed-loop temperature controller, Type K Thermocouple, all necessary feedthrough and cables. A pneumatic substrate shutter is provided for target pre-cleaning prior to deposition.

### 3.1.2.8 The Loadlock Assembly

A dual wafer load-lock is integrated with a port on the main deposition system. The loadlock has quick access door with view port for sample transfer along with a magnetically coupled linear feedthrough to insert the substrate holder into the main chamber. A wobble stick, in the main chamber transfers the substrate holder from the magnetic transport arm onto the substrate spinner assembly. The loadlock is backed by the main Pfeiffer dry pump and includes roughing, vent, and overpressure relief valves, and 70-l/sec turbo pump with its own VAT gate valve. Vacuum gauging includes an InstruTech Convectron Gauges (measures pressure from 1 mTorr to atmosphere), and Hornet Bayard Alpert ion gauge. All valves are electropneumatic except the gate valve that isolates the main chamber from the loadlock.

### 3.1.2.9 Laptop Computer Control Software Package

A laptop computer is integrated into the system. A complete software package based on a Lab View user interface is provided. The computer interface monitors and controls target
indexing and target rotation speed, target and/or laser beam raster program, substrate rotation and substrate indexing, turbo pump speed, all excimer laser functions, MFC flow rate, and substrate temperature. Furthermore, the computer also controls all the electropneumatic valves on the main chamber and load lock, shutter, IW beam splitter, and provides auto pump/auto vent features. The computer allows multilayer films to be grown via PLD. Recipes can be stored and recalled. An Ethernet port is provided for downloading large files as well as monitoring the system from remote locations.

3.1.2.10 Combinatorial Thin Film Growth Software

The software package is provided to grow combinatorial thin-films. The computer also allows for continuous, binary, ternary, and quaternary (depends on the number of targets in system) compositional spreads across 2-inch diameter substrates by indexing both the target and substrate in the appropriate fashion. The software will allow the customer to select any number of targets, index the targets and substrate appropriately along with firing the laser with the desired number of shots for each target to produce the desired compositional profile across the substrate. Combinatorial Recipes can be easily stored and recalled.

3.1.2.11 Lambda Physik COMPex PRO 110 Laser Package

A Lambda Physik COMPex PRO 110 excimer laser is mounted on top of the electronic rack system at the correct height for the optical train. The laser comes with Ceramic Tube technology and operates at repetition rates up to 100 Hz at 400 mJ per pulse (248-nm, KrF) for a maximum average power output of 30 Watts. Also included is a Spectra-Gas gas cabinet for user supplied gas pre-mix. Included in the cabinet are two high purity gas regulators for halogen gas premix and nitrogen purge.
3.1.2.12 High Pressure RHEED Set Up

A Staib 35 keV High Pressure RHEED electron gun with a voltage range of 0.5 to 35 keV and current range from 1 to 500 µA is included with the system. The gun comes with mechanical alignment capability of ±2° and a beam spot size from 100 microns to 1 mm. The electron beam can be directed at the center of the substrate spinner. System includes vacuum pressure shut-off valve. Includes a two-stage differentially pumped electron gun assembly using two Pfeiffer 70 l/s turbo pump packages. Two vacuum gauges will be provided to monitor the pressure in the electron gun housing. The RHEED gun includes the ability to adjust both the incidence and azimuthal angle of the electron beam for proper alignment on the substrate surface. A VAT isolation valve is also provided to isolate the electron gun from the main chamber when venting. A High Pressure RHEED screen will be provided mounted on a 6 CF flange. This includes a 4.5 CF viewport, reentrant screen in close proximity to the substrate heater and manual shutter assembly. Note the screen will be in close proximity to the heater and ablation plume.

A K-Space Lite 12 bit data acquisition package is provided for the RHEED unit. System includes a high sensitive 12 bit CCD Camera, frame grabber, video monitor for image display, zoom lens, with cables and basic software.

3.2 Structural Characterization Techniques

Structural characterization of the grown sample was done using wide angle X-ray diffraction (XRD). It provides the information of the crystal structure in grown thin-film heterostructures. In addition, small angle X-ray reflectivity (XRR) was performed on heterostructures to verify the thicknesses of different layers. The XRR scans also provide an idea of overall surface and interface roughness. A presence of a superlattice peak also guarantees a periodic structure.
3.2.1 Wide angle X-ray Diffraction

To describe the atomic arrangements in a given crystal, a probe that can see the lattice is required. Under this category X-rays are one of the best probing sources with the wavelength around 1 Å which is equivalent to typical inter atomic distances.

The XRD measurements are carried out on both a Rigaku D/Max-B Diffractometer and Bruker-AXS D8 Discover High-Resolution Diffractometer. X-rays are produced in an X-ray tube that consists of a source of electrons and two metallic electrodes. A voltage between these electrodes (typically tens of thousands of volts) accelerates electrons towards the anode. This bombardment of electrons on the anode with a sufficiently high energy produces X-rays, consisting of a superposition of continuous and characteristic spectra. The continuous spectrum is produced by the rapid deceleration of electrons striking the anode; collisions with nuclei produce deflections of the beam of electrons radiating X-ray photons (Bremsstrahlung radiation) which are not of our interest. On the other hand, if an electron bombarding the anode has enough energy, it can knock an electron out of the K-shell (usually done with Cu target, but holds true for other materials), leaving the anode atom in an excited state. One of the outer electrons (in the L, M, N, ... shells) falls into the vacancy in the K-shell, emitting a photon and producing one of the characteristic lines ($K_\alpha$, $K_\beta$, $K_\gamma$, ...), depending on where the electron come from. Note that the $K_\alpha$-line is the strongest among others. Due to the spin-orbit coupling, the energy levels of the shells (except K-shell) split into fine structure of the spectral lines. In particular, the L-shell split into three sublevels. Out of these three levels, the transition is possible between only two sublevels of L-shell onto K-level due to the selection rules. This gives rise to doublet of $K_{\alpha_1}$ and $K_{\alpha_2}$, with slightly different energies. The intensity of ratios of $K_{\alpha_1} : K_{\alpha_2} = 10 : 5$, showing that only the core shell electrons are necessary for consideration [99, 100, 101, 102, 103]. The Cu-$K_{\alpha_1}$-line with wave length 1.541 Å is used
for our X-ray measurements here.

Now, the produced X-ray photons collide with electrons in atoms and scatter away with same/different wavelengths. If the wavelength of these scattered X-rays does not change, the process is called elastic scattering or Thompson scattering. These are the X-rays that are measured in diffraction experiments, as the scattered X-rays that carry information about the electron distribution in materials. On the other hand, when X-ray photons collide with loosely bound electrons in the atoms, some of the energy of X-ray photon is used in providing kinetic energy for the free electron. Therefore, the scattered X-ray photon has different energies/wavelengths than incident X-ray photon gives rise to inelastic or Compton scattering. Note that in case of Compton scattering, the phase of the scattered X-ray has no fixed relation to the incident beam. Therefore, inelastic scattering is indeed incoherent scattering which will go as undesired background in the diffraction pattern [99, 100, 101, 102, 103].

Diffracted waves from different atoms interfere with each other and the resulting intensity is strongly modulated. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern, therefore, allows us to deduce the distribution of atoms in a material. However, the phase information gets lost because only intensities from scattered X-ray photons are measured in XRD but not the electric fields. Let us consider a crystalline solid where all atoms are arranged in a periodic pattern. The atoms, represented by black spheres in the figure 3.5, can be viewed as forming different sets of planes in the crystal. When a beam of monochromatic X-rays fall onto this periodic structure, the incident X-rays will be scattered by the atoms in all directions. But for some of the incident directions the scattered X-ray beams will be specularly reflected by any one plane of atoms and the reflected rays from successive adjacent planes will interfere constructively. For those two
Figure 3.5: Graphical representation of the diffraction by parallel planes of atoms (separated by a distance $d$) in a crystal. The incident X-ray makes an angle $\theta$ with lattice plans. If the path difference between successive planes ($2dsin\theta$) is equal to integral value of wavelength ($\lambda$) of the X-ray then constructive interference will be obtained.

X-ray beams to constructively interfere, the path difference between them must be an integral number of the wavelengths. Therefore, for a given set of lattice planes with an inter-plane distance of $d_{hkl}$, the condition for a diffraction to occur can be simply written as

$$n\lambda = 2d \sin \theta$$

(3.1)

The Eq. 3.1 is also known as the Bragg’s law, after W.L. Bragg and his father, W.H. Bragg proposed it. Here $\lambda$ is the wavelength of the X-ray, $\theta$ is the scattering angle, and $n$ is an integer representing the order of the diffraction peak.

The most useful method for describing diffraction phenomena in a crystal is done with the help of reciprocal lattice. The fact that the diffracting Bragg patterns are inherently three dimensional, one can remove a dimension from the problem by representing each
plane as a vector which is defined as perpendicular distance from the origin of a unit cell to the first plane in the family \((hkl)\), i.e., \(\vec{G}_{hkl} = \frac{2\pi}{d_{hkl}} \hat{n}\), where \(\hat{n}\) is the unit vector normal to the plane. Now the reciprocal lattice vectors can be constructed from the primitive vectors as shown elsewhere [99, 102].

The primitive vectors in reciprocal lattice are

\[
\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}; \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}; \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}
\]  

(3.2)

here \(\vec{a}_1, \vec{a}_2, \vec{a}_3\) are the primitive vectors of the crystal lattice. \(\vec{b}_1, \vec{b}_2, \vec{b}_3\) are the primitive vectors in corresponding reciprocal lattice which are related by \(\vec{G}_{hkl} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3\) where \(\vec{G}_{hkl}\) is the reciprocal lattice vector and \(v_1, v_2, v_3\) are the integers. The corresponding Bragg’s condition for the reciprocal lattice is given by:

\[
\vec{K} - \vec{K}_o = 2\pi \vec{G}_{hkl}
\]  

(3.3)

Where \(\vec{K}_o\) and \(\vec{K}\) are the unit wave vectors of incident and diffracted X-ray beams. It is important to point out that although we have used atoms as scattering points in this example, Bragg’s Law applies to scattering centers consisting of any periodic distribution of electron density. In other words, the law holds true if the atoms are replaced by molecules or collections of molecules, such as colloids, polymers, proteins and virus particles all of which are made out of atoms of course.

### 3.2.2 Small angle X-ray Reflectivity

The technique involves measuring the reflected X-ray intensity as a function of incidence angle over a range of angles close to the critical angle for total reflection. Above this critical angle the specularly reflected intensity (i.e. with symmetric incident and reflected...
angles) decreases, with a form that is dependent on the roughness of the interface. This can then be analyzed to obtain the electron density profile of the interface normal to the surface.

For the case of thin-films, low angle X-ray diffraction can give insight into the thickness for single films, repeated bilayers and even more complicated thin-film structures (i.e. superlattices). A change in material density (at an interface between two materials) leads to a change in the index of refraction, which will lead to reflection and transmission of the X-rays (for this reason this technique is often called X-ray reflectivity, XRR). The path difference between these interfaces also satisfies the Bragg condition and a value for \( d \), the distance between the two interfaces, can be measured. For an infinitely thick sample with a perfectly flat interface, one sees the expected Fresnel reflectivity.

When an X-ray beam impinges on a flat material, part of the incoming intensity is reflected and part of it is transmitted through the material. If the surface of the reflecting material is flat, the reflected intensity will be confined in a direction symmetric from the incident one and will be labeled as specular. X-ray reflectivity validity is limited to small angles of incidence where it is possible to consider the electron density as continuous. In this approximation, the reflection can be treated as a classical problem of reflection of an electromagnetic wave at an interface. The reflected amplitude is obtained by writing the continuity of the electric field and of the magnetic field at the interface. This leads to the Fresnel relationship, which gives the reflection coefficient in amplitude for the \( s \) and \( p \) polarization. The reflectivity, which is the modulus square of this coefficient, can be formulated in the case of X-rays as

\[
R(\theta) = rr^* = \left| \frac{\theta - \sqrt{\theta^2 - \theta_c^2 - 2i\beta}}{\theta + \sqrt{\theta^2 - \theta_c^2 - 2i\beta}} \right|^2
\]  \hspace{1cm} (3.4)
where $\beta$ is the absorption coefficient and $\theta_c$ is the critical angle. This expression is independent of the polarization \[104\].

For a thin-film, oscillations occur in the reflectivity due to interference between reflections from the two interfaces, where these two interfaces will be the substrate/film and film/air interfaces. The difference in $2\theta$ between successive maxima (or minima) relates to the thickness of the film via Bragg’s condition. With a wavelength $1.54 \text{ Å}$ this is an extremely accurate method for determining film thickness down to a few monolayers. In addition, this technique allows one to measure thickness and roughness of individual layers in a multilayer stack \[99\].

In general, XRR involves a complicated fitting routine done using fitting software with complicated algorithms; a software package from Bruker AXS called Leptos was used, which incorporates advanced X-ray scattering models and numerical methods into the package. This software allows for analysis of extremely complicated heterostructure materials, and can factor in density changes, interface roughness and instrument resolution that are difficult to analyze directly. However, for simple films there are many things that can be attained from a direct analysis, a brief example will show some of the parameters that can be obtained for a single thin-film. Assuming a grazing incidence angle, the average scattering (the atoms are no longer considered discrete at small angles but a continuous electron density) is measured and gives an index of refraction based on the electron density. The index of refraction for X-rays in any medium is always less than one and has both real and imaginary parts such that

$$n = 1 - \delta - i\beta \quad (3.5)$$
with dispersion factor

$$\delta = \left( \frac{\lambda^2}{2\pi} \right) r_e N_a \rho \left( \frac{Z + f'}{A} \right) = \left( \frac{\lambda^2}{2\pi} \right) r_e N_a \rho \quad (3.6)$$

and absorption factor

$$\beta = \left( \frac{\lambda^2}{2\pi} \right) r_e N_a \rho \left( \frac{f''}{A} \right) = \left( \frac{\lambda}{4\pi} \right) \mu \quad (3.7)$$

$\lambda$ is the X-ray wavelength, $r_e$ is the classical electron radius, $N_a$ is Avagadros number, $Z$ is the average atomic number, $A$ is the average atomic mass, $\rho_e$ the electron density, $\mu$ the linear absorption coefficient, and $f'$ and $f''$ are the real and imaginary part of the average dispersion corrections, respectively.

Then, according to Snells law (see Figure 3.6)

$$\frac{\cos \theta_i}{\cos \theta_t} = \frac{n}{n_0} \quad (3.8)$$

At the critical angle of total external reflection, $\theta_t = 0$ and $n_0 = 1$, then neglecting absorption

$$n = 1 - \delta = \cos \theta_i = \cos \theta_c \quad (3.9)$$

Expanding the cosine for small angles gives

$$\cos \theta_c = 1 - \frac{\theta_c^2}{2} = 1 - \delta \quad (3.10)$$

$$\theta_c = \sqrt{2\delta}$$

A simple approach to determine the critical angle from an XRR scan is to define the critical angle where the intensity of the reflected beam is at half intensity, or when $I = I_{max}/2$. This will be located at or near the critical edge, which signifies a drop off in the Fresnel reflectivity at the critical angle.

From this determination of critical angle there are a variety of useful parameters of
Figure 3.6: Refraction of X-rays at the interface between two media of different refractive indices, with $n < n_0$. Since the phase velocity is higher in the second medium, the angle of refraction $\theta_t$ is less than the angle of incidence $\theta_i$; that is, the ray in the lower-index medium is further away from the normal (notice that the angle convention is different from the traditional explanation of Snell's law). This implies that there is a critical incident angle, where any incidence at an angle below this angle will result in total external reflection.

A single film sample that can be determined. First, the mass density can be determined experimentally from the critical angle using Eq. 3.6, where

$$
\rho (g/cm^3) = \frac{\theta_i^2 \pi A}{r} N_a (Z + f') \lambda^2 = 1.851 \times 10^5 \frac{\theta_i^2 A}{(Z + f') \lambda^2}
$$

(3.11)

and $\lambda$ is in Å. Next, the film thickness can be determined by using a modified Bragg condition. To determine thickness, the interference peak positions must be determined. Occasionally it is quite difficult to see the small oscillations on the Fresnel reflectivity background. For this reason it is often convenient to remove this contribution, which
is often referred to as stripping off the $K^4$ signature, where $K$ is the scattering vector, $K = \frac{4\pi}{\lambda} \sin \theta$ Thus, the modified reflected intensity $I_{\text{mod}}$ is

$$I_{\text{mod}} \propto I \sin^4 \theta_i$$  \hfill (3.12)

This scaling will make it significantly easier to identify the maxima and minima positions of the reflectivity data. Once the maxima or minima positions have been determined, the modified Bragg equation

$$(m + \Delta m)\lambda = 2t\sqrt{\sin^2 \theta_m - 2\delta}$$  \hfill (3.13)

allows for the calculation of both the thickness and potentially the critical angle (if the first order reflectivity peak is known sometimes difficult to determine). Assuming the first order reflectivity peak is known exactly, then

$$(m + \Delta m)\lambda = 2t\sqrt{\sin^2 \theta_m - \theta_c^2}$$  \hfill (3.14)

where $m$ is the exact reflection order (1, 2, 3 ...) and $\Delta m$ has values $1/2$ for maxima and zero for minima if $\rho_{\text{film}} > \rho_{\text{substrate}}$ and values zero for maxima and $1/2$ for minima if $\rho_{\text{substrate}} > \rho_{\text{film}}$. A $\theta_m^2$ vs. $(m + \Delta m)^2$ plot can be made and the slope will reveal the thickness and the $y$-intercept gives the critical angle squared, where

$$t = \frac{\lambda}{2\sqrt{\text{slope}}}$$  \hfill (3.15)

Finally, in repeated bilayer structures, it is also possible to determine bilayer thickness based on a superlattice peak. For a particular angle in $2\theta$, the contributions from the interference pattern in reflectivity for a repeated bilayer add up to give a peak. The
intensity of this peak increases with an increasing number of bilayers. This superlattice peak satisfies the Bragg condition for the bilayer thickness, where the thickness of the bilayer is given by

\[ t = \frac{n\lambda}{2\sin \theta} \]  

(3.16)

where \( n \) implies that there are multiple order superlattice peaks (the order of peaks gives insight into interface roughness between bilayers). Using an off-specular technique, where \( \theta \) and \( 2\theta \) have an offset (usually between 0.1 to 1 degrees), one can remove the thickness oscillations and be left with only the Fresnel reflectivity curve accompanied by the superlattice peaks. This approach is an extremely accurate method for determining film thicknesses.

### 3.3 Magnetic Characterization

#### 3.3.1 Superconducting Quantum interference Device

Superconducting Quantum Interference Device (SQUID) is one of the most sensitive ways of measuring magnetic properties. In particular, this method allows directly determining the overall magnetic moment of a sample in absolute units. SQUID combines the physical phenomena of flux quantization and Josephson tunneling. If two superconductors are separated by an insulating film, it is found that an electric current can tunnel from one side of the junction to the other. Following the equations established by Brian David Josephson in 1962, the electrical current density through a weak electric contact between two superconductors depends on the phase difference \( \Delta \phi \) of the two superconducting wave functions. This effect is known as Josephson effect. Moreover, the time derivative of \( \Delta \phi \) is correlated with the voltage across this weak contact. In a superconducting ring with one (so-called RF – SQUID, Fig. 3.7, blue) or two (DC – SQUID) weak contacts,
\[ \Delta \phi \] is additionally influenced by the magnetic flux \( \Phi \) through this ring. Therefore, such a structure can be used to convert magnetic flux into an electrical voltage.

The magnetic signal from the sample is obtained via a superconducting pick-up coil. This coil, together with a SQUID antenna (red in Fig. 3.7), is part of a whole superconducting circuit transfers the magnetic flux from the sample to RF-SQUID device which is located away from the sample. This device acts as a magnetic flux-to-voltage converter (blue in Fig. 3.7). This voltage is then amplified and read out by the magnetometer’s electronics (brown in Fig. 3.7)

![Figure 3.7: Equivalent circuit of SQUID = flux-to-voltage converter](image)

When the sample is moved up and down it produces an alternating magnetic flux in the pick-up coil which leads to an alternating output voltage of the SQUID device. By locking the frequency of the readout to the frequency of the movement (RSO, reciprocating sample oscillation), the magnetometer system can achieve extremely high sensitivity for ultra small magnetic signals as described above.
We operate a commercial SQUID magnetometer system from Quantum Design, San
Diego (magnetic properties measurement system MPMS XL-7). The sample is located
in the center of a superconducting solenoid producing magnetic fields up to 7 Tesla.
The sample space is filled with helium at low pressures. Our SQUID can operate at
the temperature range from 2 to 400 K with sweep rates of 0.001 to 10 K/min. The
sensitivity of the system is $10^{-8}$ emu or $10^{-11}$ J/T in RSO mode. The whole system is
fully computer-controlled and operated 24 hours a day. Measuring sequences can be
programmed in advance and is executed automatically.

### 3.3.2 Magneto-Optic Kerr Effect (MOKE)

When light is reflected off a magnetized surface a change in reflectivity, polarization
and ellipticity occurs. This is similar to the Faraday Effect, except MOKE measures the
reflected light as opposed to the transmitted light. Both effects occur due to off diagonal
components of the dielectric tensor. For measurement in this setup, a lock-in technique is
used with a photo-elastic modulator (PEM).

The Kerr effect is proportional to the component of magnetization along the propaga-
tion direction; in the first-order approximation, a hysteresis loop of the magnetization can
be obtained. There are three basic MOKE configurations that are used in determining the
magnetic behavior of a thin-film sample; these three configurations are shown in figure
3.8 and described below.

In Longitudinal MOKE (LMOKE), the measured magnetization vector is parallel to
the plane of the film and is parallel to the incident plane of light. When a beam of light
with s-polarization (the electric field vector is perpendicular- originates from the fact
the s stands for “senkrecht” which is German for perpendicular) to the incident plane)
or p-polarization (the electric field vector is parallel to the incident plane) is incident
Figure 3.8: Three MOKE configurations—Polar, Longitudinal, and Transverse, where the red arrows represent the propagation direction of the light and the black arrows represent the magnetization direction.

onto the sample surface, on reflection, the beam is converted to elliptically polarized light due to an additional component perpendicular to the incident electric field vector which is induced by the magnetization. For LMOKE the laser beam should be as far from normal incidence, or more precisely, to achieve the material-dependent Brewster angle to maximize the effect. This measures the largest component of magnetization vector assuming the magnetization has an in-plane easy axis or the applied field is sufficient to pull the magnetization into the plane. Obviously, no effect is observed for a normally incident beam (see Fig. 3.8 and Fig. 3.9).

In Transverse MOKE (TrMOKE), the measured magnetization vector is parallel to the plane of the film and is perpendicular to the incident plane of light. TrMOKE only occurs for incident light with p-polarization. The reflected light is also p-polarized but there is a change in the reflected amplitude as the magnetization vector changes sign, where the reflectivity $R$ changes from $R + \Delta R$ to $R - \Delta R$. Again, the laser beam is far from normal incidence (see Fig. 3.8 and Fig. 3.9).

In Polar MOKE (PMOKE), the measured magnetization vector is perpendicular to the plane of the film and parallel to the incident plane of light. When a light beam with s
Figure 3.9: Experimental configuration for longitudinal MOKE (similar for perpendicular MOKE if the applied field $H$ was out of the page). The light passes from the laser through the polarizer at either $0$ or $90^\circ$, depending on whether the user wants $s$ or $p$ polarization. The light is then reflected from the magnetic sample surface with the addition of a polarization rotation $\theta_k$ and change in ellipticity $\epsilon_k$. It then passes through the photoelastic modulator (with principle axis along $0^\circ$) and another polarizer at $45^\circ$ before it is measured with a photodiode.

or $p$ polarization is incident on the sample surface, the reflected light will be elliptically polarized due to the induced Kerr component. For this measurement it is best to have the laser beam directly at normal incidence (see Fig. 3.8 and Fig. 3.9).

To find the variation in magnetic properties with temperature, the use of a Janis closed-cycle refrigerator (CCS-350SH) with polarization preserving optical windows was used. In practice, this allows MOKE data to be taken over a temperature range of $10$ K to $475$ K. The added constraint of large time scales made it difficult to use in the aging measurement was a problem with build up of moisture inside the glass window. With
holes through the center of the pole pieces it was possible to use them in the PMOKE setup and we were able to take measurements throughout the entire temperature range. A series of home-built codes was also developed to carry out various kind of measurements (e.g. see Appendix A).

3.3.3 Alternating Gradient Force Magnetometer

Alternating Gradient Force Magnetometer (AGFM) is an integral method that measures the bulk magnetic moment in a thin magnetic film. In AGFM, a sample of typically 1 to 3 mm square is mounted on a vertical extension rod, which is along z-axis as shown Fig. 3.10. The top end of this rod is attached to the piezoelectric element which is rigidly clamped. This piezoelectric transducer oscillates when the sample is subjected to an alternating magnetic field gradient superimposed on the DC field of an electromagnet, which is along x-axis. The force due to negative gradient of the Zeeman potential energy on a magnetized sample produces a bending moment on the piezoelectric element, which generates a voltage proportional to the force on the sample. The output from the piezoelectric element is sensitively detected at the frequency of the gradient field.

This technique is considered a force technique, which measures the force on a magnetized sample in the presence of a magnetic field gradient. The piezoelectric sample holder of AGFM, which is fragile and expensive, operates at its resonance frequency, which depends on the mass of the sample/substrate combination. Therefore, each new sample requires tuning to its resonance frequency. If the magnetic moment is very low, automatic tuning does not work out and the user has to do it manually. Even with careful manual tuning of a low moment sample, the saturation moment was found to vary by more than 5% over 10 consecutive measurements. It is necessary to make sure that the measured sample is always calibrated, placed in the same location and is of the same size.
Figure 3.10: Schematic of the Alternating Gradient Force Magnetometer

compared to the calibrated sample to avoid strong deviations from the actual magnetic moment. When measuring samples with smaller coercivity $\sim 10\text{mT}$, it is important to reduce the magnitude of gradient field in order to improve the signal-to-noise ratio.

All of our room temperature measurements were made using a Princeton Magnetics MicroMag Model 2900 AGFM. The AGFM is sensitive to about $10^{-10}$ A-m$^2$ and can apply a maximum external magnetic field of 1.35 T. This system can measure thin-film samples in two modes: The applied magnetic field perpendicular and parallel to the film.
Chapter 4

Magnetocaloric effect in Nanostructures

In this chapter I discuss the guiding mean-field theoretical concepts and experimental results of Magnetocaloric effect in Co/Cr and Fe/Cr superlattices. Magnetocaloric properties are deduced from measurements of the temperature and field dependence of the magnetization of our samples. More generally, the potential of artificial antiferromagnets for near room-temperature refrigeration is explored. The effects of intra-plane and inter-plane exchange interactions on the magnetic phase diagram in Ising-type model systems are revisited in mean-field considerations with special emphasis on tailoring magnetocaloric properties. The experimental results are discussed in light of our theoretical findings. I introduce the concept of magnetic cooling using multilayers, provide an experimental proof of principle, and introduce the involved thermodynamics by a two-sublattice mean-field model.
4.1 Concept of Nanoparticles for Magnetocaloric Applications

Almost all materials show some magnetocaloric effect, but the entropy gain is typically small and appreciable only in inconvenient field and temperature regions. Nanostructures are far more flexible with respect to the optimization of material properties, including magnetocaloric effects. One advantage is that the magnetization of suitable nanostructures can be switched by an applied magnetic field of the order one \(1\) T or less, which is easily realized by using permanent magnets and does not require superconducting magnets.

A straightforward path to enhance the field-induced entropy change is realized when isothermally increasing the applied magnetic field until technical saturation of the magnetization is reached. This brute-force approach has practical limitations. When relying on the maximum achievable flux densities of 1-2 T of modern permanent magnets, such as Nd-Fe-B and Sm-Co the feasible adiabatic temperature changes still remain below 15 K \([105, 77]\) at room temperature. Permanent magnetic fields of the order of 4 T can be created in Halbach cylinders, but the logarithmic dependence of the created field on the diameter of the cylinder makes such devices very heavy \([106]\).

A look at Eq. 2.20 provides that the total entropy change that can be achieved has an upper bound. Nevertheless, the isothermal entropy change characterizing a MC material can be tuned e.g., by controlling its particle size \([134, 135]\). To prove this let us consider the magnetic entropy of nanoparticles containing \(N\) spins of moment \(\mu_B\) (spin \(1/2\)) in a field \(H\), which can be described by a classical Hamiltonian \([135]\). Here we consider a nanoparticle as a superspin where the strong exchange interaction energy within a nanoparticle is much larger than the thermal energy \(k_B T\) and hence, all internal degrees of freedom are frozen out.
The Gibb’s free energy per nanoparticle is given by \[135\]

\[
G = -k_B T \left[ 2 \cosh \frac{\mu_B NH}{k_B T} \right] \tag{4.1}
\]

The isothermal entropy per nanoparticle is given by \[135\]

\[
S = -\left( \frac{\partial G}{\partial T} \right)_H
= k_B \ln \left( 2 \cosh \frac{\mu_B NH}{k_B T} \right) - \frac{\mu_B NH}{T} \tanh \frac{\mu_B NH}{k_B T} \tag{4.2}
\]

The entropy per nanoparticle decreases from \( S = k_B \ln 2 - \frac{\mu_B^2 N^2 H^2}{2k_B T^2} \) in small fields to zero in large fields.

Fig. 4.1 shows that mere-exchange free nanostructuring will not lead to any entropy gain although the magnetic field required to saturate the cluster decreases with increasing \( N \).

However exchange interaction is potentially helpful to enhance the entropy differences \[135\].

### 4.2 Concept of Superlattices for Magnetocaloric Applications

Past research has focused on conventionally processed bulk alloys, which can be produced in large quantities, but the range of suitable compounds is limited. Furthermore, many major constituents in MCE alloys, such as Gd, are expensive, their availability in large quantities is limited and often they are objectionable from an environmental point of view.
Figure 4.1: Main frame shows entropy per nanoparticle $S/k_B$ vs. $H$ of Ising spin cluster with $N = 300$ and $N = 1000$ spins. Inset shows $S/k_B$ vs. $N$ for $\mu_0 H = 1 \text{T}$ [135].

In spite of the remarkable advances achieved with these traditionally processed bulk samples further progress may be limited by the number of suitable compounds based on rare earth elements and due to equilibrium thermodynamic constraints. They largely reduce the flexibility of tailoring microscopic parameters. In addition, many major constituents in MC alloys like Gd are expensive and often not unobjectionable from an environmental point of view.

Our nanotechnological approach is virtually unexplored scientific terrain with all the potential benefits for materials design a nanoscale approach can offer. Our emphasis
is on tailoring magnetic interaction within and between ultra thin-films. Using simple magnetic materials like the 3d metals we realize the design of the macroscopic properties via nanostructurating. Instead of using expensive and problematic materials like Gd or As which both are extensively used in advanced MC bulk alloys we focus on conventional constituents like Fe, Co, Cr and put the innovation into the nanostructurating and composition of these materials. By tailoring magnetic properties like the critical temperature of ferromagnetic constituent films via geometrical confinement and interaction between the latter via nonmagnetic spacer layers of controlled thickness we can achieve above mentioned goals. In multilayers of ultra-thin-films, it is possible to exploit individual microscopic spin degrees of freedom, because spin fluctuations at magnetic phase transitions in reduced dimensions yield a pronounced entropy change. In this sense it is possible to harness the advantages of the bulk and the nanomagnetic world where large spin fluctuations are thermally activated using coupled two-dimensional subsystems with controlled strength and sign of the magnetic interactions.

4.3 Structure and Magnetism of Superlattices for Magnetocaloric Applications

4.3.1 Multilayer approach for negative MCE

Our multilayer growth follows two major strategies, both aiming at the realization of artificial AF multilayer structures with tailored transition temperatures and maximized isothermal entropy changes. The basic mean-field considerations are not system-specific. For simplicity we restrict ourselves to Ising systems despite the fact that our experimental systems have no pronounced uniaxial anisotropy. Hence, the theoretical results can only be considered as conceptual guiding principles. Furthermore, our exclusive magnetic
consideration does not take into account potential structural phase transitions which often accompany the magnetic first-order transition and can give rise to significant entropy contributions beyond the magnetic limit $\Delta S_{\text{max}} = Nk_B \ln 2$ or $Nk_B \ln(2S + 1)$ for non Ising systems.

Our experimental investigations presented here focus on Co/Cr and Fe/Cr superlattices. Both of these systems allow the tailoring of the intra and inter-layer magnetic properties entering the theory. In our Co/Cr multilayers, we exploit the fact that the Curie temperature of the FM Co constituents can be tailored in thin-films through thickness variation. While lowering the Curie temperature from its bulk value of 1388 K to room-temperature a dimensional crossover from 3d to 2d takes place which enhances the spin fluctuations and their contribution to the magnetic entropy. Our studies on Fe/Cr superlattice follows similar strategy of finite size scaling of Curie temperature of FM Fe films from bulk value of 1043 K to room temperature.

On the other hand, Cr is a prototypical spacer material for the realization of AF interlayer coupling. The AF coupling strength is an oscillating function of the Cr thickness and can be experimentally tailored [113, 114, 115]. Moreover, the spins of the Cr interlayer films support the MCE beyond their task in providing the RKKY-type coupling between the Co films. Note that at thicknesses below 20 monolayers the Cr films are PM [114], whereas bulk Cr orders antiferromagnetically with an incommensurate spin density wave [114]. Temperature driven AF transitions have two regions which show a potentially large MCE. On the most interesting low-temperature side the temperature derivative $\frac{\partial M}{\partial T} > 0$ of the magnetization, $M$, maximizes close to the transition temperature where the AF order parameter approaches zero. This is the region of negative MCE which is defined by an adiabatic temperature change smaller than zero when a positive magnetic field is applied. Ultimately we are aiming at an AF-to-PM transition close to the temperature where the FM-to-PM transition of the 2d FM constituent films takes place.
The 3d nature of the global AF transition will allow for an optimized MCE. This intuitive picture will be subsequently quantified in a mean-field analysis. In particular in simple layered structures the AF transition can be transformed into a first-order metamagnetic transition via the ratio of the intralayer and interlayer exchange $[31, 116, 117, 1, 118]$.

For a magnetic transition of first-order the entropy change at the transition is given by the Clausius-Claperyon equation

$$\Delta S = \mu_0 V \frac{dH_m}{dT} \Delta M$$

where $V$ is the sample volume and $\frac{dH_m}{dT}$ is the slope of the first-order phase transition line. In a metamagnetic antiferromagnet the latter is separated from the critical line, $H_c(T)$, via a tricritical point $[31]$. The slope, $\frac{dH_m}{dT}$, of the first-order transition line and the magnetization discontinuity, $\Delta M$, at the transition are determined by the microscopic exchange parameters and by the atomic coordination [section 2.1, Fig. 2.2]. Note, that additional field-induced entropy changes take place below and above the transition and can be calculated from the Maxwell relation subject to homogeneity and equilibrium conditions.

Ising metamagnets are modeled by the Hamiltonian [from Eq. 2.1]

$$\mathcal{H} = - \sum_{i,j} J_{ij} \sigma_i \sigma_j - \mu_B \mu_0 H \sum_i \sigma_i$$

where $\sigma_{i,j} = \pm 1$ are classical Ising variables, $\mu_B$ is the magnitude of the magnetic spin moment and $J_{ij}$ describes the exchange interaction between the $i$-th and $j$-th atom while the $(i,j)$-summation runs over nearest and next nearest neighbor spins. Griffiths and many others used Ising and Heisenberg localized spin Hamiltonians to investigate the thermodynamics of model systems with competing AF and FM interactions with special
emphasis, however, on the critical behavior\cite{118}. The magnetocaloric behavior of the Co/Cr superlattices is a nanoscale effect and generally involves many nonequivalent crystallographic sites (sublattices), but the involved thermodynamics can already be seen from a relatively simple two-sublattice model with competing intra and inter-sublattice interactions. Here we use $J_1$ for the FM interaction in the Co layers and $J_2$ for the AF exchange mediated by the Cr layer. By analyzing the metamagnetic phase diagrams of Ising antiferromagnets in the mean-field approximation it can be shown that the slope $\frac{dH_m}{dT}$ of the first-order transition line can be tailored by the ratio $\epsilon = z_1|J_1|/(z_2|J_2|)$, where the coordination numbers $z_{1,2}$ are the only relevant properties of the lattice structure within mean-field approximation\cite{31}. It is this dependence of $\frac{dH_m}{dT}$ and $\Delta M$ on the exchange constants and coordination numbers which guides the growth of our magnetic thin-film heterostructures with large MCE.

If $\epsilon > 3/5$ is satisfied then the critical point for the phase separation lie on the Néel-line so that the phase diagram exhibits a tricritical point. In that case using $J_{+/−} := z_1|J_1| ± z_2|J_2|$ one obtains the slope of the critical line from differentiation of\cite{31,116}

$$\frac{\mu_0 VM_s}{J_+} H_c(T) = -\frac{\epsilon - 1}{\epsilon + 1} \sqrt{1 - \frac{T}{T_N}} + \frac{T}{2T_N} \ln \frac{1 + \sqrt{1 - T/T_N}}{1 - \sqrt{1 - T/T_N}}$$

(4.5)

where $T_N = \frac{J_+}{k_B}$. At the tricritical temperature $T_{tri} = T_N \left(1 - \frac{1}{3\epsilon}\right)$ the slope read as

$$\frac{\mu_0 VM_s dH_c}{J_+ dT} \bigg|_{T=T_{tri}} = \frac{1}{2} \ln \sqrt{3\epsilon + 1} - \frac{\sqrt{3\epsilon}}{\epsilon + 1}$$

(4.6)

At $T < T_{tri}$ but close to the tricritical temperature one obtains $\frac{dH_m}{dT} \bigg|_{T=T_{tri}} \approx \frac{dH_c}{dT} \bigg|_{T=T_{tri}}$. Far below the tricritical temperature the spin-flip field, $H_{m}$, is determined by the exchange energies which an applied field has to overcome in order to flip the system from an AF into an almost saturated magnetization state. The metamagnetic transition is then
virtually temperature independent, and \( \frac{dH_m}{dT} \bigg|_{T \to 0} \to 0 \). In first approximation we can linearly interpolate between the \( T = 0 \) and \( T = T_{tri} \) behavior obtaining

\[
\frac{dH_m}{dT} \approx \frac{T}{T_{tri}} \frac{dH_c}{dT} \bigg|_{T=T_{tri}} \tag{4.7}
\]

which is used as input for the evaluation of the entropy change at the transition with the help of Eq. 4.3.

Next we derive an expression for the field-induced magnetization change \( \Delta M \) at the metamagnetic transition. While \( \frac{dH_m}{dT} \) maximizes on approaching the tricritical point, \( \Delta M \) goes to zero because the first-order transition crosses over into critical behavior [31]. At \( T \to 0 \) the field-induced metamagnetic transition drives the system from zero magnetization to saturation magnetization, \( M_s \), yielding \( \Delta M(T = 0) = M_s \). Below, we suggest an interpolating expression for the and \( T \)-dependence of \( \Delta M \). Armed with this expression, we will be able to quantitatively analyze Eq. 4.3 and predict the exchange ratio \( \epsilon \) that maximizes the entropy change in the vicinity of room-temperature.

Kincaid and Cohen studied metamagnetic phase diagrams in the mean-field approximation [31]. Others later continued their work [116]. In mean-field approximation, an Ising Hamiltonian of the type of Eq. 4.4 with FM intrasublattice and AF intersublattice interactions gives rise to two coupled equations for the two sublattice magnetizations \( M_A \) and \( M_B \) which read

\[
\frac{M_A}{M_s} = (\epsilon + 1) \left( \frac{\mu_0 V M_s H}{J_+} + \frac{\epsilon}{(\epsilon + 1)} \frac{M_B}{M_s} - \frac{T}{T_N} \ln \frac{1 + M_B/M_s}{1 - M_B/M_s} \right) \tag{4.8}
\]

and

\[
\frac{M_B}{M_s} = (\epsilon + 1) \left( \frac{\mu_0 V M_s H}{J_+} + \frac{\epsilon}{(\epsilon + 1)} \frac{M_A}{M_s} - \frac{T}{T_N} \ln \frac{1 + M_A/M_s}{1 - M_A/M_s} \right) \tag{4.9}
\]

Analysis of Eq. 4.8 and 4.9 shows that a tricritical point emerges for \( \epsilon > 3/5 \). The
asymptotic behavior of \( \Delta M = (M_A + M_B) \) has been derived for \( T \to 0 \) and \( T \to T_{tri} \) and reads [31, 119]

\[
\frac{\Delta M}{M_s} = 1 - 3e^{-2\epsilon T_N/(\epsilon+1)T}
\]  
(4.10)

for \( T \to 0 \), and

\[
\frac{\Delta M}{M_s} \propto (T - T_{tri})
\]  
(4.11)

for \( T \to T_{tri} \).

The analytic expression

\[
\frac{\Delta M(T)}{M_s} = 3 \left( e^{-2\epsilon T_N/((\epsilon+1)T_{tri})} - e^{-2\epsilon T_N/((\epsilon+1)T)} \right) + \left( 3e^{-2\epsilon T_N/((\epsilon+1)T_{tri})} - 1 \right) \frac{(T - T_{tri})}{T_{tri}}
\]  
(4.12)

reproduces the two analytically derived asymptotic expressions 4.10 and 4.11 and provides a parameter-free fit of the numerically calculated data for \( \Delta M(T)/M_s \).

Figure 4.2 shows our numerical results \( \Delta M(T)/M_s \) for \( \epsilon = 1.6 \) (open circles). They have been obtained from the magnetization discontinuities in the isotherms \( M/M_s \) vs. \( H \), as calculated from the numerical solutions of the coupled equations (4.8 and 4.9, also see Appendix C). The upper right inset shows two typical isotherms for \( \epsilon = 1.6 \) at \( T/T_N = 0.5 \) and 0.7. The \( \Delta M/M_s \) values corresponding to these isotherms are highlighted in Fig. 4.2 as solid circles. The line representing the parameter free function given by Eq. 4.12 is not a fit. The lower left inset shows the magnetic phase diagram for \( \epsilon = 0.8 \) and \( \epsilon = 3.0 \), respectively. The solid curves represent the second order phase transitions. At the tricritical point (squares) the second order transition changes into a first order transition (dotted line). The slope of the transition line at the tricritical point is visualized by tangents (solid lines). The lower left inset of Fig. 4.2 shows the magnetic phase diagram for \( \epsilon = 0.8 \) and \( \epsilon = 3.0 \), respectively. The solid curves represent the second
Figure 4.2: Temperature dependence $\Delta M(T)/M_s$ for $\epsilon = 1.6$ (open circles) obtained from the magnetization jumps in the numerically calculated isotherms $M(H)/M_s$ (see Appendix C). The upper right inset shows two isotherms for $\epsilon = 1.6$ at $T/T_N = 0.5$ and 0.7. Their $\Delta M(T)/M_s$ values are highlighted as solid circles in the main frame. The line represents the parameter free function Eq. 4.12 and is not a fit. The lower left inset shows the magnetic phase diagram for $\epsilon = 0.8$ and $\epsilon = 3.0$, respectively. The solid curves represent the second order phase transitions. At the tricritical point (squares) the second order transition changes into a first order transition (dotted line). The slope of the transition line at the tricritical point is visualized by tangents (solid lines).
order phase transitions. At the tricritical point (squares) the second order transition changes into a first order transition (dotted line). The slope of the transition line at the tricritical point is visualized by tangents (solid lines). Inspection of these phase diagrams demonstrates the mechanism of tailoring the isothermal entropy change. At temperatures $T \ll T_{\text{tri}}$ the magnetization discontinuity is very large, however, $dH_c/dT \approx 0$. At the tricritical point $dH_c/dT$ is non zero and can be tuned via $\epsilon$, however, the magnetization discontinuity goes to zero on approaching $T_{\text{tri}}$. The optimization of this competition reflects the optimization of the MCE.

Combining the results of Eq. 4.6, 4.7 and 4.12, and their substitution into Eq. 4.3 allows to look for the maximum of $|\Delta S(T, \epsilon)|$ as a function of $T$ and $\epsilon$. From

$$d|\Delta S(T, \epsilon)|/dT = 0 \quad (4.13)$$

and

$$d|\Delta S(T, \epsilon)|/d\epsilon = 0 \quad (4.14)$$

we obtain a condition for the optimized $\epsilon$ and a condition for the temperature $T^*$ which defines the optimized operating temperature of the refrigerator. For many applications, including household refrigeration applications $T^*$ must be in the vicinity of room-temperature.

Analysis of Eq. 4.14 and Eq. 4.13 yields $T^* \approx 0.53T_{\text{tri}}$ and $\epsilon = 2.9$ which in summary means $T_{\text{tri}} \approx T_N \approx 2T^*$. Choosing $T^* \approx 300$ K for near room-temperature refrigeration applications yields $T_{\text{tri}} \approx 600$ K and corresponds to an optimized $T_N \approx 600$ K. Simultaneously satisfying the condition of a high Néel temperature and of a large $\epsilon$ requires weak AF coupling such that $T_N$ is completely dominated by the FM in-plane interaction.
in accordance with
\[ T_N := T_N(H = 0) = \frac{J_+}{k_B}. \] (4.15)

The weak but finite AF coupling guarantees a crossover into 3d AF long-range order despite the strong FM interaction in the Co planes. Physically, the entropy associated with this transition originates from spins that are correlated predominantly in individual layers, with much less pronounced interlayer correlations. A crossover like this from 2d FM to 3d AF long-range order is well known from the atomic metamagnets like the prototypical system FeCl$_2$ (see sec. 2.1). The FM intra-plane interaction determines the $T_c$ of the individual Co planes and gives rise to the final optimized sample properties $T_{tri} \approx T_N \approx T_c \approx 2T^*$. 

Note that the previous considerations are based on mean-field theory and should be adopted as a guiding argument to tailor inter- and intra-layer exchange coupling for optimized MCE applications. This reflects our intuitive ideas (i)-(iii) [see chapter 1] stating that a system with an ideally tailored MCE should take advantage of a first-order transition below room-temperature while the proximity of the in-plane $T_c$ and the $T_N$ of the 3d transition thermally activates microscopic spin fluctuations. Hence in contrast to other nanoparticle based magnetocaloric systems our structures activate the microscopic spin degrees of freedom for contributions to the overall field-induced entropy change.

### 4.3.2 Multilayer approach for positive MCE

Above the AF transition temperature and in moderate magnetic fields, the magnetization follows the functional form
\[ M = \chi(T, \theta)H \] (4.16)

where $\chi(T, \theta) = C/(T - \theta)$ is the Curie-Weiss type susceptibility with Curie constant $C > 0$ and Curie Weiss temperature $\theta(H = 0) = \frac{J_-}{k_B} < T_N(H = 0) = \frac{J_+}{k_B}$. Often but not
necessarily $\theta < 0$ is realized in the case of strong AF exchange and high coordination [1]. Here we are interested in realizing systems with $\theta > 0$ for enhanced susceptibility. As a general result we obtain $\frac{\partial M}{\partial T} = -\frac{C_H}{(T-\theta)^2} < 0$ in positive applied magnetic fields. This is the region of positive MCE which is defined by an adiabatic temperature change larger than zero when a positive magnetic field is applied. This behavior of $\frac{\partial M}{\partial T}$ is at first sight very similar to ferromagnets above their Curie temperature. However, one of the major advantages of antiferromagnets over FM systems is the fact that in lowest order approximation the applied magnetic field does not perturb the AF criticality. A moderate homogeneous magnetic field is an irrelevant field meaning not conjugate to the AF order parameter. As a consequence, criticality is not destroyed by moderate fields $H$ and the shift of the critical temperature $T_N(H)$ and the Curie-Weiss temperature $\theta(H)$ are moderately evolving from $T_N(H = 0)$. This is because $(dT_N/dH)_{H=0} = 0$ according to $T_N(H) = T_N - \delta |H|^\gamma$, where $\delta > 0$ is a small parameter and $\gamma = 2$ for 3d Ising antiferromagnets for instance [120].

Similar to the arguments which lead to the optimization of the metamagnetic transition at $T^* \approx 0.53T_{tri}$ and to negative MCE, tuning of the interaction can shift the temperature and magnetic field ranges to realize appreciable entropy changes with positive MCE in the technically relevant temperature range.

Quantitative benefits of this approach become more transparent when considering the Landau theory for a ferromagnet and its isothermal entropy changes. Above $T_N$ the FM nature of the Co layers dominates the spin-fluctuation spectrum and the Landau expansion of the free energy density in powers of the FM order parameter $M$ becomes a meaningful description. It reads as

$$F/\mu_0V = \frac{1}{2}a_0(T - T_C)M^2 + \frac{1}{4}bM^4 - MH$$

(4.17)
with sample volume $V$, critical temperature $T_C$ and $a_0, b > 0$. From the equilibrium condition $\frac{\partial F}{\partial M} = 0$ one obtains the well-known equation of state

$$a_0(T - T_C)M + bM^3 = H$$

(4.18)

allowing to derive the expression

$$\frac{\partial M}{\partial T} = -a_0M\chi$$

(4.19)

via implicit differentiation with respect to $T$ and $H$. Here $\chi = \frac{\partial M}{\partial H} = \frac{1}{a_0(T - T_C) + 3bM^2}$ is the FM susceptibility in a field. Eq. 4.19 is a compact and generalized expression of corresponding results obtain from more involved mean-field considerations. In particular at $T = T_C$ Eq.4.18 yields $M(T = T_C, H) = (H/b)^{1/3}$ which leads to

$$\frac{\partial M}{\partial T} \bigg|_{T=T_C} = -\frac{a_0}{3b}\left(\frac{b}{H}\right)^{1/3}$$

(4.20)

Using Maxwell’s relation

$$\Delta S_{iso} = \mu_0V \int_{H_i}^{H_f} \frac{\partial M}{\partial T} dH$$

(4.21)

for the isothermal entropy change induced by a field increase from the initial value, $H_i$, to the final value, $H_f$, one obtains the well-known functional form

$$\Delta S_{iso}/\mu_0V = -\frac{a_0}{2}\left(\frac{H_f - H_i}{b}\right)^{2/3}$$

(4.22)

This equation has been verified for various ferromagnets like the prototypical Gd for instance [121].

In addition to the alternative derivation of the entropy change, Eq. 4.22 provides
a useful insight into the possibilities to increase the positive MCE. The major limiting factor of the positive MCE is the decay of $\chi$ with increasing field or magnetization, which reflects the loss of criticality in the presence of the conjugate field $H$. This fast decay of $|\partial M/\partial T|$ overcompensates the explicit linear increase of with increasing $M$. An antiferromagnet at $T > T_N$ but not too far above the Curie-Weiss temperature can show appreciable field-induced magnetization while at the same time $\chi$ remains virtually unchanged resulting in a potentially large positive MCE. Our approach of nanostructured materials resembles these basic ideas.

### 4.3.3 MBE growth of Co/Cr superlattices

The multilayer systems Cr(10 nm)/[Co($d_{Co}$)/Cr(0.75 nm)]$_{20}$/Cr(2 nm) with $d_{Co} = 0.35$ and 0.58 nm, Cr(10 nm)/[Co(0.6 nm)/Cr(0.78 nm)]$_{20}$/Cr(2 nm) and Cr(10 nm)/[Co(0.7 nm)/Cr(0.84 nm)]$_{20}$/Cr(2 nm) were prepared by MBE at a chamber base pressure of $1 \times 10^{-10}$ mbar. The (110)-oriented MgO substrate was heated for 30 minutes at a temperature of 1023 K in ultra-high vacuum for degassing and cleaning the surface. The substrate temperature was then reduced to 573 K at which deposition of a Cr buffer layer of 10 nm thickness took place. The Co/Cr superlattice structure of 20 Co/Cr periods was deposited at 423 K to keep inter-diffusion at a minimum. The final Co/Cr bilayer of the superstructure was capped with additional 2 nm Cr. The growth rates of Co and Cr were monitored by a calibrated quartz oscillator and were found to be 0.78 nm/min and 0.16 nm/min, respectively. A series of samples has been prepared keeping the nominal thickness of Cr constant while varying the Co thickness.

In this thickness range of a few Co monolayers, the crossover from three to two dimensions sets in, and confinement reduces the Curie temperature from $T_C(\infty) = 1388$ K to room-temperature in accordance with the finite-size scaling.[See Section 2.3]
Figure 4.3: Normalized magnetic moment $m/m_{\text{max}}$ vs. $T$ of non interacting ultrathin Co films after zero-field-cooling and subsequent field heating in $\mu_0 H = 5$ mT. The Curie temperature of bulk Co has been reduced by more than 1000 K due to a geometrical confinement of the correlation length perpendicular to the film plane.

From finite size scaling, Eq. 2.5, one would expect a $T_C$ close to room-temperature in the limit of 1 to 2 monolayers. Alloying effects at the non ideal Co/Cr interfaces, however, have already a suppressing effect on $T_C$ of Co. Hence, our deposited Co films are about 1-2 monolayers thicker than the ideal estimate above suggests. Figure 4.3 shows the normalized temperature dependence of the total magnetic moment, $m$, of non interacting ultrathin Co films after zero-field-cooling and subsequent field heating in $\mu_0 H = 5$ mT. The negligible inter-plane interaction is reached in the limit of a large Cr spacer thickness of $d_{\text{Cr}} = 5$ nm. The Curie temperature of bulk Co has been reduced by more than 1000 K due to a geometrical confinement of the correlation length perpendicular to the film plane.

Figure 4.4 shows a small-angle X-ray diffraction pattern for the multilayer sample Cr (10 nm)/[Co(0.60 nm)/Cr(0.78 nm)]$_{20}$/Cr(2 nm) as a typical example of our heterostruc-
Figure 4.4: Small-angle X-ray diffraction pattern of a nominal Cr (10 nm)/[Co(0.60 nm)/Cr(0.78 nm)]$_{20}$/Cr(2 nm) superlattice (circles). The line represents a best fit using Leptos 2. Indication of a superlattice peak at $2\theta = 6.5$ degree is found in the data in agreement with the fit (see dashed vertical line). The inset shows the wide-angle X-ray diffraction pattern indicating a Cr(211) peak from the 10 nm Cr buffer layer, the pronounced MgO (110) of the oriented single crystalline substrate and Cr (00l) peaks from the 2nm capping layer. The individual ultra-thin Co and Cr films appear as superstructure in the small angle pattern but are not resolved in the wide angle pattern.
tures. A superstructure peak is visible in the experimental data (circles) at $2\theta = 6.5^\circ$ and reproduced by the simulation (solid line) using the Leptos-2 software package. A simple estimate with the help of Bragg’s law reveals $d \approx \frac{\lambda_{\text{Cu},K_a}}{2 \sin 3.25^\circ} = 1.4$ nm with the characteristic Cu $K_a$ radiation of wavelength $\lambda_{\text{Cu},K_a} = 1.544 \text{ Å}$. This thickness represents the period produced by the sum of the Co thickness and the Cr thickness. The large angle X-ray diffraction pattern (Max-B, Rigaku-D) shown in the inset indicates a Cr(211) peak from the 10 nm Cr buffer layer, the pronounced MgO (110) of the oriented single crystalline substrate and Cr (ool) peaks from the 2 nm capping layer. The individual ultra-thin Co and Cr films are evidenced as superstructure in the small-angle pattern but are not resolved in the wide-angle pattern (inset Fig. 4.4).

### 4.3.4 Magnetic properties of Co/Cr superlattices

A superconducting quantum interference device (SQUID) magnetometer (MPMS-XL, Quantum Design) was used to carry out the magnetic measurements with magnetic fields applied in the plane of the sample. Figure 4.3 shows the presence of the well-known finite-size effect in a Cr (10 nm)/[Co(0.40 nm)/Cr(5 nm)]$_{20}$/Cr(2 nm) multilayer where the large Cr thickness of 5 nm suppresses to a large extend AF Co-Co interlayer coupling. Hence the FM to PM transition of the ultra-thin Co films is observed at a Curie temperature of $T_C(d_{\text{Co}} = 0.4 \text{ nm}) \approx 360$ K. Next we show the presence of AF coupling between the Co films. The coupling is mediated by RKKY-like exchange which depends on the Cr layer thickness $d_{\text{Cr}}$. Figure 4.5 shows a typical hysteresis loop where the zero-field magnetization (remanence) is zero. The upper left inset shows a magnified portion of the hysteresis in the vicinity of $H = 0$. Here a tendency towards moment compensation is already visible even when the applied field favors parallel alignment of the Co magnetization. This provides clear evidence for AF coupling. The
Figure 4.5: Room-temperature magnetic hysteresis of Cr (10 nm)/[Co(0.80 nm)/Cr(0.75 nm)]_{10}/Cr(2 nm). The arrows indicate the directions of field sweeps. The upper left inset shows a detailed view on the hysteresis in the vicinity of zero magnetic field. The compensation of the magnetization in small fields is clearly visible and shows that coupling between the Co films is AF. The arrows in the upper left inset represent the magnetization orientation of neighboring Co films for zero and positive applied magnetic field, respectively. The lower right inset shows a cartoon of the heterostructure and the compensation of the Co moments (arrows) close to $H = 0$.

The lower right inset shows a cartoon of the heterostructure indicating the compensation of the Co moments close to $H = 0$. Note that magnetic hysteresis gives rise to losses during cyclic magnetization reversal diminishing the magnetocaloric cooling. In the giant magnetocaloric material Gd$_5$Ge$_2$Si$_2$ hysteresis has been reduced by 90% through addition
of Fe [17]. In magnetic multilayer heterostructures, one can achieve control over the magnetic anisotropy, which is a major factor in determining and potentially reducing hysteresis. The effectiveness of such an approach remains to be investigated. Next we study the thermodynamics of various Co/Cr superlattices with AF interlayer coupling. In accordance with the mean-field equation 4.15, Fig. 4.6 suggests that the location of the temperature-driven AF to PM transition can be tuned via the intra and inter-plane
exchange interactions. The intra-layer interaction is related to the tunable $T_C(d_{Co})$ of the Co films, the inter-plane interaction is controlled via the spacing between the Co films.

Figure 4.6(a) shows $M/M_{max}$ vs. $T$ of Cr (10 nm)/[Co(d)/Cr(0.75 nm)]$_{20}$/Cr(2 nm) for $d_{Co} = 0.35$ (solid squares) and 0.58 nm (open squares), measured in an applied magnetic field of 5 mT. The increase in the Co thickness is accompanied by an increase in the $T_C$ of the Co films in accordance with Eq. 2.5. An increase in $T_C$ can be interpreted as an increase in the effective in-plane exchange constant $J_1$, even if the microscopic spin-spin exchange is unaffected by changes of the geometrical confinement. At constant Cr thickness (constant $J_2$), an increasing Co thickness ($d_{Co}$) therefore enhances the AF transition temperature.

Figure 4.6(b) allows the comparison of the temperature dependence of Cr (10 nm) / [Co( 0.60 nm) / Cr(0.78 nm)]$_{20}$/Cr(2 nm) (solid circles) and Cr (10 nm)/[Co(0.7 nm)/Cr(0.84 nm)]$_{20}$/Cr(2 nm) (open circles) with the results of Fig. 4.6(a). Again, in accordance with the guiding mean-field arguments of Eq. 4.15, we find that an increase of $d_{Co}$ from 0.35 to 0.60 nm is compensated by a reduction of the inter-plane exchange $J_2$ realized through increased Cr thickness. Similarly an increase of $d_{Co}$ from 0.58 to 0.70 nm (nominally only since X-ray results are inconclusive) implies an increase in the effective $J_1$ and, hence, enhancement of the AF transition temperature. However, the increase in $J_1$ is overcompensated by a decrease in $J_2$. The latter originates from an increase of the Cr thickness from 0.75 nm to 0.84 nm. Increasing $d_{Cr}$ for $d_{Cr}$ larger than 0.7 nm reduces the AF coupling strength. Note that the decrease of AF coupling strength is also apparent in the incomplete compensation of the low-temperature magnetization of the curves in Fig. 4.6(b) while the higher AF coupling strength gives rise to almost complete compensation of the low-temperature magnetization (Fig. 4.6(a)). A comparison between the curves in Fig. 4.6(b) is also consistent with the qualitative mean-field Eq. 4.15 showing that a strong increase of the Co thickness overcompensates for a moderate increase of the
Cr thickness and, hence, enhances the transition temperature.

Next we show the magnetization data of Cr (10 nm)/[Co(0.80 nm)/Cr(0.75 nm)]_{10}/Cr(2 nm) which can be analyzed in terms of positive MCE near room-temperature. Figure 4.7 shows representative isotherms $m$ vs. $\mu_0 H$ for $0 \leq \mu_0 H \leq 7$ T. The complete data set used for the entropy calculation via Maxwell’s relation involves the isotherms at $120 \leq T \leq 330$ K in steps of $\Delta T = 10$ K. The inset shows representative field heating and cooling curves, $m$ vs. $T$, at 5 (squares) and 100 mT (triangles). All measurements have been initialized by zero-field cooling. Note that temperature hysteresis is negligible (see arrows for indication of the direction of temperature change).

Figure 4.7: Isotherms $m$ vs. $\mu_0 H$ for $0 \leq \mu_0 H \leq 7$ T. The inset shows field heating and cooling $m$ vs. $T$ data at 5 mT (squares) and 100mT (triangles). All curves are initialized by zero-field-cooling, and the arrows indicate the direction of the temperature change.
Figure 4.8: Temperature dependence of the mass specific entropy change $\Delta S$ calculated from Eq. 4.21, using the experimental isotherms in the temperature interval $120 \leq T \leq 330$ K measured in steps of $\Delta T = \text{K}$ to numerically calculate $\frac{\partial m}{\partial T}$ vs $\mu_0 H$. for $0 \leq \mu_0 H \leq 7$ T. The dotted line shows an extrapolation of $-\Delta S$ vs. $T$ towards higher temperature going beyond our experimental data.

Figure 4.8 shows the mass specific entropy change, $\Delta S$, calculated with the help of Maxwell’s relation giving rise to Eq. 4.21 after integration. The latter allows calculating $\Delta S$ when normalizing with respect to the magnetically active mass of the sample. The mass is calculated from the sample area of 25 mm$^2$, the Co and Cr thicknesses, and their densities. We used the grid of isotherms over the temperature interval $120 \leq T \leq 330$ K to numerically calculate $\frac{\partial m}{\partial T}$ vs. $\mu_0 H$ for $0 \leq \mu_0 H \leq 7$ T where $m = VM$. The dotted line shows an extrapolation of $-\Delta S(T)$ towards higher temperature beyond our experimental data. The extrapolation implies that the maximum of the entropy change will be significantly higher than -0.4 J/kg-K but located 50 K or more above room-
temperature. It is apparent from our theoretical considerations in Section 4.3.1 and 4.3.2 that amplitude and position of the peak of the entropy change can be controlled over a wide range. As discussed throughout this chapter, the tuning of these essential magnetocaloric properties is achieved through growth controlled modification of $J_1$ and $J_2$.

The data shown in Fig. 4.8 appear encouraging enough to finally estimate the adiabatic temperature change

$$\Delta T_{ad} = -TV \mu_0J' H \int_0^1 C \left( \frac{\partial M}{\partial T} \right)_H d(\mu_0H)$$ (4.23)

This expression describes the drop in temperature of a sample with positive MCE when removing the applied magnetic field while heat exchange with the surrounding is suppressed. This is an important figure of merit for possible magnetocaloric applications, because it allows, e.g., the calculation of the refrigeration capacity.

$$RC = -\int_0^T \Delta S(T') dT'$$ (4.24)

The phenomenological expression for $\Delta T_{ad}$ deviates from the isothermal entropy expression by the additional factor $-T/C(T,H)$ where $C(H,T)$ is the field and temperature dependent heat capacity of the sample. Here, we estimate the latter with the help of the temperature and field-independent high-temperature limit of the heat capacity at constant volume, $C = 3Rn$, where $R$ is the universal gas constant and $n$ is the number of moles of Co and Cr.

With the amount of deposited Co and Cr material $M_C = 1.67 \times 10^{-9}$ kg and kg, we obtain the specific heat capacity $C \approx 461$ J/kg-K. With this and $\Delta S(T = 334K, \mu_0H = 7T) = -0.4$ J/kg-K we estimate
\[ \Delta T_{ad} \approx -\frac{T\Delta S}{C} \approx 0.3 \text{ K} \]  

an appreciable value with significant potential for further improvement.

### 4.3.5 PLD growth of Fe/Cr superlattices

Pulsed-laser deposition (PLD) is usually employed for the preparation of thin films with a thickness of at least a few nanometers, and is used especially for complex oxide films owing to the advantage of obtaining a stoichiometry consistent with the target. PLD have been used to prepare ultrathin metal films in a UHV chamber \[122\]. To do so, a low laser power (slightly above the ablation threshold) and a large target to substrate distance were employed in order to conveniently control the film thickness and to avoid droplet formation. The PLD method has also been applied to prepare ultrathin iron films on Cu(100) in the expectation of modifying the growth behavior and film structure in comparison with the extensively investigated thermally deposited (TD) films \[123\]. Compared with the TD Fe/Cu(100) films discussed, PLD films show different features regarding growth, structure and magnetism. Consistent with the layer-by-layer growth mode, PLD preparation leads to an improved film quality up to 5 ML coverage, as is revealed by the higher LEED intensity \[123\]. However, above 6 ML, thermal deposition leads to a better film quality \[123\].

The multilayer systems Cr(7.25 nm)/[Fe(1.6nm)/Cr(0.86)]\textsubscript{18}/Cr(0.8 nm) and Cr(5.22 nm)/[Fe(0.25nm)/Cr(1.12nm)]\textsubscript{20}/Cr(1.07 nm) were prepared by PLD at a chamber base pressure of \(6 \times 10^{-9}\) mbar. The pressure during the metal deposition process was below \(2.3 \times 10^{-8}\) mbar. The (100)-oriented MgO substrate was heated for 10 minutes at a temperature of 873 K in ultra-high vacuum for degassing and cleaning the surface. The substrate temperature was then reduced to 573 K at which Cr buffer layer was deposited.
Figure 4.9: Small-angle X-ray diffraction pattern of a nominal Cr(7.25 nm)/[Fe(1.6 nm)/Cr(0.86 nm)]$_{18}$/Cr(0.8 nm) superlattice (circles). The red line represents a best fit using Leptos-2 software. Indication of a superlattice peak at $2\theta = 3.6^\circ$ is clearly visible in the data in agreement with the fit. The inset shows the wide-angle X-ray diffraction pattern indicating a Cr(200) peak from the 7.25 nm Cr buffer layer, the pronounced MgO (100) of the oriented single crystalline substrate. The individual ultra-thin Fe and Cr films appear as superstructure in the small angle pattern but are not resolved in the wide angle pattern.

The temperature was then reduced by water cooling the substrate to room temperature and Fe/Cr superlattice structure was deposited at 293 K to keep inter-diffusion at a minimum. The final Fe/Cr bilayer of the superstructure was capped with additional 1 nm Cr. The energy of the laser pulse was 275mJ and the repetition rate was 5 Hz. The
substrate was rotated at 30 revolution per minute to ensure uniform film thickness. The targets was also rotated at 30 revolution per minute and the laser beam was rastered over a distance of 1 cm. The Cr thickness was chosen so that it gives rise to antiferromagnetic coupling between Fe layers. For comparison AF coupling and FM coupling a multilayer system \( \text{Cr}(5.5 \text{ nm})/\text{[Fe}(0.49 \text{ nm})/\text{Cr}(0.56\text{nm})]_{20}/\text{Cr}(1.15 \text{ nm}) \) was prepared. The laser energy in this case was 300 mJ and the repetition rate was 5 Hz. The growth rates of Fe and Cr were calibrated per laser pulse and were found to be \( 6 \times 10^{-3} \text{Å} \) and \( 6 \times 10^{-3} \text{Å} \), respectively.

Figure 4.9 shows a small-angle X-ray diffraction pattern for the multilayer sample \( \text{Cr}(7.25 \text{ nm})/\text{[Fe}(1.6 \text{ nm})/\text{Cr}(0.86 \text{ nm})]_{18}/\text{Cr}(0.8 \text{ nm}) \) as a typical example of our heterostructures. A superstructure peak is visible in the experimental data (solid black line in main frame) at \( 2\theta = 3.6^\circ \) and reproduced by the simulation (solid red line) using the Leptos-2 software package. A simple estimate with the help of Bragg’s law reveals 
\[ d \approx \frac{\lambda_{\text{Cu},K\alpha}}{2 \sin 1.8^\circ} = 2.45 \text{ nm} \]
with the characteristic Cu \( K\alpha \) radiation of wavelength \( \lambda_{\text{Cu},K\alpha} = 1.54 \text{ Å} \). This thickness represents the period produced by the sum of the Fe thickness and the Cr thickness. The large angle X-ray diffraction pattern (Max-B, Rigaku-D) shown in the inset indicates a Cr(200) peak from the 7.25 nm Cr buffer layer, the pronounced MgO (200) and (400) of the (100)-oriented single crystalline substrate. The absence of any additional X-ray peaks from any other orientation of Cr and Fe supports that the growth has followed an uniaxial orientation unlike Co/Cr superlattices. The individual ultra-thin Fe and Cr films are evidenced as superstructure in the small-angle pattern but are not resolved in the wide-angle pattern (inset Fig. 4.9).
4.3.6 Magnetic properties of Fe/Cr superlattices

A superconducting quantum interference device (SQUID) magnetometer (MPMS-XL, Quantum Design) was used to carry out the magnetic measurements with magnetic fields applied in the plane of the sample. Figure 4.10 shows the presence of the well-known finite-size effect in a Cr(5.5 nm) / [Fe(0.49 nm) /Cr(0.56 nm) ]_{20} /Cr(1.15 nm) multilayer where the Cr thickness of 0.56 nm provides FM Fe-Fe interlayer coupling. Hence the FM to PM transition of the ultra-thin Fe films is observed at a Curie temperature of $T_C(d_{Fe} = 0.49 \text{ nm}) \approx 325 \text{ K}$. In the thickness range of a few Fe monolayers, the crossover from three to two dimensions sets in, and confinement reduces the Curie temperature from $T_C^\infty(Fe) = 1043 \text{ K}$ to room-temperature in accordance with the finite-size scaling [see section 2.3].

From finite size scaling, Eq. 2.5, one would expect a $T_C$ close to room-temperature in the limit of 1 to 2 monolayers. Alloying effects at the non ideal Fe/Cr interfaces, however, have already a suppressing effect on $T_C$ of Fe. Hence, our deposited Fe films are about $\leq$ 1 monolayers thicker than the ideal estimate above suggests. Figure 4.10 shows the temperature dependence of the total magnetic moment, $m$, of ferromagnetically interacting ultrathin Fe films after zero-field-cooling and subsequent field heating in $\mu_0 H = 2, 10$ and 30 mT. The FM inter-plane interaction is reached in the limit of a Cr spacer thickness of $d_{Cr} \approx 0.5 \text{ nm}$ [124]. The Curie temperature of bulk Fe has been reduced by more than 700 K due to a geometrical confinement of the correlation length perpendicular to the film plane. The inset shows the temperature dependence of $dm/dT$ with with applied magnetic field. Analogous to behavior of bulk FM, $dm/dT$ decreases with applied magnetic. Such a behavior is not advantageous for optimized MCE materials, where a increase of $dm/dT$ with increasing field, approach in the direction of maximizing the isothermal entropy change.
Figure 4.10: Magnetic moment $m$ vs. $T$ of ferromagnetically interacting ultrathin Fe films of multilayer Cr(5.5 nm) / [Fe(0.49 nm) /Cr(0.56 nm)]$_{20}$/Cr(1.15 nm) after zero-field-cooling and subsequent field heating in $\mu_0 H = 2, 10$, and 30 mT respectively. The Curie temperature of bulk Fe has been reduced by more than 700 K due to a geometrical confinement of the correlation length perpendicular to the film plane. The inset show the derivative $dm/dT$ vs. $T$ of the in the main frame corresponding to $\mu_0 H = 2, 10$ and 30 mT respectively.

Next we show the presence of AF coupling between the Fe films. The coupling is mediated by RKKY-like exchange which depends on the Cr layer thickness. Figure 4.11 shows a typical hysteresis loop where the zero-field magnetization (remanence) is close to zero. The upper left inset shows a magnified portion of the hysteresis in the vicinity of $H = 0$. Here a tendency towards moment compensation is already visible even when the applied field favors parallel alignment of the Fe magnetization. This provides clear evidence for AF coupling.
Figure 4.11: Magnetic hysteresis of Cr(7.25 nm)/[Fe(1.6 nm)/Cr(0.86 nm)]_{18}/Cr(0.8 nm) measured at $T = 20$ K. The upper left inset shows a detailed view on the hysteresis in the vicinity of zero magnetic field. The arrows indicate the directions of field sweeps. The compensation of the magnetization in small fields is clearly visible and shows that coupling between the Fe films is AF.

Next we study the thermodynamics of Cr(5.22 nm)/[Fe(0.25 nm)/Cr(1.12 nm)]_{20}/Cr(1.07 nm) superlattice with AF interlayer coupling. In accordance with the mean-field equation 4.15. Fig. 4.12 suggests that the location of the temperature-driven AF to PM transition can be tuned via the intra and inter-plane exchange interactions. The intra-layer interaction is related to the tunable $T_C(d_{Fe})$ of the Fe films, the inter-plane interaction is controlled via the spacing between the Fe films.

Figure 4.12 shows $m$ vs. $T$ of antiferromagnetically interacting Cr(5.22 nm)/ [Fe(0.25 nm)/ Cr(1.12 nm)]_{20}/Cr(1.07 nm) superlattice after zero-field-cooling and subsequent field heat-
Figure 4.12: Magnetic moment $m$ vs. $T$ of antiferromagnetically interacting Cr(5.22 nm) / [Fe(0.25 nm) /Cr(1.12 nm)]$_{20}$ / Cr(1.07 nm) superlattice after zero-field-cooling and subsequent field heating in $\mu_0 H = 2, 10, 30$ mT. The Curie temperature of bulk Fe has been reduced by more than 700 K due to a geometrical confinement of the correlation length perpendicular to the film plane. The inset show the derivative $dm/dT$ vs. $T$ of the in the main frame corresponding to $\mu_0 H = 2, 10$ and 30 mT respectively. Unlike in FM case, here $dm/dT$ increases with applied magnetic filed. This is an ideal situation to study MCE in this superlattice since from Eq. 4.3 it is clear that will maximize $\Delta S$ in case of positive MCE. Note that temperature hysteresis is negligible in this regime (see arrows for indication of the direction of temperature
Figure 4.13: magnetization data of Cr(5.22 nm)/[Fe(0.25nm)/Cr(1.12nm)]20/Cr(1.07 nm) which can be analyzed in terms of positive MCE near room-temperature. Figure 4.13 shows representative isotherms $m$ vs. $\mu_0 H$ for $0 \leq \mu_0 H \leq 7$ T. The complete data set used for the entropy calculation via Maxwell’s relation involves the isotherms at $170 \leq T \leq 360$ K in steps of $\Delta T = 10$ K. All measurements have been initialized by zero-field cooling.

Next we show the magnetization data of Cr(5.22 nm)/[Fe(0.25nm)/Cr(1.12nm)]20/Cr(1.07 nm) which can be analyzed in terms of positive MCE near room-temperature. Figure 4.13 shows representative isotherms $m$ vs. $\mu_0 H$ for $0 \leq \mu_0 H \leq 7$ T. The complete data set used for the entropy calculation via Maxwell’s relation involves the isotherms at $170 \leq T \leq 360$ K in steps of $\Delta T = 10$ K. All measurements have been initialized by zero-field cooling from $T = 400$ K.

Figure 4.14 shows the mass specific entropy change, $\Delta S$, calculated with the help of
Figure 4.14: Temperature dependence of the mass specific entropy change $\Delta S$ calculated from Eq. 4.21, using the experimental isotherms in the temperature interval $170 \leq T \leq 360$ K measured in steps of $\Delta T = 10$ K to numerically calculate $\frac{dm}{dT}$ vs $\mu_0 H$. for $0 \leq \mu_0 H \leq 7$ T. The inset shows RCP (See Eq. 2.20) for $\mu_0 H = 7$ T calculated by integrating the $-\Delta S$ vs. $T$ with our experimental data.

Maxwell’s relation giving rise to Eq. 4.21 after integration. The latter allows calculating $\Delta s_{iso}$ which provides $\Delta S$ when normalizing with respect to the magnetically active mass of the sample. The mass is calculated from the sample area of $50$ mm$^2$, the Fe and Cr thicknesses, and their densities. We used the grid of isotherms over the temperature interval $170 \leq T \leq 360$ K to numerically calculate $\frac{dm}{dT}$ vs. $\mu_0 H$ for $0 \leq \mu_0 H \leq 7$ T where $m = VM$. It is apparent from our theoretical considerations in Section 4.3.1 and 4.3.2 that amplitude and position of the peak of the entropy change can be controlled over a wide range. As discussed throughout this chapter, the tuning of these essential magnetocaloric

properties is achieved through growth controlled modification of $J_1$ and $J_2$.

The inset shows RCP (See Eq. 2.20) for $\mu_0H = 7$ T calculated by integrating the $-\Delta S$ vs. $T$ with our experimental data. By applying Eq. 4.24 the refrigerant capacity was calculated using the $-\Delta S$ curve for $\mu_0H = 7$ T. This was achieved by interpolating the curve. The limits of integration were from $T = 76$ K to $T = 340$ K. The limits were chosen with standard consideration in literature for corresponding to half value of maximum of $-\Delta S$.

With the amount of deposited Fe and Cr material the isothermal entropy change is $\Delta S(T = 260K, \mu_0H = 7T) = -1.3$ J/kg-K and maximum RCP = 253 J/Kg.

At this point it is worth discussing how this approach compare to bulk materials and nanoparticles in application to MCE. Bulk Gd at $T_c = 292$ K and $\mu_0H = 5$ T has $\Delta S = 10.2$ J/Kg-K and $RCP = 410$ J/Kg [14]. Gd based alloys as Gd$_5$Si$_2$Ge$_2$ at $T_c = 276$ K and $\mu_0H = 5$ T has $\Delta S = 18.4$ J/Kg-K and $RCP = 535$ J/Kg [14]. The alloy Gd$_5$Si$_2$Ge$_2$ is considered as a standard for comparison for bulk MC materials. Nanoparticles based on different materials have more modest entropy changes. Nanoparticles based on e.g. La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ of size 50 nm, at $T = 215$ K with $\mu_0H = 5$ T has $\Delta S = 6.2$ J/Kg-K and $RCP = 225.6$ J/Kg [125]. All these materials are based on rare earth elements. In spite of our approach based on 3d transitional metals the value of $\Delta S$ is modest and RCP is comparable with rare earth bulk alloys. Further scope of improvement lies with incorporation of elastic degrees of freedom as in case of bulk Gd$_5$Si$_2$Ge$_2$. 
Chapter 5

Probing equilibrium by non-equilibrium dynamics: Aging in Co/Cr superlattices

In this chapter I discuss our magnetization relaxation studies on a structurally ordered magnetic Co/Cr superlattice. Tailored nanoscale periodicity creates mesoscopic spatial magnetic correlations with slow relaxation dynamics when quenching the system into a non-equilibrium state. Magnetization transients are measured after exposing the heterostructure to a magnetic set-field for various waiting times. Scaling analysis reveals an asymptotic power-law behavior in accordance with a full aging scenario. The temperature dependence of the relaxation exponent shows pronounced anomalies at the equilibrium phase transitions of the antiferromagnetic superstructure and the ferromagnetic to paramagnetic transition of the Co layers. The latter leaves only weak fingerprints in the equilibrium magnetic behavior but gives rise to a prominent change in non-equilibrium properties. These findings suggest scaling analysis of non-equilibrium data as a probe for weak equilibrium phase transitions.
5.1 Superlattices for Tailored Spin-Spin Correlation

Magnetic model systems serve traditionally as workhorses in equilibrium statistical mechanics. They maintain their importance in the challenging field of non-equilibrium thermodynamics. Magnetic aging phenomena are conceptually simple with well-defined experimental protocols. At the same time, even macroscopically complex magnetic behavior can be described by simple model Hamiltonians. Similarly to the celebrated concept of universality in equilibrium statistical mechanics where symmetry of the interactions and dimensionality unify otherwise microscopically different systems into classes with common critical behavior, there are magnetic control parameters grouping microscopically distinct model systems into classes with universal aspects of non-equilibrium thermodynamics.

Magnetic multilayer thin-films and their controlled growth via modern molecular beam epitaxy (MBE) methodology provide experimental access to a wide range of microscopic parameters. Superlattice structures allow tailoring the intra and inter-layer exchange as well as the spin fluctuation spectra through geometrical confinement. We tailor those properties in Co/Cr thin-film superlattices to study magnetic aging phenomena in the framework of scaling analysis. For example, the Curie temperature of the Co constituent films can be tailored between $0 < T^\text{Co}_C(d) \leq 1388$K by geometrical confinement through variation of the film thickness, $d$. Cr spacer layers provide AF exchange coupling between these Co films. The oscillating thickness dependence of the RKKY-type interlayer exchange becomes tunable in strength through control of the Cr interlayer film thickness [113, 114, 115].
5.2 Magnetic Relaxation in Ordered Magnetic Systems

Magnetization relaxation in weakly correlated spin systems is typically a fast process on a laboratory time scale since it depends on the microscopic spin-flip time of about $10^{-8}$ s. From an experimental point of view it is convenient to study magnetic relaxation phenomena on a time scale from seconds to hours. However, this requires the presence of non-exponentially decaying spin-spin correlation. Glassy systems in general and spin glasses in particular provide experimental access to a non-ergodic regime below the glass transition temperature where the dynamics of the system becomes very slow in comparison with the microscopic spin flip time. The magnetic glass properties with their slow spin dynamics require disorder and frustration in the magnetic interactions. While disordered glassy systems have been extensively studied, only little work has been done on the relaxation of ordered magnetic systems. With rare exceptions, experimental investigations in ordered bulk systems face the problem of fast dynamics. The situation improves when taking advantage of an analogy of the phenomenon of critical slowing down with the spin dynamics in ordered magnetic nanostructures. Critical slowing down is observed when entering the critical regime of, e.g., a magnetic second order phase transition. Here, on approaching the critical temperature, the diverging magnetic correlation length gives rise to diverging relaxation times. However, the smallness of the critical regime makes it almost impossible to experimentally observe this phenomenon in ordered bulk systems [126].

Our novel approach to study magnetic relaxation in ordered magnetic systems builds on the increase of the characteristic spin-spin correlation length in comparison to atomic bulk systems when taking advantage of magnetic nanostructuring. We use magnetic superlattices, structured on the nanoscale, to increase relaxation times when replacing atomic spins through mesoscopically correlated regions. More specifically, we grow
three-dimensional artificial AF superlattices of two-dimensional FM Co films with in-plane anisotropy coupling antiferromagnetically perpendicular to the plane across Cr spacer layers. As a result, we obtain temperature-dependent magnetic metastability and slow relaxation dynamics in the absence of disorder and frustration. Our experimental results on magnetic aging can be interpreted in the framework of a dynamic scaling analysis which is based on the assumption of a full aging scenario. This scenario predicts asymptotic power-law relaxation, \(M(t, S) \propto S^{-\theta}(t/S)^{-\lambda/z}\), with non-universal exponents \(a\) and \(\lambda/z\). Here \(z\) is the dynamical exponent that governs the algebraic growth of the time-dependent correlation length. The exponents \(a\) and \(\lambda\), the latter being sometimes called the autoresponse exponent, are non-equilibrium exponents that describe the dynamical scaling behavior of the response in the asymptotic aging regime [119].

Here we show the correlation between anomalies in the temperature dependence of \(\lambda/z\) vs. \(T\) with magnetic equilibrium phase transitions. \(\lambda/z\) vs. \(T\) reveals the breakdown of three-dimensional AF order at the Néel temperature, \(T_N(H = 0)\), followed by a transition at \(T_C\) from FM order of the uncorrelated Co films to global paramagnetism of the sample. The latter transition is very weakly pronounced in the equilibrium magnetic data but creates a prominent drop of about 60% in \(\lambda/z\) at \(T_C\). These findings pave the way to probe particularly equilibrium phase transitions via pronounced non-equilibrium properties [127].

5.3 Results and Analysis

Figure 5.1 shows the temperature dependence, \(M\) vs. \(T\), of the magnetic moment, \(M\), of our Cr (10 nm)/[Co(0.60 nm)/Cr(0.78 nm)]\(_{20}\)/Cr(2 nm) heterostructure. The data are taken with the help of a superconducting quantum interference device (SQUID MPMS-XL, Quantum Design) on field-heating (FH) and field-cooling (FC) in \(\mu_0H=5\).
Figure 5.1: ZFC-FH and FC $M$ vs. $T$ data measured in $\mu_0 H = 5$ (solid triangles (FH) and circles (FC)) and 30 mT (open triangles (FH) and circles (FC)). $T_N (\mu_0 H = 5mT) = 53K$ is indicated by a vertical arrow. Inset (a) shows small-angle X-ray diffraction data (blue lower line) and the corresponding simulation (red upper line). Inset (b) shows a hysteresis loop, $M$ vs. $\mu_0 H$, measured at $T = 50K$. Inset (c) shows the corresponding hysteresis loop at $T = 200K$ [127].

(solid triangles (FH) and circles (FC)) and 30 mT (open triangles (FH) and circles (FC)) in-plane magnetic fields after initial zero-field cooling (ZFC). The ZFC-FH/FC branches of the 5mT $M_{ZFC-FH}$ vs. $T$ / $M_{FC}$ vs. $T$, exhibit pronounced irreversibilities close to $T_N (\mu_0 H = 5mT) = 53 \text{ K}$ of the superlattice. In analogy to atomic bulk antiferromagnets, homogenously applied magnetic fields weaken the AF order parameter and reduce the
AF ordering temperature such that $T_N = T_N(H)$ where $T_N(H)$ is given by the inflection point of $M_{ZFC-FH}$ vs. $T$. This field dependence is seen in Fig. 5.1 in the decrease from $T_N(\mu_0 H = 5mT) = 53K$ to $T_N(\mu_0 H = 30mT) = 25K$.

The Co/Cr superlattice periodicity of 1.4 nm is shown in Fig. 5.1a via small-angle X-ray diffraction measured with the help of characteristic Cu $K_{\alpha}$ radiation of wavelength $\lambda_{\text{Cu}, K_{\alpha}} = 0.1544$ nm. A superstructure peak appears in the data at $2\theta = 6.5^\circ$ (blue lower line) and is reproduced by simulation (red upper line). Details of the structural analysis including wide angle X-ray diffraction can be found in Fig. 4.4.

Figure 5.1b shows an isothermal magnetization hysteresis loop, $M$ vs. $H$, measured at $T = 50K \ll T_N(H = 0)$. Contraction of the loop at the coercive fields is a fingerprint of AF coupling. Fig. 5.1c shows the corresponding hysteresis loop at $T = 200K \gg T_N(H = 0)$. Here the AF inter-layer correlation is thermally broken and, hence, the contraction of the hysteresis loop is absent. This behavior is in close analogy to atomic layered AF systems such as the prototypical metamagnets FeCl$_2$ and FeBr$_2$.

The insets of Fig. 5.2 show typical log-log plots of our magnetic aging data measured at $T = 20$ (left frame) and 160K (right frame) below and above the AF transition. The displayed data are 5-point adjacent averages. A small homogenizing field of $\mu_0 H = 5$ mT, which brings the individual Co layers into single domain states, has been applied on cooling the sample from $T = 330$ K down to various target temperatures where magnetization relaxation is measured, respectively. At each target temperature the sample is exposed to a set-field of $\mu_0 H = 30$ mT for various waiting times $S=10$ (squares), 100 (circles), and 1000 s (triangles). After field exposure the magnetic field is quickly removed on a time scale $t \ll S$ and isothermal relaxation, $M$ vs. $t$, is recorded using SQUID magnetometry.

Our magnetization transients confirm the asymptotic power-law behavior, $M(t, S) \propto S^{-a}(t/S)^{-\lambda/z}$, when represented in a log-log scaling plot, $S^a M(t, S)$ vs. $t/S$ where
Figure 5.2: Insets show log-log plots of magnetic aging data, $M$ vs. $t$, measured after cooling in $\mu_0 H = 5$ mT, from $T = 330$ K to $T = 20$ (left frame) and 160 K (right frame) and subsequent exposure to a set-field of $\mu_0 H = 30$ mT for various waiting times $S = 10$ (squares), 100 (circles), and 1000 s (triangles) followed by field removal on a timescale $t \ll S$. Main frames show the same data in a scaling plot, $S^a M(t, S)$ vs. $t/S$ with data collapse in the asymptotic regimes on respective master curves (green lines) [127].

asymptotic linear behavior with slope $\lambda/z$ is expected. Optimized exponents $a = 1.32 \times 10^{-3}$, $\lambda/z = 1.9 \times 10^{-3}$ at 20K and $a = 3.0 \times 10^{-3}$, $\lambda/z = 4.3 \times 10^{-3}$ at 160 K give rise to data collapse on respective master curves (green lines in Fig. 5.2) in the asymptotic regime. In accordance with the scaling law we obtain identical $\lambda/z$-values for a given temperature at all waiting times within less than 5% error. Note, that without changing $\lambda/z$ a shift of the master curve along the $S^a M$-axis (away from the middling position) will give rise to virtually perfect collapse with the $S = 10$ s relaxation data
(Fig. 5.2 blue squares), which approximate best the approach of the true asymptotic regime for $t/s > 100$. It is the temperature dependence of $\lambda/z$ which we will discuss below as a non-equilibrium parameter with extreme sensitivity on equilibrium magnetic transitions. Alternatively, when plotting $F(t) = \frac{M(t, S) - M(t_1, S)}{M(t_2, S) - M(t_1, S)}$ for various waiting times,

![Figure 5.3: Inset shows a log-log plot of $M$ vs. $t$ for $T = 140K$ and waiting times $S = 10$ (squares), 100 (circles), and 1000s (triangles). Main frame shows corresponding scaling plot in log-log representation of $F(t)$ (see text) calculated for $t_1 = 1000$ and $t_2 = 5000$ with master curve (green line).](image)

$S$, at a given temperature one expects data collapse in the asymptotic regime onto the waiting-time independent master curve $F(t) = \frac{t^{-\lambda/z} - t_1^{-\lambda/z}}{t_2^{-\lambda/z} - t_1^{-\lambda/z}}$. Here $t_{1,2}$ are two arbitrary but fixed times in the asymptotic regime. Note that the structure of the experimentally
motivated scaling function $F(t)$ eliminates the impact of time independent background signals. In addition, data collapse is achieved through the single parameter $\lambda/z$, which is determined independently from the asymptotic region of the log-log plots of the relaxation data. Note, that attempts to determine $\lambda/z$ via a single parameter least squares fit is not recommended due to the insensitivity of $F(t)$ on variation of $\lambda/z$. The inset of Fig. 5.3 shows a log-log plot of the magnetization transients at $T = 140$ K and waiting times $S = 10$ (squares), 100 (circles), and 1000 s (triangles). The corresponding scaling plot is shown in log-log representation of $F(t)$ calculated for $t_1 = 1000$ and $t_2 = 5000$ s. The green line is the master curve calculated from $t_{1,2}$ and $\lambda/z = 4.6 \times 10^{-3}$. The residual $S$-dependence at small $t$ is in accordance with the expected breakdown of the scaling law when leaving the asymptotic regime.

MOKE magnetometry offers the advantage to probe low end regime of waiting time $S$ because the magnetic field can be set to zero in a time interval $\ll 0.1$ s unlike SQUID magnetometry where the resulting flux in the superconducting coils takes relatively more time to settle. In Fig. 5.4 we show the scaling plot of MOKE relaxation data obtained by field cooling the sample in a small homogenizing field of $\mu_0H = 5$ mT, which brings the individual Co layers into single domain states, has been applied on cooling the sample from $T = 330$ K down to $T = 40$ K where magnetization relaxation is measured, respectively. The sample is then exposed to a set-field of $\mu_0H = 40$ mT for various waiting times $S = 3$ (squares), 10 (circles), 30 s (triangles), 100 s (inverted triangles) and 2000 s (rhombohedral). After field exposure the magnetic field is quickly removed on a time scale $t \ll S$ and isothermal relaxation, $M$ vs. $t$, is recorded using MOKE magnetometry. It can be clearly concluded that the scaling with $F(t)$ works in excellent agreement even though long time of measurement suffers from moisture condensation at the window of the cryostat.

Figure 5.5 represents the culmination of our findings. It shows a hitherto unexplored
Figure 5.4: Shows a log-log scaling plot of MOKE data $T = 40$ K and waiting times $S = 3$ (squares), 10 (circles), 30 (triangles), 100 (inverted triangles) and 2000 s (rhombohedral) in log-log representation of $F(t)$ (see text) calculated for $t_1 = 5$ and $t_2 = 5000$ s.

bridge between traditional equilibrium and progressive non-equilibrium thermodynamics. Fig. 5.5 substantiates that we can identify weak equilibrium phase transitions in $M$ vs. $T$ via anomalies in the temperature dependence of $\lambda/z$. To this end we compare the ZFC-FH/FC $M$ vs. $T$ data measured in $\mu_0 H = 1$ mT (solid circles) with $\lambda/z$ vs. $T$ (open circles) obtained from the scaling analysis of the relaxation data (see Fig. 5.2 for typical examples). The vertical line highlights the correlation between the equilibrium AF transition temperature $T_N(\mu_0 H = 1 mT) = 90$ K and the local minimum in $\lambda/z$ vs. $T$. Note that in theoretical studies of model systems a change in the value of $\lambda/z$ is routinely
Figure 5.5: ZFC-FH/FC $M$ vs. $T$ equilibrium data measured in $\mu_0 H = 1 \text{ mT}$ (solid circles) and $\lambda/z$ vs. $T$ (open circles) obtained from the scaling analysis of the relaxation data. The vertical dashed line highlights $T_N(\mu_0 H = 1 \text{ mT}) = 90 \text{ K}$ coinciding with the local minimum in $\lambda/z$ vs. $T$. A second vertical dashed line marks the weak ferromagnetic transition at $T_C \approx 225 \text{ K}$. The inset displays the dc susceptibility, $\chi$ vs. $T$ (solid squares), and $(M_{FC} - M_{ZFC-FH})^2$ vs. $T$, measured at $\mu_0 H = 0.1$ (blue lower line), 0.2 (black center line), and 0.4 mT (green upper line). Linear best fits (red dashed linear lines) intercept at $T_m(H)$, respectively. A power law (dashed dark curved yellow line) extrapolates $T_m(H)$ to $T_m(\mu_0 H = 0) = T_C \approx 225 \text{ K}$. 
observed when approaching a phase transition by changing external parameters [84]. This decrease of $\lambda/z$ reveals a faster decorrelation of non-equilibrium states due to the presence of enhanced fluctuations at different length scales. With increasing temperature, $\lambda/z$ vs. $T$ shows a second, more pronounced, anomaly at $T \approx 225$ K. Note that the $\lambda/z$ data in the main frame extend continuously into the inset of Fig. 5.5. An abrupt 60% drop of $\lambda/z$ vs. $T$ is indicated by a second vertical line. Interestingly, at first glance the equilibrium $M$ vs. $T$ data appear featureless at this temperature. However, the results of closer inspection of equilibrium isotherms, $M$ vs. $H$ and isofields, $M$ vs. $T$, reveal various weak anomalies. The inset of Fig. 5.5 displays the detailed analysis of the equilibrium data exposing the weak phase transition around 225K. Note the synchronization of the temperature axes of the main frame and the inset.

First, we determine the dc susceptibility, $\chi$ vs. $T$, from the slopes of various magnetization isotherms (not shown) in the vicinity of $H = 0$. These $\chi$ vs. $T$ data are displayed as solid squares in the inset revealing a peak at $T \approx 225$ K. We interpret this peak as a weak singularity of the FM transition of the individual ultra-thin Co layers. The rounding results from the finite value of the amplitude $\mu_0 \delta H = \pm 0.5$ mT probing the magnetization response around $H = 0$. A strongly reduced $T_C$ of the Co layers in comparison to bulk cobalt ($T_C = 1388$ K) is expected from thickness confinement of the spin correlations and additional interface alloying. This interpretation is strongly supported by additional analysis of various interpolated ZFC-FH/FC $M$ vs. $T$ data. The inset shows, $(M_{FC} - M_{ZFC-FH})^2$ vs. $T$, measured at $\mu_0 H$ = 0.1 (blue lower line), 0.2 (black center line), and 0.4 mT (green upper line). This analysis is motivated by mean-field considerations and the question of what happens to the critical temperature in the presence of a conjugate field lifting criticality. We show that the temperature, $T_{m}$, of maximum slope in $M$ vs. $T$ at $H > 0$ shifts with increasing $H$ towards higher temperatures away from $T_C$ with a power law $H^{2/3}$ fulfilling the condition $\lim_{H \to 0} \frac{T_m(H)}{T_C} = T_C$. In the vicinity of $T_C$,
mean-field and Landau theory are equivalent. We thus discuss the Landau free energy

\[ F = \frac{1}{2}a_0 (T - T_C) M^2 + \frac{1}{4}b M^4 - MH \].

From \( \partial F / \partial M = 0 \) we obtain the cubic equation for the equilibrium magnetization \( M = M(T, H) \). For further analytic investigation we simplify the latter in the limit \( T \approx T_C \) and small magnetic field-induced magnetization. In the spirit of successive approximations we substitute the magnetization in the cubic term through \( M = \frac{H}{a_0(T - T_C)} \). The resulting approximate \( M = M(T, H) \) expression allows for the analytic calculation of \( \partial^2 M / \partial T^2 = 0 \). Its solution with respect to \( T \) provides the temperature of maximum slope which reads \( T_m(H) = T_C + \frac{(10 b)^{1/3}}{a_0} H^{2/3} \) (see Appendix D).

We determine \( T_m(H) \) of our data through analysis of \( (M_{FC} - M_{ZFC-FH})^2 \) vs. \( T \) for various \( H \). Again, motivated by mean-field results where the square of the order parameter is a linear function of temperature, we use linear best fits (red dashed linear lines in inset of Fig. 5.5) and their intercepts to approximate \( T_m(H) \). Since \( \lim_{H \to 0} T_m(H) = T_C \) is expected to hold also for our experimental data we extrapolate the intercept temperatures, \( T_m(H) \), towards \( H = 0 \) using a power law (dashed dark curved yellow line) and obtain \( T_m(H = 0) = T_C \approx 225 \) K. This extrapolated \( T_C \) is in good agreement with the maximum of \( \chi \) vs. \( T \). Most importantly both of these equilibrium signatures coincide with the far more pronounced non-equilibrium \( \lambda/z \) anomaly at \( T_C \approx 225 \) K.
Chapter 6

Overcoming the spin-multiplicity limit of entropy

The discovery of the giant magnetocaloric effect with isothermal field-induced entropy change beyond the spin-multiplicity limit gave rise to some confusion in the literature regarding the applicability of fundamental thermodynamics in data analysis. Those misleading interpretations concerning for instance the rigorousness of phenomenological thermodynamics are clarified in this chapter. Specifically, it is shown that the Maxwell relation incorporates contributions from the spin degrees of freedom and potential lattice degrees of freedom into the isothermal entropy change. A minimalist model involving pairs of exchange coupled, mobile Ising spins is investigated. It is explicitly shown that lattice degrees of freedom can be activated via applied magnetic fields and the integrated Maxwell relation contains this lattice contribution. A simple and intuitive analytic expression for the isothermal entropy change in the presence of field-activated lattice degrees of freedom is provided. Also, we quantify the impact of quantum corrections in the low-temperature limit. We compare calculations which include elastic interaction with the rigid exchange model in the high-temperature limit. We find that quantum
effects provide quantitative corrections in the low temperature limit. In addition we show that the elastic contributions to the isothermal entropy change can be additive but, remarkably, it can also give rise to reduced isothermal entropy change in certain temperature regions.

6.1 Insufficient Clarity in Literature

The search for advanced magnetocaloric materials has intensified in recent years due to their potential role in future energy-efficient and environmentally friendly refrigeration technologies [128, 129, 130, 131, 132]. An appreciable magnetocaloric effect (MCE) with sizeable isothermal entropy change and adiabatic temperature change in moderate applied magnetic fields requires new magnetic materials with tailored magnetocaloric properties. Most of the contemporary on-going research focuses on the giant MCE found in bulk rare-earth alloys. Recently, various nanotechnological approaches based on nanoparticles [133, 134, 135, 136, 137, 138] and thin-film heterostructures [119, 139, 140] have been attempted to tailor microscopic magnetic parameters such as exchange and anisotropy for advanced magnetocaloric materials design. Discoveries of a giant MCE overcoming the magnetic limit for the isothermal entropy change reveal a mechanism based on coupling between structure and magnetism [141, 142, 143]. Hence, optimization of magnetic interactions alone does no longer suffice for ultimate MCE of highest refrigeration capacity. However, recent discoveries of a giant MCE, which permit overcoming the magnetic limit [141, 142, 143] for the isothermal entropy change, make it evident that optimization of magnetic interactions alone will not suffice for ultimate optimization of the MCE. Sparked by this insight, an even more intensified but perhaps somewhat unfocused search for new giant MCE materials can be observed in recent years.

Despite the growing quantity of publications and growth of insight it seems clear that
some fundamental aspects of thermodynamics and statistical mechanics appear to be overlooked by some in the literature, leading to statements such as “the colossal MCE was obtained from magnetic measurements using Maxwell’s relation, which only reflects changes in magnetic entropy” \[144\]. More commonly, many authors refer to the isothermal entropy change, which is the entropy change at constant temperature, \( T \), induced by a change of the magnetic field, as magnetic entropy change \[145, 146, 147, 148, 149\]. This nomenclature can be very misleading and appears to be subliminally interpreted by others, not explicitly referenced here, as a contribution to the entropy change which exclusively originates from spin degrees of freedom. This interpretation is in general wrong and can only be applied in the absence of magnetoelastic interactions. We argue here that the use of \( \Delta S_M \) should be avoided, the index, \( M \), should be suppressed, and the term isothermal entropy change should be used instead. In contrast to certain statements in the literature it is not a matter of debate whether the integrated Maxwell relation contains all of the field-induced isothermal entropy change for systems in a homogeneous phase. If the Maxwell relation is applicable, meaning the second order mixed derivatives of the Gibbs free energy are mathematically well defined and identical, the isothermal entropy change obtained from integration of the magnetization derivative contains all possible field-induced contributions.

In addition, there seems to be some confusion about the conditions allowing for contributions of lattice degrees of freedom to the isothermal entropy change. The vagueness often seen in discussions on this subject has the potential to confuse materials scientists searching for magnetocaloric materials which overcome the magnetic limit for the isothermal entropy change. The latter is determined by the logarithm of \( 2J + 1 \), where \( J \) is the total atomic angular moment when a localized moment picture can be applied. One can anticipate that magnetic materials relying only on the limited \( J \)-multiplicity for isothermal entropy change will not be able to compete with the proposed electrocaloric
materials. Here, quantization is not the limiting factor and large changing electric fields are much easier realized than changing magnetic fields. Therefore, competitive magnetocaloric materials need to make use of entropy contributions of non-magnetic degrees of freedom which still can be activated through magnetic fields.

The objective of this chapter is three-fold. First, the aim is to reemphasize the rigorous nature of relations from phenomenological thermodynamics such as the Maxwell relation. Special emphasis is on the fact that the isothermal entropy change determined via Maxwell’s relation is not limited to magnetic degrees of freedom. Second, a model system is investigated which is as simple as possible and as complex as necessary to show under which conditions lattice degrees of freedom can be activated and contribute to the magnetic field-induced isothermal entropy change. It is shown explicitly that the integrated Maxwell relation contains this lattice contribution, if present, despite the fact that the field integral is taking place over the temperature derivative of the magnetization. It is the absence of elastic variables in the Maxwell relation which, in a naïve view, may appear counterintuitive and, hence, can lead to the wrong conclusion that field-dependent lattice effects are not included in this integral. Thirdly, the quantization of the vibrational mode and its effect on the isothermal entropy change in the low temperature regime is considered, where the thermal energy is lower than the ground state energy of the quantum harmonic oscillator. We study the impact of finite mass of atoms carrying the magnetic moments on the entropy change in the low temperature limit. Moreover, we compare in the high temperature limit the case of rigid exchange with the position dependent exchange model. The former is obtained from our quantum approach in the limit of large atomic mass and high curvature of the elastic potential. The latter is our model of mobile Ising spins where the classical approximation becomes exact in the high temperature limit. The comparison provides the temperature dependent contribution of the elastic degree of freedom to the isothermal entropy change. The latter can be additive
and, hence, favorable for increased entropy change, but remarkably it can also give rise to reduced isothermal entropy change.

Contributions to the isothermal entropy change which are not magnetic in origin can only exist if there is coupling between spin and elastic degrees of freedom giving rise to a free-energy coupling-term with a dependence on the magnetic field, \( H \), such that the total Gibbs free energy, \( G \), reads
\[
G_{\text{total}}(T, H) = G_{\text{spin}}(T, H) + G_{\text{lattice}}(T) + G_{\text{spin-lattice}}(T, H).
\]

It is the field dependent spin-lattice contribution, \( G_{\text{spin-lattice}}(T, H) \), which creates the possibility of overcoming the multiplicity limit
\[
\Delta S_{\text{spin-lattice}}(T, H) = S_{J}(H = 0) - S_{J}(H \to \infty) = nR \ln (2J + 1)
\]
originates from
\[
S_{J}(T, H) := - \left( \frac{\partial G_{\text{spin}}}{\partial T} \right)_{H}.
\]

We show explicitly in a minimalist microscopic model that a term of the form \( G_{\text{spin-lattice}}(T, H) \) contributing to the isothermal entropy change requires non-linear spin-lattice coupling. Evidently, magnetocaloric materials can only take advantage of lattice degrees of freedom if non-linear coupling is sizable. We use our minimalistic Hamilton function to calculate the Gibbs free energy and from that the isothermal entropy change showing the possibility of overcoming \( \Delta S_{\text{spin-lattice}}^{\text{J}} \). Moreover, we calculate the magnetization, \( M(T, H) \), and show for the latter that in fact the numerically integrated Maxwell relation can generate an isothermal entropy change
\[
\Delta S > nR \ln (2J + 1)
\]
which of course is identical with the analytically derived using the free-energy expression. This explicit proof given by our specific model may retrospectively appear redundant because one may argue that there is no need to reconsider established thermodynamics. However, the existing tendency to reason on the basis of models and microscopic considerations together with a general propensity to consider statistical physics superior to phenomenological thermodynamics is motivation enough for the explicit confirmation of the integrated Maxwell relation. The work outlined here serves as an explicit reminder that the Maxwell relation, when the
prerequisites for its application are fulfilled, provides the complete isothermal entropy change and not just a “magnetic contribution” in case there is more. It is hoped that these considerations will help to clarify some of the recent confusions such as those about Maxwell’s relation in the framework of discussions of the lattice contributions to the isothermal entropy change.

## 6.2 Minimalist Classical Model

We briefly recall the model of pairs of interacting, mobile Ising spins. When aiming at a classical approximation it is meaningful to neglect the kinetic energy. In this truncated case the main features of the elastic degree of freedom are already included since the momentum-dependent term has no coupling to the spin degrees of freedom. It will give rise to a free energy contribution which is temperature dependent but field independent. Therefore kinetic energy terms in the Hamilton function will not contribute to the isothermal entropy change. Thus the minimalist model [see Fig. 6.1] of an individual
Ising spin-pair reads \([150, 151]\)

\[
H = \frac{1}{2} D (x_2 - x_1)^2 + J(x_1, x_2) \sigma_1 \sigma_2 - h (\sigma_1 + \sigma_2)
\]  

(6.1)

Here, \(D\) is the curvature of the harmonic elastic energy, \(J(x_1, x_2)\) is the exchange integral, \(\sigma_{1,2} = \pm 1\) are the classical Ising spin variables, and \(h\) is an applied magnetic field where constants like the Bohr magneton, the \(g\)-factor and the vacuum permeability have been absorbed such that \(h\) is measured in units of energy. Eq.6.1 is a minimalistic version of the 1-dimensional Ising model with mobile spins similar to the one discussed in the appendix of Ref.([151]). We allow for an additional Zeeman term and enable non-linear spin-lattice interaction via the general dependence of the exchange integral on \(x_{1,2}\) quantifying the deviations from the equilibrium positions of the atoms 1 and 2. We make the assumption of an exponential dependence of the exchange integral on the spatial separation of the two spins which reads [152]

\[
J(x_1, x_2) = J_0 e^{-\frac{(x_2 - x_1)}{a}}
\]  

(6.2)

where \(a\) determines the length scale on which the exchange interaction decays. We restrict our consideration to the case of small deviations from the equilibrium positions such that \((x_2 - x_1)/a\) becomes a small parameter. We use the latter to expand Eq.6.2 up to first order and second order, respectively. Substituting this expansions into Eq.6.1 leaves us with two systematically progressing approximations \(H_\alpha\) and \(H_\beta\) of our minimalistic model Hamiltonian \([150]\)

\[
H_\alpha = \frac{1}{2} D y^2 + J_0 \left[ 1 - \frac{y^2}{a^2} \right] \sigma_1 \sigma_2 - h (\sigma_1 + \sigma_2)
\]

\[
H_\beta = \frac{1}{2} D y^2 + J_0 \left[ 1 - \frac{y^2}{a^2} + \frac{y^4}{2a^4} \right] \sigma_1 \sigma_2 - h (\sigma_1 + \sigma_2)
\]  

(6.3)
where \( y = x_2 - x_1 > 0 \) is proportional to the normal coordinate of the vibrational motion.

Next we evaluate the canonical partition function and from that the Gibbs free energy per spin pair for \( H_\alpha \) and \( H_\beta \), respectively. We integrate out the classical variable \( 0 \leq y/a \leq \infty \) and take into account the spin products \( \{\sigma_1\sigma_2\} = \{1, -1, -1, 1\} \) and spin sums \( \{\sigma_1 + \sigma_2\} = \{2, 0, 0, -2\} \) of the 4 spin configurations. As a result we obtain for \( H_\alpha \) in the limit of small exchange energy in comparison with the elastic and the thermal energy \( k_BT \). This limit justifies neglecting quantum considerations including the kinetic energy term in the Hamiltonian and leads to

\[
G_\alpha(T, h) = (2h + J_0) - \frac{J_0^2}{2a^2D} - k_BT \ln \left(1 + e^{\frac{4h}{k_BT}} + 2e^{\frac{2(h+|J_0|)}{k_BT}}\right) - k_BT \ln \sqrt{\frac{\pi k_BT}{2a^2D}} \quad (6.4)
\]

We are interested in the isothermal entropy change \( \Delta S = S(T, h = 0) - S(T, h \to \infty) \). Therefore, only the term \( \tilde{G}_\alpha = -k_BT \ln \left(1 + e^{\frac{4h}{k_BT}} + 2e^{\frac{2(h+|J_0|)}{k_BT}}\right) \) of Eq. 6.4 which depends on \( h \) and \( T \) needs to be considered. It is straightforward to show from the temperature derivative of \( \tilde{G}_\alpha \) and intuitively that asymptotically for \( k_BT \gg |J_0| \) the maximum isothermal entropy change becomes \( \Delta S_\alpha = S_\alpha(T, h = 0) - S_\alpha(T, h \to \infty) = k_B \ln 4 \). This is in accordance with \( \Delta S_{\text{max}} = 2k_B \ln 2 \) obtained from the limiting expression given by the logarithm of the spin-multiplicity of a quantum mechanical spin \( 1/2 \) system where 2 such spins are involved in our model Hamiltonian. Evidently, the spin-lattice coupling in linear approximation has no effect on the isothermal entropy change induced by a magnetic field in the classical limit. In fact the term \( \tilde{G}_\alpha \), which completely determines the isothermal entropy change, does not depend on the parameter \( a \) which controls the spin-lattice coupling. A model Hamiltonian of the form \( H_\alpha \) is therefore not able to create an entropy contribution which originates from non-magnetic degrees of freedom.

The situation changes when considering \( H_\beta \). Again we restrict ourselves to the limiting case where the elastic energy is large in comparison to the exchange energy and
temperatures are sufficiently high. Then the Gibbs free energy $G_\beta$ reads [see Appendix E]

$$G_\beta(T,h) = (2h + J_0) - k_B T \ln \left( e^{-\frac{J_0 (4h + 3h_0) - 4a^2 D (k + J_0)}{2(a^2 D - J_0) k_B T}} + \sqrt{\frac{2\pi k_B T}{a^2 D - J_0}} \left( e^{\frac{4h}{k_B T}} + \frac{J_0^2}{2(a^2 D + J_0)} + e^{\frac{2J_0}{k_B T(a^2 D + J_0)}} \right) \right)$$

(6.5)

It is straightforward to show that in the limit of large $a$ Eq. 6.5 reduces to Eq. 6.4 up to an irrelevant field and temperature independent constant. In contrast to Eq. 6.4 we see that the non-linear Hamiltonian $H$ generates terms in the free energy, which depend on the magnetic field, temperature, and exchange as well as the elastic constant $D$. Next we show that this is the ingredient allowing for $\Delta S > k_B \ln (2J + 1)$ via a magnetic field-activation of non-magnetic degrees of freedom through non-linear spin-lattice coupling.

From $S = -\left( \frac{\partial G_\beta}{\partial T} \right)_h$ we calculate $\Delta S_\beta(T,h) = S_\beta(T,h = 0) - S_\beta(T,h)$ in the limit which simplifies in the limit

$$\Delta S_\beta(T,h \to \infty) = S_\beta(T,h = 0) - S_\beta(T,h \to \infty)$$

into the intuitive approximate expression

$$\Delta S_\beta(T,h \to \infty) = \frac{k_B J_0}{2a^2 D} + k_B \ln 4$$

(6.6)

showing that the conventional limit determined by the logarithm of the spin-multiplicity is exceeded by the term $\frac{k_B J_0}{2a^2 D}$ which allows for an intuitive interpretation.

Clearly, in the absence of spin-spin exchange such as paramagnetic materials, entropy originating from elastic degrees of freedom cannot be harnessed. Likewise, a sensitive dependence of the exchange on the spatial spin separation, expressed in accordance with Eq. 6.2 through a small characteristic exponential decay length $a$, increases spin-lattice
coupling and enhances the impact of the lattice degree of freedom on the entropy change. Finally, if the elastic energy $a^2D$ is large in comparison with $k_B T$, there is no significant thermal excitation of the elastic degree of freedom and, hence, no significant contribution from the latter to the isothermal entropy change.

### 6.3 Comparison between integrated Maxwell relation and entropy of the model Hamiltonian

Next we calculate the magnetization $M = -\left(\frac{\partial G}{\partial h}\right)_{T}$ and use the resulting $M$ vs. $h$ isotherms for numerical integration of the Maxwell relation, $(\frac{\partial M}{\partial T})_h = (\frac{\partial S}{\partial h})_T$. The latter provides the isothermal entropy change $\Delta S$ as a function of $h$. The result from the Maxwell relation is then compared with the analytically calculated isothermal entropy change determined directly from $S = -\left(\frac{\partial G}{\partial T}\right)_h$. This comparison provides explicit confirmation that the Maxwell relation includes the lattice degrees of freedom.

Specifically, we calculate the magnetic moment per spin pair for the set of parameters $J_0/k_B = 0.1$ K and $a^2D/k_B = 0.49$ K. These values fulfill the constraint $a^2D \gg J_0$ under which we performed the classical calculation of the Gibbs free energy based on the Hamiltonian $H_\beta$. In addition we limit our investigation to a temperature region such that $k_B T$ is large in comparison with elastic and exchange energies such that our classical consideration becomes meaningful.

Figure 6.2 shows a representative set of isotherms $M$ vs. $h$ for $4 \leq T \leq 100$ in temperature steps of $\Delta T = 2$ K. The complete data set used for the entropy calculation via Maxwell’s relation involves the isotherms for $3 \leq T \leq 100$ in steps of $\Delta T = 0.01$ K [also see Appendix F].

Figure 6.3 shows the entropy calculated via the integrated Maxwell relation (magenta
Figure 6.2: Representative isotherms $M$ vs. $h$ for $0 \leq h/k_B \leq 30$ K calculated with $J_0/k_B = 0.1$ K and $a^2D/k_B = 0.49$ K for $4K \leq T \leq 100$ K displayed in steps $\Delta T = 2$ K [150].

open circles) using the magnetization data selectively displayed in Figure 6.2. The black solid lines in Figure 6.3 show the isothermal entropy change $\Delta S_{\beta}(T, h)$ calculated analytically from $S = -\left(\partial G_{\beta}/\partial T\right)_h$. For clarity $\Delta S_{\beta}(T, h)$ curves are displayed in field step of $\Delta h/k_B = 2$ K. The perfect coincidence of circles with the lines implies that the Maxwell relation contains the entropy contributions of both the spin degrees of freedom as well as the lattice degrees of freedom. There is, within numerical uncertainties, no difference between the result from the integrated Maxwell relation and $\Delta S_{\beta}(T, h)$ calculated analytically from $S = -\left(\partial G_{\beta}/\partial T\right)_h$. 
Figure 6.3: Entropy $\Delta S_T(T,h)$ (black solid lines) versus $T$ calculated from Gibbs free energy derivatives for $J_0 = 0.1$ K and $a^2D/k_B = 0.49$ K displayed at constant magnetic fields $2K \leq h/k_B \leq 100$K in field steps $\Delta h/k_B = 2$ K. Open circles (magenta) show entropy calculated via Maxwell relation using magnetization data such as the isotherms shown in Fig.6.2. The lower dotted blue line represents the maximum entropy limit based of spin-multiplicity only. The upper dotted red line shows the maximum isothermal entropy change which includes the magnetoelastic contribution using the microscopic parameters $J_0 = 0.1$ K and $a^2D/k_B = 0.49$ K. The inset shows the result of the temperature dependent area determined from numerical integration of the $-\Delta S$ vs. $T$ curve for $h/k_B = 30$ K. The dashed horizontal line marks its theoretical limiting value of 60 K [150].

The lower dotted blue line in Figure 6.3 represents the value of $\Delta S_{\text{max}}^{I}$ which for $J = 1/2$ reads $\Delta S_{\text{max}}^{I}/k_B = 2 \ln 2 = 1.38$. The upper dotted red line shows the maximum isothermal entropy change achievable in our model with magnetoelastic coupling.
using the microscopic parameters above. This limit is clearly above the magnetic limit
\[ \Delta S_{\text{max}}^J/k_B = 2 \ln 2 \]
indicating explicitly that lattice degrees of freedom can contribute to the
isothermal field-induced entropy change as they do in real systems in the case of the giant
MCE. The validity of our simple approximate Eq. 6.6 is also prominently evident in this fig-
ure. A calculation of the limiting approximate expression \[ \Delta S_\beta (T, h \to \infty) = \frac{k_B h_0}{2a^2 D} + k_B \ln 4 \]
yields \[ \Delta S_\beta (T, h \to \infty) = 1.488k_B \] which is in excellent agreement with our numerically
calculated value of \[ \Delta S_\beta (T, h \to \infty) = 1.494k_B. \]

The inset of Fig. 6.3 shows a semi-logarithmic plot of \[ \text{Area}(T) = -\frac{1}{k_B} \int_0^T \Delta S(T') \, dT' \]
evaluated through numerical integrations of the \(-\Delta S/k_B\) vs. \(T\) data for \(h/k_B = 30\) K. An
area sum rule is known to hold (See also Eq. 2.20) such that

\[ \lim_{T \to \infty} \text{Area}(T) = \mu_0 V M_s \Delta H/k_B \]

where \(V M_s\) is the saturation magnetic moment and \(\Delta H\) is the magnetic field change
which induces the isothermal entropy change. In accordance with the area sum rule [Eq.
2.20], our numerically calculated function \(\text{Area}(T)\) shows an asymptotic approach of the
limiting value \(\mu_0 V M_s \Delta H\) which is given by the saturation value \((\sigma_1 + \sigma_2) h = 60\) K in the
reduced variables of our model with \(h/k_B = 30\) K and \(\sigma_{1,2} = 1\). The fact that the sum
rule applies is further evidence that the Maxwell relation includes all contributions to the
entropy change, including those originating from elastic degrees of freedom.

### 6.4 Quantum corrections and comparisons

In the previous section we assessed the interpretation of what is sometimes called in
the literature magnetic-entropy change. The magnetic field-induced isothermal entropy
change can contain additions from the lattice which accompany the conventional contri-
Figure 6.4: Temperature dependence of $\text{erf} \left( \sqrt{\frac{J_0^2}{2T(a^2D-J_0)}} \right)$ showing the fast decay as $T$ increases. Note the $T$-axis is logarithmic.

butions originating from spin degrees of freedom. We showed in a minimalist model of Ising spin pairs that the activation of lattice degrees of freedom requires non-linear magnetoelastic coupling. Additionally, we showed explicitly that lattice degrees of freedom can help to overcome the spin-multiplicity limit of entropy as it does in the giant MCE.

The statistical analysis of our simple model was done in a classical approximation for the elastic degree of freedom. An additional high-temperature simplification, valid in the limit of thermal energies large in comparison to elastic and exchange energy, allowed us to derive a simple analytic result for excess isothermal entropy change beyond the spin-multiplicity limit. We calculated the Gibbs free energy with $H_{\beta}$, using the classical approximation for the elastic degree of freedom together with a high-temperature
approximation of the Gauss error function $\text{erf} \left( \sqrt{\frac{J_0^2}{2T (a^2D - J_0)}} \right) \approx 0$ valid for $k_B T >> |J_0|$ and $a^2D >> J_0$. Note that the approximation of the error function does not affect the significance of the results obtained in the classical approximation because the classical approximation has a priori only meaning at high-temperatures. In this context, it is useful to recall a few textbook examples of classical approximations. Without exception they show unphysical behavior in the low temperature limit. Most prominent examples are the ideal gas and its unphysical low-temperature entropy limit and the classical Dulong-Petit value of the specific heat capacity violating the third law of thermodynamics. Remarkably high-temperatures with respect to the Debye temperature of a solid have to be attained such that the classical limit becomes a reasonable approximation.

The Hamiltonian of Eq. 6.3 can be rearranged into the quadratic form as

$$H_\beta = \frac{1}{2} m \omega_0^2 \left( 1 + \frac{J_0 \sigma_1 \sigma_2}{D a^2} \right) \eta^2 - \frac{1}{2} \frac{J_0^2}{D a^2 + J_0 \sigma_1 \sigma_2} + J_0 \sigma_1 \sigma_2 - h (\sigma_1 + \sigma_2) \quad (6.7)$$

which is free from the linear term. Here $\eta = y - \frac{J_0 \sigma_1 \sigma_2}{a^2D + J_0 \sigma_1 \sigma_2}$ and $\omega_0^2 = D/m$.

In order to generalize the classical approximation of the Gibbs free energy into a result which takes into account the quantization of the vibrational mode, Eq. 6.7 has to be transformed into a Hamilton operator which necessarily has to include the kinetic energy terms of the two masses. This generalization adds the mass, $m$, or equivalently $\omega_0$ as an additional parameter which potentially affects the isothermal entropy change. This new property is a fundamental consequence of the quantum harmonic oscillator having a ground state energy which is determined by the Heisenberg uncertainty principle demanding a minimum amount of kinetic energy due to partial localization of the particles.

We solve the resulting Schrödinger equation in the approximate case where the harmonic oscillator is constrained to its vibrational ground state while we allow for thermal
spin excitations. The significance of this approximation lies in its correct description of the asymptotic low-temperature behavior. Here quantized vibrational excitations are frozen out when approaching the limit \( k_B T < \hbar \omega = \hbar \omega_0 \sqrt{1 + \frac{J_0 \sigma_1 \sigma_2}{D a^2}} \), but the vibrational zero-point fluctuations can still modify the isothermal entropy change. Within this approximation the eigenenergies read

\[
E(\sigma_1, \sigma_2) = \frac{1}{2} \hbar \omega_0 \sqrt{1 + \frac{J_0 \sigma_1 \sigma_2}{D a^2}} - \frac{1}{2} \frac{J_0^2}{D a^2 + J_0 \sigma_1 \sigma_2} + J_0 \sigma_1 \sigma_2 - h (\sigma_1 + \sigma_2)
\] (6.8)

With Eq.6.8 we calculate the partition function of the canonical ensemble, the Gibbs free energy, and finally the isothermal entropy change [see Appendix G].

The upper black line in the main panel of the figure 6.5 shows the temperature dependence of the isothermal entropy change \( \Delta S_{cl}/k_B = S_{cl}(T, h = 30) - S_{cl}(T, h = 0) \) on a logarithmic T-scale calculated for \( a^2D/k_B = 0.49 \) K and \( J_0/k_B = 0.1 \) K in the classical approximation using the Hamiltonian \( H_\beta \). The blue vertical arrow indicates a temperature above which the classical approximation is meaningful. The triangles and dashed line show the corresponding results of the quantum corrected isothermal entropy change with the parameter \( \omega_0/k_B = .245 \) K(triangles) and \( \hbar \omega_0/k_B = 0 \) K(dashed line). The motivation for the choice \( \hbar \omega_0/k_B = 0.245 \) K = \( \frac{D a^2}{2k_B} \) originates from the virial theorem and the fact that the maximum potential energy which can be deposited into the elastic degree of freedom is limited by the spacing \( a \) of the two spins \( \sigma_1, \sigma_2 \). The circles show the \( T \)-dependence of the isothermal entropy change in the rigid limit which is determined by \( \omega_0/k_B = 0 \) and \( D \to \infty \). Inspection of Eq.6.8 shows that this limit reproduces the eigenenergies of the Hamiltonian of two rigidly exchange coupled Ising spins.

First we note that all of the quantum results have the same \( T \to 0 \) limit of the entropy change per spin-pair given by \( -\Delta S/k_B = k_B \ln 2 \). For the rigidly coupled Ising spins this is trivial. In zero magnetic field, there are two degenerate ground states of the parallel
Figure 6.5: The upper black line shows the temperature dependence of the isothermal entropy change $\Delta S = S(T, h = 30) - S(T, h = 0)$ calculated for $a^2 D / k_B = 0.49$ K and $J_0 / k_B = 0.1$ K in the classical approximation. The blue vertical arrow indicates a temperature above which $k_B T \gg |J_0|$ is fulfilled. Triangles and dashed line show the isothermal entropy change for the quantum approximation with $\hbar \omega_0 / k_B = 0.245$ (triangles) and $\omega_0 / k_B = 0$ K (blue dashed line) with $a^2 D / k_B = 0.49$ K and $J_0 / k_B = 0.1$ K, respectively. Circles show the temperature dependence of the isothermal entropy change in the rigid limit $\omega_0 / k_B = 0$ and $D \to \infty$. The dashed horizontal line marks the spin-multiplicity limit $-\Delta S / k_B = \ln 4$. The inset quantifies the difference $-\Delta S_{cl} + \Delta S_{qm}^{rigid}$ vs. T (dark yellow line, left ordinate), vs. $T$ (green line, right ordinate), and $(-\Delta S_{qm}(\omega = 0) + \Delta S_{qm}(\omega)) / k_B$ vs. $T$ (red line, right ordinate). The vertical arrow in the inset marks a temperature regime where the elastic degree of freedom is not favorable for large isothermal entropy change.
spins while a magnetic field lifts this degeneracy such that only a single state of both spins parallel to the field remains. This will not change even if coupling between spins and the elastic degree of freedom is introduced, because the vibrational degree of freedom has to freeze out for $T \to 0$ in a quantum description.

As expected, the classical approximation (upper line) fails in the limit $T \to 0$. Note, that our constraint imposed to the quantum calculation confining the harmonic oscillator in its ground state still leaves room for an influence of the elastic degree of freedom on the $T$-dependent isothermal entropy change. This can be seen when comparing the three quantum calculations for the rigid case (circles) with $\omega_0 = 0$ (dashed line) and $\hbar \omega_0/k_B = 0.245$ K (triangles). Difference curves (arrows pointing to right ordinate of the panel in the inset) $(-\Delta S_{qm}(\omega = 0) + \Delta S_{qm}(\omega))/k_B$ vs. $T$ and $(-\Delta S_{qm}^{rigid} + \Delta S_{qm}(\omega = 0))/k_B$ vs. $T$ highlight this fact.

Nevertheless, the vibrational ground state constraint prevents thermal excitation of the quantized vibrational mode and thus does not allow for excess of isothermal entropy change above the spin multiplicity limit $-\Delta S/k_B = \ln 4$ indicated by a horizontal dashed line in the Fig. 6.5. This excess of elastic origin, which is at the heart of the physical mechanism of the giant MCE, is clearly seen when comparing the classical approximation for $k_B T >> |J_0|$ (vertical arrow) with the quantum calculations. This difference is quantified in the inset of the figure by $(-\Delta S_{cl} + \Delta S_{qm}^{rigid})/k_B$ vs. $T$ with a virtually temperature-independent plateau-value of $(-\Delta S_{cl} + \Delta S_{qm}^{rigid})/k_B \approx 0.1 \approx \frac{J_0}{2a^2D}$.

Note the interesting fact that the presence of an elastic degree of freedom can also decrease the entropy change when compared to the rigid exchange case (see vertical arrow in the inset). We intuitively interpret this behavior as a result of the exponential decay of the exchange with spin separation. For high temperatures the spins get increasingly mobile. As a result the exchange increases and decreases periodically. If the oscillation of the spins takes place around the equilibrium distance $<x_0> = <x_2 - x_1>$ according
Figure 6.6: Plot of Modified Bessel function of first kind with $n=0$, $I_0(\delta x/a)$.

to $x(t) = <x_0> + \delta x \sin(\omega t)$ we obtain $\langle J \rangle = I_0 e^{-<x_0>/a} I_0(\delta x/a)$ with $\langle \ldots \rangle$ indicating temporal average. Here $I_0(\delta x/a)$ is the modified Bessel function of first kind with the property $I_0(\delta x/a) > 1$ [see Fig. 6.6] thus making $\langle J \rangle > I_0 e^{-<x_0>/a}$. The enhanced exchange introduces an additional competition with the thermal tendency towards disorder which can to some extent reduce the isothermal entropy change.
Chapter 7

Conclusion

The tuning of magnetocaloric properties in nanostructured materials for near room-temperature refrigeration applications has been investigated experimentally and theoretically. Our focus is on artificial antiferromagnetic superlattices with tailored metamagnetic transitions allowing for a negative and a positive magnetocaloric effect below and above the antiferromagnetic transition, respectively. The phase diagram and, hence, the magnetocaloric properties of these metamagnets are largely determined by the in-plane and inter-plane exchange interactions. We show that a large ratio of intra to inter-layer exchange is favorable for spin-flip transitions with large entropy change. Here the tricritical temperature approaches the Néel temperature which at the same time is near the critical temperature of the ferromagnetic constituent films activating microscopic spin fluctuations for the magnetic entropy change. The maximum field-induced entropy change occurs at about half of the tricritical temperature. We realize layered artificial antiferromagnets experimentally with the help of MBE grown Co/Cr superlattices of ultra-thin Co and Cr films and PLD growth of Fe/Cr superlattices. SQUID magnetometric studies of the temperature and field dependence of the magnetization are performed for various Co/Cr multilayer and Fe/Cr multilayer systems. The positive magnetocaloric
effect is explored for one of the Co/Cr samples with a detailed investigation of the isothermal entropy and the corresponding adiabatic temperature change. For a Fe/Cr sample showing increase of $dM/dT$ with increase of magnetic field MCE was studied and RCP was calculted.

It was also shown that equilibrium magnetic phase transitions can strongly affect the non-equilibrium magnetic properties in an ordered nanostructured superlattice. Nanos- tructuring creates magnetic correlations which bring relaxation times into the experimentally easily accessible domain of seconds to hours. MBE grown Co/Cr superlattice with antiferromagnetic coupling between ferromagnetic Co layers was used as a model system with extended temperature regions far from equilibrium. Magnetization transients are analyzed using the theoretically expected scaling function in the aging regime. The scaling exponent has a surprisingly sensitive temperature dependence originating from the subtle temperature dependence of the spin-spin correlations. Our approach has the potential to evolve into a new tool to investigate weak phase transitions in magnetically nanostructured systems with sensitivity hitherto not achieved by equilibrium methodology. In addition, our system should also allow future verifications of detailed theoretical predictions of the scaling forms of non-equilibrium response functions, coming from the theory of local scale invariance.

We also clarified some misleading interpretation of what is sometimes called in the literature magnetic entropy change. The magnetic field-induced isothermal entropy change can in fact contain lattice contributions other than just spin degrees of freedom. In addition we reemphasized that those contributions are fully contained in the Maxwell relation if the latter is applicable. We used a minimalistic model of Ising spin pairs and made it as complex as necessary to show that the activation of lattice degrees of freedom requires non-linear magnetoelastic coupling. Moreover, we showed explicitly that lattice degrees of freedom can help to overcome the spin-multiplicity limit of entropy as it does
in the giant magnetocaloric effect. Here, however, we show the impact of elastic coupling on the magnetocaloric effect already in the absence of magnetic long range order.

The classical approximation has the advantage to provide analytic results in the high-temperature limit taking into account the elastic contribution, but fails in the low-temperature limit. We use a quantum approach with an approximation which constrains the elastic mode in its quantum ground state to investigate the correct asymptotic low-temperature regime. We find that quantum effects leave the qualitative picture unchanged. Quantitative corrections affect the low-temperature limit which is given by its statistical limit $-\Delta S = k_B \ln 2$. The quantum approximation which leaves the spin-pair in its vibrational ground state prevents the correct description of the entropy excess of the elastic degree of freedom. This contribution allows overcoming the spin multiplicity limit $-\Delta S = k_B \ln 4$. At temperatures where the elastic excitations become relevant our classical approximation is fully appropriate. We find that non-linearity of the position dependent exchange integral can give rise to reduced isothermal entropy change at high temperatures.
Appendix A

An example of MOKE Labview Code

This is one example code out of various codes that I have developed with Keithley 2420, 6221/2182A, 2000, 2010, GMW magnet, Kepco power supply, Janis cryostat, SRS 830.
Connector Pane

Moke WITH 2420 current source_SRS lock-in.vi
Use a +ve sign for increment and a -ve sign for decrement in step array otherwise the program will not run properly.
Express VI Configuration Information

**Build XY Graph**

Build XY Graph

formats the data displayed on an X-Y Graph.

---

This Express VI is configured as follows:

Clear data on each call: Off
Write LabVIEW Measurement File
Write LabVIEW Measurement File
Writes data to a LabVIEW measurement data file.

This Express VI is configured as follows:

Mode: Save to one file
Filename: test.lvm
Ask Operator to choose file
If a file already exists: Append to file
Description:

Convert to Dynamic Data5
Convert to Dynamic Data

Convert to Dynamic Data6
Convert to Dynamic Data

Elapsed Time
Elapsed Time
Keeps track of time by indicating when a certain amount of time has elapsed. The elapsed time is the present time minus the start time that you specify.

This Express VI is configured as follows:

Time Target: 12 s
Auto Reset: On

Convert to Dynamic Data
Convert to Dynamic Data

Convert to Dynamic Data3
Convert to Dynamic Data

Convert to Dynamic Data2
Convert to Dynamic Data

Convert to Dynamic Data4
Convert to Dynamic Data
Appendix B

RHEED Labview Code

This an code summary of the RHEED code that I developed for our RHEED system. The original code consists of about 130 subVIs and is not included here.
**Write LabVIEW Measurement File**
Write LabVIEW Measurement File
Writes data to a LabVIEW measurement data file.

This Express VI is configured as follows:

- **Mode:** Save to one file
- **Filename:** test.lvm
- **Ask Operator to choose file**
- **If a file already exists:** Append to file
- **Description:**

**Elapsed Time**
Elapsed Time
Keeps track of time by indicating when a certain amount of time has elapsed. The elapsed time is the present time minus the start time that you specify.

This Express VI is configured as follows:

- **Time Target:** 1E-54 s
- **Auto Reset:** Off

**Convert to Dynamic Data**
Convert to Dynamic Data

**Convert to Dynamic Data2**
Convert to Dynamic Data

**Build XY Graph**
Build XY Graph
formats the data displayed on an X-Y Graph.

This Express VI is configured as follows:

- **Clear data on each call:** Off

**Convert to Dynamic Data3**
Convert to Dynamic Data
Appendix C

Mathematica code for numerical calculation of magnetization jumps

An example mathematica code for calculation of magnetization jumps from Eq. 4.8 and 4.9 for $\epsilon = 0.7$ (here ‘a’) and $T = 0.48$ (here ‘t’).

Clear [ma, mb, x, k]
a = 0.7
ho = 0.25
t = 0.48
xo = -0.87
size = 50
Array[b, size]
Array[c, size]
Array[M, size]
Array[Ms, size]
k = 1
h = ho + k/100;
Clear[x];

fa = (a + 1)*(h +
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]) -
t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h + a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))])
);

FindRoot[fa - x == 0, {x, xo}];

ma = x /. %;

mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);

b[k] = Re[ma];
c[k] = Re[mb];

k = 2;

h = h0 + k/100;

Clear[x];

xo = Re[ma];

fa = (a + 1)*(h +
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]) -
t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h + a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))])
);

FindRoot[fa - x == 0, {x, xo}];

ma = x /. %;

mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
\begin{verbatim}
b[k] = Re[ma];
c[k] = Re[mb];
k = 3;
h = ho + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h +
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]) -
t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h +
a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))]);
FindRoot[fa - x == 0, {x, x0}];
ma = x /. %;
mb = (a + 1)*((h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]));
b[k] = Re[ma];
c[k] = Re[mb];
k = 4;
h = ho + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h +
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]) -
t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]))))]);
FindRoot[fa - x == 0, {x, x0}];
ma = x /. %;
mb = (a + 1)*((h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]));
\end{verbatim}
\[
t/2\times \log\left[\frac{1+x}{1-x}\right]\right)/(1 - ((a + 1)\times(h + a/(a + 1)\times x - t/2\times \log\left[\frac{1+x}{1-x}\right]\right))
\]

FindRoot\[fa - x == 0, \{x, xo\}\];

\[
ma = x \ / . \%;
\]

\[
mb = (a + 1)\times(h + a/(a + 1)\times ma - t/2\times \log\left[\frac{1+ma}{1-ma}\right]\right);
\]

\[
b[k] = \text{Re}[ma];
\]

\[
c[k] = \text{Re}[mb];
\]

\[
k = 5;
\]

\[
h = h_0 + k/100;
\]

Clear[x];
\[
x_0 = \text{Re}[ma];
\]

\[
f_a = (a + 1)\times(h +
\[
\quad a/(a + 1)\times((a + 1)\times(h + a/(a + 1)\times x -
\quad t/2\times \log\left[\frac{1+x}{1-x}\right]\right)) -
\quad t/2\times \log\left[\frac{1 + ((a + 1)\times(h + a/(a + 1)\times x -
\quad t/2\times \log\left[\frac{1+x}{1-x}\right]\right))/(1 - ((a + 1)\times(h +
\quad a/(a + 1)\times x - t/2\times \log\left[\frac{1+x}{1-x}\right]\right))))\right]);
\]

FindRoot\[f_a - x == 0, \{x, xo\}\];

\[
ma = x \ / . \%;
\]

\[
mb = (a + 1)\times(h + a/(a + 1)\times ma - t/2\times \log\left[\frac{1+ma}{1-ma}\right]\right);
\]

\[
b[k] = \text{Re}[ma];
\]

\[
c[k] = \text{Re}[mb];
\]

\[
k = 6;
\]

\[
h = h_0 + k/100;
\]

Clear[x];
\[ x_0 = \text{Re}[ma]; \]
\[ f_a = (a + 1)*(h + \]
\[ \quad a/(a + 1)*((a + 1)*(h + a/(a + 1)*x - \]
\[ \quad \quad t/2*\log[(1 + x)/(1 - x)])) - \]
\[ \quad t/2*\log[(1 + ((a + 1)*(h + a/(a + 1)*x - \]
\[ \quad \quad \quad t/2*\log[(1 + x)/(1 - x)])/(1 - ((a + 1)*(h + \]
\[ \quad \quad \quad \quad a/(a + 1)*x - t/2*\log[(1 + x)/(1 - x)])])])); \]
\[ \text{FindRoot}[f_a - x == 0, \{x, x_0\}]; \]
\[ ma = x /. \%; \]
\[ mb = (a + 1)*(h + a/(a + 1)*ma - t/2*\log[(1 + ma)/(1 - ma)]); \]
\[ b[k] = \text{Re}[ma]; \]
\[ c[k] = \text{Re}[mb]; \]
\[ k = 7; \]
\[ h = h_0 + k/100; \]
\[ \text{Clear}[x]; \]
\[ x_0 = \text{Re}[ma]; \]
\[ f_a = (a + 1)*(h + \]
\[ \quad a/(a + 1)*((a + 1)*(h + a/(a + 1)*x - \]
\[ \quad \quad t/2*\log[(1 + x)/(1 - x)])) - \]
\[ \quad t/2*\log[(1 + ((a + 1)*(h + a/(a + 1)*x - \]
\[ \quad \quad \quad t/2*\log[(1 + x)/(1 - x)])/(1 - ((a + 1)*(h + \]
\[ \quad \quad \quad \quad a/(a + 1)*x - t/2*\log[(1 + x)/(1 - x)])])])); \]
\[ \text{FindRoot}[f_a - x == 0, \{x, x_0\}]; \]
\[ ma = x /. \%; \]
\[ mb = (a + 1)*(h + a/(a + 1)*ma - t/2*\log[(1 + ma)/(1 - ma)]); \]
\[ b[k] = \text{Re}[ma]; \]
\[ c[k] = \text{Re}[mb]; \]
\[ k = 8; \]
\[ h = h_0 + k/100; \]
\[ \text{Clear}[x]; \]
\[ x_0 = \text{Re}[ma]; \]
\[ \text{fa} = (a + 1)*(h + \]
\[ a/(a + 1)*((a + 1)*(h + a/(a + 1)*x - \]
\[ t/2*\log[(1 + x)/(1 - x)]]) - \]
\[ t/2*\log[(1 + ((a + 1)*(h + a/(a + 1)*x - \]
\[ t/2*\log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h + \]
\[ a/(a + 1)*x - t/2*\log[(1 + x)/(1 - x)]))/])])]; \]
\[ \text{FindRoot}[\text{fa} - x == 0, \{x, x_0\}]; \]
\[ \text{ma} = x/.\%; \]
\[ \text{mb} = (a + 1)*(h + a/(a + 1)*ma - t/2*\log[(1 + ma)/(1 - ma)]); \]
\[ b[k] = \text{Re}[ma]; \]
\[ c[k] = \text{Re}[mb]; \]
\[ k = 9; \]
\[ h = h_0 + k/100; \]
\[ \text{Clear}[x]; \]
\[ x_0 = \text{Re}[ma]; \]
\[ \text{fa} = (a + 1)*(h + \]
\[ a/(a + 1)*((a + 1)*(h + a/(a + 1)*x - \]
\[ t/2*\log[(1 + x)/(1 - x)]]) - \]
\[ t/2*\log[(1 + ((a + 1)*(h + a/(a + 1)*x - \]
\[ t/2*\log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h + \]
\[ a/(a + 1)*x - t/2*\log[(1 + x)/(1 - x)]))/])])]; \]
\[
t \times \log \left( \frac{1 + x}{1 - x} \right) / \left(1 - ((a + 1)(h + a/(a + 1)x - t/2 \times \log \left( \frac{1 + x}{1 - x} \right))\right)
\]

\text{FindRoot}\left[f(a - x == 0, \{x, x_0\}\right] ;
\text{ma} = x / . \% ;
\text{mb} = (a + 1)(h + a/(a + 1)ma - t/2 \times \log \left( \frac{1 + ma}{1 - ma} \right));
\text{b}[k] = \text{Re}[\text{ma}] ;
\text{c}[k] = \text{Re}[\text{mb}] ;
k = 10 ;
h = h_0 + k/100 ;
\text{Clear}[x] ;
x_0 = \text{Re}[\text{ma}] ;
\text{fa} = (a + 1)(h + a/(a + 1)((a + 1)(h + a/(a + 1)x - t/2 \times \log \left( \frac{1 + x}{1 - x} \right)) - t/2 \times \log \left( \frac{1 + ((a + 1)(h + a/(a + 1)x - t/2 \times \log \left( \frac{1 + x}{1 - x} \right))\right)/(1 - ((a + 1)(h + a/(a + 1)x - t/2 \times \log \left( \frac{1 + x}{1 - x} \right))))\]);
\text{FindRoot}\left[f(a - x == 0, \{x, x_0\}\right] ;
\text{ma} = x / . \% ;
\text{mb} = (a + 1)(h + a/(a + 1)ma - t/2 \times \log \left( \frac{1 + ma}{1 - ma} \right));
\text{b}[k] = \text{Re}[\text{ma}] ;
\text{c}[k] = \text{Re}[\text{mb}] ;
k = 11 ;
h = h_0 + k/100 ;
\text{Clear}[x] ;
\[ x_0 = \text{Re}[ma]; \]
\[ fa = (a + 1)(h + a/(a + 1)(h + a/(a + 1)x - \\
\quad t/2\times \text{Log}[(1 + x)/(1 - x)]) - \\
\quad t/2\times \text{Log}[(1 + ((a + 1)(h + a/(a + 1)x - \\
\quad t/2\times \text{Log}[(1 + x)/(1 - x)]))/((1 - ((a + 1)(h + \\
\quad a/(a + 1)x - t/2\times \text{Log}[(1 + x)/(1 - x)])))])]; \]
\[ \text{FindRoot}[fa - x == 0, \{x, x_0\}]; \]
\[ ma = x /. %; \]
\[ mb = (a + 1)(h + a/(a + 1)ma - t/2\times \text{Log}[(1 + ma)/(1 - ma)]); \]
\[ b[k] = \text{Re}[ma]; \]
\[ c[k] = \text{Re}[mb]; \]
\[ k = 12; \]
\[ h = h_0 + k/100; \]
\[ \text{Clear}[x]; \]
\[ xo = \text{Re}[ma]; \]
\[ fa = (a + 1)(h + a/(a + 1)(h + a/(a + 1)x - \\
\quad t/2\times \text{Log}[(1 + x)/(1 - x)]) - \\
\quad t/2\times \text{Log}[(1 + ((a + 1)(h + a/(a + 1)x - \\
\quad t/2\times \text{Log}[(1 + x)/(1 - x)]))/((1 - ((a + 1)(h + \\
\quad a/(a + 1)x - t/2\times \text{Log}[(1 + x)/(1 - x)])))])]; \]
\[ \text{FindRoot}[fa - x == 0, \{x, xo\}]; \]
\[ ma = x /. %. \]
\[ mb = (a + 1)(h + a/(a + 1)ma - t/2\times \text{Log}[(1 + ma)/(1 - ma)]); \]
\begin{verbatim}
b[k] = Re[ma];
c[k] = Re[mb];
k = 13;
h = ho + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h +
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)])) -
t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h +
a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])))]));
FindRoot[fa - x == 0, {x, x0}];
ma = x /. %;
mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
b[k] = Re[ma];
c[k] = Re[mb];
k = 14;
h = ho + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h +
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)])) -
t/2*Log[(1 + x)/(1 - x)]));
\end{verbatim}
Log[(1 + ((a + 1)*(h + a/(a + 1)*x - 
    t/2*Log[(1 + x)/(1 - x)])/(1 - ((a + 1)*(h + 
    a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])))))/
(1 - ((a + 1)*(h + a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))));

FindRoot[fa - x == 0, {x, xo}];
ma = x /. %;
mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
b[k] = Re[ma];
c[k] = Re[mb];
k = 15;
h = ho + k/100;
Clear[x];
xo = Re[ma];
fa = (a + 1)*(h + 
    a/(a + 1)*((a + 1)*(h + a/(a + 1)*x - 
    t/2*Log[(1 + x)/(1 - x)]) - 
    t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x - 
    t/2*Log[(1 + x)/(1 - x)])/(1 - ((a + 1)*(h + 
    a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])))))])

FindRoot[fa - x == 0, {x, xo}];
ma = x /. %;
mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
b[k] = Re[ma];
c[k] = Re[mb];
k = 16;
h = ho + k/100;
Clear\[x\];
x0 = Re[ma];
fa = (a + 1)*(h +
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]) -
t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)])))/(1 - ((a + 1)*(h +
a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])))]));
FindRoot[fa - x == 0, \{x, x0\}];
ma = x /. %;
mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
b[k] = Re[ma];
c[k] = Re[mb];
k = 17;
h = ho + k/100;
Clear\[x\];
x0 = Re[ma];
fa = (a + 1)*(h +
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)]) -
t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)])))/(1 - ((a + 1)*(h +
a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])))]));
FindRoot[fa - x == 0, \{x, x0\}];
ma = x /. %;
\[ mb = (a+1)(h + a/(a+1)ma - t/2*\log((1+ma)/(1-ma)));
\]
\[ b[k] = \text{Re}[ma];\]
\[ c[k] = \text{Re}[mb];\]
\[ k = 18;\]
\[ h = h_0 + k/100;\]
\[ \text{Clear}[x];\]
\[ xo = \text{Re}[ma];\]
\[ fa = (a + 1)(h + \\
\quad a/(a + 1)((a + 1)(h + a/(a + 1)x - \\
\quad t/2*\log((1 + x)/(1 - x)))) - \\
\quad t/2*\log((1 + ((a + 1)(h + a/(a + 1)x - \\
\quad t/2*\log((1 + x)/(1 - x)))))/(1 - ((a + 1)(h + \\
\quad a/(a + 1)x - t/2*\log((1 + x)/(1 - x))))));\]
\[ \text{FindRoot}[fa - x == 0, \{x, xo\}];\]
\[ ma = x/.%;\]
\[ mb = (a + 1)(h + a/(a + 1)ma - t/2*\log((1 + ma)/(1 - ma)));
\]
\[ b[k] = \text{Re}[ma];\]
\[ c[k] = \text{Re}[mb];\]
\[ k = 19;\]
\[ h = h_0 + k/100;\]
\[ \text{Clear}[x];\]
\[ xo = \text{Re}[ma];\]
\[ fa = (a + 1)(h + \\
\quad a/(a + 1)((a + 1)(h + a/(a + 1)x - \\
\quad t/2*\log((1 + x)/(1 - x)))) - \\
\quad t/2*\log((1 + x)/(1 - x))));\]
\[
t/2 \log \left( 1 + \left( (a + 1)(h + a/(a + 1)x - \right.ight.
\left. t/2 \log \left( (1 + x)/(1 - x) \right) \right) \right) / \left( 1 - ((a + 1)(h + a/(a + 1)x - \right. \\
\left. t/2 \log \left( (1 + x)/(1 - x) \right) \right) \right)
\]

FindRoot[fa - x == 0, \{x, xo\}];

ma = x /. %;

mb = (a + 1)(h + a/(a + 1)ma - t/2 \log \left( (1 + ma)/(1 - ma) \right));
b[k] = Re[ma];
c[k] = Re[mb];
k = 20;
h = ho + k/100;
Clear[x];

xo = Re[ma];

fa = (a + 1)(h +
\left. a/(a + 1) \left( (a + 1)(h + a/(a + 1)x - \right. \right.
\left. t/2 \log \left( (1 + x)/(1 - x) \right) \right) \right)
\left. - \right. \\
\left. t/2 \log \left( (1 + ((a + 1)(h + a/(a + 1)x - \right. \right. \\
\left. t/2 \log \left( (1 + x)/(1 - x) \right) \right) \right) / \left( 1 - ((a + 1)(h + a/(a + 1)x - \right. \right. \\
\left. t/2 \log \left( (1 + x)/(1 - x) \right) \right) \right) \right)
\right)

FindRoot[fa - x == 0, \{x, xo\}];

ma = x /. %;

mb = (a + 1)(h + a/(a + 1)ma - t/2 \log \left( (1 + ma)/(1 - ma) \right));
b[k] = Re[ma];
c[k] = Re[mb];
k = 21;
h = ho + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h +
        a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
        t/2*Log[(1 + x)/(1 - x)])) -
        t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
        t/2*Log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h +
        a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))]);
FindRoot[fa - x == 0, {x, x0}];
ma = x /. %;
mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
b[k] = Re[ma];
c[k] = Re[mb];
k = 22;
h = h0 + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h +
        a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
        t/2*Log[(1 + x)/(1 - x)])) -
        t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
        t/2*Log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h +
        a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))]);
FindRoot[fa - x == 0, {x, x0}];
ma = x /. %;
\[ mb = (a + 1) \cdot (h + a/(a + 1) \cdot ma - t/2\cdot \log[1 + ma)/(1 - ma)]) \; ; \\
\text{b}[k] = \text{Re}[ma] \; ; \\
\text{c}[k] = \text{Re}[mb] \; ; \\
k = 23 \; ; \\
h = h_0 + k/100 \; ; \\
\text{Clear}[x] \; ; \\
x_0 = \text{Re}[ma] \; ; \\
\text{fa} = (a + 1) \cdot (h + \\
a/(a + 1) \cdot ((a + 1) \cdot (h + a/(a + 1) \cdot x - \\
t/2\cdot \log[1 + x)/(1 - x)]) - \\
t/2\cdot \log[1 + ((a + 1) \cdot (h + a/(a + 1) \cdot x - \\
t/2\cdot \log[1 + x)/(1 - x)])))/(1 - ((a + 1) \cdot (h + \\
a/(a + 1) \cdot x - t/2\cdot \log[1 + x)/(1 - x)]))) ]]; \\
\text{FindRoot}[\text{fa} - x == 0, \{x, x_0\}] \; ; \\
\text{ma} = x \; /. \% \; ; \\
\text{mb} = (a + 1) \cdot (h + a/(a + 1) \cdot ma - t/2\cdot \log[1 + ma)/(1 - ma)]) \; ; \\
\text{b}[k] = \text{Re}[ma] \; ; \\
\text{c}[k] = \text{Re}[mb] \; ; \\
k = 24 \; ; \\
h = h_0 + k/100 \; ; \\
\text{Clear}[x] \; ; \\
x_0 = \text{Re}[ma] \; ; \\
\text{fa} = (a + 1) \cdot (h + \\
a/(a + 1) \cdot ((a + 1) \cdot (h + a/(a + 1) \cdot x - \\
t/2\cdot \log[1 + x)/(1 - x)])) - \\
t/2\cdot \log[1 + x)/(1 - x)])) -
\frac{t}{2} \log \left( 1 + \frac{(a + 1)(h + a/(a + 1)x - \frac{t}{2} \log \left( \frac{1 + x}{1 - x} \right))}{(1 - ((a + 1)(h + a/(a + 1)x - \frac{t}{2} \log \left( \frac{1 + x}{1 - x} \right))) / (1 - ((a + 1)(h + a/(a + 1)x - t/2 \log \left( \frac{1 + x}{1 - x} \right)))} \right) ;

\text{FindRoot}\left[ f_a - x == 0, \{x, x_0\} \right];

ma = x /. \%;

mb = (a + 1)(h + a/(a + 1)ma - \frac{t}{2} \log \left( \frac{1 + ma}{1 - ma} \right));

b[k] = \text{Re}[ma];

c[k] = \text{Re}[mb];

k = 25;

h = h_0 + k/100;

\text{Clear}[x];

x_0 = \text{Re}[ma];

f_a = (a + 1)(h + a/(a + 1)((a + 1)(h + a/(a + 1)x - \frac{t}{2} \log \left( \frac{1 + x}{1 - x} \right)) - \frac{t}{2} \log \left( \frac{1 + ((a + 1)(h + a/(a + 1)x - \frac{t}{2} \log \left( \frac{1 + x}{1 - x} \right))) / (1 - ((a + 1)(h + a/(a + 1)x - t/2 \log \left( \frac{1 + x}{1 - x} \right)))} \right) ;

\text{FindRoot}\left[ f_a - x == 0, \{x, x_0\} \right];

ma = x /. \%;

mb = (a + 1)(h + a/(a + 1)ma - \frac{t}{2} \log \left( \frac{1 + ma}{1 - ma} \right));

b[k] = \text{Re}[ma];

c[k] = \text{Re}[mb];

k = 26;

h = h_0 + k/100;
Clear[x];

xo = Re[ma];

fa = (a + 1)*(h +
    a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
      t/2*Log[(1 + x)/(1 - x)]) -
      t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
      t/2*Log[(1 + x)/(1 - x)])))/((1 - ((a + 1)*(h +
      a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])))/(1 - ((a + 1)*(h +
      a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))));

FindRoot[fa - x == 0, {x, xo}];

ma = x /. %;

mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);

b[k] = Re[ma];

c[k] = Re[mb];

k = 27;

h = ho + k/100;

Clear[x];

xo = Re[ma];

fa = (a + 1)*(h +
    a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
      t/2*Log[(1 + x)/(1 - x)]) -
      t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
      t/2*Log[(1 + x)/(1 - x)])))/((1 - ((a + 1)*(h +
      a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])))/(1 - ((a + 1)*(h +
      a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))));

FindRoot[fa - x == 0, {x, xo}];

ma = x /. %;
\[
mb = (a + 1)(h + a/(a + 1)\cdot ma - \frac{t}{2}\cdot \log \left[ \frac{1 + ma}{1 - ma} \right]) ;
\]
\[
b[k] = \text{Re}[ma] ;
\]
\[
c[k] = \text{Re}[mb] ;
\]
\[
k = 28 ;
\]
\[
h = h_0 + k/100 ;
\]
\[
\text{Clear}[x] ;
\]
\[
x_0 = \text{Re}[ma] ;
\]
\[
fa = (a + 1)(h + \frac{a}{a + 1}\cdot((a + 1)(h + a/(a + 1)\cdot x - \frac{t}{2}\cdot \log \left[ \frac{1 + x}{1 - x} \right])) - \frac{t}{2}\cdot \log \left[ \frac{1 + ((a + 1)(h + a/(a + 1)\cdot x - \frac{t}{2}\cdot \log \left[ \frac{1 + x}{1 - x} \right]))}{1 - ((a + 1)(h + a/(a + 1)\cdot x - \frac{t}{2}\cdot \log \left[ \frac{1 + x}{1 - x} \right]))} \right]) ;
\]
\[
\text{FindRoot}[fa - x == 0, \{x, x_0\}] ;
\]
\[
ma = x /. \%;
\]
\[
mb = (a + 1)(h + a/(a + 1)\cdot ma - \frac{t}{2}\cdot \log \left[ \frac{1 + ma}{1 - ma} \right]) ;
\]
\[
b[k] = \text{Re}[ma] ;
\]
\[
c[k] = \text{Re}[mb] ;
\]
\[
k = 29 ;
\]
\[
h = h_0 + k/100 ;
\]
\[
\text{Clear}[x] ;
\]
\[
x_0 = \text{Re}[ma] ;
\]
\[
fa = (a + 1)(h + \frac{a}{a + 1}\cdot((a + 1)(h + a/(a + 1)\cdot x - \frac{t}{2}\cdot \log \left[ \frac{1 + x}{1 - x} \right])) - \frac{t}{2}\cdot \log \left[ \frac{1 + x}{1 - x} \right]) ;
\]
FindRoot[\(fa - x == 0, \{x, x0\}\)];
ma = x /. %;
mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
b[k] = Re[ma];
c[k] = Re[mb];
k = 30;
h = ho + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h + 
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)])) -
t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
t/2*Log[(1 + x)/(1 - x)])))/(1 - ((a + 1)*(h +
a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])))]);
FindRoot[fa - x == 0, \{x, x0\}\)];
ma = x /. %;
mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
b[k] = Re[ma];
c[k] = Re[mb];
k = 31;
h = ho + k/100;
Clear[x];

xo = 0.4509;

fa = (a + 1)*(h +
    a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
        t/2*Log[(1 + x)/(1 - x)]) -
        t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
            t/2*Log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h +
            a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))]));

FindRoot[fa - x == 0, {x, xo}];

ma = x /. %;

mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);

b[k] = Re[ma];

c[k] = Re[mb];

k = 32;

h = h0 + k/100;

Clear[x];

xo = Re[ma];

fa = (a + 1)*(h +
    a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
        t/2*Log[(1 + x)/(1 - x)]) -
        t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
            t/2*Log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h +
            a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))]));

FindRoot[fa - x == 0, {x, xo}];

ma = x /. %;
mb = \( (a + 1) \times (h + a/(a + 1) \times ma - t/2 \times \log((1 + ma)/(1 - ma))) \);

b[k] = Re[ma];
c[k] = Re[mb];
k = 33;
h = ho + k/100;
Clear[x];

xo = Re[ma];

fa = \( (a + 1) \times (h + a/(a + 1) \times x - t/2 \times \log((1 + x)/(1 - x))) - t/2 \times \log((1 + ((a + 1) \times (h + a/(a + 1) \times x - t/2 \times \log((1 + x)/(1 - x))))/(1 - ((a + 1) \times (h + a/(a + 1) \times x - t/2 \times \log((1 + x)/(1 - x))))))));

FindRoot[fa - x == 0, \{x, xo\}];

ma = x /. %;

mb = \( (a + 1) \times (h + a/(a + 1) \times ma - t/2 \times \log((1 + ma)/(1 - ma))) \);

b[k] = Re[ma];
c[k] = Re[mb];
k = 34;
h = ho + k/100;
Clear[x];

xo = Re[ma];

fa = \( (a + 1) \times (h + a/(a + 1) \times ((a + 1) \times (h + a/(a + 1) \times x - t/2 \times \log((1 + x)/(1 - x)))) - ...) \);
\[
t/2\text{Log}[(1 + ((a + 1)*(h + a/(a + 1)*x - \\
t/2\text{Log}[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h + a/(a + 1)*x - t/2\text{Log}[(1 + x)/(1 - x)])))])
\]

\text{FindRoot}[fa - x == 0, \{x, xo\}];

\text{ma} = x \/. \%

\text{mb} = (a + 1)*(h + a/(a + 1)*ma - t/2\text{Log}[(1 + ma)/(1 - ma)]);

b[k] = \text{Re}[ma];

c[k] = \text{Re}[mb];

k = 35;

h = ho + k/100;

\text{Clear}[x];

xo = \text{Re}[ma];

fa = (a + 1)*(h + \\
a/(a + 1)*((a + 1)*(h + a/(a + 1)*x - \\
t/2\text{Log}[(1 + x)/(1 - x)])) - \\
t/2\text{Log}[(1 + ((a + 1)*(h + a/(a + 1)*x - \\
t/2\text{Log}[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h + a/(a + 1)*x - t/2\text{Log}[(1 + x)/(1 - x)])))])])

\text{FindRoot}[fa - x == 0, \{x, xo\}];

\text{ma} = x \/. \%

\text{mb} = (a + 1)*(h + a/(a + 1)*ma - t/2\text{Log}[(1 + ma)/(1 - ma)]);

b[k] = \text{Re}[ma];

c[k] = \text{Re}[mb];

k = 36;

h = ho + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h +
    a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
        t/2*Log[(1 + x)/(1 - x)]) -
        t/2*Log[(1 + ((a + 1)*(h + a/(a + 1)*x -
            t/2*Log[(1 + x)/(1 - x)]))/
            (1 - ((a + 1)*(h +
            a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))]));
FindRoot[fa - x == 0, {x, x0}];
ma = x /. %;
mb = (a + 1)*(h + a/(a + 1)*ma - t/2*Log[(1 + ma)/(1 - ma)]);
b[k] = Re[ma];
c[k] = Re[mb];
k = 37;
h = h0 + k/100;
Clear[x];
x0 = Re[ma];
fa = (a + 1)*(h +
    a/(a + 1)*((a + 1)*(h + a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)])
        - t/2*Log[(1 + ((a + 1)*(h +
            a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))/
            (1 - ((a + 1)*(h +
            a/(a + 1)*x - t/2*Log[(1 + x)/(1 - x)]))))]));
FindRoot[fa - x == 0, {x, x0}];
ma = x /. %;
\[ mb = (a + 1)(h + a/(a + 1)ma - t/2\log[(1 + ma)/(1 - ma)]); \]
\[ b[k] = \text{Re}[ma]; \]
\[ c[k] = \text{Re}[mb]; \]
\[ k = 38; \]
\[ h = h_0 + k/100; \]
\[ \text{Clear}[x]; \]
\[ xo = \text{Re}[ma]; \]
\[ fa = (a + 1)(h + \]
\[ a/(a + 1)((a + 1)(h + a/(a + 1)x - \]
\[ t/2\log[(1 + x)/(1 - x)]) - \]
\[ t/2\log[(1 + ((a + 1)(h + a/(a + 1)x - \]
\[ t/2\log[(1 + x)/(1 - x)])/(1 - ((a + 1)(h + \]
\[ a/(a + 1)x - t/2\log[(1 + x)/(1 - x)]))); \]
\[ \text{FindRoot}[fa - x == 0, \{x, xo\}]; \]
\[ ma = x / . \%; \]
\[ mb = (a + 1)(h + a/(a + 1)ma - t/2\log[(1 + ma)/(1 - ma)]); \]
\[ b[k] = \text{Re}[ma]; \]
\[ c[k] = \text{Re}[mb]; \]
\[ k = 39; \]
\[ h = h_0 + k/100; \]
\[ \text{Clear}[x]; \]
\[ xo = \text{Re}[ma]; \]
\[ fa = (a + 1)(h + \]
\[ a/(a + 1)((a + 1)(h + a/(a + 1)x - \]
\[ t/2\log[(1 + x)/(1 - x)])); \]
\[
t/2\log\left(1 + ((a + 1)\frac{h + a/(a + 1)x - \frac{t}{2}\log\left(1 + x\right)/(1 - x)}{(1 - ((a + 1)\frac{h + a/(a + 1)x - \frac{t}{2}\log\left(1 + x\right)/(1 - x))}}\right)
\]

FindRoot[fa - x == 0, \{x, xo\}];

ma = x /. %;

mb = (a + 1)\frac{h + a/(a + 1)ma - \frac{t}{2}\log\left(1 + ma\right)/(1 - ma)}{};

b[k] = Re[ma];

c[k] = Re[mb];

k = 40;

h = ho + k/100;

Clear[x];

xo = Re[ma];

fa = (a + 1)\frac{h + a/(a + 1)((a + 1)\frac{h + a/(a + 1)x - \frac{t}{2}\log\left(1 + x\right)/(1 - x)}) - \frac{t}{2}\log\left(1 + ((a + 1)\frac{h + a/(a + 1)x - \frac{t}{2}\log\left(1 + x\right)/(1 - x)))/(1 - ((a + 1)\frac{h + a/(a + 1)x - \frac{t}{2}\log\left(1 + x\right)/(1 - x))}}\right)};
Clear[\(x\)];

\(x_0 = \text{Re}[\text{ma}];\)

\(fa = (a + 1)(h +
\quad a/(a + 1)((a + 1)(h + a/(a + 1)x -
\quad t/2*\text{Log}[(1 + x)/(1 - x)]) -
\quad t/2*\text{Log}[(1 + ((a + 1)(h + a/(a + 1)x -
\quad t/2*\text{Log}[(1 + x)/(1 - x)]))/(1 - ((a + 1)(h +
\quad a/(a + 1)x - t/2*\text{Log}[(1 + x)/(1 - x)])))))];\)

\text{FindRoot}[fa - x == 0, \{x, x_0\}];

\(ma = x / . \%;\)

\(mb = (a + 1)(h + a/(a + 1)ma - t/2*\text{Log}[(1 + ma)/(1 - ma)]);\)

\(b[k] = \text{Re}[\text{ma}];\)

\(c[k] = \text{Re}[\text{mb}];\)

\(k = 42;\)

\(h = h_0 + k/100;\)

Clear[\(x\)];

\(x_0 = \text{Re}[\text{ma}];\)

\(fa = (a + 1)(h +
\quad a/(a + 1)((a + 1)(h + a/(a + 1)x -
\quad t/2*\text{Log}[(1 + x)/(1 - x)]) -
\quad t/2*\text{Log}[(1 + ((a + 1)(h + a/(a + 1)x -
\quad t/2*\text{Log}[(1 + x)/(1 - x)]))/(1 - ((a + 1)(h +
\quad a/(a + 1)x - t/2*\text{Log}[(1 + x)/(1 - x)])))))];\)

\text{FindRoot}[fa - x == 0, \{x, x_0\}];

\(ma = x / . \%;\)
\[ mb = (a + 1)(h + a/(a + 1)ma - t/2\log[(1 + ma)/(1 - ma)]); \]
\[ b[k] = \text{Re}[ma]; \]
\[ c[k] = \text{Re}[mb]; \]
\[ k = 43; \]
\[ h = h_0 + k/100; \]
\[ \text{Clear}[x]; \]
\[ x_0 = \text{Re}[ma]; \]
\[ f_a = (a + 1)(h + \]
\[ a/(a + 1)((a + 1)(h + a/(a + 1)x - \]
\[ t/2\log[(1 + x)/(1 - x)]) - \]
\[ t/2\log[(1 + ((a + 1)(h + a/(a + 1)x - \]
\[ t/2\log[(1 + x)/(1 - x)])/(1 - ((a + 1)(h + \]
\[ a/(a + 1)x - t/2\log[(1 + x)/(1 - x)])))); \]
\[ \text{FindRoot}[f_a - x == 0, \{x, x_0\}]; \]
\[ ma = x /. \%; \]
\[ mb = (a + 1)(h + a/(a + 1)ma - t/2\log[(1 + ma)/(1 - ma)]); \]
\[ b[k] = \text{Re}[ma]; \]
\[ c[k] = \text{Re}[mb]; \]
\[ k = 44; \]
\[ h = h_0 + k/100; \]
\[ \text{Clear}[x]; \]
\[ x_0 = \text{Re}[ma]; \]
\[ f_a = (a + 1)(h + \]
\[ a/(a + 1)((a + 1)(h + a/(a + 1)x - \]
\[ t/2\log[(1 + x)/(1 - x)]) - \]
\[ t/2\log[(1 + x)/(1 - x)])]; \]
\[
\frac{t}{2} \log\left(1 + ((a + 1) \cdot (h + a/(a + 1)) \cdot x - \frac{t}{2} \log\left(\frac{1 + x}{1 - x}\right))\right) / (1 - ((a + 1) \cdot (h + a/(a + 1)) \cdot x - \frac{t}{2} \log\left(\frac{1 + x}{1 - x}\right)))
\]

\begin{verbatim}
FindRoot[fa - x == 0, {x, xo}];
ma = x /. %;
mb = (a + 1) \cdot (h + a/(a + 1)) \cdot ma - \frac{t}{2} \log\left(\frac{1 + ma}{1 - ma}\right);
b[k] = Re[ma];
c[k] = Re[mb];
fname = "simu44";
k = 45;
h = h0 + k/100;
Clear[x];
ox0 = Re[ma];
fa = (a + 1) \cdot (h +
a/(a + 1) \cdot ((a + 1) \cdot (h + a/(a + 1)) \cdot x -
\frac{t}{2} \log\left(\frac{1 + x}{1 - x}\right)) -
\frac{t}{2} \log\left(\frac{1 + ((a + 1) \cdot (h + a/(a + 1)) \cdot x -
\frac{t}{2} \log\left(\frac{1 + x}{1 - x}\right))\right) / (1 - ((a + 1) \cdot (h +
a/(a + 1)) \cdot x - \frac{t}{2} \log\left(\frac{1 + x}{1 - x}\right)))\right) ;
FindRoot[fa - x == 0, {x, xo}];
ma = x /. %;
mb = (a + 1) \cdot (h + a/(a + 1)) \cdot ma - \frac{t}{2} \log\left(\frac{1 + ma}{1 - ma}\right);
b[k] = Re[ma];
c[k] = Re[mb];
k = 46;
\end{verbatim}
\[
\begin{align*}
h &= h_0 + \frac{k}{100}; \\
&\text{Clear}[x]; \\
x_0 &= \text{Re}[ma]; \\
fa &= (a + 1)(h + \\
&\quad\frac{a}{(a + 1)}((a + 1)(h + a/(a + 1)x - \\
&\quad\frac{t}{2}\log((1 + x)/(1 - x))) - \\
&\quad\frac{t}{2}\log((1 + ((a + 1)(h + a/(a + 1)x - \\
&\quad\quad\frac{t}{2}\log((1 + x)/(1 - x))))/(1 - ((a + 1)(h + \\
&\quad\quad\quad\frac{a}{(a + 1)x - \frac{t}{2}\log((1 + x)/(1 - x)))))); \\
&\text{FindRoot}[fa - x == 0, \{x, x_0\}]; \\
&\text{ma} = x /. %; \\
b[k] &= \text{Re}[ma]; \\
c[k] &= \text{Re}[mb]; \\
k &= 47; \\
h &= h_0 + \frac{k}{100}; \\
&\text{Clear}[x]; \\
x_0 &= \text{Re}[ma]; \\
fa &= (a + 1)(h + \\
&\quad\frac{a}{(a + 1)}((a + 1)(h + a/(a + 1)x - \\
&\quad\quad\frac{t}{2}\log((1 + x)/(1 - x))) - \\
&\quad\quad\frac{t}{2}\log((1 + ((a + 1)(h + a/(a + 1)x - \\
&\quad\quad\quad\quad\frac{t}{2}\log((1 + x)/(1 - x))))/(1 - ((a + 1)(h + \\
&\quad\quad\quad\quad\quad\quad\quad\frac{a}{(a + 1)x - \frac{t}{2}\log((1 + x)/(1 - x))))))); \\
&\text{FindRoot}[fa - x == 0, \{x, x_0\}];
\end{align*}
\]
\[
\begin{align*}
ma &= x \ . \ %; \\
mb &= \frac{(a + 1)\left(h + \frac{a}{a + 1}\right) - t/2\log\left(\frac{1 + ma}{1 - ma}\right)}{2}; \\
b[k] &= \text{Re}[ma]; \\
c[k] &= \text{Re}[mb]; \\
k &= 48; \\
h &= h_0 + k/100; \\
\text{Clear}[x]; \\
x_0 &= \text{Re}[ma]; \\
fa &= \frac{(a + 1)\left(h + \frac{a}{a + 1}\right) - t/2\log\left(\frac{1 + x}{1 - x}\right)}{2}; \\
\text{FindRoot}[fa - x == 0, \{x, x_0\}]; \\
ma &= x \ . \ %; \\
mb &= \frac{(a + 1)\left(h + \frac{a}{a + 1}\right) - t/2\log\left(\frac{1 + ma}{1 - ma}\right)}{2}; \\
b[k] &= \text{Re}[ma]; \\
c[k] &= \text{Re}[mb]; \\
k &= 49; \\
h &= h_0 + k/100; \\
\text{Clear}[x]; \\
x_0 &= \text{Re}[ma]; \\
fa &= \frac{(a + 1)\left(h + \frac{a}{a + 1}\right) - t/2\log\left(\frac{1 + x}{1 - x}\right)}{2}; \\
\text{FindRoot}[fa - x == 0, \{x, x_0\}]; \\
\end{align*}
\]
\[
t/2\log[(1 + x)/(1 - x))] - \\
t/2\log[1 + ((a + 1)*(h + a/(a + 1)*x - \\
t/2\log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h + \\
a/(a + 1)*x - t/2\log[(1 + x)/(1 - x)])))];
\]

FindRoot[fa - x == 0, \{x, xo\}];

ma = x/.%;

mb = (a + 1)*(h + a/(a + 1)*ma - t/2\log[(1 + ma)/(1 - ma)]);

b[k] = Re[ma];
c[k] = Re[mb];
k = 50;

h = h0 + k/100;

Clear[x];

xo = Re[ma];

fa = (a + 1)*(h +

   a/(a + 1)*((a + 1)*(h + a/(a + 1)*x -
   t/2\log[(1 + x)/(1 - x)])) - \\
t/2\log[(1 + ((a + 1)*(h + a/(a + 1)*x - \\
t/2\log[(1 + x)/(1 - x)]))/(1 - ((a + 1)*(h + \\
a/(a + 1)*x - t/2\log[(1 + x)/(1 - x)])))] ];

FindRoot[fa - x == 0, \{x, xo\}];

ma = x/.%;

mb = (a + 1)*(h + a/(a + 1)*ma - t/2\log[(1 + ma)/(1 - ma)]);

b[k] = Re[ma];
c[k] = Re[mb];

fname = "ao7simu48";
strm = OpenWrite["c:\\Temp\\" <> fname <> ".dat"];
For[k = 1, k <= size, k += 1, 
   WriteString[strm, FortranForm[N[ho + k/100]]];
   WriteString[strm, " "];
   WriteString[strm, FortranForm[N[b[k]]]];
   WriteString[strm, " "];
   WriteString[strm, FortranForm[N[c[k]]]];
   WriteString[strm, " "];
   M[k] = (b[k] + c[k])/2;
   Ms[k] = (c[k] - b[k])/2;
   WriteString[strm, FortranForm[N[M[k]]]];
   WriteString[strm, " "];
   WriteString[strm, FortranForm[N[Ms[k]]]];
   WriteString[strm, " "];
   WriteString[strm, "\n"];
];
Close[strm];
Exit[];
Appendix D

Deriving the field-dependence of $T_m$

$$F = \frac{1}{2} a_0 (T - T_c) M^2 + \frac{1}{4} b M^4 - MH$$

$$\frac{\partial F}{\partial M} = 0;$$

$$a_0 (T - T_c) M + b M^3 - H = 0$$

$$M = \frac{H}{a_0 (T - T_c)} - \frac{b}{a_0 (T - T_c)} M^3$$

$$M = \chi H = \frac{H}{a_0 (T - T_c)}$$

$$M = \frac{H}{a_0 (T - T_c)} - \frac{b}{a_0 (T - T_c)} \left[ \frac{H}{a_0 (T - T_c)} \right]^3$$

The following is the Mathematica code used for calculation. Here $A = a_0$.

```mathematica
M = 1/(A*(T-Tc))*(H-b*(H/(A*(T-Tc)))^3)
```
\( \frac{H - \left( b \frac{H^3}{A^3 (T - T_c)^3} \right)}{A (T - T_c)} \)

\[ \text{d}M = \text{D}[M, T] \]

\( \frac{3 b \frac{H^3}{A^4 (T - T_c)^5}}{A^4 (T - T_c)^5} - \frac{H - \left( b \frac{H^3}{A^3 (T - T_c)^3} \right)}{A (T - T_c)^2} \)

\[ \text{dd}M = \text{D}[\text{dd}M, T] \]

\( -\frac{(18 b \frac{H^3}{A^4 (T - T_c)^6})}{A^4 (T - T_c)^6} + \frac{2 \left( H - \left( b \frac{H^3}{A^3 (T - T_c)^3} \right) \right)}{A (T - T_c)^3} \)

\[ \text{Solve}[\text{dd}M == 0, T] \]

\{ \{ T \rightarrow \left( \frac{10^{1/3} b^{1/3} H^{2/3}}{A} + T_c \right) \}, \{ T \rightarrow \left( \frac{-5^{1/3} (1 - i \sqrt{3}) b^{1/3} H^{2/3}}{2^{2/3} A} + T_c \right) \}, \{ T \rightarrow \left( \frac{-5^{1/3} (1 + i \sqrt{3}) b^{1/3} H^{2/3}}{2^{2/3} A} + T_c \right) \} \}

\[ M = \frac{1}{(A*({\text{T-Tc}}))} \left( H - b*\left( H/(A*({\text{T-Tc}})) \right) \right)^3 \]

\[ H = \frac{\frac{b H^3}{A^3 (T - T_c)^3}}{A (T - T_c)} \]

\[ \text{d}M = \text{D}[M, T] \]

\[ \frac{3 b H^3}{A^4 (T - T_c)^5} - \frac{H - \frac{b H^3}{A^3 (T - T_c)^3}}{A (T - T_c)^2} \]
ddM = D[dM, T]

\[- \frac{18bH^3}{A^4(T - Tc)^6} + \frac{2\left( H - \frac{bH^3}{A^3(T - Tc)^3} \right)}{A(T - Tc)^3}\]

Solve[ddM == 0, T]

\[
\begin{cases}
T \rightarrow \frac{10^{1/3} b^{1/3} H^{2/3}}{A} + Tc \\
T \rightarrow -\frac{5^{1/3} (1 - i\sqrt{3}) b^{1/3} H^{2/3}}{2^{2/3} A} + Tc \\
T \rightarrow -\frac{5^{1/3} (1 + i\sqrt{3}) b^{1/3} H^{2/3}}{2^{2/3} A} + Tc
\end{cases}
\]
Appendix E

Mathematica code for calculating \(-\Delta S\) with \(H_\beta\)

Clear[h, d, a, J0, T]

\[ E_1 = \frac{d}{2} y^2 + (1 - \frac{y}{a} + \frac{1}{2} \frac{y^2}{a^2}) J_0 - 2h \]

\[ -2h + (\frac{d}{2} y^2)/2 + J_0 \left(1 - \frac{y}{a} + \frac{y^2}{2a^2}\right) \]

\[ E_2 = \frac{d}{2} y^2 - (1 - \frac{y}{a} + \frac{1}{2} \frac{y^2}{a^2}) J_0 \]

\[ (\frac{d}{2} y^2)/2 - J_0 \left(1 - \frac{y}{a} + \frac{y^2}{2a^2}\right) \]

\[ E_3 = \frac{d}{2} y^2 - (1 - \frac{y}{a} + \frac{1}{2} \frac{y^2}{a^2}) J_0 \]

\[ (\frac{d}{2} y^2)/2 - J_0 \left(1 - \frac{y}{a} + \frac{y^2}{2a^2}\right) \]

\[ E_4 = \frac{d}{2} y^2 + (1 - \frac{y}{a} + \frac{1}{2} \frac{y^2}{a^2}) J_0 + 2h \]
2 h + (d y^2)/2 + J0 (1 - y/a + y^2/(2 a^2))


E^((-2 h - (d y^2)/2 - J0 (1 - y/a + y^2/(2 a^2)))/T) + E^((
2 h - (d y^2)/2 - J0 (1 - y/a + y^2/(2 a^2)))/T) +
2 E^((-((d y^2)/2) + J0 (1 - y/a + y^2/(2 a^2)))/T)

y = a*x

Z = Integrate[g, {x, 0, Infinity}]

a x

If[Re[(a^2 d - J0)/T] >= 0 && Re[(a^2 d + J0)/T] < 0 &&
Re[(a^2 d + J0)/T] > 0,
E^((-((2 h + J0)/
T))) ((E^-((-((-4 a^2 d (h + J0) + J0 (4 h + 3 J0))/(
2 (a^2 d - J0) T)))) Sqrt[
2 \[Pi]] (J0 -
Sqrt[(a^2 d - J0)/T] T Sqrt[J0^2/(a^2 d T - J0 T)]
Erf[Sqrt[J0^2/(2 a^2 d T - 2 J0 T)]])/(J0 Sqrt[(a^2 d - J0)/T])) +
E^((J0^2/(2 a^2 d T + 2 J0 T)) Sqrt[\[Pi]]/
2] (1/Sqrt[(a^2 d + J0)/T] + (T Sqrt[J0^2/(a^2 d T + J0 T)]
\[\frac{\text{Erf}\left[\sqrt{\frac{J_0^2}{2a^2dT + 2J_0T}}\right]}{J_0} + \frac{e^{\left(\frac{8a^2dh + 8hJ_0 + J_0^2}{2a^2dT + 2J_0T}\right)}}{\sqrt{\pi/2}}\left(\frac{T}{\sqrt{\frac{a^2d + J_0}{T}}} + \frac{T\sqrt{\frac{J_0^2}{a^2dT + J_0T}}}{J_0}\right),\]

\[
\text{Integrate}\left[\frac{e^{-\left(\frac{4h + a^2dx^2 + J_0(2 - 2x + x^2)}{2T}\right)}}{1 + e^{\left(\frac{4h}{T}\right)} + 2e^{\left(\frac{2h + J_0(2 - 2x + x^2)}{T}\right)}}\right], \{x, 0, \infty\}, \text{Assumptions} \rightarrow \text{Re}\left[\frac{a^2d - J_0}{T}\right] < 0 || \text{Re}\left[\frac{-a^2d + J_0}{T}\right] \geq 0 || \text{Re}\left[\frac{a^2d + J_0}{T}\right] \leq 0\]

\[F = \text{Simplify}\left[-T\star\log\left(e^{-\left(\frac{4h + J_0}{T}\right)}\frac{\left(e^{-\left(\frac{-4a^2dh + J_0(4h + 3J_0)}{2(a^2d - J_0)}\right)}\sqrt{2\pi}\left(J_0 - \sqrt{\frac{a^2d - J_0}{T}}T\sqrt{\frac{J_0^2}{a^2dT - J_0T}}\right)}{J_0\sqrt{\frac{a^2d - J_0}{T}}} + \frac{e^{\left(\frac{8a^2dh + 8hJ_0 + J_0^2}{2a^2dT + 2J_0T}\right)}}{\sqrt{\pi/2}}\left(\frac{T}{\sqrt{\frac{a^2d + J_0}{T}}} + \frac{T\sqrt{\frac{J_0^2}{a^2dT + J_0T}}}{J_0}\right)\right)\right]\]
\[
\begin{align*}
&T \sqrt{J_0^2/(a^2 d T + J_0 T)} \times 0)/J_0)) \]

\[-T \log[E^{-(2 h + J_0)/} T) \times (E^{-(4 a^2 d (h + J_0) - J_0 (4 h + 3 J_0))/(2 (a^2 d - J_0) T)} \]
\[&\text{Sqrt}[2 \Pi]/\text{Sqrt}[(a^2 d - J_0)/T] + (E^{-(J_0^2/(2 a^2 d T + 2 J_0 T))} \text{Sqrt}[(Pi)/2]/\text{Sqrt}[(a^2 d + J_0)/T] + (E^{-(8 a^2 d h + 8 h J_0 + J_0^2)/(2 a^2 d T + 2 J_0 T)} \]
\[&\text{Sqrt}[(Pi)/2]/\text{Sqrt}[(a^2 d + J_0)/T])] \]

\[S = -D[F, T] \]

\[1/((E^{-(4 a^2 d (h + J_0) - J_0 (4 h + 3 J_0))/(2 (a^2 d - J_0) T)} \text{Sqrt}[2 \Pi]/\text{Sqrt}[(a^2 d - J_0)/T] + (E^{-(J_0^2/(2 a^2 d T + 2 J_0 T))} \text{Sqrt}[(Pi)/2]/\text{Sqrt}[(a^2 d + J_0)/T] + (E^{-(8 a^2 d h + 8 h J_0 + J_0^2)/(2 a^2 d T + 2 J_0 T)} \]
\[&\text{Sqrt}[(Pi)/2]/\text{Sqrt}[(a^2 d + J_0)/T])] \]

\[E^{-(2 h + J_0)/}
\[T \times (E^{-(2 h + J_0)/} T)) \times (2 h + J_0) \times (E^{-(4 a^2 d (h + J_0) - J_0 (4 h + 3 J_0))/(2 (a^2 d - J_0) T)} \]
\[&\text{Sqrt}[2 \Pi]/\text{Sqrt}[(a^2 d - J_0)/T] + (E^{-(J_0^2/(2 a^2 d T + 2 J_0 T))} \text{Sqrt}[(Pi)/2]/\text{Sqrt}[(a^2 d + J_0)/T] + (E^{-(8 a^2 d h + 8 h J_0 + J_0^2)/(2 a^2 d T + 2 J_0 T)} \]
\[&\text{Sqrt}[(Pi)/2]/\text{Sqrt}[(a^2 d + J_0)/T]) \times T^2 +
\[E^{-(2 h + J_0)/} \]
\[
T) \left( (E^{-((4 a^2 d (h + J0) - J0 (4 h + 3 J0)))/(2 (a^2 d - J0) T)} ((a^2 d - J0) Sqrt[\[Pi] /
2])/(((a^2 d - J0)/T)^{(3/2) T^{-2}}) - (E^{-((4 a^2 d (h + J0) - J0 (4 h + 3 J0))/((a^2 d - J0)/T)^{(3/2) T^{-2}})} (4 a^2 d (h + J0) -
J0 (4 h + 3 J0)) Sqrt[\[Pi]/2])/(Sqrt[((a^2 d - J0)/T)^{(3/2) T^{-2}}] (a^2 d - J0) Sqrt[\[Pi] /
2] Sqrt[2] + (E^{(J0^2/(2 a^2 d T + 2 J0 T))} (a^2 d + J0) Sqrt[\[Pi]/2])/(Sqrt[((a^2 d + J0)/T)^{(3/2) T^{-2}}] (a^2 d + J0) Sqrt[\[Pi]/2])/(E^{((8 a^2 d h + 8 h J0 + J0^2)/(2 a^2 d T + 2 J0 T))} (a^2 d + J0) Sqrt[\[Pi]/2])/(Sqrt[((a^2 d + J0)/T)^{(3/2) T^{-2}}] (a^2 d + J0) Sqrt[\[Pi]/2])/(E^{(J0^2/(2 a^2 d T + 2 J0 T))} (2 a^2 d + 2 J0) Sqrt[\[Pi]/2])/(Sqrt[((a^2 d + J0)/T)^{(3/2) T^{-2}}] (2 a^2 d + 2 J0) Sqrt[\[Pi]/2])/(E^{((8 a^2 d h + 8 h J0 + J0^2)/(2 a^2 d T + 2 J0 T))} (2 a^2 d T +
2 J0 T)) (2 a^2 d + 2 J0) (8 a^2 d h + 8 h J0 +
J0^2) Sqrt[\[Pi]/2])/(Sqrt[((a^2 d + J0)/T)^{(3/2) T^{-2}}] (2 a^2 d T + 2 J0 T)^2])) +
Log[E^{-((2 h + J0)/
T)) \left( (E^{-((4 a^2 d (h + J0) - J0 (4 h + 3 J0)))/(2 (a^2 d - J0) T)} Sqrt[2 \[Pi]])/Sqrt[(a^2 d - J0)/T] + (E^{(J0^2/(2 a^2 d T + 2 J0 T))} Sqrt[\[Pi]/2])/(Sqrt[(a^2 d + J0)/
T] + (E^{((8 a^2 d h + 8 h J0 + J0^2)/(2 a^2 d T + 2 J0 T))} (2 a^2 d + J0) Sqrt[\[Pi]/2])/(Sqrt[(a^2 d + J0)/
T])]
\right)\]
h = 0
S0 = Simplify[S]

0

\[
(a^2 d J_0^2 \left(E^{((2 a^2 d J_0^2 + J_0^3)/(a^4 d^2 T - J_0^2 T))} \sqrt{\left(a^2 d - J_0\right)/T}\right) + E^{((2 a^2 d J_0)/(a^2 d T - J_0 T))} \sqrt{(a^2 d + J_0)/T}) + J_0^2 \left(E^{((2 a^2 d J_0)/(a^2 d T - J_0 T))} \sqrt{(a^2 d + J_0)/T} \right) (-J_0 + T) + E^{((2 a^2 d J_0^2 + J_0^3)/(a^4 d^2 T - J_0^2 T))} \sqrt{(a^2 d - J_0)/T}) (J_0 + T) - a^4 d^2 \left(E^{((2 a^2 d J_0)/(a^2 d T - J_0 T))} \sqrt{(a^2 d + J_0)/T}\right) -\]

\[
T) (-2 J_0 + T) + E^{((2 a^2 d J_0^2 + J_0^3)/(a^4 d^2 T - J_0^2 T))} \sqrt{(a^2 d - J_0)/T}) \left(2 J_0 + T)\right)/\left(2 (-a^2 d + J_0) (a^2 d + J_0) \left(E^{((2 a^2 d J_0^2 + J_0^3)/(a^4 d^2 T - J_0^2 T))} \sqrt{(a^2 d - J_0)/T}\right) + E^{((2 a^2 d J_0)/(a^2 d T - J_0 T))} \sqrt{(a^2 d + J_0)/T}) \right) T) + \]

\[
\log\left[E^{(-(J_0/T))} \left((E^{((4 a^2 d J_0 - 3 J_0^2)/(2 a^2 d T - 2 J_0 T))} \sqrt{2 \pi})/\sqrt{(a^2 d - J_0)/T}\right) + \left(E^{(J_0^2/(2 a^2 d T + 2 J_0 T))} \sqrt{2 \pi}/\sqrt{(a^2 d + J_0)/T}\right) \right] \]
\]
Clear[h]

dS = Simplify[S - S0]

\( (E^(-((2 \ h + J0)/T)) \ (E^(-(-((2 \ h + J0)/T))))) \)

\( \left( (E^(((4 \ a^2 \ d \ (h + J0) - J0 \ (4 \ h + 3 \ J0))/((a^2 \ d - J0)/T)^(3/2) \ T^3) - (E^((J0^2/(2 \ a^2 \ d \ T + 2 \ J0 \ T)) \ J0^2 \ Sqrt[\[Pi]/2])/(2 ((a^2 \ d + J0)/T)^(3/2) \ T^3) - (E^((8 \ a^2 \ d \ h + 8 \ h \ J0 + J0^2)/(2 ((a^2 \ d + J0)/T)^(3/2) \ T^3)) + (E^((4 \ a^2 \ d \ (h + J0) - J0 \ (4 \ h + 3 \ J0))/(2 (a^2 \ d - J0) \ T)) \ Sqrt[\[Pi]]]/(Sqrt[(2 a^2 \ d - 2 J0)/T] \ T) + (E^((J0^2/(2 \ a^2 \ d \ T + 2 \ J0 \ T)) \ Sqrt[\[Pi]/2])/(2 \ Sqrt[(a^2 \ d + J0)/T] \ T) + (E^((8 \ a^2 \ d \ h + 8 \ h \ J0 + J0^2)/(2 \ a^2 \ d \ T + 2 \ J0 \ T)) \ Sqrt[\[Pi]/2])/(2 \ Sqrt[(a^2 \ d + J0)/T] \ T)) + (E^(-((2 \ h + J0)/T))) \right) \)
\[
\begin{align*}
E^\left(J_0^2/(2 a^2 d T + 2 J_0 T)\right) \sqrt{\frac{\pi}{2}}/\sqrt{(a^2 d + J_0)/T} & + \\
E^\left((8 a^2 d h + 8 h J_0 + J_0^2)/(2 a^2 d T + 2 J_0 T)\right) \sqrt{\frac{\pi}{2}}/\sqrt{(a^2 d + J_0)/T} & + \\
\left(E^\left((4 a^2 d (h + J_0) - J_0 (4 h + 3 J_0))/(2 (a^2 d - J_0) T)\right) \sqrt{\frac{\pi}{2}}/\sqrt{(a^2 d - J_0)/T} + \right.
\end{align*}
\]
E^((J0^2/(2 a^2 d T + 2 J0 T)) Sqrt[\[Pi]/2])/Sqrt[(a^2 d + J0)/T] + (E^((8 a^2 d h + 8 h J0 + J0^2)/(2 a^2 d T + 2 J0 T)) Sqrt[\[Pi]/2])/Sqrt[(a^2 d + J0)/T]) - Log[E^(-(J0/T)) ((E^((4 a^2 d J0 - 3 J0^2)/(2 a^2 d T - 2 J0 T)) Sqrt[2 \[Pi]])/Sqrt[(a^2 d - J0)/T] + (E^(J0^2/(2 a^2 d T + 2 J0 T)) Sqrt[2 \[Pi]])/Sqrt[(a^2 d + J0)/T])]

T = 3
J0 = 1.1
a = 1.5
d = 0.5

3
1.1
1.5
0.5

Plot[dS, {h, 10, 30}]

Clear[a]
\[\text{dns} = \text{Simplify}[dS]\]

\[
(-2 (-1 + E^{-2 h}) (E^{2 + 2 h} (-1 + h) + h + E^{-2 h} h + E^2 (1 + h)) - (1 + E^2) (1 + E^{4 h} + 2 E^{2 + 2 h}) \log[2 E^{(-1 + a^2/2) (1 + E^{-2})} Sqrt[2 \[\pi]]] + (1 + E^{-2}) (1 + E^{-4 h} + 2 E^{2 + 2 h}) \log[2 E^{(-1 + a^2/2 - 2 h) (1 + E^{-4 h})} Sqrt[2 \[\pi]]]) / ((1 + E^2) (1 + E^{-2} (1 + E^{4 h} + 2 E^{2 + 2 h})))
\]

\[h = 0.2\]

0.2
Appendix F

Mathematica code for calculating Magnetization isotherms with $H_\beta$

Clear[h, J0, T, a, d]

F = -T Log[
    E^-((2 h + J0)/
        T)) ((E^((4 a^2 d (h + J0) - J0 (4 h + 3 J0))/(2 (a^2 d - J0) T))
          Sqrt[2 \[Pi]])/Sqrt[(a^2 d - J0)/T] + (E^(J0^2/(2 a^2 d T + 2 J0 T)) Sqrt[\[Pi]/2])/Sqrt[(a^2 d + J0)/
          T] + (E^-((8 a^2 d h + 8 h J0 + J0^2)/(2 a^2 d T + 2 J0 T))
          Sqrt[\[Pi]/2])/Sqrt[(a^2 d + J0)/T])
]

-T Log[E^-((2 h + J0)/
    T)) ((E^((4 a^2 d (h + J0) - J0 (4 h + 3 J0))/(2 (a^2 d - J0) T))
          Sqrt[2 \[Pi]])/Sqrt[(a^2 d - J0)/T] + (E^(J0^2/(2 a^2 d T + 2 J0 T)) Sqrt[\[Pi]/2])/Sqrt[(a^2 d + J0)/
          T] + (E^-((8 a^2 d h + 8 h J0 + J0^2)/(2 a^2 d T + 2 J0 T)))
\[ \text{Sqrt}\left[\frac{\pi}{2}\right]/\text{Sqrt}\left[\frac{a^2 d + J_0}{T}\right] \]

\[-T \log\left( E^{-\left((2 h + J_0)/T\right)} \left( \left( E^{-\left((4 a^2 d (h + J_0) - J_0 (4 h + 3 J_0))/(2 (a^2 d - J_0) T)\right)} \text{Sqrt}\left[\frac{2 \pi}{a^2 d - J_0}/T\right] + \left( E^{\left(J_0^2/(2 a^2 d T + 2 J_0 T)\right)} \text{Sqrt}\left[\pi/2\right]/\text{Sqrt}\left[a^2 d + J_0\right]/T\right] + \left( E^{-\left(8 a^2 d h + 8 h J_0 + J_0^2)/(2 a^2 d T + 2 J_0 T)\right)} \text{Sqrt}\left[\pi/2\right]/\text{Sqrt}\left[a^2 d + J_0\right]/T\right) \right) \right) \]
\[
\begin{align*}
&\frac{E^{-((4a^2d(h+J0) - J0(4h + 3J0))/(2(a^2d - J0)T))}(4a^2d - 4J0)}{2}\left(\frac{E^{-((8a^2d h + 8h J0 + J0^2)/(2a^2dT + 2J0T))}(8a^2d + 8J0)}{Sqrt[\pi]/2}\right)
\end{align*}
\]

\[
\begin{align*}
&+ \frac{E^{-((4a^2d(h+J0) - J0(4h + 3J0))/(2(a^2d - J0)T))}}{Sqrt[\pi]}\frac{E^{(J0^2/(2a^2dT + 2J0T))}}{Sqrt[(a^2d + J0)/T]} + (E^{-((8a^2d h + 8h J0 + J0^2)/(2a^2dT + 2J0T))}}\frac{E^{(8a^2d h + 8h J0 + J0^2)}}{Sqrt[\pi]/2}\frac{E^{(8a^2d h + 8h J0 + J0^2)/(2a^2dT + 2J0T))}}{Sqrt[(a^2d + J0)/T]}
\end{align*}
\]

size = 1500
J0 = 0.1
a = 0.7
d = 1
For[T = 3, T <= 5, T += 0.1,
    fname1 = "F";
    strm = OpenWrite["C:\\T\\" <> fname1 <> ToString[T] <> ".dat"];
    Array[M, size];
    WriteString[strm, "\n"];

    For[k = 1, k <= size, k += 1,
        Clear[h, M];
        M = -D[F, h];
    ]
]
\[ h = \frac{k}{50}; \]
\[ M[k] = M; \]

WriteString[strm, FortranForm[N[M]]];
WriteString[strm, " "]; WriteString[strm, FortranForm[N[h]]];
WriteString[strm, " "];
WriteString[strm, "\n"];
]; Close[strm];

]; Exit[];

1500

0.1

0.7

1
Appendix G

Mathematica code for calculating \( -\Delta S \) with Quantum Corrections

Clear[a, d, T, J0, h, om]

\[
E1 = \frac{1}{2}\text{om}(1 + \frac{J0}{(d*a^2)})^{\frac{1}{2}} - \frac{1}{2}\frac{J0^2}{d*a^2 + J0} - 2h + J0
\]

\[
E2 = \frac{1}{2}\text{om}(1 - \frac{J0}{(d*a^2)})^{\frac{1}{2}} - \frac{1}{2}\frac{J0^2}{d*a^2 - J0} - J0 - \frac{J0^2}{2(d*a^2 - J0)} + \frac{1}{2}\sqrt{1 + \frac{J0}{d*a^2}} \cdot \text{om}
\]

\[
E3 = \frac{1}{2}\text{om}(1 - \frac{J0}{(d*a^2)})^{\frac{1}{2}} - \frac{1}{2}\frac{J0^2}{d*a^2 - J0} - J0 - \frac{J0^2}{2(d*a^2 - J0)} + \frac{1}{2}\sqrt{1 - \frac{J0}{d*a^2}} \cdot \text{om}
\]
E4 = (1/2)*\(\omega m*(1 + J_0/(d*a^2))^{(1/2)} - (1/2)*J_0^2/(d*a^2 + J_0) + 2 h + J_0\)

\[2 h + J_0 - J_0^2/(2 (a^2 d + J_0)) + 1/2 Sqrt[1 + J_0/(a^2 d)] \omega m\]


\[2 E^\left((J_0 + J_0^2/(2 (a^2 d - J_0)) - 1/2 Sqrt[1 - J_0/(a^2 d)] \omega m)/T\right) + E^\left((-2 h - J_0 + J_0^2/(2 (a^2 d + J_0)) - 1/2 Sqrt[1 + J_0/(a^2 d)] \omega m)/T\right) + E^\left((2 h - J_0 + J_0^2/(2 (a^2 d + J_0)) - 1/2 Sqrt[1 + J_0/(a^2 d)] \omega m)/T\right)\]

\[F = \text{Simplify}[-T*\text{Log}[Z]]\]

\[-T \text{Log}[2 E^\left((2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m)/(2 T\right)) + E^\left((-4 h + 2 J_0 - J_0^2/(a^2 d + J_0) + Sqrt[1 + J_0/(a^2 d)] \omega m)/(2 T\right))\]

\[S = -\text{D}[F, T]\]

\((-((E^\left((2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m)/(2 T\right)) (2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m))/(T^-2) - (E^\left((-4 h - 2 J_0 + J_0^2/(a^2 d + J_0) - Sqrt[1 + J_0/(a^2 d)] \omega m)/(2 T\right))\]

\[((-((E^\left((2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m)/(2 T\right)) (2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m))/(T^-2) - (E^\left((-4 h + 2 J_0 + J_0^2/(a^2 d + J_0) + Sqrt[1 + J_0/(a^2 d)] \omega m)/(2 T\right))\]

\[((-((E^\left((2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m)/(2 T\right)) (2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m))/(T^-2) - (E^\left((-4 h + 2 J_0 - J_0^2/(a^2 d + J_0) + Sqrt[1 + J_0/(a^2 d)] \omega m)/(2 T\right))\]

\[((-((E^\left((2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m)/(2 T\right)) (2 J_0 + J_0^2/(a^2 d - J_0) - Sqrt[1 - J_0/(a^2 d)] \omega m))/(T^-2) - (E^\left((-4 h + 2 J_0 - J_0^2/(a^2 d + J_0) + Sqrt[1 + J_0/(a^2 d)] \omega m)/(2 T\right))\]
\[2 \frac{\text{h} - 2 \text{J0} + \text{J0}^2/(a^2 \text{d} + \text{J0}) - \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T}^2) + (E^{-((4 \text{h} + 2 \text{J0} - \text{J0}^2/(a^2 \text{d} + \text{J0}) + \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T}))} (4 \text{h} + 2 \text{J0} - \text{J0}^2/(a^2 \text{d} + \text{J0}) + \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T}^2)) T)/(2 \text{E}^{((2 \text{J0} + \text{J0}^2/(a^2 \text{d} - \text{J0}) - \text{Sqrt}[1 - \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T})) + E^{-((4 \text{h} - 2 \text{J0} + \text{J0}^2/(a^2 \text{d} + \text{J0}) - \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T})) + E^{-((4 \text{h} + 2 \text{J0} - \text{J0}^2/(a^2 \text{d} + \text{J0}) + \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T}))}) + \text{Log}[2 \text{E}^{-((2 \text{J0} + \text{J0}^2/(a^2 \text{d} - \text{J0}) - \text{Sqrt}[1 - \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T})) + E^{-((4 \text{h} - 2 \text{J0} + \text{J0}^2/(a^2 \text{d} + \text{J0}) - \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T})) + E^{-((4 \text{h} + 2 \text{J0} - \text{J0}^2/(a^2 \text{d} + \text{J0}) + \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T}))})

h = 0
S0 = \text{Simplify}[S]

0

(E^{-((2 \text{J0} + (\text{Sqrt}[1 - \text{J0}/(a^2 \text{d})] + \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})])] \text{om})/(2 \text{T})) ((E^{-((2 \text{J0} + \text{J0}^2/(a^2 \text{d} - \text{J0}) - \text{Sqrt}[1 - \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T}))} (-2 \text{J0} - \text{J0}^2/(a^2 \text{d} - \text{J0}) + \text{Sqrt}[1 - \text{J0}/(a^2 \text{d})] \text{om}))\text{T}^2 + (E^{-((-2 \text{J0} + \text{J0}^2/(a^2 \text{d} + \text{J0}) - \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om})/(2 \text{T}))} (2 \text{J0} - \text{J0}^2/(a^2 \text{d} + \text{J0}) + \text{Sqrt}[1 + \text{J0}/(a^2 \text{d})] \text{om}))/
\[ T^2 \frac{T}{2} \left( e^{\left( \frac{4J0 + J0^2/(a^2 d - J0) + \sqrt{1 + J0/(a^2 d)} \cdot \omega}{2T} \right)} + e^{\left( \frac{4J0 + J0^2/(a^2 d - J0) - \sqrt{1 - J0/(a^2 d)} \cdot \omega}{2T} \right)} \right) + \ln \left( 2 e^{-\left( \frac{2J0 + (\sqrt{1 - J0/(a^2 d)} + \sqrt{1 + J0/(a^2 d)}) \cdot \omega}{2T} \right)} \left( e^{\left( \frac{J0^2/(a^2 d + J0) + \sqrt{1 - J0/(a^2 d)} \cdot \omega}{2T} \right)} + e^{\left( \frac{4J0 + J0^2/(a^2 d - J0) + \sqrt{1 + J0/(a^2 d)} \cdot \omega}{2T} \right)} \right) \right) \]

Clear[h]

dS = Simplify[S - S0]

\[-\left( e^{\left( 2J0 + (\sqrt{1 - J0/(a^2 d)} - \sqrt{1 + J0/(a^2 d)}) \cdot \omega \right) \frac{1}{2T}} \left( e^{\left( 2J0 + J0^2/(a^2 d - J0) - \sqrt{1 - J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \right) \right) \frac{1}{2T^2} \frac{T}{2} \left( e^{\left( 2J0 + J0^2/(a^2 d - J0) + \sqrt{1 - J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \left( e^{\left( 2J0 + J0^2/(a^2 d - J0) - \sqrt{1 - J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \right) \right) \frac{1}{2T} \]

\[-\left( e^{\left( 4J0 + J0^2/(a^2 d - J0) - \sqrt{1 + J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \left( e^{\left( 4J0 + J0^2/(a^2 d - J0) + \sqrt{1 + J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \right) \right) \frac{1}{2T^2} \frac{T}{2} \left( e^{\left( 4J0 + J0^2/(a^2 d - J0) - \sqrt{1 + J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \left( e^{\left( 4J0 + J0^2/(a^2 d - J0) + \sqrt{1 + J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \right) \right) \frac{1}{2T} \]

\[-\left( e^{\left( 4J0 + J0^2/(a^2 d - J0) - \sqrt{1 + J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \left( e^{\left( 4J0 + J0^2/(a^2 d - J0) + \sqrt{1 + J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \right) \right) \frac{1}{2T^2} \frac{T}{2} \left( e^{\left( 4J0 + J0^2/(a^2 d - J0) - \sqrt{1 + J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \left( e^{\left( 4J0 + J0^2/(a^2 d - J0) + \sqrt{1 + J0/(a^2 d)} \cdot \omega \right) \frac{1}{2T}} \right) \right) \frac{1}{2T} \]
\[
\begin{align*}
\text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T^2} + ( \\
E^{-\left(-(4 h + 2 J0 - J0^2/(a^2 d + J0) + \text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T})\right)} \left(4 h + 2 J0 - J0^2/(a^2 d + J0) + \text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T^2}\right) \\
\left(2 E^{-\left((2 J0 + J0^2/(a^2 d - J0) - \text{Sqrt}[1 - J0/(a^2 d)] \frac{\text{om}}{2 T})\right)} + E^{-\left((4 h - 2 J0 + J0^2/(a^2 d + J0) - \text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T})\right)}\right) \\
\left(2 E^{-\left((4 h + 2 J0 - J0^2/(a^2 d + J0) + \text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T})\right)} + E^{-\left((4 h - 2 J0 + J0^2/(a^2 d + J0) - \text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T})\right)}\right)^{-1} \\
\left(2 E^{-\left((2 J0 + J0^2/(a^2 d - J0) - \text{Sqrt}[1 - J0/(a^2 d)] \frac{\text{om}}{2 T})\right)} + E^{-\left((4 h - 2 J0 + J0^2/(a^2 d + J0) - \text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T})\right)}\right) \\
\left(2 E^{-\left((4 h + 2 J0 - J0^2/(a^2 d + J0) + \text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T})\right)} + E^{-\left((4 h - 2 J0 + J0^2/(a^2 d + J0) - \text{Sqrt}[1 + J0/(a^2 d)] \frac{\text{om}}{2 T})\right)}\right)^{-1} \\
\end{align*}
\]

\[a = .7\]
\[h = 30\]
\[J0 = 0.1\]
\[d = 1\]
\[om = 1/2*d*a^2\]
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1. “Thermodynamics and Magnetocaloric properties of Fe/Cr superlattices” (in preparation)

2. S. Michalski, R. Skomski, Xingzhong Li, Damien Le Roy, T. Mukherjee, Ch. Binek and D. J. Sellmyer, “Isothermal Entropy Changes in Nanocomposite Co: Ni_{67}Cu_{33}” (Accepted J. Appl. Phys.)

3. T. Mukherjee, R. Skomski, S. Michalski, D. J. Sellmyer and Ch. Binek ”Spin and Lattice Contributions to the Isothermal Entropy Change” (Accepted J. Appl. Phys.)

4. Sarbeswar Sahoo, Srinivas Polisetty, Yi Wang, Tathagata Mukherjee, Xi He, Sitaram S. Jaswal, and Christian Binek, ” Asymmetric magnetoresistance in an exchange bias Co/CoO bilayer” (submitted)

5. Yi Wang, Xi He, T. Mukherjee, M.R. Fitzsimmons, S. Sahoo, and Ch. Binek, ”Magnetometry and transport data complement polarized neutron reflectometry in magnetic depth profiling”(Accepted J. Appl. Phys.)


