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Non-Equilibrium States of Matter: Ultrafast Dynamics and Phase Transitions

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Cover: Damped nutation and precession motion of a macrospin towards the preferred axis. The background symbolizes the environment surrounding the spin.

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Abstract

Although increasingly accessible by experiments and present in nanotechnology, non-equilibrium dynamics still pose challenges for theoretical physics. That includes the description of ultrafast demagnetization processes, magnetic phase transitions, and induced magnetization. This thesis is a contribution to the advancement of coarse-grained mesoscopic descriptions of non-equilibrium dynamics of magnetization.

Thermodynamics provides a framework to include fluctuations and coarse-grained dynamics. We extend it to non-equilibrium collective phenomena on subpicosecond timescales, although it was originally developed for slower timescales, and introduce the concept of *ultrafast thermodynamics*. We use three examples to demonstrate its potential.

First, the entropy production in ultrafast magnetization is considered using the Landau-Lifshitz-Gilbert equation, and the path-integral formalism is applied to it. This yields the entropy production that strongly depends on the nutation of the magnetization.

Second, we use entropy production as a measure of Markovianity in magnetization dynamics. Using three different Landau-Lifshitz-Gilbert equations (without nutation, with nutation, with nutation and higher orders), we numerically compute their entropy production rates. Negative entropy production rates indicate non-Markovian dynamics, making them a good measure of the Markovianity.

Third, we investigate the phase transition into quadrupole ordering, observed slightly above the magnetic transition. Using a field-theoretical approach, we find the transition temperatures and coupling to strain, explain why quadrupole order is visible only in anisotropic materials, and derive an analytical expression for the transition temperatures.

Finally, this thesis includes a review of recent theories of the phono-magnetic effect, a non-equilibrium magnetization phenomenon subject to significant debate. Altogether, the work broadens the theoretical foundations for understanding ultrafast non-equilibrium magnetization dynamics.

Keywords:

thermodynamics, non-equilibrium, phase transitions, magnetism, entropy production

LIST OF APPENDED PAPERS

This licentiate thesis consists of seven introductory chapters and the following papers:

I **Ultrafast Entropy Production in Nonequilibrium Magnets**
Finja Tietjen and R. Matthias Geilhufe
***PNAS Nexus* 4, pgaf055 (2025)**

doi:10.1093/pnasnexus/pgaf055

II **Axial phono-magnetic effects**
Natalia Shabala, Finja Tietjen and R. Matthias Geilhufe
in manuscript

III **Entropy Production as Markovianity Measure in Magnetization Dynamics**
Felix Hartmann, Finja Tietjen, Janet Anders and R. Matthias Geilhufe
in manuscript

The author's contribution to the papers:

I I did most of the analytical calculations and numerical implementation. R. M. Geilhufe and I analyzed the results together. We both wrote and reviewed the manuscript. I was contributing to and with formal analysis, investigation, methodology, code, validation, visualization, writing of the original draft, reviewing, and editing.

II I read and summarized parts of the literature. I contributed to analyzing the different approaches, writing the first draft, visualizing, and reviewing.

III F. Hartmann and I were responsible for planning the project. I contributed to the background and foundations of the theory. We both analyzed the data and formulated conclusions. I wrote the first draft of the manuscript. We reviewed the manuscript together.

Contents

1

Introduction

Theoretical physics is used to explain and predict experiments, but the currently existing theories cannot explain some of the experiments. This is especially true for out-of-equilibrium phenomena, since the experimental technology has only recently advanced into that regime. There are, for example, experiments on ultrafast demagnetization [1], inertial dynamics of magnetization [2], giant magnetic effects from excited phonons [3, 4], and new types of magnetic ordering [5].

But not only are experimental techniques constantly improving. The same is true for applied technology for data storage and processing. For even further advancements, it would be advantageous to reach sub-nanosecond timescales, but it comes with the cost of non-equilibrium processes. This cost includes heat and entropy production, irreversibility and efficiency loss, decoherence and noise, increased demands for the used materials.

Therefore, the demand for explanations and predictions for ultrafast and non-equilibrium dynamics is high. Yet many existing theories have been developed for slow and/or equilibrium phenomena. In addition, the unprecedentedly short timescales in the magnetization experiments raise the question of whether theories developed for significantly slower timescales are still valid.

Therefore, we investigate possible expansions and improvements of mesoscopic theories and thermodynamics. These are then compared to existing experimental data or used to predict the outcome of future experiments.

Mesoscopic theories use a coarse-graining approach and have an advantage over microscopic theories: they can explain phenomena in a wider range of systems because they are independent of the exact microscopic interactions. Microscopic theories, on the other hand, consider the exact underlying interactions and are consequently restricted to systems with the included types of interaction. Therefore, we are going to use mesoscopic theories and focus on the effect of the interactions, while keeping in

mind the microscopic origin of these interactions.

Of course, we are building on existing and successful theories. They are then expanded to higher orders of interactions or changed by combining known problems and techniques in a new way.

Research Question How can we improve, expand, and adjust existing mesoscopic theories to correctly explain and predict outcomes from non-equilibrium experiments?

What do we do? To answer this question generally is too big a scope for one researcher's career. Therefore, we focus on selected examples in the area of magnetism. Magnetism has been studied for centuries and still does not cease to fascinate with new, unexplained phenomena. It is possible to measure magnetization at ultrafast (femtosecond) timescales and with high spatial precision as well. Phase transitions, different orders, relaxation dynamics, and different origins have all been observed in magnets. But not all of the phenomena have been understood on a mesoscopic level yet.

We take thermodynamics as a starting point and further develop it to ultrafast thermodynamics to capture non-equilibrium dynamics and states of magnetization. Consequently, the refined research question is

Refined Research Question How can we combine thermodynamics, collective phenomena and mesoscopic theories of magnetism to describe non-equilibrium magnetization dynamics?

Structure This thesis starts with an introduction to thermodynamics, where, for this work, the central concept of entropy production is introduced. We continue with defining and explaining ultrafast thermodynamics. It enables us to study the non-equilibrium dynamics of collective excitations and is the basic framework for Paper I, Paper II and Paper III. Since magnetization experiments play a key role in all the papers, the experimental technique of magneto-optical Kerr effect measurements is presented in Chapter 4. It is followed by an explanation of externally excited magnetization dynamics in Chapter 5, which is the process of interest in Paper I and Paper III.

Paper II focuses on a specific way to induce magnetism, and the basics for that are given in Chapter 6. The last background chapter is about changes in magnetization, with a special focus on phase transitions and quadrupolar ordering. It provides the background for ongoing work and contains some of the first results.

Finally, the included papers are summarized, before the entire work is concluded by an overall summary and outlook.

2

Introduction to Thermodynamics

Historically, the invention of steam engines led to a macroscopic theory involving pressure, volume, heat, work, and entropy. This theory led to improved efficiencies in engines and sparked theoretical interest.

What started out as a phenomenological description turns out to be a rather universal description of nature. Together with mechanics and information theory, it is one of the pillars of classical physics, and today known as *classic thermodynamics* [6, 7].

Generally, there are two components to any physical problem in thermodynamics: the system and the bath or medium. The system is a subsystem of the entire problem, which is observed closely. The bath or medium denotes the environment surrounding and interacting with the system.

The increased theoretical interest in classic thermodynamics led to the development of *statistical mechanics*. Based on microscopic interactions, statistical predictions are made regarding thermodynamic evolutions. This works because statistical mechanics focuses on the averages over many particles and trajectories. The microscopic foundation of the theory results in rigorous definitions for quantities like temperature and entropy. With that, it provides mathematical proof for the phenomenological classic thermodynamics, but it is still a theory on its own.

The following section introduces the most important concepts of thermodynamics relevant to this work. The laws of thermodynamics and the definition of equilibrium conclude this chapter.

2.1 Entropy, Heat and Work

The three quantities central to classic thermodynamics have each been defined in many ways.

Starting from the outside, *work* can be defined as the energy added into the system from external sources. This energy can take the form of, for example, a change of pressure.

Such work leads to a change of energy within the system. This change can be quantified in two ways. One is the *heat* of the system. It is the amount of energy transferred due to microscopic processes like thermal conduction or friction. The other one is the *entropy* S, which quantifies the number of microscopic states Ω possible for a given macroscopic configuration of the system [7]. In statistical mechanics, it is defined as

$$S_B = k_B \ln \Omega \,. \tag{2.1}$$

Entropy is a central quantity of thermodynamics because it explains why some processes do not happen despite obeying energy conservation laws. It is possible to make such general statements because the entropy is defined for the entire physical system. The entropy is one single quantity capturing important information about the system and the bath simultaneously. As a consequence, we cannot investigate the system and bath separately.

From an information theory point of view, entropy is the amount of information lost between the forward and backward processes. The most common definition of entropy in information theory is the Shannon entropy

$$S_S = \sum p(x) \ln \left(p(x)\right) , \tag{2.2}$$

which sums over the probability distribution $p(x)$ for all possible states x of a certain macroscopic configuration [7]. Here, the entropy is not defined for the entire problem, but only for the system. The entropy of the bath is viewed as a separate quantity.

The Shannon entropy also finds its applications in ultrafast thermodynamics, as further explored in Chapter 3.

2.2 Laws of Thermodynamics

Similar to mechanics, thermodynamics has fundamental principles that apply to all problems addressed with this framework. They are called the *laws of thermodynamics* [7].

The first law is the thermodynamic version of the law of conservation of energy. It is formulated based on the *internal energy* U, which is the amount of energy necessary to bring the system into its current state. It accounts for all changes that occur during the transformation from the ground state to the current state. The first law tells us that these energy changes are equal to the heat added to the system, reduced by the work of the system done to the environment:

$$\Delta U = Q - W \,. \tag{2.3}$$

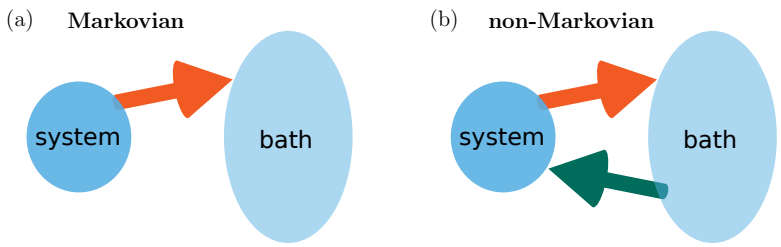

Figure 2.1: Sketch of Markovian and non-Markovian information flow. In Markov processes, information flow only happens from the system to the bath (indicated by the orange arrow). In non-Markovian processes, information can also flow back from the bath into the system (indicated by the green arrow).

The second law says that a system is always increasing its entropy S. Consequently, the state of maximal entropy is the equilibrium of the system. This equals the statement that no heat flows from a colder to a hotter medium. It is conventionally formulated as

$$\delta_t S \geq 0\,. \tag{2.4}$$

Recent works show when the second law applies and when it can seemingly be broken. Fluctuations are one example, because they can lead to a transient decrease in entropy. They only become visible when investigating individual trajectories or very small systems [8–10].

Another exemption can be understood with the help of information theory. Since entropy is defined as information flow in that context, an increase in entropy means the flow of information from the system into the medium. In the moment, when the information flow is reversed, the entropy of the system decreases. This can happen in systems that have a memory effect, i.e., their future state depends on their past trajectory. A system, whose evolution only ever depends on its current state, is called *Markovian*. If that is not the case, the system is called non-Markovian. Fig. 2.1 illustrates the information flow between system and bath for (a) the Markovian dynamics and (b) the non-Markovian dynamics.

The third law governs the limiting case of zero temperature. It states that the entropy of a system approaching zero temperature becomes a constant:

$$S \to const. \quad \text{for} \quad T \to 0 \tag{2.5}$$

The entropy is related to the number of possible states. Therefore, the entropy might become zero at zero temperature, but only if the system has a unique ground state.

2.3 Equilibrium and beyond

A system is in thermodynamic *equilibrium* if there is no macroscopic change and no tendency to such a change.

To go beyond the equilibrium case, it is necessary to study the microscopic processes as in statistical mechanics. The emergence of order parameters from statistical mechanics provides a tool to describe the evolution of a system by following only the changes in relevant parameters. One example of such an order parameter is temperature.

In classic thermodynamics, for a valid physical description, the bath has to have a well-defined temperature. That means the bath has to be big enough not to change its state because of the presence of the system. This is not always given in ultrafast non-equilibrium dynamics, which poses additional challenges for the description.

One crucial thermodynamic tool for a physical description of ultrafast non-equilibrium dynamics is *entropy production*

$$\Sigma = \Delta S_S + \sum_i \frac{Q_i}{T_i} \,. \tag{2.6}$$

The total entropy production Σ consists of the change in entropy in the system ΔS_S and the combined heat Q_i of the baths i scaled by their temperatures T_i [11]. Entropy production has long been a tool in classic thermodynamics, but it proves useful when extending thermodynamics beyond the classic framework. One example is stochastic thermodynamics and its extension to ultrafast dynamics, which we make use of in Paper I. Generally, entropy production is a way to quantify change within a system and is connected to the non-equilibrium aspects of ultrafast dynamics. As a consequence, the entropy production holds information about the Markovianity of the system [9], which we explain and use in Paper III.

The next chapters show possibilities to formulate a thermodynamic framework for ultrafast non-equilibrium processes.

3

Ultrafast Thermodynamics

A system needs time to reach its new equilibrium after it has been subject to an excitation by, for example, a laser pulse. This relaxation has a characteristic time scale, and everything faster than it is inherently non-equilibrium. The observed non-equilibrium dynamics are therefore ultrafast, because they are faster than the shortest characteristic timescale of the system.

Nonetheless, it is interesting to investigate the thermodynamics of these ultrafast non-equilibrium processes. Since experiments track only specific degrees of freedom, it is useful to apply the principles of stochastic thermodynamics [12]. These degrees of freedom often represent collective excitations of the studied material.

Therefore, we develop the concept of *ultrafast thermodynamics* using methods from stochastic thermodynamics.

The following sections introduce stochastic thermodynamics and collective excitations, along with the widely used path-integral method and free energy approach.

3.1 Stochastic Thermodynamics

In stochastic thermodynamics, the system is one single particle, organism or object, while the bath is treated as a stochastic background [13]. The system itself is non-equilibrium, and studying its dynamics is the main focus. One example is active matter, where the single objects perform random motions fueled by the interaction with the environment.

Stochastic thermodynamics combines ideas of classic thermodynamics and statistical mechanics. The bath is described by averages and expectation values, and there is no knowledge about the individual constituents. The system is a single object or particle, and its individual behavior is studied, while the rest remains a statistical background with well-defined temperature [8].

The result is a combination of deterministic and random variables that gives the full description of the dynamics. The randomness does not always come from the environment, but can also be intrinsic, as for active matter. Regardless of the exact origin or form, this randomness is often called *noise*. It always means that there are degrees of freedom that are not explicitly included, i.e., deterministically described in stochastic thermodynamics. A common example of noise is fluctuations due to finite temperature.

Besides temperature for the bath and the system, stochastic thermodynamics uses heat, work, entropy production, and other thermodynamic quantities to describe the non-equilibrium processes, which are defined trajectory-dependently. The stochastic entropy production is

$$s(\tau) = -\ln\left(p(x(\tau), \tau\right), \tag{3.1}$$

where τ is the time, $x(\tau)$ the trajectory, and p is the probability for that trajectory to occur at the given time [?]. Therefore, the stochastic entropy production does not depend on a single trajectory alone, but on the distribution of all trajectories.

The mathematical form for equations of motion in stochastic thermodynamics is stochastic differential equations. That prevents obtaining a unique solution for the dynamics, which makes averaging over many different trajectories crucial. The averages are what can be understood as predictions for experimental measurements.

An example of a process described by stochastic thermodynamics is the Ornstein–Uhlenbeck process, which is a form of Langevin process. Generally, the equation of motion for Ornstein–Uhlenbeck processes can be written as

$$\dot{\boldsymbol{X}} = \boldsymbol{F}(\boldsymbol{X}) + \boldsymbol{\eta}\,, \tag{3.2}$$

where $\boldsymbol{F}$ is a vector force, which includes all external and internal deterministic contributions. The vector $\boldsymbol{\eta}$ is the so-called noise vector and stems from coarse-graining some degrees of freedom that are slower than the characteristic time-scales of the variable $\boldsymbol{X}$. The coarse-graining takes away information about some parts of the dynamics, which results in a certain degree of randomness.

Without loss of generality, we can set the first moment (expectation value) of the noise to zero $\langle\boldsymbol{\eta}\rangle$. The second moment is expressed by a two-time correlation matrix

$$\langle \eta_i(s)\eta_j(t)\rangle = \nu_{ij}(t-s)\,. \tag{3.3}$$

This correlation matrix reduces to a simple delta-function if the noise is Gaussian and uncorrelated, i.e., white noise. Consequently, it is characterized entirely by its mean value and correlation. It also contains a correlation factor, which depends on the type of noise and system in question. If the source of the noise is of thermal nature, the correlation factor includes the factor $k_B T$.

Each realization of the evolution in the time interval between the initial time t_i and the final time t_f will give a different path $\underline{\boldsymbol{X}} = \{\boldsymbol{X}\}_{t_i}^{t_f}$. The probability of observing

this path is denoted by $P\left[\underline{\boldsymbol{X}}\right]$, assuming that all paths start with a defined initial condition $\boldsymbol{X}_0 = \boldsymbol{X}(t_i)$. These path probabilities are a useful tool for computing entropy production, as detailed in the next section.

3.1.1 Path-Integral Method

The path-integral method is an extension of the classical action principle. It considers many stochastic trajectories, instead of one deterministic one. Therefore, it is a perfect tool for stochastic thermodynamics.

The following example of entropy production of an Ornstein-Uhlenbeck process shows how it can be used [14]. The underlying definition of entropy production is the stochastic entropy production in Eq. (3.1).

The previous section introduced path probabilities and defined Gaussian white noise. The actual path probability can be calculated via a path integral:

$$P\left[\underline{\boldsymbol{\eta}}\right] \propto \exp\left(-\frac{1}{2}\int \mathrm{d}t \int \mathrm{d}s\, \boldsymbol{\eta}(s)\boldsymbol{\nu}^{-1}(t-s)\boldsymbol{\eta}(t)\right). \tag{3.4}$$

We dropped a normalization factor because it will cancel out in later calculations. The integral is calculated in the relevant time interval and $\boldsymbol{\nu}^{-1}$ is the inverse of the two-time correlator $\boldsymbol{\nu}$, which is defined as

$$\int \mathrm{d}t' \boldsymbol{\nu}^{-1}(t-t')\boldsymbol{\nu}(t'-s) = \mathbb{I}\delta(t-s)\,. \tag{3.5}$$

For Gaussian uncorrelated noise, the probability for the trajectory of the noise path is given by

$$P\left[\underline{\boldsymbol{\eta}}\right] \propto \exp\left(-\frac{1}{2}\int \mathrm{d}t\, \boldsymbol{\eta}(t)^2\right). \tag{3.6}$$

The time evolution of the noise, however, can be expressed in terms of the evolution of the system variables $\boldsymbol{X}$. Note that the potentially non-trivial correlation factor is assumed to be within the evolution equation.

Formally, we can relate the path probability of the noise to the path probability of the system variables:

$$\ln P\left[\underline{\boldsymbol{X}}\right] = \ln P\left[\underline{\boldsymbol{\eta}}\right] + \left(\det\left[\frac{\partial\boldsymbol{\eta}}{\partial\boldsymbol{X}}\right]\right). \tag{3.7}$$

The last term is the Jacobian of the transformation between $\boldsymbol{X}$ and $\boldsymbol{\eta}$. It vanishes under rather general conditions, which include the process here [15–17].

All discussions so far were for the forward process. But to determine the entropy production of the evolution, the backward process is necessary as well. It can be determined with the same logic, except that now the time-reversed variables are involved. This can formally be achieved by applying the time-reversal operator $\boldsymbol{\Theta}\, o(t) = o(t_f - t)$.

Consequently, the entropy production of the medium is

$$\Sigma = k_B \ln \frac{P\left[\underline{\boldsymbol{X}}\right]}{P\left[\underline{\boldsymbol{\Theta X}}\right]} \,. \tag{3.8}$$

Note that all terms quadratic in $\boldsymbol{\nu}^{-1}$ contribute trivially as boundary terms [18].

The path-integral method for calculating the entropy production rate concludes the introduction to stochastic thermodynamics. The next part of the definition of ultrafast thermodynamics is *collective excitations*, which are introduced in the next section.

3.2 Collective Excitations and Ordering

In condensed matter systems, many particles interact and show collective behavior. This leads to quantized disturbances or modes of motion in the ground state of the system when slightly perturbed.

Condensed matter systems often show collective excitations, which are described by quasiparticles. Relevant here are phonons, which are quantized lattice vibrations with acoustic and optical modes, and magnons, which are quantized spin waves with band-dependent dispersions. Both can be coherently excited by tailored light beams, where the resulting excitation depends on beam frequency, intensity, and system structure.

Another consequence of the interaction between particles is the order of the system. This order and its changes depend on the type of interaction, as well as temperature, pressure, external fields, and numerous other factors. A system that has a specific order is said to be in a specific phase. Magnetization is one type of order and describes the collective alignment of electronic spins, as described in more detail in Chapter 4. As an order parameter, magnetization depends on temperature and has a critical temperature T_c that divides the magnetic from the non-magnetic phase of the system as depicted in Fig. 3.1.

The onset of a phase can include more changes to the system than just the ones described by the order parameter. For example, the magnetic phase of a material can have a different geometric structure than the non-magnetic phase. Additionally, a system can have more than two phases and more than one order parameter describing it. That leads to potentially complicated phase diagrams.

The benefit of defining and analyzing order parameters is the possibility to measure, e.g., transition temperatures experimentally. That can validate or invalidate theoretical models.

3.2.1 Free Energy and Partition Function

Studying the dynamics of order parameters is interesting, but can be tedious. A useful approach is to express the equation of motion not in terms of the microscopic, under-

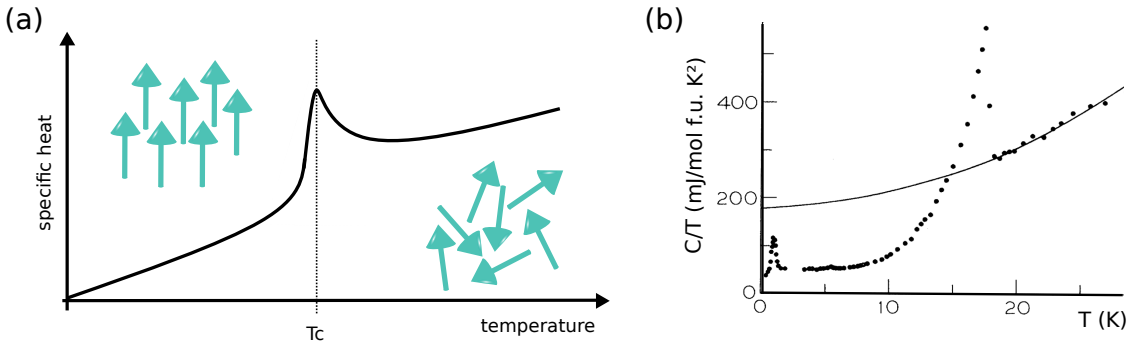

Figure 3.1: Peaks in the specific heat can indicate phase transitions. (a) The disordered spin state above T_C becomes ordered below a critical temperature T_c. (b) Experimental data of the specific heat of URu_2Si_2 indicate two phase transitions: a magnetic one at 17.5 K and a superconducting one at 0.8 K [19].

lying dynamics, but rather to coarse-grain it and express it in terms of the effective dynamics of the order parameter itself. That is possible when focusing on the regimes close to the phase transition associated with the order parameter, because the order parameter becomes small at the phase transition, which makes different approximations possible. Such a phase transition depends on at least one macroscopic variable, such as temperature or pressure.

The quantity capturing the behavior of the order parameter is the free energy, which depends on the order parameter and the corresponding macroscopic variable. Since the expressions are for many-particle systems, the free energy is usually normalized to yield the free energy density.

One approach to the free energy density is provided by Landau theory [20]. Its general form is

$$f(\boldsymbol{A}, T) = c\,(\nabla \boldsymbol{A})^2 + \alpha(T - T_c)\boldsymbol{A}^2 + \beta \boldsymbol{A}^4 + \text{anisotropy} + \text{coupling} \tag{3.9}$$

and can contain even higher orders of the order parameter $\boldsymbol{A}$. The constants c and α are material-dependent and can be found experimentally. The anisotropy and coupling terms can lead to terms dependent on different components of the order parameter simultaneously. They also include symmetry constraints and possible coupling to external forces or other orders of the system.

The minimization of the free energy gives the equilibrium state of the system for the given parameters. In this way, it is possible to capture the evolution of the system as it changes with varying temperature, pressure, or any other environmental variable.

The *partition function* is a spatially independent and dimensionless quantity. It is calculated from the free energy density as

$$Z = \exp\left(-\beta \int d^d r f\right), \tag{3.10}$$

where $\beta = \frac{1}{k_b T}$ is the inverse temperature.

With knowledge of the free energy and the partition function, we can calculate all thermodynamic variables and observables, as well as the probabilities for different states given specific parameters.

For example, the specific heat can be calculated as

$$c_V(T) = -T \frac{\partial^2 f_{min}}{\partial T^2} \tag{3.11}$$

and, in turn, it contains information about phase transitions and the bulk behavior of the material. Fig. 3.1 shows how the specific heat indicates a phase transition with a peak. Since a material can have more than one phase transition, the specific heat might exhibit more than one peak as illustrated in Fig. 3.1 at the example of the intermetallic compound URu_2Si_2 [19]. The benefit of the specific heat as an observable is that it is directly measurable in experiments. Therefore, it can be used to verify the theoretical approach leading to the specific formulation of the free energy.

In general, the free energy approach has the benefit that no knowledge about the microscopic processes is necessary. It is possible to extend this approach to operators represented by a field or fields. The framework is called *statistical field theory* and can be used close to phase transitions as well.

Similar to quantum field theory, path integrals and renormalizations are common tools within statistical field theory.

In the context of phase transitions, the *saddle point approximation* of the free energy leads to the gap equation. It means that the derivative of the free energy with respect to the order parameter of the phase of interest is set to zero. The solution to this equation gives the gap equation.

4

MOKE for Magnetization Dynamics

Magnetism is a long-known phenomenon and one of the cases where quantum mechanics becomes visible in macroscopic observables. Its origin and prevalence have been studied ever since its discovery, but there are still open questions. They are about the different possible origins of magnetism, the influence of magnetism on other degrees of freedom, the different types of magnetism, and the dynamics of magnetization processes.

The latter is not only becoming more relevant with advancing technology, but also more accessible. Already about thirty years ago, the first experiments on ultrafast magnetization dynamics were performed [21]. They revealed that the established explanations for changes in magnetization did not suffice to explain the speed of the observed dynamics. That sparked a new field of investigations, which got much attention as ultrafast pump-probe experiments became more available. The increasing temporal and spatial resolution leads to measurements of previously inaccessible dynamics [2, 22–25].

These ultrafast magnetization dynamics include demagnetization processes, as well as relaxation processes of excited states. Consequently, they are out of equilibrium.

The following sections revisit the basic formalism of magnetism and explain the frequently used experimental setup for magneto-optical Kerr effect measurements.

4.1 Magnetization

The microscopic origin of macroscopic magnetization is the alignment of electronic spins. Their collective order depends on the interaction potential and results in a magnetization.

The Heisenberg Hamiltonian

$$H = \sum J_{ij} \boldsymbol{S}_i \boldsymbol{S}_j \tag{4.1}$$

captures different alignments of spins, depending on the sign and form of the interaction coefficient J_{ij}. Therefore, it can be used to describe ferro and anti-ferro magnetic orders. More complex magnetic orders are possible, as we discuss in more detail in Chapter 7.

A single spin can be interpreted as a single magnetic dipole, but the order parameter of magnetization is more commonly described as the average over many spins

$$\boldsymbol{M} = \frac{1}{N} \sum_i \boldsymbol{S}_i \,. \tag{4.2}$$

Note that not every magnetic ordering leads to an effective magnetic field. For example, the magnetic dipoles in anti-ferromagnetic ordering cancel each other, which leads to zero effective magnetization. Consequently, the total magnetization of a material contains only part of the information about its microscopic order. A high spatial resolution can reveal more information because it can capture local variations.

4.2 Magneto-Optical Kerr-Effect

A widely used technique to measure magnetization dynamics relies on the magneto-optical Kerr-effect (MOKE). This effect describes the change in polarization and ellipticity when a linearly polarized light beam reflects off a magnetized surface. Its microscopic origin is in the dielectric permittivity [26], which is the dipole moment obtained as the response of a system to an electric field.

For magnetic materials, the dielectric tensor ϵ has off-diagonal elements because of anisotropic permittivity. If the material is additionally isotropic, the dielectric tensor takes the form

$$\epsilon = \begin{pmatrix} \epsilon & \epsilon' & 0 \\ \epsilon' & \epsilon & 0 \\ 0 & 0 & \epsilon \end{pmatrix} . \tag{4.3}$$

This leads to a different absorption rate of left and right-polarized light components. Consequently, the polarization of reflected light is changed.

The off-diagonal elements of the dielectric tensor can have different origins. In ferro- and ferrimagnetic materials, it is the spin-orbit coupling that makes the off-diagonal elements proportional to the magnetization of the sample [27]. Therefore, the changes between incident and reflected light are proportional to the surface magnetization. Note that the dielectric tensor is position-dependent, which enables the study of local surface magnetization with MOKE.

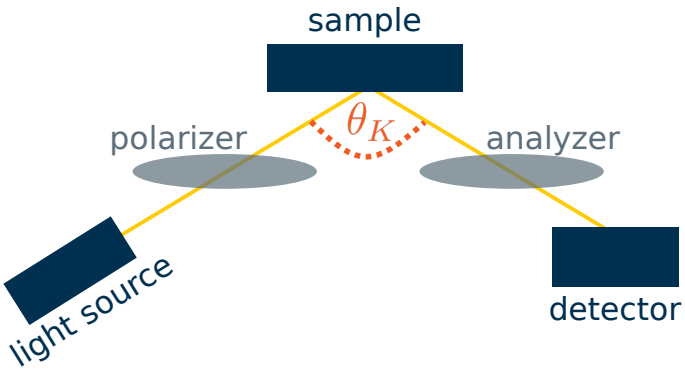

Figure 4.1: Schematic of a MOKE experiment set-up.

The experimental setup for measuring the MOKE is depicted in Fig. 4.1. The light beam is first polarized before it reaches the sample. The reflected beam is then guided through an analyzer, which translates the polarization into intensity data. The intensity is then detected by a microscope.

The change in polarization between the incoming and the outgoing light is defined as the Kerr rotation angle θ_K. Its analytical form depends on the complex index of reflection and combines the real and imaginary parts of it. In addition, the exact geometry of the setup influences the analytical Kerr angle.

The combination of MOKE measurements with pump-and-probe setups allows the study of magnetization dynamics with high temporal and spatial precision. The pump laser excites the magnetic degrees of freedom of the sample, and the following probe laser beams track the relaxation process of the magnetization as MOKE signals.

The diffraction limits of the beam, as well as the variation of incidence angle for each ray, render the analysis of MOKE signals tedious. Despite that, the accuracy of MOKE measurements is high.

One example is the measurement of small changes in magnetization to find the nutation frequency [2], the magnetization induced by excited phonons [3], or in general ultrafast magnon dynamics [28].

5

Excited Magnetization

There are many ways to excite a magnet, and many ways to describe the subsequent evolution of the magnetization. One routinely used approach is the Landau-Lifshitz-Gilbert (LLG) equation. It uses the fact that every magnet will react with torque to an external magnetic field, regardless of the timescale. This makes it suitable to describe the ultrafast magnetization dynamics in solid magnets, where we can approximate the magnetization of a unit cell by a macrospin.

Investigating the ultrafast dynamics after excitations comes with the difficulty of being completely out of equilibrium. Consequently, extensions of the original LLG equation are necessary, which are presented in this chapter. Including them enables us to study the energy dissipation and entropy production in these ultrafast processes with the help of ultrafast thermodynamics, as done in Paper I.

Additionally, a thorough study of the microscopic origins of the extensions reveals possible memory effects in the dynamics. Sect. 5.2 explains the emergence of memory in more detail. This opens the possibility to study the signatures of non-Markovianity in magnetization dynamics with the help of ultrafast entropy production, as done in Paper III.

5.1 Landau-Lifshitz-Gilbert Equation

Although magnetism is a quantum mechanical effect, it is possible to describe its dynamics by a classical equation of motion. This is possible by focusing only on the quantities directly relevant to the dynamics.

One widely used and successful description is the Landau-Lifshitz-Gilbert (LLG) equation [29]. It is based on the torque effect that an external magnetic field $\boldsymbol{B}$ has on a magnetization $\boldsymbol{M}$. Note that this magnetization is a three-component vector, which can represent either a single spin or the average of many spins, known as a macrospin.

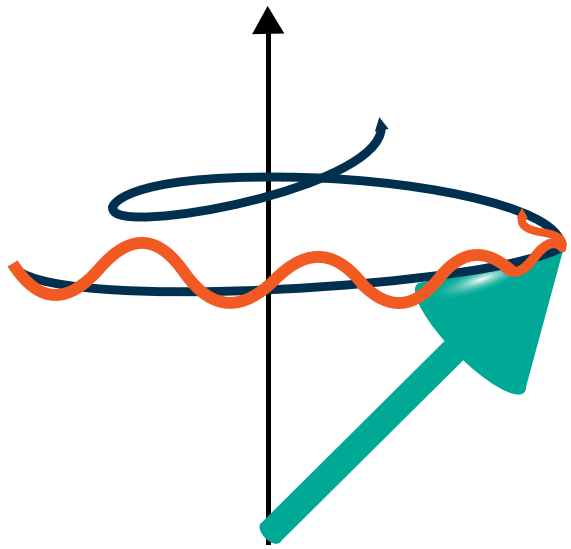

Figure 5.1: Spin dynamics as described by the inertial LLG equation. The slower precession motion is in dark blue, and the faster nutation motion is in orange. The damping leads to a decrease in the amplitude of both motions.

The form relevant to this work and describing the motion depicted in Fig. 5.1 is

$$\dot{\boldsymbol{M}} = -\gamma\, \boldsymbol{M} \times \left(\boldsymbol{B} + \eta \dot{\boldsymbol{M}} + \eta\tau \ddot{\boldsymbol{M}} + \sqrt{2D'}\boldsymbol{h} \right). \tag{5.1}$$

The first term is the torque interaction as introduced by Landau and Lifshitz and describes the precession motion. It only depends on the magnetization and the external field. This field can be constant or explicitly time-dependent. The constant γ is the electronic gyromagnetic ratio.

The second term is the Gilbert damping, which slows down the precession and any other movement. The Gilbert damping constant α is dimensionless, and in the formulation in Eq. (5.1), it is rescaled by the saturation magnetization M_s as $\eta = \alpha/(\gamma M_s)$.

The third term captures the nutation motion and is scaled by the angular momentum relaxation time τ [30]. This is an inertial effect and its exact form can be derived in different ways. It emerges when treating the magnetization dynamics relativistically [31], or quantum mechanically [32], as detailed later, or within first principles [33]. Despite it being a relatively new expansion, the nutation frequencies have been measured in experiments [2, 22, 25, 34–36].

Finally, the last term is stochastic noise in the form that arises from a quantum mechanical approach [32]. Its origin is the interaction of the (macro)-spin with the environment, and the details of the interaction and bath are encoded in the correlation factor D'. This includes interactions with neighboring spins and other degrees of freedom, e.g., phonons.

It can also be understood from a phenomenological point of view: Damping or dissipation is tightly bound to fluctuations, according to the well-known fluctuation-dissipation theorem. Microscopically, the Gilbert damping can be derived from the dissipation of energy from magnetic degrees of freedom to electrons [37] or a bosonic bath, e.g., due to phonons [38]. This dissipation introduces fluctuations, which are taken into account by adding a stochastic noise term.

According to the LLG Eq.(5.1), the magnetic fluctuations only concern the transverse component of the magnetization. However, longitudinal fluctuations can be incorporated [39], giving rise to the following stochastic Landau-Lifshitz-Gilbert (sLLG) equation,

$$\dot{\boldsymbol{M}} = -\gamma\, \boldsymbol{M} \times \left(\boldsymbol{B} + \eta \dot{\boldsymbol{M}} + \eta\tau \ddot{\boldsymbol{M}} \right) - \gamma M_s \sqrt{2D}\boldsymbol{h}\,. \tag{5.2}$$

The exact form of the noise depends on the system. A common choice is uncorrelated (white) noise. It obeys the correlation relations

$$\begin{aligned} \langle \boldsymbol{h}(t) \rangle &= 0 \\ \left\langle h_i(t) h_j(t') \right\rangle &= \delta(t-t')\delta_{ij}, \qquad \boldsymbol{D} = \eta k_B T \end{aligned} \tag{5.3}$$

with unit $1/\sqrt{\text{time}}$ and correlation factor $\boldsymbol{D}$. Since the noise arises from interaction with different degrees of freedom and the energy in each degree of freedom depends on the accessible energy and, therefore, the temperature of the system, the noise is often considered thermal. Consequently, $k_B T$ stems from the thermal nature of the noise.

The final form of the LLG Eq. (5.2) is that of a stochastic differential equation. Since it describes the evolution of a collective excitation and includes dissipation, ultrafast thermodynamics can be used to study its behavior. That is done in Paper I, where the entropy production by the magnetization dynamics is determined.

5.2 Open System LLG Equation

Although the original LLG equation started as a phenomenological description, quantum mechanics provides a rigorous derivation, including higher interaction terms like nutation [32].

The starting point is a single spin $\boldsymbol{S}$ interacting with a magnetic field $\boldsymbol{B}(t)$, other spins and a bath:

$$H_{tot} = H_{\text{spin}} + H_{\text{bath}} + V_{\text{interaction}}\,. \tag{5.4}$$

If the bath is now assumed to consist of harmonic oscillators and to couple to the spin in all three dimensions, an exchange tensor emerges. After considering the equations of motion of the harmonic oscillators, two features emerge for the equation of motion

of a single spin. It is straightforward to map from a single spin to magnetization and therefore the features also hold for magnetization. The equation reads:

$$\dot{\boldsymbol{M}} = -\gamma \boldsymbol{M} \times \left(\boldsymbol{B}_{\text{eff}} + \boldsymbol{h}(t) + \int_{-\infty}^{t} \mathrm{d}t' \, \mathscr{K}(t - t') \boldsymbol{M}(t') \right) . \tag{5.5}$$

The first feature is the noise term, which is denoted h and describes the thermal fluctuations of the bath. It is determined by the type of coupling between spin and bath, as well as the harmonic oscillators in phononic form. In the original LLG equation, the stochastic term had to be added explicitly, while it naturally emerged in the quantum mechanical derivation. Additionally, the dependence on the coupling encodes possible frequency dependencies of the noise automatically. Therefore, it is always potentially colored.

Secondly, all motion except for precession and spin-spin interaction is encoded in a single interaction kernel $\mathscr{K}(t - t')$. This kernel only depends on the type of coupling between spin and bath. Therefore, it encodes all possible orders of coupling leading to all possible motions. That includes nutation, but is not limited to it. Since the coupling and not the effect leads to motion, the interaction kernel also acts as a memory kernel. Depending on the type of coupling, this leads to non-Markovian magnetization dynamics.

Importantly, here, the fluctuation and memory kernel (dissipation) are linked due to the underlying thermodynamic principles and microscopic dynamics. That is in contrast to the original LLG equation, where the addition of stochastic noise was only justified by phenomenological arguments, but never derived from thermodynamic principles.

The choice of the spectral density $I(\omega)$ further specifies the dynamics, because it details the coupling of the system to the bath. The Lorentzian spectral density is a possible choice as the kernel because its parameters can be chosen such that the Ohmic limit of Eq. (5.5) is obtained. That allows for comparison of the os-LLG to the original LLG equation with only precession, damping and noise terms.

It is not possible to choose the parameters to obtain a valid comparison to the inertial LLG equation, because the damping and the nutation term are the first and second term of the kernel expansion, respectively.

Therefore, any other choice of parameters for the Lorentzian includes more higher-order interaction terms than the other two LLG equations. This makes the os-LLG equation interesting from a theoretical point of view. In Paper III, we use it to investigate the Markovianity of ultrafast magnetization processes.

6

Induced Magnetization

Magnetization can arise intrinsically or can be induced by external forces. These forces include magnetic fields, electro-magnetic fields, and strain or stress [40]. Some of these mechanisms couple directly to the magnetization, while others do so indirectly. One example of an indirect way is axial phonon-induced magnetism. This phenomenon has been know experimentally for a few decades already [41], but has recently gained renewed attention [42].

That makes the phono-magnetic effect the main topic of this chapter.

6.1 Axial phonons

Phonons are the collective excitation of crystalline materials. They can be described in terms of the small ionic displacements $\boldsymbol{\tau}_{l\alpha}$ around their equilibrium positions $\boldsymbol{R}^{(0)}_{l\alpha}$. Due to the periodic lattice structure, it is convenient to Fourier transform the displacement $\mathscr{F}(\boldsymbol{\tau}_{l\alpha}) \rightarrow \boldsymbol{\tau}_{\boldsymbol{k}\alpha}$. Furthermore, it is common to incorporate the ionic mass M_α and define

$$\boldsymbol{u}_{\boldsymbol{k}\alpha} = \sqrt{M_\alpha}\boldsymbol{\tau}_{\boldsymbol{k}\alpha}. \tag{6.1}$$

This is the phonon mode for wave vector $\boldsymbol{k}$ and atom α in the unit cell.

Axial phonons are phonons carrying phonon angular momentum, which originates in the lattice vibrations [43, 44]:

$$\boldsymbol{J}^{\mathrm{ph}} = \sum_{l\alpha} M_\alpha \, \boldsymbol{\tau}_{l\alpha} \times \dot{\boldsymbol{\tau}}_{l\alpha} = \sum_{l\alpha} \boldsymbol{u}_{l\alpha} \times \dot{\boldsymbol{u}}_{l\alpha} \, . \tag{6.2}$$

Note that this notation is in real space again, where l denotes the lattice position and α the atom of the unit cell.

Such phonon angular momentum can be excited, e.g., by coherent laser excitation [3, 45], phonon-phonon scattering [46], ultrafast demagnetization [47], or thermal gradients [48]. Additionally, phonons should inherently carry angular momentum in magnetic materials with broken time-reversal symmetry.

6.2 Phono-magnetic effect

The naive approach to explaining the experimentally observed magnetization is to assume that the angular momentum of the axial phonon causes the magnetization directly. Since angular momentum is directly proportional to magnetization, the resulting magnetization takes the form

$$\boldsymbol{M} = \gamma \boldsymbol{J}^{\mathrm{ph}} \propto \boldsymbol{u}_{l\alpha} \times \dot{\boldsymbol{u}}_{l\alpha} \,. \tag{6.3}$$

This approach yields an induced magnetization of approximately $|\boldsymbol{M}| = 10^{-4}\mu_B$. But that is at least two orders of magnitude smaller than experimental results [23, 49–51].

This has sparked the theoretical interest, and the explanation is the topic of ongoing debate. There are several theories as to how the phonons induce the magnetization, and many include a coupling to the spin degrees of freedom.

Every theory uses different regimes and approximations, each fitting to a different situation. Paper II is a review of the different theoretical approaches and highlights three main frameworks—Floquet, adiabatic, and perturbative theories—that capture the interplay between electrons and phonons from different limiting perspectives. We discuss how these approaches are interconnected, as well as additional explanations invoking inertial effects. By investigating the limiting cases and finding the connections between perturbative, adiabatic, and Floquet-based approaches, the review shows that many of the theories are talking about the same microscopic effects.

7

Magnetic Quadrupoling

Magnetic phase transitions are not a new phenomenon, and they already played a role in induced magnetization (Chapter 6). On a more fundamental level, they are connected to non-equilibrium dynamics and can be described by the framework of free energy because they are a form of critical dynamics [52]. But they are neither theoretically, nor experimentally fully understood.

One interesting aspect is the possibility that two or more components of the magnetic order parameter interact and describe a new order. This is called a composite order and leads to many different possible phases. One example that has already been observed in magnetic systems is the quadrupole order. Both are explained in the following two sections and the last section of this chapter gives a preview of the work we are currently conducting.

Generally, quadrupoling in magnetic systems is interesting because it happens above the critical temperature of the magnetic phase but only at finite temperatures. That is because the thermal fluctuations that are present above the transition into the magnetic phase play a crucial role in making quadrupoling possible. A fluctuation of the local magnetization has a strong effect on the global magnetization if there is no coherent magnetic order present. These relatively large fluctuations lead to local orders of magnetization, and quadrupoling is one of them.

7.1 Composite Order

Order parameters are defined such that their expectation value vanishes in the non-ordered phase, and is non-zero within the phase.

There are materials and conditions under which the expectation value of a single

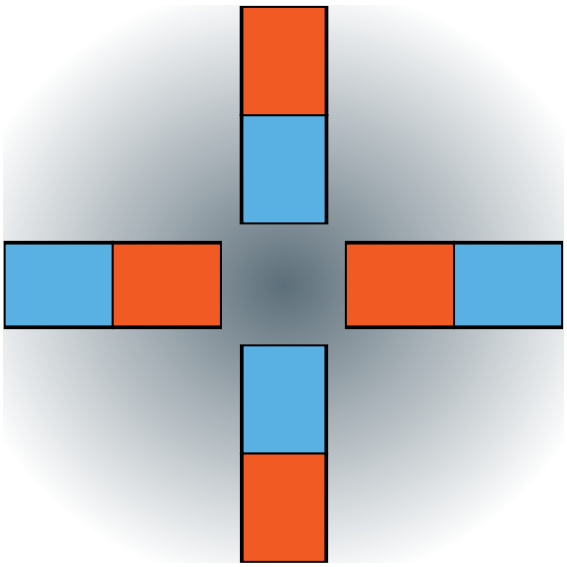

Figure 7.1: Four magnetic dipoles form a magnetic quadrupole. The resulting field vanishes quickly outside the pole itself.

order parameter vanishes, but the combination of two gives a non-zero contribution:

$$\langle \boldsymbol{A} \rangle = 0\,, \quad \langle \boldsymbol{B} \rangle = 0 \tag{7.1}$$

$$\langle \boldsymbol{A}\boldsymbol{B} \rangle \neq 0\,. \tag{7.2}$$

This indicates a new ordered phase, in addition to the phases of the respective single order parameters. It is described by the combination of two order parameters and therefore termed *composite order*.

There are many theoretical examples for composite orders. They include odd-frequency pairing [53, 54], composite U(1) orders, such as those composed of 2-component superconducting order parameters [55]. Recently, experiments found evidence that supports the existence of composite orders [5, 56–59]. Another example of a composite order is the magnetic quadrupole order, which is introduced in the next section.

7.2 Quadrupoling

A quadrupole order can, for example, occur in magnetic or electric systems. In the magnetic case, the quadrupole order looks as depicted in Fig. 7.1. Four magnetic dipoles are arranged such that they point towards a common center. The opposing magnets each have the same pole, positive-positive or negative-negative. As a consequence, there are four poles to be detected outside the arrangement, and the overall field vanishes more quickly than the field of a single dipole. In the electric case, the arrangement is

similarly composed of four electric dipoles, but the field of the quadrupole vanishes completely.

From a theoretical perspective, quadrupole order in magnetic systems generally emerges from the multipole expansion of the interaction energy

$$H_{int} = -\int \boldsymbol{\mu}(\boldsymbol{r}) \cdot \boldsymbol{H}(\boldsymbol{r}) d\boldsymbol{r} \tag{7.3}$$

between the magnetization density $\boldsymbol{\mu}$ and a magnetic field $\boldsymbol{H}$. The integration is performed over all space $\boldsymbol{r}$. This interaction energy can be expanded to the second order of the multipole expansion

$$H_{int}^{ME} = -\int r_i \mu_j(\boldsymbol{r}) \partial_i H_j(0) d\boldsymbol{r}\,, \tag{7.4}$$

where we assumed a homogeneous magnetic field. Consequently, the field is only a constant, and the remaining integral can be expressed as a sum over three terms

$$a = \frac{1}{3}\int \boldsymbol{r} \cdot \boldsymbol{\mu} d\boldsymbol{r} \tag{7.5}$$

$$\boldsymbol{t} = \frac{1}{2}\int \boldsymbol{r} \times \boldsymbol{\mu}(\boldsymbol{r}) d\boldsymbol{r} \tag{7.6}$$

$$q = \frac{1}{2}\int \left[r_i \mu_j + r_j \mu_i - \frac{2}{3}\delta_{ij} \boldsymbol{r} \cdot \boldsymbol{\mu}(\boldsymbol{r})\right] d\boldsymbol{r}\,. \tag{7.7}$$

The first one consists of the diagonal components of the magnetoelectric tensor and is referred to as the monopole. The second one is the toroidal moment, consisting of the symmetric and antisymmetric components. The third one is the quadrupole and contains the traceless components of the magnetoelectric tensor [60].

The order parameter for quadrupole order is a rank-two tensor. Imposing a vanishing trace and considering the symmetry of the system, five of the nine components are independent. For spin systems, the five components are combinations of the spin components making the quadrupole order a composite order.

In cubic symmetry, combinations of spin components transform as the two-dimensional representation E_g and the three-dimensional irreducible representation T_{2g}. The basis functions for the representations are

$$\Phi_{E_g} = \left(\frac{1}{\sqrt{2}}(\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2)\,, \frac{1}{\sqrt{6}}(\boldsymbol{S}_x^2 + \boldsymbol{S}_y^2 - 2\boldsymbol{S}_z^2)\right) \tag{7.8}$$

$$\boldsymbol{\Phi}_{T_g} = \sqrt{2}(\boldsymbol{S}_x\boldsymbol{S}_y\,, \boldsymbol{S}_y\boldsymbol{S}_z\,, \boldsymbol{S}_z\boldsymbol{S}_x)\,, \tag{7.9}$$

Each of these can be the order parameter of a quadrupole phase.

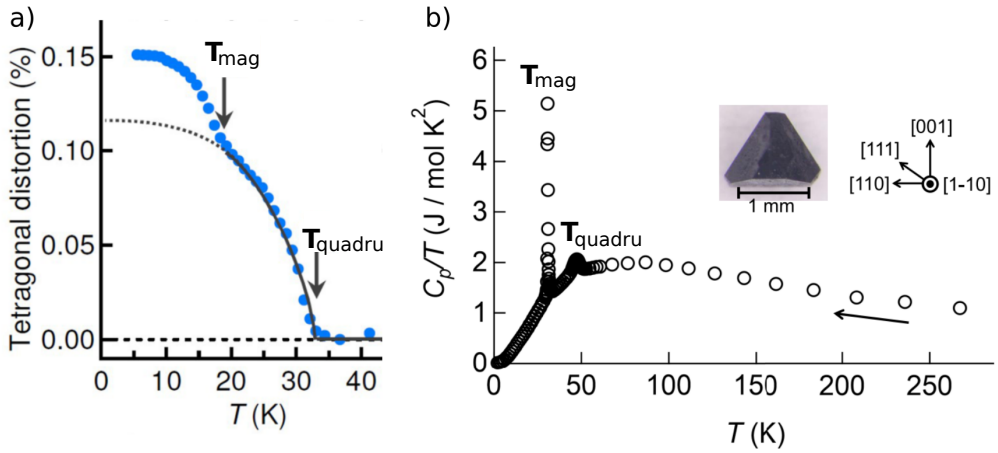

Figure 7.2: The tetragonal distortion and specific heat C_p indicate two phase transitions – one into magnetic and one into quadrupole ordering. a) The experimental data for the distortion of Ba_2MgReO_6 are obtained with x-ray diffraction [5]. b) The specific heat of $GdNb_4Se_8$ is obtained with optical measurements of the thermal relaxation [61].

7.3 Interesting Materials

Several experiments have looked into quadrupole order in different materials. Two of them found strong evidence of quadrupole order in Ba_2MgReO_6 [5, 57] and $GaNb_4Se_8$ [56, 61], respectively.

Both materials are Mott insulators and have strong spin-spin or spin-orbit interactions, which lead to strong magnetic anisotropies.

Two clear peaks in the specific heat of $GaNb_4Se_8$ are observed at $T_q = 50\,\mathrm{K}$ and $T_c = 33\,\mathrm{K}$ [56], shown in Fig. 7.2 b). The first one is the critical temperature of quadrupolar order, while the second one is the critical temperature of magnetic ordering. Their appearance in the specific heat means that we are talking about bulk phase transitions. Measurements of the magnetic susceptibility result in the same critical temperatures [61].

For Ba_2MgReO_6, the peaks in specific heat are at $T_q = 33\,\mathrm{K}$ and $T_c = 18\,\mathrm{K}$ [57]. These temperatures agree with the results from crystal structure distortion measurements [5], which are depicted in Fig. 7.2 a).

These experimental data already show that there is no universal ratio between the transition temperature for quadrupoling and magnetic ordering. Additionally, the crystal structure distortion seems to have a dependence on the quadrupole order.

Our current work investigates these statements with the help of statistical field theory as well as microscopic principles.

7.4 Field Theory for Quadrupoling

There are different explanations for the quadrupole order measured in experiments, but they are only valid for very specific materials or conditions [5, 62, 63]. A more general and unifying description is missing.

To address this, we employ statistical field theory and determine the gap equation and transition temperature independently of the underlying microscopic interactions.

We begin with the Landau free energy of magnetization $\boldsymbol{M}$ for cubic symmetry [64–66]

$$f(\boldsymbol{M},T) = f_0(T) + c\,(\nabla \boldsymbol{M})^2 + \frac{\alpha(T-T_c)}{2}\boldsymbol{M}^2 + \beta_1\left(M_x^4 + M_y^4 + M_z^4\right) + \beta_2\left(M_x^2M_y^2 + M_y^2M_z^2 + M_z^2M_x^2\right). \quad (7.10)$$

The anisotropies are dependent on the material-specific coefficients β_1 and β_2. In contrast to the critical temperature T_c, at which the phase transition to the ordered state happens, the anisotropy factors are not easily accessible individually in experiments.

After performing a Hubbard-Stratonovich transformation into the order parameter space of the quadrupole order (compare Eq. (7.8)), we can develop the interaction terms to second order. That gives us a gap equation, which becomes

$$1 = -\frac{3}{2}\frac{\beta_-}{\beta}\Gamma_0 = \frac{3}{16\pi c^{\frac{3}{2}}}\frac{\left(\beta_2 - 2\beta_1\right)k_BT}{\sqrt{\alpha(T-T_c)}} \quad (7.11)$$

when assuming a s-wave gap. We can immediately see that the gap strongly depends on the anisotropy of the material, which is illustrated in Fig. 7.3, where three different cases of the gap equation, which differ by the anisotropy of the material, are presented. Firstly, some systems have no solution to the gap equation because their anisotropies are too strong. There are systems where the minimum at $2\,T_c$ exactly coincides with the solution of Eq. (7.11). This is the case for

$$\beta_-^* = -\frac{8\pi c^{\frac{3}{2}}\sqrt{\alpha}}{3k_B\sqrt{T_c}} \quad (7.12)$$

If $\beta_- > \beta_-^*$, then the gap equation has a solution $T_q < 2T_c$. In these cases, the first solution of the gap equation appears at $T_q > T_c$ and has the general expression

$$T_q = \frac{\alpha - \sqrt{\alpha\left(\alpha - \left(\frac{3k_B}{8\pi c^{\frac{3}{2}}}\right)^2 T_c\beta_-^2\right)}}{2\left(\frac{3k_B}{16\pi c^{\frac{3}{2}}}\right)^2\beta_-^2} \quad (7.13)$$

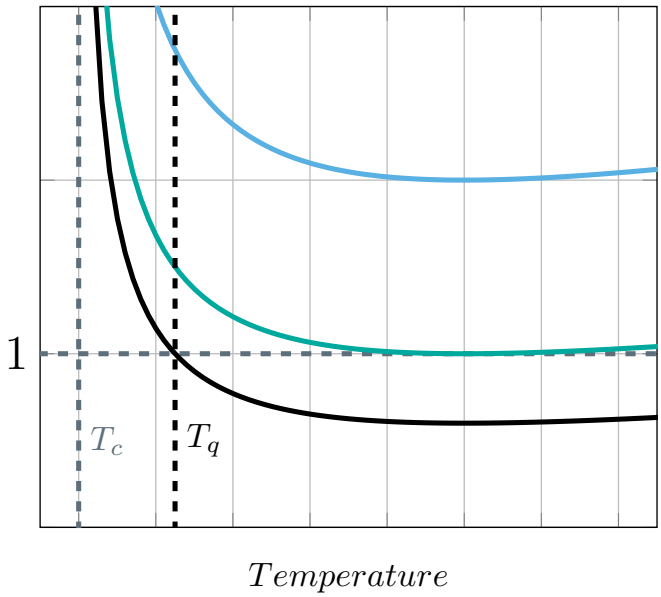

Figure 7.3: Gap equation for quadrupole transition. Depending on the anisotropy, the gap equation has no solutions ($\beta_- < \beta_-^*$), one solution at $T_q = 2\,T_c$ ($\beta_- = \beta_-^*$), or two solutions with $T_c < T_q < 2\,T_c$ ($\beta_- > \beta_-^*$).

and depends strongly on the anisotropy parameters.

The next steps in this work involve formulating the free energy of the quadrupole phase. It contains information about the interaction with other order parameters and properties of the system. One of the interacting properties is strain, which has been experimentally measured [5] and theoretically predicted [62]. Consequently, finding an explicit expression for the coupling between quadrupole order and strain gives a strategy to verify our theoretical approach and predict measurement outcomes for experiments with other materials.

8

Summary of papers

Paper I

Ultrafast Entropy Production in Driven Magnets

We present an ultrafast thermodynamics framework to model heat generation and entropy production in laser-driven ferromagnetic systems. By establishing a connection between the magnetic field strength of the laser pulse and magnetization dynamics, we model time-dependent entropy production rates and deduce the associated heat dissipation in epitaxial and polycrystalline FeNi and CoFeB thin films. Our theoretical predictions are validated by comparison to experimental magnetization dynamics data, shedding light on thermodynamic processes on picosecond timescales. Crucially, we incorporate recently observed inertial spin dynamics, to describe their impact on heat generation in pump-probe experiments. As such, this formalism provides novel insights into controlling heat production in magnetic systems and contributes to advancing the understanding of nonequilibrium thermodynamics in magnetic systems, with implications for future experimental protocols in spintronics and nanotechnology.

Paper II

Axial phono-magnetic effects

Recent experimental findings for the strength of magnetization induced by circularly polarized phonons have sparked great theoretical interest. The measured strength of magnetization is orders of magnitude higher than predicted by theories based on classic ionic motion. This review presents an overview of the many theoretical explanations

developed to resolve this discrepancy, and of the experimental evidence for different material classes and with different experimental techniques. Most explanations can be categorized into Floquet, adiabatic, and perturbative approaches. They all have in common that electrons and phonons interact, and we show that they are limiting cases of each other. Furthermore, there are explanations based on inertial effects, which we also contextualize.

Paper III

Entropy Production as Markovianity Measure in Magnetization Dynamics

Ultrafast magnetization processes are routinely described by the Landau-Lifshitz-Gilbert equation. Recent experimental and theoretical advancements sparked extensions of its original form by inertial terms and gave a microscopic derivation of the original and additional terms. Since inertial terms and ultrafast dynamics are both known to cause non-Markovian behavior, we investigate the Markovianity of spin dynamics, spin dynamics including inertial effects, and spin dynamics of an open system.

We use entropy production rates as the quantitative measure for Markovianity, assuming that their negativity is a sufficient condition for non-Markovian dynamics. Our simulations are based on the Kullback-Leibler divergence. We find different degrees of Markovianity for the different spin dynamics. We also show a dependence of the Markovianity on the geometry of the system, which has implications for experimental setups.

9

Summary and Outlook

The research question at the beginning of this work was:

> How can we combine thermodynamics, collective phenomena and mesoscopic theories of magnetism to describe non-equilibrium magnetization dynamics?

The answer has been approached in three different ways. Firstly, the framework of ultrafast thermodynamics has been defined based on stochastic thermodynamics. We showed that it can describe the entropy production in ultrafast magnetization dynamics. The entropy production depends only on the magnetization dynamics and the pump laser. Consequently, the entropy production becomes experimentally accessible. Additionally, we see clear changes in the magnitude of the entropy production with different material parameters like damping and relaxation times. This makes the entropy production also a material-sensitive measure. Furthermore, we managed to show with simulations of entropy production for different types of magnetization dynamics that the entropy production rate is an indicator for the Markovianity of the system.

Secondly, we investigated the currently debated phono-magnetic effects. The resulting review includes an overview of many of the magnetization experiments. This reveals that the strength of the magnetization resulting from phonon excitation depends on the material and the excited phonon mode. Furthermore, the strength ranges over three orders of magnitude. However, the main focus of the review is the theoretical explanation of the phono-magnetic effect. The numerous theories can be grouped into perturbative, adiabatic, and Floquet-based approaches. Although they start with slightly different assumptions, we were able to show that they all agree in the limiting cases. This is a great step towards finding a general mesoscopic theory to explain the vast range of experimental results.

Thirdly, we investigate the quadrupole phase transition with statistical field theory. We derived exact analytical forms for the gap equation, which shows a strong dependence of the gap on the anisotropy of the underlying material. The possibility of linking the quadrupole order to strain makes predictions about the lattice distortion upon entering the quadrupole phase possible. The lattice distortions have been measured before, which links our mesoscopic theory to experimental results.

Therefore, we conclude that the combination of thermodynamics, collective phenomena, and mesoscopic theories of magnetization is a strong tool to investigate the non-equilibrium dynamics of magnetization.

There are three possible ways to continue our work and further advance in answering our research questions.

In Chapter 5, we briefly introduced two different forms of stochastic noise in the magnetization dynamics. These two types are called “additive” and “multiplicative” after their form of appearance. Currently, there is no thorough understanding of the microscopic origin of additive noise, although it is commonly used. The multiplicative noise can be derived directly from quantum mechanical coupling between system and bath, but it does not capture the longitudinal fluctuations. Therefore, it is of interest to not only find the missing microscopic origin of additive noise but also to investigate the consequences of using one or the other form of noise to describe magnetization dynamics.

The dependencies of the quadrupole order derived in Sect. 7.4 suggest the possibility of manipulating the phase transition. Especially the direct coupling to strain makes it interesting to investigate driving protocols of quadrupole order. That could make this otherwise rarely observed ordering more accessible, which could give experimental proof to our mesoscopic theory.

The broadest resulting research question is, however, whether we can use entropy production to investigate and describe phase transitions. Entropy production has proven to give an interesting perspective on non-equilibrium dynamics within an ordered phase. Directly at the phase transition, there are two competing orders, and the system should choose the one with the higher entropy. But there is no theoretical model describing this situation yet. Additionally, the system has to go through some kind of transient order, which is neither disordered nor completely ordered. If this state maximizes the entropy under certain conditions, it would become metastable and experimentally accessible. That would open up new possibilities for targeted material design. Therefore, it would be interesting to extend the framework of entropy production to phase transitions.

Acknowledgments

This work has happened in the last two years - alongside many other things. Many people and hours of sport helped me stay sane and motivated during the highs and lows. I want to specifically thank my supervisor Matthias, who guided me through this journey so far, and I'm happy to have him in my corner for the next years as well. I want to thank my colleagues and friends Esmée and Natalia for sharing the daily stories of successes, frustrations and administrative hustles. I want to thank my parents and my best friend. You helped me to stay motivated and positive when I was not so sure anymore.

At last, I also want to thank DrGENIE for giving me the opportunity to work on equality, diversity and inclusion during my PhD and therefore to shape our community towards an even more welcoming place.

Sometimes, all it takes is 8 minutes from a friend, colleague or stranger to stop you from drowning in your own thoughts. So thank you to all of the people above and everyone else who gave me 8 minutes of their time.

Bibliography

[1] S. R. Tauchert, M. Volkov, D. Ehberger, D. Kazenwadel, M. Evers, H. Lange, A. Donges, A. Book, W. Kreuzpaintner, U. Nowak, *et al.*, *Polarized phonons carry angular momentum in ultrafast demagnetization,* Nature **602**, 73 (2022). doi:10.1038/s41586-021-04306-4.

[2] V. Unikandanunni, R. Medapalli, M. Asa, E. Albisetti, D. Petti, R. Bertacco, E. E. Fullerton, and S. Bonetti, *Inertial Spin Dynamics in Epitaxial Cobalt Films,* Physical Review Letters **129**, 237201 (2022). doi:10.1103/PhysRevLett.129.237201.

[3] M. Basini, M. Pancaldi, B. Wehinger, M. Udina, V. Unikandanunni, T. Tadano, M. C. Hoffmann, A. V. Balatsky, and S. Bonetti, *Terahertz electric-field-driven dynamical multiferroicity in $SrTiO_3$,* Nature **628**, 534 (2024). doi:10.1038/s41586-024-07175-9.

[4] A. Kirilyuk, A. V. Kimel, and T. Rasing, *Ultrafast optical manipulation of magnetic order,* Reviews of Modern Physics **82**, 2731 (2010). doi:10.1103/RevModPhys.82.2731.

[5] D. Hirai, H. Sagayama, S. Gao, H. Ohsumi, G. Chen, T.-h. Arima, and Z. Hiroi, *Detection of multipolar orders in the spin-orbit-coupled 5d Mott insulator Ba_2MgReO_6,* Physical Review Research **2**, 022063 (2020). doi:10.1103/PhysRevResearch.2.022063.

[6] M. Kardar, *Statistical physics of fields* (Cambridge University Press, 2007).

[7] M. Kardar, *Statistical physics of particles* (Cambridge University Press, 2007).

[8] U. Seifert, *Stochastic thermodynamics, fluctuation theorems and molecular machines,* Reports on Progress in Physics **75**, 126001 (2012). doi:10.1088/0034-4885/75/12/126001.

[9] P. Strasberg and M. Esposito, *Non-Markovianity and negative entropy production rates,* Physical Review E **99**, 012120 (2019). doi:10.1103/PhysRevE.99.012120.

[10] P. Strasberg, *Quantum Stochastic Thermodynamics* (Oxford University Press, 2022). ISBN 0192895583. doi:10.1093/oso/9780192895585.001.0001.

[11] G. T. Landi and M. Paternostro, *Irreversible entropy production: From classical to quantum,* Reviews of Modern Physics **93**, 035008 (2021). doi:10.1103/RevModPhys.93.035008.

[12] L. Caprini, H. Löwen, and R. M. Geilhufe, *Ultrafast entropy production in pump-probe experiments,* Nature Communications **15**, 94 (2024). doi:10.1038/s41467-023-44277-w.

[13] U. Seifert, *Stochastic thermodynamics* (Cambridge University Press, 2025). doi:10.1017/9781009024358.

[14] L. Caprini, U. M. B. Marconi, A. Puglisi, and A. Vulpiani, *The entropy production of Ornstein–Uhlenbeck active particles: a path integral method for correlations,* Journal of Statistical

Mechanics: Theory and Experiment **2019**, 053203 (2019). doi:10.1088/1742-5468/ab14dd.

[15] R. E. Spinney and I. J. Ford, *Nonequilibrium Thermodynamics of Stochastic Systems with Odd and Even Variables,* Physical Review Letters **108**, 170603 (2012). doi:10.1103/PhysRevLett.108.170603.

[16] R. E. Spinney and I. J. Ford, *Entropy production in full phase space for continuous stochastic dynamics,* Physical Review E **85**, 051113 (2012). doi:10.1103/PhysRevE.85.051113.

[17] D. Chaudhuri, *Entropy production by active particles: Coupling of odd and even functions of velocity,* Physical Review E **94**, 032603 (2016). doi:10.1103/PhysRevE.94.032603.

[18] F. Zamponi, F. Bonetto, L. F. Cugliandolo, and J. Kurchan, *A fluctuation theorem for non-equilibrium relaxational systems driven by externalforces,* Journal of Statistical Mechanics: Theory and Experiment **2005**, P09013 (2005). doi:10.1088/1742-5468/2005/09/P09013.

[19] T. Palstra, A. Menovsky, J. Van den Berg, A. Dirkmaat, P. Kes, G. Nieuwenhuys, and J. Mydosh, *Superconducting and magnetic transitions in the heavy-fermion system URu_2Si_2,* Physical Review Letters **55**, 2727 (1985). doi:10.1103/PhysRevLett.55.2727.

[20] R. Livi and P. Politi, *Nonequilibrium statistical physics: a modern perspective* (Cambridge University Press, 2017). doi:10.1017/9781107278974.

[21] E. Beaurepaire, J.-C. Merle, A. Daunois, and J.-Y. Bigot, *Ultrafast spin dynamics in ferromagnetic nickel,* Physical Review Letters **76**, 4250 (1996). doi:10.1103/PhysRevLett.76.4250.

[22] K. Neeraj, N. Awari, S. Kovalev, D. Polley, N. Zhou Hagström, S. S. P. K. Arekapudi, A. Semisalova, K. Lenz, B. Green, J.-C. Deinert, *et al.*, *Inertial spin dynamics in ferromagnets,* Nature Physics **17**, 245 (2021). doi:10.1038/s41567-020-01040-y.

[23] M. Basini, M. Pancaldi, B. Wehinger, M. Udina, V. Unikandanunni, T. Tadano, M. C. Hoffmann, A. V. Balatsky, and S. Bonetti, *Terahertz electric-field-driven dynamical multiferroicity in $SrTiO_3$,* Nature , (2024). doi:10.1038/s41586-024-07175-9.

[24] D. Bossini, D. M. Juraschek, R. M. Geilhufe, N. Nagaosa, A. V. Balatsky, M. Milanović, V. V. Srdić, P. Šenjug, E. Topić, D. Barišić, *et al.*, *Magnetoelectrics and multiferroics: theory, synthesis, characterisation, preliminary results and perspectives for all-optical manipulations,* Journal of Physics D: Applied Physics **56**, 273001 (2023). doi:10.1088/1361-6463/acc8e1.

[25] A. De, J. Schlegel, A. Lentfert, L. Scheuer, B. Stadtmüller, P. Pirro, G. von Freymann, U. Nowak, and M. Aeschlimann, *Nutation: separating the spin from its magnetic moment,* arXiv:2405.01334 , (2024). https://doi.org/10.48550/arXiv.2405.01334.

[26] M. Mansuripur, *The magneto-optical Kerr effect,* Optics and Photonics News **11**, 34 (2000). doi:10.1017/CBO9780511803796.016.

[27] P. Pershan, *Magneto-optical effects,* Journal of Applied Physics **38**, 1482 (1967). doi:10.1063/1.1709678.

[28] D. Bossini, S. Dal Conte, G. Cerullo, O. Gomonay, R. Pisarev, M. Borovsak, D. Mihailovic, J. Sinova, J. Mentink, T. Rasing, *et al.*, *Laser-driven quantum magnonics and terahertz dy-*

namics of the order parameter in antiferromagnets, Physical Review B **100**, 024428 (2019). doi:10.1103/physrevb.100.024428.

[29] T. L. Gilbert, *A phenomenological theory of damping in ferromagnetic materials,* IEEE Transactions on Magnetics **40**, 3443 (2004). doi:10.1109/TMAG.2004.836740.

[30] J.-E. Wegrowe and M.-C. Ciornei, *Magnetization dynamics, gyromagnetic relation, and inertial effects,* American Journal of Physics **80**, 607 (2012). doi:10.1063/1.4712056.

[31] R. Mondal, M. Berritta, A. K. Nandy, and P. M. Oppeneer, *Relativistic theory of magnetic inertia in ultrafast spin dynamics,* Physical Review B **96**, 024425 (2017). doi:10.1103/PhysRevB.96.024425.

[32] J. Anders, C. R. Sait, and S. A. Horsley, *Quantum Brownian motion for magnets,* New Journal of Physics **24**, 033020 (2022). doi:10.1088/1367-2630/ac4ef2.

[33] S. Bhattacharjee, L. Nordström, and J. Fransson, *Atomistic Spin Dynamic Method with both Damping and Moment of Inertia Effects Included from First Principles,* Physical Review Letter **108**, 057204 (2012). doi:10.1103/PhysRevLett.108.057204.

[34] D. Böttcher and J. Henk, *Significance of nutation in magnetization dynamics of nanostructures,* Physical Review B **86**, 020404 (2012). doi:10.1103/PhysRevB.86.020404.

[35] Y. Li, A.-L. Barra, S. Auffret, U. Ebels, and W. E. Bailey, *Inertial terms to magnetization dynamics in ferromagnetic thin films,* Physical Review B **92**, 140413 (2015). doi:10.1103/PhysRevB.92.140413.

[36] M. d'Aquino, S. Perna, M. Pancaldi, R. Hertel, S. Bonetti, and C. Serpico, *Micromagnetic study of inertial spin waves in ferromagnetic nanodots,* Physical Review B **107**, 144412 (2023). doi:10.1103/PhysRevB.107.144412.

[37] H. Ebert, S. Mankovsky, D. Ködderitzsch, and P. J. Kelly, *Ab Initio Calculation of the Gilbert Damping Parameter via the Linear Response Formalism,* Physical Review Letters **107**, 066603 (2011). doi:10.1103/PhysRevLett.107.066603.

[38] J. Anders, C. R. J. Sait, and S. A. R. Horsley, *Quantum Brownian motion for magnets,* New Journal of Physics **24**, 033020 (2022). doi:10.1088/1367-2630/ac4ef2.

[39] P.-W. Ma and S. L. Dudarev, *Longitudinal magnetic fluctuations in Langevin spin dynamics,* Physical Review B **86**, 054416 (2012). doi:10.1103/PhysRevB.86.054416.

[40] J. C. Maxwell, *Induced Magnetization.* In , *A Treatise on Electricity and Magnetism* (Oxford, 1998). doi:10.1093/oso/9780198503743.003.0004.

[41] G. Schaack, *Magnetic field dependent splitting of doubly degenerate phonon states in anhydrous cerium-trichloride,* Zeitschrift für Physik B Condensed Matter and Quanta **26**, 49 (1977). doi:10.1007/BF01313371.

[42] R. M. Geilhufe, V. Juričić, S. Bonetti, J.-X. Zhu, and A. V. Balatsky, *Dynamically induced magnetism in $KTaO_3$,* Physical Review Research **3**, L022011 (2021). doi:10.1103/PhysRevResearch.3.L022011.

[43] D. M. Juraschek, R. M. Geilhufe, H. Zhu, M. Basini, P. Baum, A. Baydin, S. Chaudhary, M. Fechner, B. Flebus, G. Grissonnanche, *et al.*, *Chiral phonons,* Nature Physics , 1 (2025). doi:10.1038/s41567-025-03001-9.

[44] L. Zhang and Q. Niu, *Angular Momentum of Phonons and the Einstein–de Haas Effect,* Physical Review Letters **112**, 085503 (2014). doi:10.1103/PhysRevLett.112.085503.

[45] C. S. Davies, F. G. N. Fennema, A. Tsukamoto, I. Razdolski, A. V. Kimel, and A. Kirilyuk, *Phononic switching of magnetization by the ultrafast Barnett effect,* Nature **628**, 540 (2024). doi:10.1038/s41586-024-07200-x.

[46] O. Minakova, C. Paiva, M. Frenzel, M. S. Spencer, J. M. Urban, C. Ringkamp, M. Wolf, G. Mussler, D. M. Juraschek, and S. F. Maehrlein, *Direct observation of angular momentum transfer among crystal lattice modes,* arxiv:2503.11626 , (2025).

[47] S. R. Tauchert, M. Volkov, D. Ehberger, D. Kazenwadel, M. Evers, H. Lange, A. Donges, A. Book, W. Kreuzpaintner, U. Nowak, and P. Baum, *Polarized phonons carry angular momentum in ultrafast demagnetization,* Nature **602**, 73 (2022). doi:10.1038/s41586-021-04306-4.

[48] H. Zhang, N. Peshcherenko, F. Yang, T. Ward, P. Raghuvanshi, L. Lindsay, C. Felser, Y. Zhang, J.-Q. Yan, and H. Miao, *Observation of phonon angular momentum,* arXiv:2409.13462 , (2024).

[49] B. Cheng, T. Schumann, Y. Wang, X. Zhang, D. Barbalas, S. Stemmer, and N. P. Armitage, *A Large Effective Phonon Magnetic Moment in a Dirac Semimetal,* Nano Letters **20**, 5991 (2020). doi:10.1021/acs.nanolett.0c01983.

[50] A. Baydin, F. G. G. Hernandez, M. Rodriguez-Vega, A. K. Okazaki, F. Tay, G. T. Noe, I. Katayama, J. Takeda, H. Nojiri, P. H. O. Rappl, E. Abramof, G. A. Fiete, and J. Kono, *Magnetic Control of Soft Chiral Phonons in PbTe,* Physical Review Letters **128**, 075901 (2022). doi:10.1103/PhysRevLett.128.075901.

[51] F. G. G. Hernandez, A. Baydin, S. Chaudhary, F. Tay, I. Katayama, J. Takeda, H. Nojiri, A. K. Okazaki, P. H. O. Rappl, E. Abramof, M. Rodriguez-Vega, G. A. Fiete, and J. Kono, *Observation of interplay between phonon chirality and electronic band topology,* Science Advances **9**, eadj407 (2023). doi:10.1126/sciadv.adj4074.

[52] P. C. Hohenberg and B. I. Halperin, *Theory of dynamic critical phenomena,* Reviews of Modern Physics **49**, 435 (1977). doi:10.1103/RevModPhys.49.435.

[53] A. Balatsky and J. Bonca, *Even-and odd-frequency pairing correlations in the one-dimensional t-J-h model: A comparative study,* Physical Review B **48**, 7445 (1993).

[54] J. Linder and A. V. Balatsky, *Odd-frequency superconductivity,* Reviews of Modern Physics **91**, 045005 (2019). doi:10.1103/RevModPhys.91.045005.

[55] E. Babaev, A. Sudbø, and N. Ashcroft, *A superconductor to superfluid phase transition in liquid metallic hydrogen,* Nature **431**, 666 (2004). doi:10.1038/nature02910.

[56] H. Ishikawa, T. Yajima, A. Matsuo, Y. Ihara, and K. Kindo, *Nonmagnetic ground states and a possible quadrupolar phase in 4d and 5d lacunar spinel selenides GaM_4Se_8 (M= Nb, Ta),* Physical review letters **124**, 227202 (2020). doi:10.1103/PhysRevLett.124.227202.

[57] J. Pásztorová, A. M. Tehrani, I. Živković, N. A. Spaldin, and H. M. Rønnow, *Experimental and theoretical thermodynamic studies in Ba_2MgReO_6—the ground state in the context of Jahn-Teller effect,* Journal of Physics: Condensed Matter **35**, 245603 (2023). doi:10.1088/1361-648X/acc62a.

[58] C.-w. Cho, J. Lyu, L. An, T. Han, K. T. Lo, C. Y. Ng, J. Hu, Y. Gao, G. Li, M. Huang, *et al.*, *Nodal and nematic superconducting phases in $NbSe_2$ monolayers from competing superconducting channels,* Physical Review Letters **129**, 087002 (2022).

[59] V. Grinenko, D. Weston, F. Caglieris, C. Wuttke, C. Hess, T. Gottschall, I. Maccari, D. Gorbunov, S. Zherlitsyn, J. Wosnitza, *et al.*, *State with spontaneously broken time-reversal symmetry above the superconducting phase transition,* Nature Physics **17**, 1254 (2021).

[60] F. Thöle and N. A. Spaldin, *Magnetoelectric multipoles in metals,* Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences **376**, 20170450 (2018). doi:10.1098/rsta.2017.0450.

[61] S. Kitou, M. Gen, Y. Nakamura, Y. Tokunaga, and T.-h. Arima, *Cluster Rearrangement by Chiral Charge Order in Lacunar Spinel $GaNb_4Se_8$,* Chemistry of Materials **36**, 2993 (2024). doi:10.1021/acs.chemmater.4c00118.

[62] D. Fiore Mosca, C. Franchini, and L. V. Pourovskii, *Interplay of superexchange and vibronic effects in the hidden order of Ba_2MgReO_6 from first principles,* Physical Review B **110**, L201101 (2024). doi:10.1103/PhysRevB.110.L201101.

[63] M.-T. Suzuki, H. Ikeda, and P. M. Oppeneer, *First-principles theory of magnetic multipoles in condensed matter systems,* Journal of the Physical Society of Japan **87**, 041008 (2018). doi:10.7566/JPSJ.87.041008.

[64] R. M. Geilhufe and W. Hergert, *GTPack: A Mathematica group theory package for application in solid-state physics and photonics,* Frontiers in Physics **6**, 86 (2018). doi:10.3389/fphy.2018.00086.

[65] O. V. Barabanov and A. Kosogor, *Landau theory of ferroelastic phase transitions: Application to martensitic phase transformations,* Low Temperature Physics **48**, 206 (2022). doi:10.1063/10.0009538.

[66] A. Devonshire, *Theory of ferroelectrics,* Advances in Physics **3**, 85 (1954). doi:10.1080/00018735400101173.