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**Magnetic and dilatometric studies of the
correlated systems TbInO_3 , $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$,
 $\text{Er}_2\text{Te}_4\text{O}_{11}$, and Fe_3GaTe_2**

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Abstract

The correlated systems TbInO_3 , $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$, $\text{Er}_2\text{Te}_4\text{O}_{11}$, and Fe_3GaTe_2 are investigated by means of high-resolution capacitance dilatometry, AC & DC SQUID magnetometry and high-field/frequency electron spin resonance (HF-ESR) spectroscopy down to low temperatures and in high magnetic fields. Magnetic ordering at low temperatures is suppressed in these systems. For the quantum spin liquid candidate TbInO_3 dilatometric and magnetometric data confirm the absence of long-range magnetic order. A pronounced easy-plane anisotropy is confirmed. Low temperature ($T \geq 0.4$ K) DC and AC magnetometry is used to study the evolution of a glassy regime in $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ ($x = 0$ & 0.5). A hysteresis in field and temperature and freezing processes below 1 K serve as evidence for the glassy phase. Above 7 K a field induced slow relaxation regime is observed. The phase diagram is constructed which shows the suppression of the glassy phases upon increased Ti doping. For $\text{Er}_2\text{Te}_4\text{O}_{11}$, the phase diagram is determined by magnetization studies. The data reveal a field stabilized region of slow spin relaxation above 2 K as well as a crossover into an antiferromagnetically dominated regime below 0.5 K. High-field magnetization data further evidence geometric frustration. The two-dimensional van der Waals ferromagnet Fe_3GaTe_2 is investigated using HF-ESR with $B \parallel c$. While the resonance branches suggest a behavior qualitatively similar to the related compounds Fe_nGTe_2 ($n = 3 \dots 5$; $G = \text{Ga}, \text{Ge}$), the occurrence of a gapless branch is unreported to date in this class of materials.

Kurzzusammenfassung

Mittels hochauflösender Kapazitätsdilatometrie, AC & DC SQUID Magnetometrie und hochfrequenter Elektronenspinresonanz-Spektroskopie (HF-ESR) sind die stark korrelierten Materialien TbInO_3 , $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$, $\text{Er}_2\text{Te}_4\text{O}_{11}$ und Fe_3GaTe_2 im Tieftemperatur- und Hochfeldbereich untersucht worden. Diese Systeme zeichnen sich alle durch eine unterdrückte magnetische Ordnung bei tiefen Temperaturen aus. TbInO_3 wird als mögliche Realisation einer Quantenspinflüssigkeit (QSL) angesehen. Mithilfe von Dilatometrie und Magnetometrie wurden darin keine Anzeichen einer langreichweitigen magnetischen Ordnung gefunden. Das Vorliegen einer signifikanten magnetischen Anisotropie mit einer leichten Ebene konnte bestätigt werden. Mithilfe von niedrig-Temperatur AC und DC Magnetometrie bis zu 0.4 K wurde ein glass-artiges Regime im Terbiumzirconat $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ ($x = 0$ & 0.5) nachgewiesen. Insbesondere dienen magnetische Hysterese- und Einfrierprozesse unterhalb von 1 K sowie ein im Magnetfeld stablierter Bereich langsamer Spinrelaxation oberhalb von 7 K als Hinweise darauf. Aus diesen Beobachtungen wird ein magnetisches Phasendiagramm konstruiert. Daraus wird ersichtlich, dass die Spinglass-artigen Eigenschaften durch eine Erhöhung des Titan-Anteils unterdrückt werden. Für $\text{Er}_2\text{Te}_4\text{O}_{11}$ wird das Phasendiagramm präsentiert, welches sich auf Magnetometrie-Daten im Tieftemperaturbereich stützt. Darin ist eine im Magnetfeld stabilisierte Region langsamer Spinrelaxationen oberhalb von 2 K beschrieben. Außerdem wurde ein Crossover in einen antiferromagnetisch dominierten Bereich unterhalb von 0.5 K gefunden. Aus Hochfeld-Magnetisierungsdaten wird die zugrundeliegende geometrische Frustration bis 14 T ersichtlich. Die magnetischen Eigenschaften des zweidimensionalen van der Waals Ferromagnets Fe_3GaTe_2 entlang der c -Achse wurden mittels HF-ESR untersucht. Die so gefundenen Resonanzlinien sind analog zu dem Verhalten der verwandten Systeme der Klasse Fe_nGTe_2 ($n = 3 \dots 5$; $G = \text{Ga}, \text{Ge}$), wohingegen eine zweite, Energielücken-freie Resonanzlinie wurde bisher in der Literatur noch nicht erwähnt ist.

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1 Introduction

A real scientific mystery is worth pursuing
to the end of the Earth for its own sake,
independently of any obvious practical
importance or intellectual glamour.

Philip W. Anderson [1]

Naively, one expects that physical systems with finite interactions assume an ordered ground state. There are however systems which defy this expectation. They possess a structure which prevents a well-defined singular ground state and allow the system to avoid long-range ordering. Underlying this are competing interactions and geometric constraints [2]. A famous example of a system with those constraints and strong interactions are so-called quantum spin liquids (QSL). They have a manifold of low energy states which hinder them from developing long-range spin order even at very low temperatures [3]. One class of materials where these conditions are predicted to be met are those in which their magnetic interactions are restricted to certain lower dimensional structures such as two-dimensional planes with triangular arrangements of spins as described by Wannier in 1950 [4]. This would later be referred to as frustration. Additional disorder in the interaction- or crystalline environment may result in many closely spaced metastable states, causing a rich glassy behavior characterized by nontrivial effects such as slow spin dynamics and memory effects in their magnetization [5] [6] [7]. Geometric constraints in the spin arrangement and disorder allow the quantum nature of the magnetism in correlated materials to persevere to the macroscopic scale.

Research on Quantum Spin Liquids began in 1973 when Anderson proposed Resonating Valence Bond (RVB) states as a new antiferromagnetic state [8]. About its nature he said: "we really know very little about it". In QSLs quantum fluctuations of the spins prevent order even in the absence of thermal fluctuations. To date, no definite QSL has been found [9]. The reason for the difficult search is that it is not yet clear which experimental feature would unambiguously indicate a QSL state as its definition of *not* being "a symmetry-broken state with conventional order" is negative. Experimentally, there are a few systems which are vigorously investigated

with regards to possibly possessing a QSL state [3], some of them are based on organic compounds like κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_2$ [10] [11] or EtMe $_3$ Sb[Pd(dmit) $_2$] $_2$ [12], others are inorganic like volborthite [13], herbertsmithite [14], vesignieite [15], Na $_4$ Ir $_3$ O $_8$ [16], or α -RuCl $_3$ [17]. They take on different crystal structures like triangular or Kagomé lattices [3]. On a (triangular) honeycomb lattice, QSLs are predicted to exist by means of the Kitaev model [18].

Canella and Mydosh found the first evidence for a different phenomenon, spin glasses, by studying the low temperature magnetic behavior of a highly dilute Au:Fe alloy. This revealed "a more perfect antiferromagnetic order than that expected for a random alloy" and a peak in the ac susceptibility [19]. In spin glasses, the random distribution of spins and their local environments suppress magnetic ordering. Spin glass behavior has been found in both dilute alloys such as Au:Fe and Cu:Mn [20] [21] and in insulators such as Eu $_x$ Sr $_{1-x}$ S $_y$ Se $_{1-y}$ [22]. Anderson [23] characterized spin glasses as possessing both frustrations and randomness [24]. Early theoretical models for spin-glasses such as those presented by Sherrington and Kirkpatrick [25] or Edwards and Anderson [26] have been improved upon by the likes of e.g. Nobel laureate Giorgio Parisi [27].

This thesis is concerned with investigations of the magnetic properties of four systems, in which magnetic ordering is suppressed. Their behavior at low temperatures down to 400 mK and in high static and dynamic magnetic fields up to 14 T is observed. From the systems' response, more insight into the concrete interactions and their structure can be gained. **Chapter 2** introduces a relevant theoretical basis of the physics treated in later chapters. This is followed by **Chapter 3**, which explains the necessary experimental techniques and used devices. Dilatometry and magnetometry can reveal magnetic phases and show how spin dynamics change as a function of temperature and magnetic field strength. In order to understand magnetic excitations, High-Field Electron Spin Resonance is a useful tool.

The first material investigated is terbium indate TbInO $_3$, which crystallizes in a triangular lattice, where Terbium ions occupy two nonequivalent lattice positions in two-dimensional layers described as a stuffed honeycomb lattice. The resulting magnetic behavior is anisotropic in that the magnetic moments possess an easy plane. It is suggested both in previous experimental as well as theoretical work, that TbInO $_3$ may host a Quantum Spin Liquid (QSL) ground state. To date, the thermal expansion and magnetostriction of TbInO $_3$ have not been investigated. As a part of this thesis, these two behaviors are investigated in TbInO $_3$ and supplemented with DC magnetization measurements. The results of this are presented in **Chapter 4**.

Tb $_2$ Zr $_2$ O $_7$ and Tb $_2$ Zr $_{1.5}$ Ti $_{0.5}$ O $_7$ belong to a class of materials, Tb $_2$ Zr $_{2-x}$ Ti $_x$ O $_7$, which crystallize in a pyrochlore or fluorite lattice with significant disorder between the Tb

and Zr ions on their respective lattice sites. Only the terbium ions contribute magnetically to the lattice. It is reported that this disorder results in glass-like characteristics in $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$. Upon full substitution of Zr for Ti, $\text{Tb}_2\text{Ti}_2\text{O}_7$, possesses a QSL ground state. In **Chapter 5** results of AC and DC magnetization measurements (between 2 K and 300 K and 0.4 K and 300 K respectively) are presented for both materials as a powder. This information is used in order to investigate the influence of cationic site disorder on the glassiness and general magnetic properties of the $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ family of materials. A B - T phase diagram sums up and compares the results for both systems.

For the rare-earth oxotellurate $\text{Er}_2\text{Te}_4\text{O}_{11}$ magnetization measurements were performed in the same manner as for $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$. Its crystal structure has the Er ions arranged on a buckled honeycomb lattice. This lattice may be a realization of the Kitaev model, which predicts a QSL ground state. **Chapter 6** reports on the results of the AC and DC magnetization measurements (probed in the same temperature range as used for $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$). A comparison between the two systems is made using a constructed phase diagram.

Chapter 7 reports on high field electron spin resonance measurements performed on the two-dimensional van der Waals ferromagnet Fe_3GaTe_2 with $B||c$. This conducting material orders magnetically at the comparatively high Curie temperature $T_C = 350$ K. Resonance-frequency-magnetic-field diagrams are recorded at $T = 2$ K and 220 K. Furthermore, measuring the temperature dependence of the resonance positions allows a comparison with other two-dimensional van der Waals ferromagnets.

Chapter 8 sums up the conclusions drawn from the data presented in chapters 4-7.

2 Theoretical Background

2.1 Thermodynamics of a solid

Many relevant quantities discussed in this thesis are fundamentally thermodynamic response functions. Thus, it is necessary to introduce thermodynamic potentials [28], in particular the internal energy U , of a general body of matter. Its total differential at constant entropy S , volume V , particle number N and magnetic field $\vec{B}$ is a function of the state of the system characterized by its temperature T , pressure p , chemical potential μ , and magnetization $\vec{M}$:

$$\begin{aligned} U(S, V, N, \vec{B}) &= TS - pV + \mu N - V\vec{M} \cdot \vec{B} \\ dU(S, V, N, \vec{B}) &= TdS - pdV + \mu dN - (V\vec{M}) \cdot d\vec{B}. \end{aligned} \quad (2.1)$$

The particle number N is conserved in solids: $dN = 0$. Since maintaining a constant entropy and volume is experimentally difficult, it makes sense to switch to Gibbs' Free Energy G , which is a Legendre transform of U [29]:

$$G(T, p, \vec{B}) = U - TS + pV \quad (2.2)$$

with a total differential

$$dG(T, p, \vec{B}) = dU - d(TS) + d(pV) = -SdT + Vdp - (V\vec{M}) \cdot d\vec{B}. \quad (2.3)$$

The following section aims to give an overview of the thermodynamic response functions, which will be measured later in this work. It is based on chapter 2-II A *Thermodynamical Potential of a Magnet* of [30] and derives various response functions in an elegant way: The experiments presented in the subsequent chapters are sensitive to the system's orientation as their partial aim is the quantification of anisotropic effects. In particular, this means applying pressures along one direction and measuring not the volume change but the change of length along a particular axis.

Gibbs' Free Energy (density) and its differential in a magnetic field are then given as

$$dG = -SdT - \sum_{i,j} \varepsilon_{ij} d\sigma_{ij} - \sum_i B_i dH_i \quad (2.4)$$

It depends on the temperature T , entropy density S , stress tensor $\boldsymbol{\sigma} = \frac{\partial \vec{F}}{\partial \vec{A}}$ ($\vec{F}$: force applied, $\vec{A}$: oriented surface) and strain tensor $\boldsymbol{\varepsilon} = \frac{\partial \Delta \vec{L}}{\partial \vec{L}}$ ($\vec{L}$: position, $\Delta \vec{L}$: displacement) [31], and external $\vec{H}$ and $\vec{B} = \mu_0 (\vec{H} + \vec{M})$ are the magnetic field and flux density. Since measurements are typically conducted in a thermodynamical equilibrium $dG = 0$ leading to the following equations

$$S = -\frac{\partial G}{\partial T} \quad \varepsilon_{ij} = -\frac{\partial G}{\partial \sigma_{ij}} \quad B_i = -\frac{\partial G}{\partial H_i} \quad (2.5)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_{\sigma, H} dT + \sum_{i,j} \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{T, H} d\sigma_{ij} + \sum_i \left(\frac{\partial S}{\partial H_i} \right)_{T, \sigma} dH_i \quad (2.6)$$

$$d\varepsilon_{ij} = \left(\frac{\partial \varepsilon_{ij}}{\partial T} \right)_{\sigma, H} dT + \sum_{k,l} \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right)_{T, H} d\sigma_{kl} + \sum_k \left(\frac{\partial \varepsilon_{ij}}{\partial H_k} \right)_{T, \sigma} dH_k \quad (2.7)$$

$$dB_i = \left(\frac{\partial B_i}{\partial T} \right)_{\sigma, H} dT + \sum_{k,l} \left(\frac{\partial B_i}{\partial \sigma_{kl}} \right)_{T, H} d\sigma_{kl} + \sum_j \left(\frac{\partial B_i}{\partial H_j} \right)_{T, \sigma} dH_j \quad (2.8)$$

Equation (2.6) - (2.8) give rise to the relevant thermodynamic response functions:

- The specific heat (at constant pressure p)

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{\sigma, H} = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{\sigma, H} \quad (2.9)$$

- The components of the stiffness tensor $\mathbf{s}$ (where the known symmetries have to be accounted for, see e. g. [31])

$$s_{ijkl} = \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right)_{T, H} = - \left(\frac{\partial^2 G}{\partial \sigma_{ij} \partial \sigma_{kl}} \right)_{T, H} \quad (2.10)$$

- The magnetic permeabilities, which can be converted to magnetic susceptibilities using $\chi_{ij} = \frac{1}{\mu_0} (\mu_{ij} - 1)$

$$\mu_{ij} = \left(\frac{\partial B_i}{\partial H_j} \right)_{T, \sigma} = - \left(\frac{\partial^2 G}{\partial H_i \partial H_j} \right)_{T, \sigma} \quad (2.11)$$

- The thermal expansion coefficients

$$\alpha_{ij} = \left(\frac{\partial \varepsilon_{ij}}{\partial T} \right)_{\sigma, H} = \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{T, H} \quad (2.12)$$

- The pyromagnetic coefficients

$$i_j = \left(\frac{\partial B_j}{\partial T} \right)_{\sigma, H} = \left(\frac{\partial S}{\partial H_j} \right)_{T, \sigma} \quad (2.13)$$

- The piezomagnetic coefficients

$$d_{ijk} = \left(\frac{\partial B_k}{\partial \sigma_{ij}} \right)_{T, H} = \left(\frac{\partial \varepsilon_{ij}}{\partial H_k} \right)_{T, \sigma} \quad (2.14)$$

2.1.1 Thermal expansion

Equation (2.12) defines the thermal expansion (TE) tensor as the temperature derivative of the strain tensor ε . In practice, often only the diagonal elements of the tensor, $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$, are measured. Given an initial length L_0 (chosen at a convenient temperature) and a temperature-dependent length $L(T)$, the strain and appropriate on-diagonal thermal expansion coefficient $\alpha_{L,i}$ can be written as

$$\varepsilon_{ii} = \frac{L_i - L_i^0}{L_i^0} = \frac{\Delta L_i}{L_i^0} \quad (2.15)$$

$$\alpha_{L,i} = \frac{\partial \varepsilon_{ii}}{\partial T} = \frac{\partial((L_i - L_i^0)/L_i^0)}{\partial T} = \frac{1}{L_i^0} \frac{\partial(L_i - L_i^0)}{\partial T} = \frac{1}{L_i^0} \frac{\partial L_i}{\partial T} \quad (2.16)$$

This can be expanded rather straightforwardly to get an expression for the volumetric thermal expansion α_V

$$\alpha_V = \frac{1}{V_0} \frac{\partial V}{\partial T} = \sum_{i \in xyz} \alpha_{L,i} \quad (2.17)$$

In a homogeneous medium $\alpha_{L,\{x,y,z\}} = \alpha_L$. This leads to [31]

$$\alpha_V^{\text{homogeneous}} = 3\alpha_L \quad (2.18)$$

2.1.2 Magnetostriction

A similar treatment can be taken to describe the magnetostrictive (MS) behavior of a system where a strain is induced by an external magnetic field $\vec{B}$ onto a sample. The magnetostriction coefficient λ is defined analogously to eq. (2.12), eq. (2.15) &

eq. (2.16) as

$$\lambda_{ijk} = \frac{\partial \varepsilon_{ij}}{\partial H_k} \rightarrow \lambda_{ij} = \frac{\partial \Delta L_i / L_0^i}{\partial H_j}$$

$$\lambda_L = \frac{1}{L_0} \frac{\partial L}{\partial H} \quad (2.19)$$

$$\lambda_V = \frac{1}{V_0} \frac{\partial V}{\partial H} \quad (2.20)$$

In a paramagnet, an approximate expression for the magnetostriction with sufficiently low induced strain can be derived thermodynamically by considering the fact that both a magnetization M and a stress σ cause free energy to be stored in the system:

$$F_{\text{elastic}} = \int_0^\varepsilon \sigma(\varepsilon') d\varepsilon' \stackrel{\text{Hooke's law}}{=} \int_0^\varepsilon C \varepsilon' d\varepsilon' = \frac{1}{2} C \varepsilon^2 \quad (2.21)$$

$$F_{\text{magnetic}} = - \int_0^H M(H') dH' \stackrel{\text{paramagnetic}}{=} - \int_0^H \chi H' dH' = -\frac{1}{2} \chi H^2 \quad (2.22)$$

From this a simple approximation of the magnetostrictive behavior of a paramagnet can be derived. The free energy of the material is

$$F = F_0 + F_{\text{elastic}} + F_{\text{magnetic}} = F_0 + \frac{1}{2} C \varepsilon^2 - \frac{1}{2} \chi H^2. \quad (2.23)$$

Generally couplings between χ and ε lead to magnetoelastic effects and the susceptibility can be expressed as a function of strain

$$\chi = \chi(\varepsilon) \approx \chi|_{\varepsilon=0} + \left. \frac{d\chi}{d\varepsilon} \right|_{\varepsilon=0} \varepsilon =: \chi_0 + \chi_1 \varepsilon. \quad (2.24)$$

To find the relationship between ε and H for this approximation in a thermodynamic equilibrium, eq. (2.23) is minimized with respect to ε :

$$\frac{\partial F}{\partial \varepsilon} = C \varepsilon - \frac{1}{2} \chi_1 H^2 \stackrel{!}{=} 0 \quad \implies \quad \varepsilon = \frac{\chi_1}{2C} H^2 \propto H^2, \quad (2.25)$$

$$\lambda = \frac{\partial \varepsilon}{\partial H} = \frac{\chi_1}{C} H \propto H^1. \quad (2.26)$$

The magnetostriction is generally dependent on the direction of the applied field and induced strain direction as well as the anisotropy of the tensor $\mathbf{C}$. A quadratic dependence of magnetostriction on the applied field is often observed [32].

2.2 Magnetic behavior of a system

Equation (2.11) defined the magnetic permeability $\mu = \frac{\partial \vec{B}}{\partial \vec{H}}$. The two quantities $\vec{B}$, $\vec{H}$ are linked through the magnetization $\vec{M}$ of the system [33]:

$$\vec{B} \stackrel{\text{SI}}{=} \mu_0 (\vec{H} + \vec{M}) \stackrel{\text{cgs}}{=} \vec{H} + 4\pi \vec{M}. \quad (2.27)$$

μ_0 relates the magnetic field strength H and the magnetic flux density B in vacuum. Inside a finitely sized sample, its shape influences the internal magnetization and the internal magnetic flux density $\vec{B}_i$ is changed relative to the externally applied field $\vec{B}_a$ [2]:

$$\vec{B}_i = \vec{B}_a + \mu_0(1 - N)\vec{M} \quad (2.28)$$

where N is the shape dependent demagnetization factor. In vacuum, the two fields are equal up to constants depending on the chosen unit system. The magnetic permeability relates the $\vec{B}$ and $\vec{H}$ fields. However, as shown in eq. (2.27), $\vec{B}$ contains $\vec{H}$ already, so the case can be made that the relationship between either one of the two fields and the magnetization $\vec{M}$ is more physically interesting. This leads to the definition of the magnetic susceptibility

$$\chi = \frac{\partial \vec{M}}{\partial \vec{H}} \stackrel{\text{SI}}{=} \frac{\partial}{\partial \vec{H}} \left(\frac{1}{\mu_0} \vec{B} - \vec{H} \right) \stackrel{\text{cgs}}{=} \frac{1}{4\pi} \frac{\partial}{\partial \vec{H}} (\vec{B} - \vec{H}) \quad (2.29)$$

In many situations, the magnetization is rather small compared to the applied field and so it is valid to assume $\vec{B} \approx \vec{H}$ (or analogously in SI). If this holds, χ can be approximated as a response to the applied external flux density $\vec{B}$, which is easier to control in experiment [34]:

$$\chi = \frac{\partial \vec{M}}{\partial \vec{H}} \approx \frac{\partial \vec{M}}{\partial \vec{B}} \quad (2.30)$$

2.2.1 Dynamic and static magnetic susceptibility

Equation (2.30) is directly derived from the definition of the magnetic susceptibility as a thermodynamic response function. In practice, the mathematical derivative $\chi = \frac{\partial M}{\partial B}$ is not accessible because infinitesimal changes in neither of the measured quantities are attainable.

In thermal equilibrium B is constant. In order to obtain a differential quotient $\frac{\Delta M}{\Delta B} \rightarrow \frac{\partial M}{\partial B} = \chi$, one needs to compare the measured value $M(B)$ to a reference. The two

types of magnetization measurements with constant fields (dc) performed in this work are $M(T)$ and $M(B)$. In the latter, the isothermal magnetization measurement, B is measured at many field values, subsequent data points can be used to obtain a value for χ . Typically, $\Delta B \approx 10^2$ Oe. The temperature sweep $M(T)$ measured the magnetization strength as a function of sample temperature at a chosen flux density B . The choice of reference for the differential requires more consideration than with the field sweep: For small applied fields, the magnetization can be approximated to be linear with respect to the magnetic field so that

$$\chi = \frac{\partial M}{\partial B} \approx \frac{M(B) - M(0)}{B - 0} = \frac{M}{B}. \quad (2.31)$$

In practice, this approximation is used even for larger fields, even though it fails at higher fields, see for example the saturation in the Brillouin function [2] (as introduced in the next subchapter).

If a time-dependent field B_{ac} is applied additionally to a constant field B_{dc} , the magnetization cannot be taken to be constant anymore [35]. In the case of a sinusoidal ac field $B_{ac}(t) = b_{ac} \sin(\omega t)$ with frequency ω , the measurement can be discussed in the complex plane [36] with $B_{\text{applied}} = B_{dc} + b_{ac} \exp(i\omega t)$, where only the real part is measured. The response to this excitation is a magnetization $M(t)$ with phase θ

$$M(t) = M_{dc} + m_{ac} \exp(i(\omega t - \theta)) \quad (2.32)$$

The ac component of the magnetization can be differentiated (see eq. (2.30)) with respect to the ac field. This yields the complex valued *ac susceptibility*

$$\chi_{ac} = \frac{\partial M_{ac}}{\partial B_{ac}} = \frac{\partial m_{ac}}{\partial b_{ac}} \exp(-i\theta) := \chi_{ac}^0 \exp(-i\theta) = \chi' + i\chi''. \quad (2.33)$$

χ' and χ'' are in and out of phase with the excitation field respectively and referred to as reactive and absorptive component, respectively [35].

In the case of only one relaxation timescale τ , a quantitative description is given through the Debye relaxor model [35]. Its predictions are shown in figure 2.1 and can be summarized as follows: In the limit of $\omega \rightarrow 0$, one expects the reactive component χ' to approach the dc value and the absorptive term to vanish:

$$\omega\tau \rightarrow 0 : \chi' \rightarrow \chi_{dc}, \chi'' \rightarrow 0 \quad (2.34)$$

One benefit of using ac magnetometry can be derived directly from eq. (2.34): At sufficiently slow excitation fields, χ' is the differential quotient $\frac{\Delta M}{\Delta B}$ and approaches the field derivative of the magnetization for small excitation fields

$$\chi' = \frac{\Delta M}{\Delta B} \rightarrow \frac{\partial M}{\partial B} = \chi_{dc}. \quad (2.35)$$

χ' only depends on ΔM and not the absolute value of M . This allows for a high sensitivity of the susceptibility in both variable field and temperature measurements, even at non-negligible magnetic moments in the sample which would degrade the quality of dc measurements.

If the excitation field has a frequency, where the magnetic moments cannot follow, both components vanish since no reaction is possible

$$\omega\tau \rightarrow \infty : \chi' \rightarrow 0, \chi'' \rightarrow 0. \quad (2.36)$$

Should ω induce an excitation on a timescale similar to the relaxation timescale τ of the magnetic state, a phase difference between the induced magnetization and the external field will emerge. This leads to a non-vanishing absorptive term peaking at $\omega\tau = 1$.

$$\omega\tau \approx 1 : \chi'' \approx \chi''_{\max}. \quad (2.37)$$

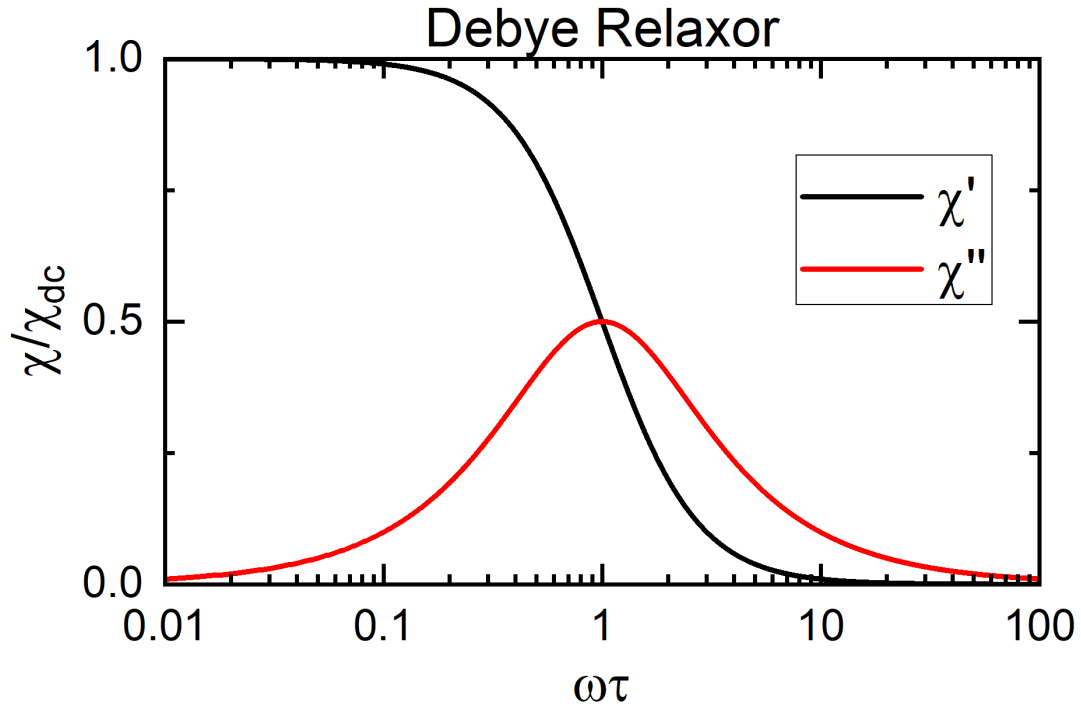


Figure 2.1: Behavior of the ac susceptibility according the Debye relaxor model. (after [35])

2.2.2 Paramagnetism and diamagnetism

The magnetic response of matter can take many forms. Two qualitatively simple kinds of response are diamagnetism (DM) and paramagnetism (PM). In all atoms, even those with vanishing total magnetic moment, there is still a magnetic response of the individual electrons to an external magnetic field $\vec{B}_{\text{ext}}$ [2]. This results in an energy shift of states favoring the build up of dipoles which oppose the external field. The induced magnetization $\vec{M}$ and the associated susceptibility χ_{dia} are thereby negative. This diamagnetic response is typically small and temperature independent but present regardless of the total angular and magnetic momentum of the atom [34].

Looking at the same situation for a simple atomic system with a non-zero magnetic moment, a different response behavior arises: Each atom's/ion's dipole moment $\vec{\mu}$ gets polarized by the field. The relevant interaction between it and the moment is the Zeeman contribution to the total energy

$$\Delta E_{\text{Zeeman}} = -\vec{\mu} \cdot \vec{B} \quad (2.38)$$

For a singular ion with total spin $\vec{S}$ and total orbital angular momentum $\vec{L}$, the total angular momentum is $\vec{J} = \vec{S} + \vec{L}$. The magnetic moment of a system with $\vec{J}$ and quantum number m_J ($-J \leq m_J \leq +J$) is given by

$$\mu = -m_J g_J \mu_B. \quad (2.39)$$

These results can be used to derive [2] the Brillouin function of a system of localized paramagnetic spins in a statistical framework. It determines the magnetization as a function of the external magnetic field and temperature

$$\begin{aligned} M(B, T) &= M_s B_J(B, T) \\ &= n g_J \mu_B J \left[\frac{2J+1}{2J} \coth \left(\frac{2J+1}{2J} \frac{g_J \mu_B J B}{k_B T} \right) - \frac{1}{2J} \coth \left(\frac{1}{2J} \frac{g_J \mu_B J B}{k_B T} \right) \right] \end{aligned} \quad (2.40)$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}, \quad (2.41)$$

$$\mu_{\text{eff}} = g_J \mu_B \sqrt{J(J+1)}. \quad (2.42)$$

For $\frac{g_J \mu_B J B}{k_B T} \ll 1$, the Brillouin function can be approximated as linear in that term. This yields the Curie law describing the magnetization/susceptibility for variable time at sufficiently small fields:

$$\chi_{\text{para}} = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \frac{n \mu_0 \mu_{\text{eff}}^2}{3 k_B T} = \frac{C}{T} \propto T^{-1}, \quad (2.43)$$

$$C = \frac{n \mu_0 \mu_{\text{eff}}^2}{3 k_B}. \quad (2.44)$$

C is the Curie constant. This term typically dominates over the aforementioned diamagnetism. Using Curie's law permits an evaluation of the temperature range, in which paramagnetic behavior can be assumed. Furthermore it is found that

$$\mu_{\text{eff}}^{\text{cgs}} \equiv \sqrt{8C} \mu_B \quad (2.45)$$

A system can also exhibit paramagnetism with other T -behavior. This can be due to van Vleck paramagnetism which is a result of higher order perturbation terms in its Hamiltonian.

$$\chi_{\text{vV}} \propto T^0 \quad (2.46)$$

and it is usually smaller than the Curie term. The van Vleck contribution can become significant if the ion in question has $J = 0$ and allows a non-vanishing population of excited states by, for example, small excitation gaps. This may be the case in Eu^{3+} and Sm^{3+} systems [34].

2.2.3 Magnetically ordered systems

Both previously mentioned cases assumed non-interacting magnetic moments (or at least negligible interactions). This assumption is often reasonable if the interaction strengths between two magnetic moments J is much smaller than the thermal energy $k_B T$ because interactions are suppressed by thermal fluctuations. If the interaction strengths are on the order of thermal noise, they have to be accounted for. A direct consequence of this are much more complex macroscopic magnetic states. Interactions between any two moments typically favor either parallel or antiparallel alignment; in the case of the anisotropic exchange/Dzyaloshinsky-Moriya interaction, the alignment may even be at an angle. Which state a system assumes, depends on the thermodynamic environment, i.e. on the temperature, pressure, magnetic field, size, etc. This work investigates variations of the parameters T and $\vec{B}$.

Pairwise interactions between moments in a magnetic field are described by an interaction Hamiltonian [37]

$$H = - \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j + g \mu_B \sum_i \vec{S}_i \cdot \vec{B} \quad (2.47)$$

which is a sum over all pairs of moments being coupled through their individual interaction J_{ij} . In the case of non-interacting spins $J = 0$. The second term describes the previously introduced Zeeman interaction eq. (2.38). In many systems at finite temperatures, interactions can be neglected to distant neighbors. An example for this is the (anyway relatively small) dipolar interaction, which decays cubically with

distance. If the exchange is mediated through other ions (superexchange) or through conduction electrons (RKKY), more than only the next neighbor ions need to be considered [2]

Under certain conditions, a positive interaction $J > 0$ can lead to the formation of a ferromagnetic (FM) state. The system's magnetic moments are aligned in parallel and enhance each other. This tendency of the ensemble to take on a parallel orientation leads to a non-vanishing magnetization even without an applied magnetic field as, in the mean field approximation, the aligned moments represent a fictional mean field which prevents a flipping of the magnetization. Taking into account the mean field, eq. (2.43) can be generalized to the Curie-Weiss law

$$\chi = \frac{C}{T - \theta_W} \propto (T - \theta_W)^{-1} \quad (2.48)$$

which is valid for $T \gg \theta_W$. $\theta_W > 0$ is the Weiss temperature. In the ferromagnetic case this is also referred to as the Curie temperature $T_C = \theta_W$. This law is only valid in the case of temperatures (thermal energies) much larger than the magnetic interactions because dominating thermal fluctuations are the factor which gives the Curie-Weiss approximation its merit; as soon as they become too small, the magnetic states need to be quantized and they can no longer be taken as uncorrelated anymore [38] [34].

The opposite case of a negative interaction strength $J < 0$ favors an antiferromagnetic (AFM) alignment of magnetic moments; an antiparallel orientation of any two antiferromagnetically interacting spins is the configuration with the lowest energy. Individual moments in a borderless perfectly antiferromagnetically ordered system cancel each other out and lead to a state of zero magnetization. Similarly to the ferromagnetic case, a Curie-Weiss law eq. (2.48) can also be applied to an antiferromagnet. The main difference is that the antiferromagnetic Weiss temperature is negative $\theta < 0$; the Néel temperature T_N is defined as $T_N = -\theta_W$.

Real world systems often do not clearly fall into one of the two extreme cases of ferro- and antiferromagnetism. Exchange mechanisms can compete with each other, i.e. a system may simultaneously be driven to parallel and antiparallel alignments of moments by different mechanisms. Reasons for this are lattice geometries or competing interactions with different spatial behaviors [2]. The textbook example of a system in which the geometry forbids a state with perfectly fulfilled alignment is shown in figure 2.2a. On a triangle with Ising spins (only the up/down orientations are possible), not all three pairs of moments can be antiparallel to each other. There are three classical states with the lowest energy (due to the rotational symmetry). Such a system is referred to as geometrically frustrated [6]. another two dimensional system with the same property is the Kagomé lattice which consists of corner sharing triangles

[2]. A three dimensional geometrically frustrated lattice is the pyrochlore lattice [39]. It consists of two interpenetrating sublattices of edge sharing tetrahedra, as shown in figure 2.2b. The tetrahedral sublattices are especially interesting in the sense that its constituent corner-sharing tetrahedra host both Kagomé as well as triangular planes if viewed along the [111] axis. Another mechanism for frustration are competing interactions on a geometrically non-frustrated lattice [38]. Limitations to the above ideal systems can arise from anisotropy, deviations from the Ising-like behavior or interactions that act further than the nearest neighbors [38], although the latter may also cause frustration itself. Frustration is quantified through the frustration index [34], the quotient of Weiss temperature and the transition temperature to the ground state

$$f = -\frac{\theta_W}{T_{\text{order}}}. \quad (2.49)$$

Since order does not occur at θ_W directly, it is argued in the literature that frustrated systems may adhere to the Curie-Weiss law (with a negative Weiss temperature) even at temperatures lower than θ_W [38].

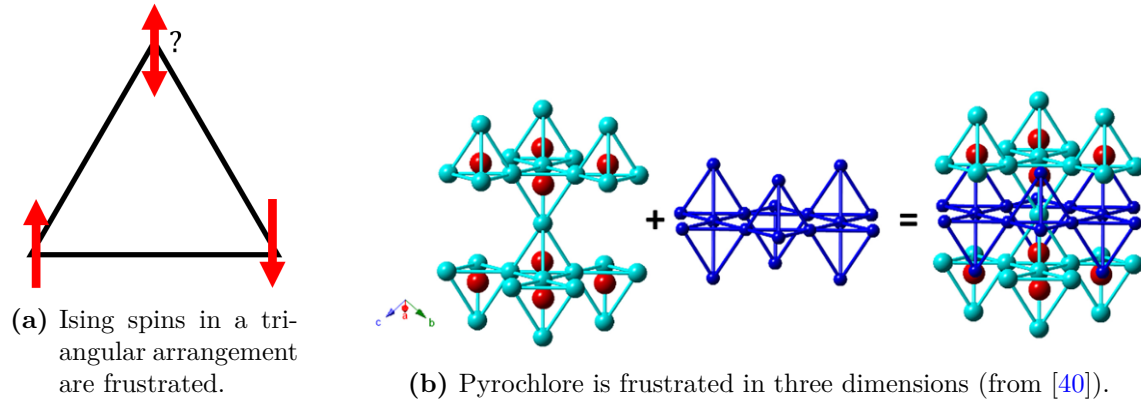


Figure 2.2: Two examples of geometrically frustrated spin configurations.

2.2.4 Spin glasses/Magnetically disordered systems

There are systems which lack a periodicity in their magnetic site locations. If they are frustrated on top, either due to the geometry of their magnetic moments or due to competing exchange interactions, then they might fall into the class of spin glasses or magnetically glassy materials. These materials' low temperature ground state lacks a magnetic long range order [6]. There are at least two different realizations of glassy states [41]: The more commonly talked about case - which is referred to as canonical

spin glass [42] - describes a non-magnetic, often conducting host lattice with a low concentration doping (below the percolation threshold) of magnetic atoms [35]. Here, the dominating magnetic exchange mechanism of the magnetic spins are either the briefly aforementioned RKKY interaction [2] [5], where

$$J_{\text{RKKY}} \propto \frac{\cos(2k_F r)}{r^3} \quad (2.50)$$

(only for a conducting host lattice) and the dipolar interaction

$$J_{\text{dipolar}} \propto \frac{1 - 3 \cos^2 \theta}{r^3} \quad (2.51)$$

which is anisotropic with the relative angle θ between two moments. The sign of the RKKY exchange oscillates with radial distance which means that, due to the random distribution of the dopants, most magnetic atoms will be subject to a mix of opposing interactions [27]. The anisotropy of the dipolar interaction causes an azimuthally varying sign of the exchange. Further anisotropy is caused by the coordination of the individual magnetic moments in the lattice. This causes a frustration which may suppress long range-ordering. Another realization of glassiness may occur in magnetic lattices with frustrations (e.g. magnetic pyrochlore type materials) and substituting atoms on magnetically relevant sites with diamagnetic ones [38]. The introduced disorder facilitates frustrations and, if the dilution of the magnetic structure is close to percolating, allows a glassy state. Because this situation differs from the canonical spin glass mentioned earlier, it is often cautiously named glassy instead of glass. In both realizations of glassiness, it must be remembered that the interactions are not spatially ordered.

In any case, a network of non-periodically distributed moments is created which results in frustrated interactions. The disordered spatial distribution allows many local minima in the energy manifold. By sufficiently rapid cooling, the system can be frozen into one of these metastable states.

Phenomenology of spin glasses

Spin glasses exhibit several features that together help in identifying them [2][41][42]: If the system is cooled in the presence of a magnetic field (field cooled, FC), at the freezing temperature T_f , it will freeze into one of its low energy states that allows the magnetic moments to align with the magnetic field. During a subsequent warming up (in field), the magnetization remains on a plateau since it is frozen into the magnetized state. This behavior is different if the warming happens after zero field cooling (ZFC): In that case, the post-cooling state will be unmagnetized and so the heating and the

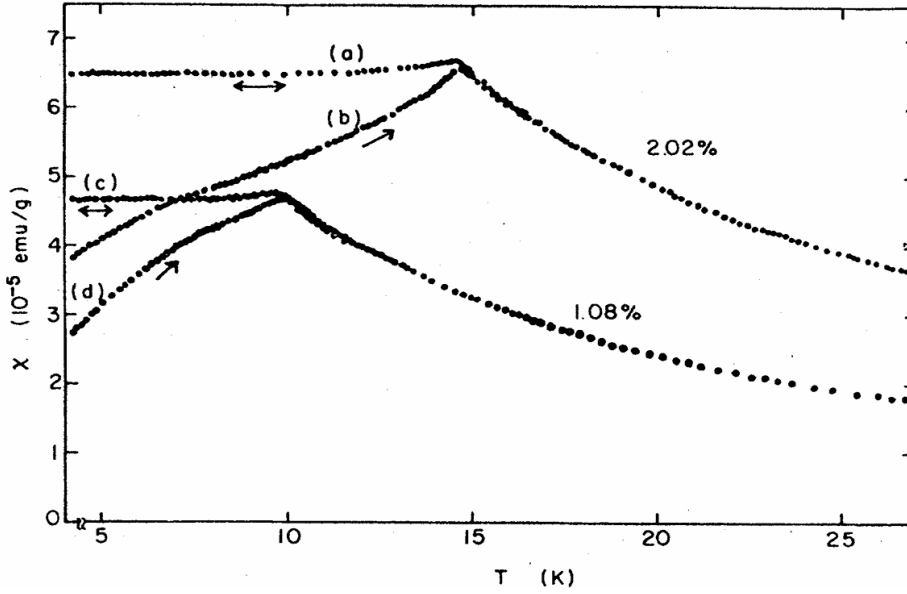


Figure 2.3: DC susceptibility of spin glass CuMn with two Mn doping levels with ZFC (b&d) and FC (a&c) data. From [6].

associated thermal fluctuations of the spins gradually allows the system to move into a more magnetized state, thereby increasing the magnetization up to T_f [35]. At higher temperatures, a Curie-Weiß law is approximated. Exemplary experimental data for this phenomenon is shown in figure 2.3. If a glassy system is zero field cooled below its freezing temperature T_f , it is in a disordered configuration. Upon subsequent field application, the magnetization process of such a frozen system causes the magnetic moments to reorient along the field. Due to the disordered nature of a glassy state, this does not happen synchronously for all moments because the environments (and the associated anisotropy) follow a statistical distribution. The magnetization curve $M(B)$ takes on an S-shape [6] [43] [44] [45]. When isothermally removing the field, the inflection vanishes and a field-hysteresis is noticed because some of the spins are frozen in metastable configurations with a larger magnetization than during the initial field ramp [46].

Another signature of glassiness is seen in the static (ac) magnetic susceptibility χ_{ac} (see section 2.2.1). Both components of the dynamic susceptibility, χ' and χ'' , are expected to show a frequency dependent temperature maximum [35] [5]. The drop after the maximum in χ' can be understood as a slowing down in the spin dynamics caused by the freezing into one of the low temperature states. Due to this slowing down because of the timescale mismatch, the spin dynamics can no longer follow a driving field, resulting in a peak in the absorptive component $\chi''(T)$ [47].

2.3 Magnetic resonance

Equation (2.38) describes the interaction energy between a magnetic dipole and a magnetic field. This principle is exploited in magnetic resonance spectroscopy, of which Electron Spin Resonance (ESR) is a part. In this, resonance is detected between the magnetic substates of a system and incident photons with frequency f and energy

$$E = hf \quad (2.52)$$

For a quantum system with total angular momentum $\vec{J}$, this is described by eq. (2.39). Subsequently, the energy difference ΔE between two states with a difference in quantum numbers Δm_J is

$$\Delta E = -\Delta m_J g_J \mu_B B = hf. \quad (2.53)$$

The second part of this equation describes the resonance condition. Normally, transitions are of dipolar order, i.e. $\Delta m_J = \pm 1$, higher order processes are suppressed. According to the above equation, the transition energy is directly proportional to the magnetic field. In the case of non-isolated ions, excitations are collective. Those so called spin waves or magnons may need an energy gap to be overcome in order to excite them [2]; in an ESR experiment, this means that the resonance positions in a $f(B)$ diagram will not form a line passing through the origin because of the finite gap energy/frequency $E_{\text{gap}}/f_{\text{gap}}$. Furthermore, since these excitations arise from the crystalline forms of the system, the $f(B)$ relationship is generally not isotropic. Both magnetic ordering and the magnetic interactions themselves are rarely isotropic as can be seen when considering magnetically hard and easy axes, implying that both the gap as well as the g factor are potentially anisotropic.

3 Experimental Methods

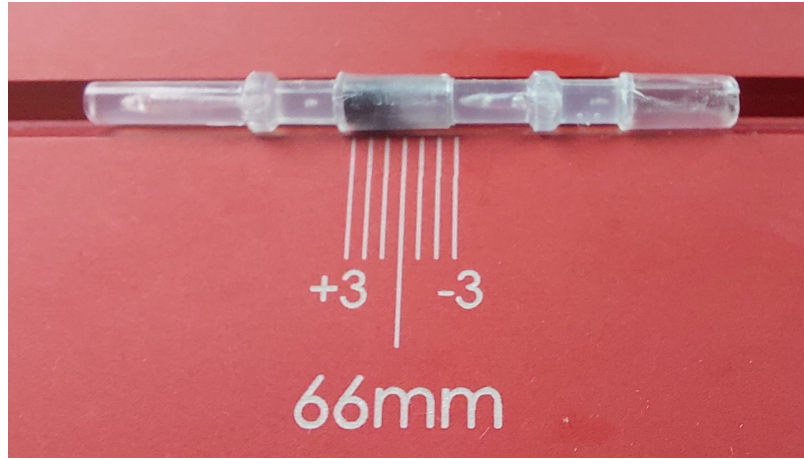
3.1 Magnetization measurements

Magnetization measurements were performed in *Quantum Design's Magnetic Properties Measurement System* MPMS3, a commercially available SQUID magnetometer [48]. When operated in standard DC mode, it offers a maximum resolution of $\Delta M < 5 \times 10^{-8}$ emu if working with a field smaller than 2500 Oe or $\Delta M < 6 \times 10^{-7}$ emu if $H > 2500$ Oe. The field control has a resolution of 0.5 Oe and remanence of < 5 Oe. The temperature inside the chamber can be varied between 1.8 K and 400 K (nominally) and does not deviate from the set point by more than 1%. These chosen temperatures are reached through a multi-stage temperature control consisting of a liquid He-4 and a liquid nitrogen cooling stage [49]. MPMS3 contains a vertical sample chamber, in which a magnetic field of up to 7 T can be applied in parallel to the vertical axis. Samples are mounted onto a sample holder and inserted into the chamber, their vertical position is controlled by a motor. A second-order gradiometer configuration [50] of superconducting coils picks up the magnetic signature, suppressing external noise signals to a high degree. This particular arrangement of coils offers a higher selectivity for the sample and thus enhances the accuracy to above mentioned values compared to a single pickup coil.

Depending on the type of sample, the preparation method in the measurement chamber varies: Mechanically stable bulk samples are best connected to a brass or (plastic) straw holder with Apiezon N cryo grease [51]. Photos of the two setups are shown in figure 3.1. It may prove useful to additionally clamp samples between two quartz blocks in the brass holder, especially if larger magnetic moments are expected. This is not possible for powdered materials due to the risk of losing parts of the sample inside the chamber and thus contaminating the device. Studies of such samples require them to be placed inside plastic capsules provided by Quantum Design (see figure 3.1b). These capsules have a non-zero magnetic signature which needs to be taken into account. Quantum Design could not provide reliable data on the capsules' magnetic properties and warned that the signal was not consistent between individual units. This means that (for small signatures) each capsule needs to be characterized before inserting the sample. However, the actual signature of a capsule measurement depends on the exact orientation and configuration of the capsule which may



(a)



(b)

Figure 3.1: Sample holders for the MPMS3. (a) Brass sample holder, upper one with quartz clamps (b) Gel capsule for powder samples.

be altered when preparing the sample.

The temperature measurement range can be extended beyond the 1.8 K using the iQuantum Helium 3 dilution refrigerator setup. This system is complementary to the MPMS and enables dc $M(T)$ and $M(B)$ measurements at temperatures as low as 350 mK with the full field range of up to 7 T. In the Helium 3 setup, the sample is contained in a closed He-3 chamber using the conventional cooling cycle of the MPMS as a pre-cooling stage. He-3 measurements require exclusively the use of the straw sample holders.

3.1.1 DC magnetometry

A significant part of the magnetization measurements described in this work were performed in "DC mode" which is described in [48] and can be briefly summarized as follows: Any sufficiently small (relative to the pickup coil dimensions) magnetized sample is accompanied by a magnetic field which can be approximated in space by a dipole response function shown in figure 3.2 [52]. In the gradiometer setup of the MPMS, the picked up response is described by the function

$$f(Z) = X_1 + X_2 Z + X_3 \left(2 \left[R^2 + (Z + X_4)^2 \right]^{-\frac{3}{2}} - \left[R^2 + (\Lambda + Z + X_4)^2 \right]^{-\frac{3}{2}} - \left[R^2 + (-\Lambda + Z + X_4)^2 \right]^{-\frac{3}{2}} \right) \quad (3.1)$$

f is the field strength, Z the sample position along the magnet's axis, R coil's radius, Λ the separation of the coils and X_1, X_2, X_3, X_4 are parameters describing the particular measurement, i.e. background, drift, moment and sample position. The sample is mechanically driven through the pickup coils, allowing probing of the sample position z . Moving the magnetic moment relative to the pickup coils induces a voltage in the SQUID sensor. By fitting the dipole response function eq. (3.1) to the recorded sweeps, a simple and mostly automated retrieval of the magnetic moment [53] can be done, as X_3 is proportional to the magnetic moment. Environmental parameters, which are varied during the course of this work, were the temperature T and the magnetic field B . In order to obtain a higher accuracy or to analyze smaller signals, the application SquidLab [52] can be used. It allows the user to manually correct the measured signal by performing background and drift subtraction and fitting of the raw data for each data point, enabling a more accurate result.

3.1.2 AC magnetometry

Investigating a system's dynamic magnetization properties poses different challenges than a dc measurement and thus requires different methods: The dynamic property introduces the frequency f or the timescale $\tau = 1/f$ as a further parameter; additionally, the amplitude of the ac excitation B_{ac} can be varied. No setup can cover every possible value for f or B_{ac} , the MPMS3's ac capabilities allow frequencies in the range $0.1 \text{ Hz} < f < 1 \text{ kHz}$ and $0.1 \text{ Oe} < B_{ac} < 10 \text{ Oe}$. Experimentally, this is realized by adding another set of coils into the dc setup. In the MPMS3, these are arranged concentrically relative to all the other coils, allowing measurements with $B_{ac} \parallel B_{dc}$. The read out of the signals presented in this work is not done through recording a

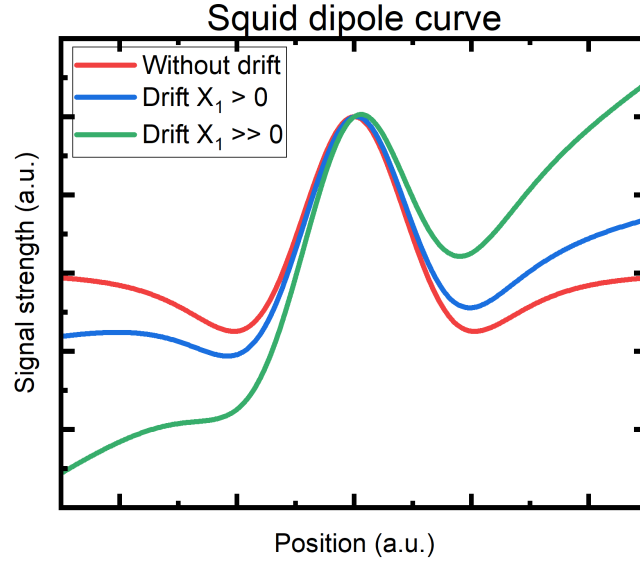


Figure 3.2: Simulated dipole response function of samples in the MPMS. Two curves have a non-zero drift.

sweep through all positions but by measuring three defined positions, the peak, a null point and a highest order side peak as described in [54].

A decision which needs to be made for each ac measurement is the employed sample holder. While offering an improved mechanical stability, the brazen tubes carry the significant disadvantage of being metallic. The varying magnetic fields induce eddy currents in the material which will both add additional noise to the signal and partially shield the sample from the excitation signal.

3.2 High Field Electron Spin Resonance

Electron spin resonance (ESR) is a spectroscopic technique to investigate the microscopic magnetic properties of a system. Microwave radiation is used to induce transitions between magnetic states in a magnetic field B . The ESR setup utilized for this thesis is home built [55], it is schematically shown in figure 3.3. Microwaves with $f = 8-18$ GHz generated in an *AB Millimeter Millimeter Vector Network Analyser model-8-350* (MVNA) are guided into a harmonic generator (HG) to generate higher frequency radiation. The frequency multiplication is defined by the factor N (which can be chosen between $N = 4$ and $N = 64$). The high frequency microwaves

are subsequently guided to a sample placed inside a variable temperature inset (VTI) in an *Oxford Instruments* cryostat. With the aforementioned setup, frequencies between 30 GHz and 1000 GHz can be tuned almost continuously. In a harmonic mixer (HM), the signal is read out at the original frequency. Comparing the input signal with the transmitted signal yields an attenuation strength in amplitude (typically in dB) and a phase shift. Inside the ESR setup, the sample can be exposed to a variable temperature (down to 1.7 K) and uniaxial magnetic fields up to 16 T, which are swept with a rate of $dB/dT \leq 1$ T/min. For each measurement the frequency is kept constant while the field is swept to the maximum and down to zero again.

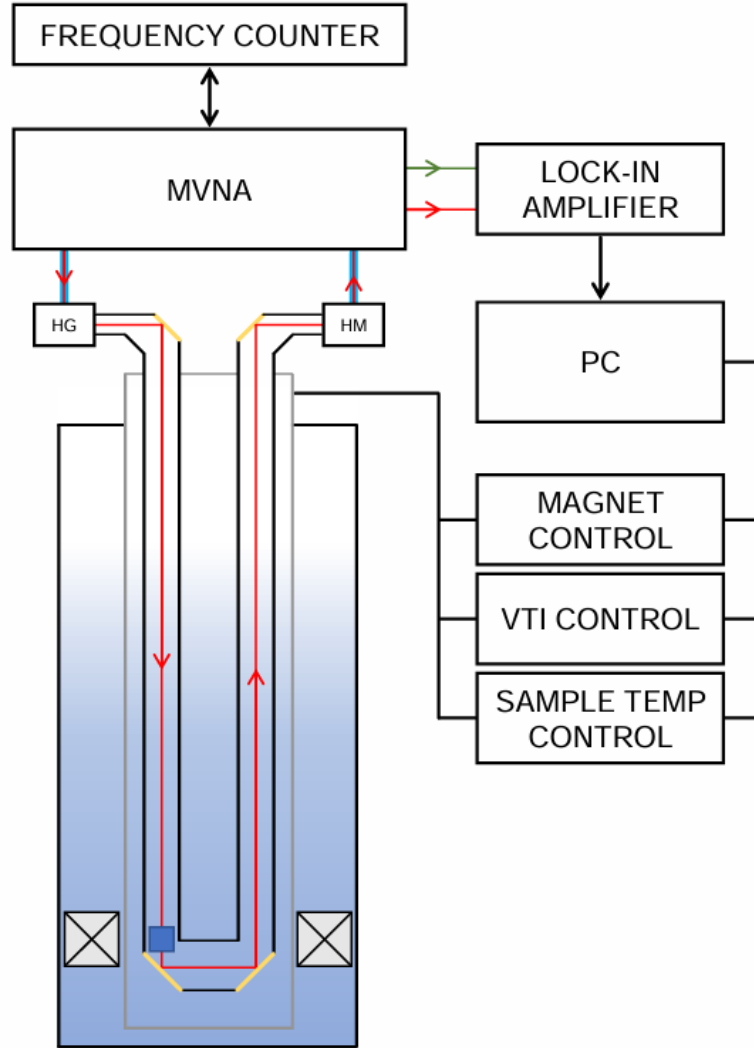


Figure 3.3: Schematic of the HF-ESR setup, from [55].

Crystalline samples are kept inside a brass ring that is closed off on both ends with Kapton tape. The sample dimensions generally do not match the ring's inner diameter and length. It is thus necessary to further fixate it to suppress sample motion, either due to vibrations or magnetically induced torque. A standard approach is clamping the crystal between Teflon blocks that are matched in size to minimize the potential for wiggling, an example for this is shown in figure 3.4a. Teflon is mostly incompressible and chemically inert and can thus be used for sample mounting even in an Argon filled glovebox with air sensitive samples. The downsides of Teflon fixation is that, especially for small samples, it is difficult to get a tight clamp because this requires precise fitting of the blocks. An alternative approach is stabilization in one of various bonding agents like icosane, GE varnish (used as glue) or possibly even standard issue superglue. This can be seen in figure 3.4b where a thin-plate sample is kept in molten and re-solidified icosane. Advantages of this second approach are that the fixation is generally more stable because the grease adapts to the shape of the sample, especially thin samples are better kept in place this way. However, inserting icosane requires melting it which is incompatible with the protected Argon environment of a glovebox as it risks contaminating the protective atmosphere. Other glues like N grease, GE varnish or superglue cannot be easily introduced into a glovebox either because they come in containers that are not well suited for the vacuum of an airlock, and might even begin to solidify because their solvents are removed during the voiding stage and might damage it or other contents of the glovebox.

In order to probe the anisotropy of a sample, it is necessary to remove it from the setup and reinstall it oriented accordingly. This may cause the aforementioned issues if it results in unfavorable sample alignments.

Microwaves consist of an oscillating electric and magnetic field. It is known [31] that electromagnetic waves have a finite penetration depth δ into a conductor. This length scale is frequency f and conductivity σ dependent

$$\delta = \sqrt{\frac{2}{2\pi\mu_0\sigma f}} \propto \sqrt{\frac{\sigma}{f}} \quad (3.2)$$

For practical measurements on conductors (either metals or semiconductors at sufficiently high temperatures), this reduces the interaction volume between the microwave radiation and the material. A smaller volume means an overall reduced signal.

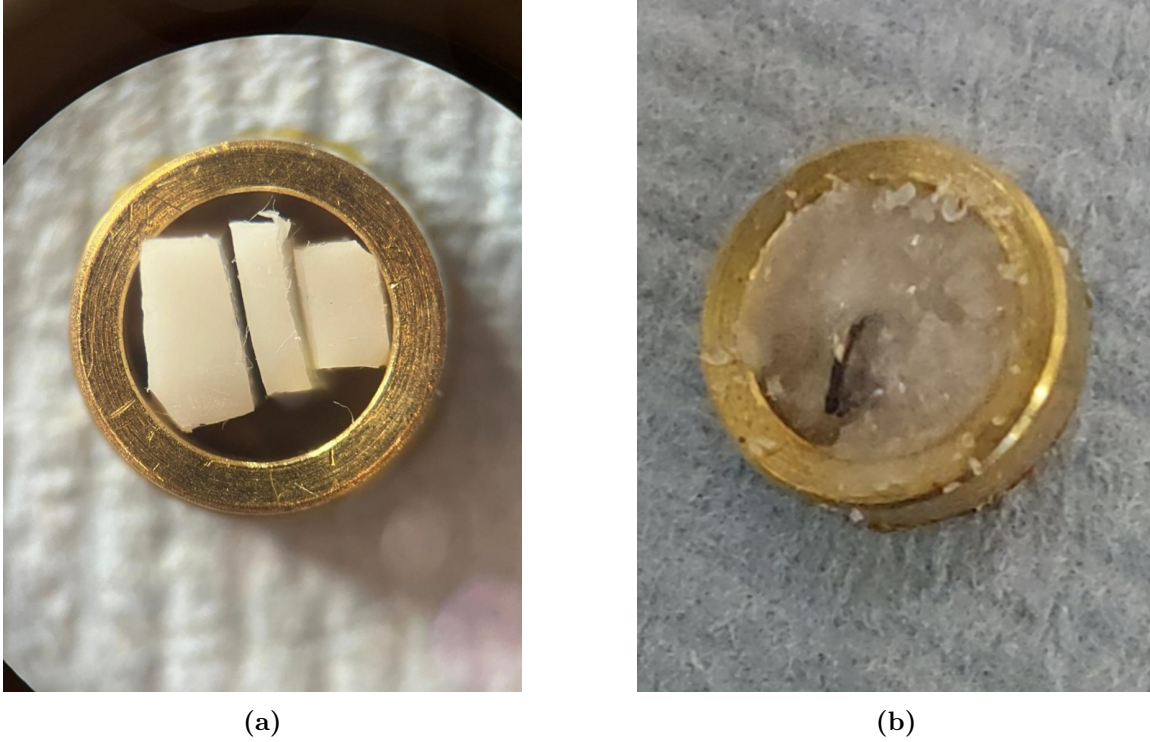


Figure 3.4: Sample mounting in brass ring for ESR. (a) is fixed using cut Teflon blocks (b) is fixed in grease.

3.3 Capacitance dilatometry

Section 2.1.1 & 2.1.2 introduced the thermal expansion and magnetostriction phenomena in solids. Both have in common that a strain $\varepsilon = \Delta L/L$ is induced in the system of interest by changing the thermodynamic variable (either temperature T or magnetic field B). Experimental techniques measuring this strain are referred to as dilatometric techniques. Dilatometry can be attacked from multiple angles: One can use X-Ray diffraction (XRD) [56] or elastic neutron diffraction [57]. Another approach to dilatometric measurements uses bulk samples and the strain induced on them. Laser dilatometry [58] and capacitance dilatometry [59] both measure the macroscopic length of the sample along a chosen axis with high precision. This work uses capacitance dilatometry, which exploits the fact that the capacitance of a parallel-plate capacitor is both proportional to the inverse distance between the plates and can be measured with very high precision. The relationship between the capacitance C and the distance L between the two plates with area A and an inter-plate medium

with dielectric constant $\varepsilon = \varepsilon_0 \varepsilon_r$ is given by

$$C = \varepsilon_r \varepsilon_0 \frac{A}{L} \quad (3.3)$$

In capacitance dilatometry, the sample is contained in a frame between a moving and a fixed part of the cell. Each part is coupled to the two plates of a plate capacitor. A strain $\Delta L/L$ in the sample then changes this capacitance [60]. Measurements are performed with a reference capacitance C_0 , which is chosen to be the one corresponding to the length L_0 at the lowest measured temperature/field. The length change ΔL is then expressed as a function of the capacitances as

$$\Delta L = L - L_0 = \varepsilon A \frac{C - C_0}{C \cdot C_0} \quad (3.4)$$

Available dilatometers for this work have circular plates with radius $r = 5 \text{ mm}^2$ and area $A = \pi r^2$. Equation (3.3) assumes perfectly parallel plates; this assumption is too crude for the desired measurements (strains measured here are on the order of $\Delta L/L \approx 10^{-8}$). A correction term for tilted circular plates is derived in [61]:

$$\Delta L = \varepsilon_0 \pi r^2 \frac{C - C_0}{C \cdot C_0} \left(1 - \frac{C \cdot C_0}{C_{\max}^2} \right) \quad (3.5)$$

$C_{\max}$ is the capacitance in the limit of physical contact, i.e. directly before a short circuit is established.

All dilatometric measurements presented in the course of this work, were performed using high-resolution capacitance dilatometers developed by *Kuechler Innovative Measurement Technology*. In particular, the in-situ PPMS-Dilatometry probe (in the following referred to as *Mini-dilatometer PPMS* [60]) were employed. Sketches of the dilatometers cell are shown in figure 3.5.

The working principle of these cells is the following [59]: A sample (4, red) is locked in position between the upper half of the setup (1, golden), which is mobile and holds the upper capacitor plate (5, green), and a piston (10, grey). The piston's vertical position can be adjusted with an adjusting screw (9, yellow). After the sample is fixated to its position, the piston is locked horizontally by the fixing screw (12, orange). The mobile part of the cell is connected to the external frame (3, golden) with two 0.3 mm leaf springs (2), it is contacted electrically. The bottom plate of the capacitor (6, green) is mounted on the external frame (3, grey) and connected with wires (15, green) to readout electronics. Also installed are electrical insulation elements (13 and 14) and protective guard rings (7 and 8). The adjusting screw (9) is housed in a sample adjustment aid (11, grey) that can be removed before measurement and mechanically

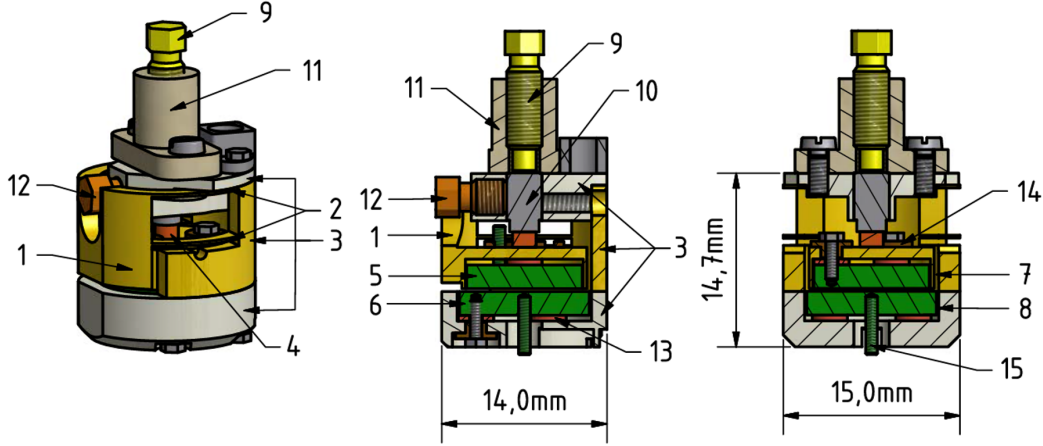


Figure 3.5: Technical sketches of the dilatometer cell of the used dilatometer. The left image shows a generic 3D rendering, the center shows a cut through the middle as viewed from the side, the right panel shows the same but seen from the front. 1: Upper mobile half of the cell 2: Connecting springs 3: Housing 4: Sample 5&6: Plate capacitor halves 7&8: Guard rings 9: Adjusting screw 10: Adjusting piston 11: Housing for 9 12: Fixing screw 13: Sapphire washer 14: Vespel insulation of the capacitor plates 15: Electrical connection. From [59].

connects to the cell. Optimal working conditions are achieved at the working capacity of approximately 20 pF, this can be approached by selecting an appropriate initial capacity during installation.

Due to the compact design, the cell has a size of $14.0 \times 15.0 \times 14.7 \text{ mm}^3$ (without the detachable housing for the adjusting screw). All parts, barring the insulating elements, are manufactured from a Be-Cu mixture (1.84% Cu) where the Beryllium serves to increase the setup's electrical resistance by a factor of 30 in order to suppress eddy currents from a changing magnetic field.

To facilitate the installation of samples and to allow measurements with angular dependence, the Mini-dilatometer PPMS is mounted in a cage [60], as shown in figure 3.6. This setup allows rotations around an axis perpendicular to the field direction in an angular range between -90° and $+90^\circ$ (which can be extended to 360° with some effort), to achieve this, the dilatometer is housed in a C-shaped holder. In addition to the rotating mechanism, the cage also houses the wiring necessary for accessing the dilatometer cell, which is done using coaxial cables (for insulating the fields to the cables). The cage holds additional springs and elements to improve rotation performance and thermal stability.

The read-out for the capacitive component of the dilatometer is carried out by an

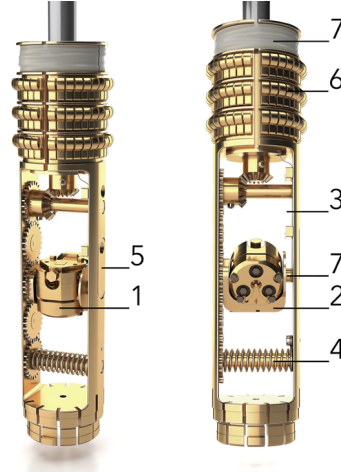


Figure 3.6: PPMS dilatometer in the cage setup. 1: Dilatometer 2: Dilatometer holder in C-shape 3: Cage 4: Spiral spring 5: Leaf spring 6: Gold-plated contact springs 7: Housing of the coax cables. From [60].

Andeen-Hagerling AH2550A *ultra-precision capacitance bridge* [62].

3.3.1 Cell effect

When performing capacitance dilatometry in the described dilatometer cell, in particular when measuring thermal expansion, the measured length change ΔL^{meas} is not purely due to the sample. The cell material also shows a length change ΔL_{cell} , the *cell effect*, under temperature change, which must be accounted for to obtain the real the sample length change ΔL

$$\Delta L = \Delta L^{\text{meas}} + \Delta L_{\text{cell}} \quad (3.6)$$

In order to measure the cell effect, reference measurements are performed on ultra pure copper samples with length $L_{\text{Cu}}^{\text{RT}}$ at room temperature (RT). Pure Copper is used as it is understood and approximates the cell material very well, reference data for $(\Delta L/L)_{\text{Cu}}^{\text{lit}}$ can be obtained from the literature [63]. The cell effect is the difference between the expansion data of the Cu reference measurements $\Delta L_{\text{Cu}}^{\text{meas}}$ (taken in the same cell) and the literature values

$$\Delta L_{\text{cell}} = \Delta L_{\text{Cu}}^{\text{lit}} - \Delta L_{\text{Cu}}^{\text{meas}} = \left(\frac{\Delta L}{L} \right)_{\text{Cu}}^{\text{lit}} L_{\text{Cu}}^{\text{RT}} - \Delta L_{\text{Cu}}^{\text{meas}} \quad (3.7)$$

Using this, the actual sample length change relative to the sample length at RT, L^{RT} , can be expressed as

$$\left(\frac{\Delta L}{L^{\text{RT}}}\right) = \frac{1}{L^{\text{RT}}} \left[\Delta L^{\text{meas}} - \Delta L_{\text{Cu}}^{\text{meas}} + \left(\frac{\Delta L}{L}\right)_{\text{Cu}}^{\text{lit}} L_{\text{Cu}}^{\text{RT}} \right] \quad (3.8)$$

In practice it is observed that the cell effect is dependent on the reference sample. This can be seen in figure 3.7 which shows how $d\Delta L/dT$ differs for varying initial lengths. A similar variance is also observed when comparing cell effects over time, possibly due to varying exact positions of cell elements.

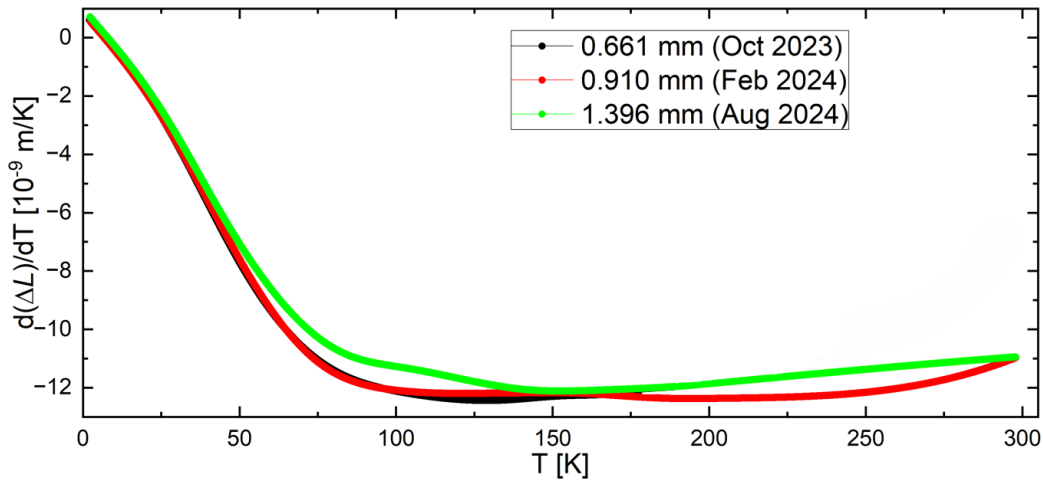


Figure 3.7: Comparison of cell effects: Strains of differently dimensioned copper reference samples recorded at different times. This demonstrates the dependence of the sample on measured effects.

4 TbInO₃

4.1 Introduction

TbInO₃ has a triangular crystal structure which is classified as part of the space group $P6_3cm$, as determined by [64], see table 4.1 for the lattice parameters and figure 4.1 for renderings of the crystal lattice. The Tb³⁺ ions are arranged in layers in the ab plane. They are divided into two species, which are slightly shifted against each other along the crystallographic c axis (figure 4.1b). The Tb2 sites are arranged in a honeycomb lattice with the Tb1 ions at the centers of the resulting hexagons (figure 4.1a). InO₅ layers sit in-between the Tb layers. Only the Tb ions carry a non-zero magnetic moment. The structure of the Tb planes is referred to as a *stuffed honeycomb lattice* [65]. This is idealized as the Tb inter-site distances vary slightly (by ca. 0.6%) [66].

This system has been previously magnetically studied, both as single crystals and as powders [66] [67] [68] [69] [70] [71]. Its high temperature magnetic susceptibility $\chi(T)$ shows a behavior which can be approximated by a Curie-Weiss law for polycrystalline and single crystalline samples. Effective moments in the powder indicate a fitted value of $\mu_{\text{eff}} \approx 9.6 \mu_B/\text{Tb}$, which is close to the free ion moment $\mu_{\text{eff}} = 9.7 \mu_B/\text{Tb}$ and a significant anisotropy in the form of a magnetically hard c axis with $\chi_{ab}/\chi_c \approx 4 - 6$ at $T \approx 14$ K is reported from previous measurements on single-crystals [67] [68] [69]. Reported Weiss temperatures are not consistent across multiple studies but the c axis seems to have a relatively smaller θ_W than the ab plane. No magnetic ordering is detected down to 100 mK in either case. Field-induced phase transitions are not observed in polycrystalline TbInO₃ at 550 mK up to 60 T [70]. The specific heat of a TbInO₃ polycrystal was measured down to 150 mK, more than an order of magnitude below all Weiss temperatures. It did not yield any evidence of phase transitions either [69]. Recent investigations in a thin-film sample generally corroborate these findings [71]. The reported absence of magnetic ordering in combination with a clearly non-vanishing θ_W hints at a high degree of frustration.

Due to the high level of frustration and yet strong magnetic interactions, it is hypothesized that TbInO₃ may be a Quantum Spin Liquid (QSL) [66] [68]. A QSL is a magnetic state of a correlated system characterized by significant interactions but a notable absence of magnetic ordering at any temperature. Besides magnetometry, this

Ion	x	y	z	Lattice parameter [$\text{\AA}$]
Tb1	0.33330	0.66670	0.03210	$a = 6.3186(3)$
Tb2	0.00000	0.00000	-0.00004	$b = 6.3186(3)$
In	0.33400	0.00000	0.26873	$c = 12.306(1)$
O1	0.31700	0.00000	0.10010	
O2	0.36540	0.00000	0.43670	
O3	0.66670	0.33330	0.24600	
O4	0.00000	0.00000	0.30000	

Table 4.1: Structural parameters of the TbInO_3 lattice according to [64].

hypothesis is furthermore corroborated by muon and inelastic neutron spectroscopy [66] [68]. This is supported by simulations which indicate a possible QSL state in a stuffed honeycomb lattice [65].

4.2 Magnetometry

A monocrystalline sample of TbInO_3 was grown by N. Yuan [67]. It is shown in figure 4.2. The sample shape is best described as a thin plate with width $\sim 170 \mu\text{m}$ and in plane dimensions $3.2 \text{ mm} \times 8.5 \text{ mm}$. The sample mass is $0.97(1) \text{ mg}$.

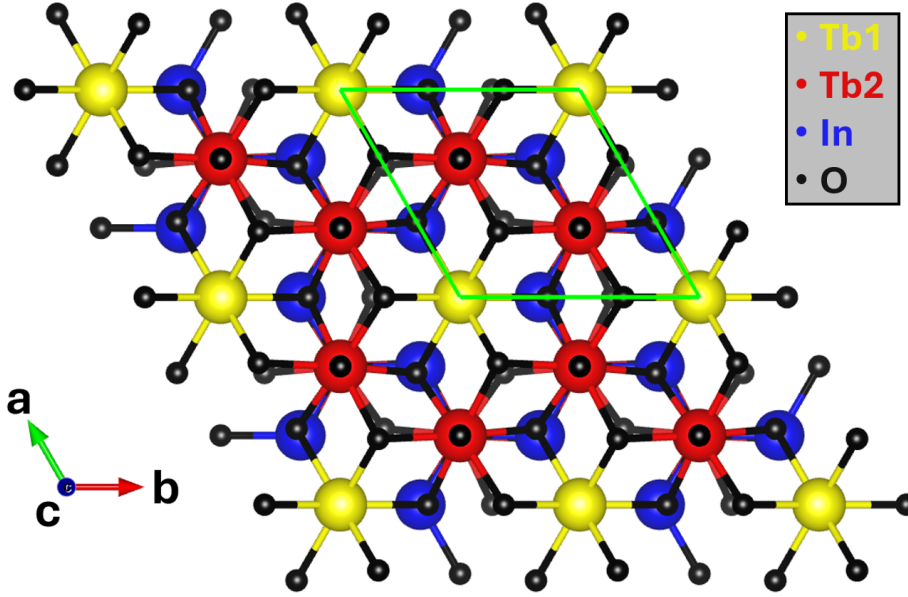
The magnetic properties of TbInO_3 are measured using the brass sample holders with quartz clamps in the MPMS3. In particular its temperature dependent magnetization $M(T)$ and isothermal magnetization $M(B)$ were probed parallel and perpendicular to the c axis. The results of the temperature dependent measurements are shown in figure 4.3 as magnetic susceptibilities $\chi(T) = M(T)/B$, respectively. This plot is extended by including a powder average as follows

$$\chi_{\text{powder}} = \frac{1}{3} \sum_{i \in \text{axes}} \chi_i = \frac{2}{3} \chi_{ab} + \frac{1}{3} \chi_c. \quad (4.1)$$

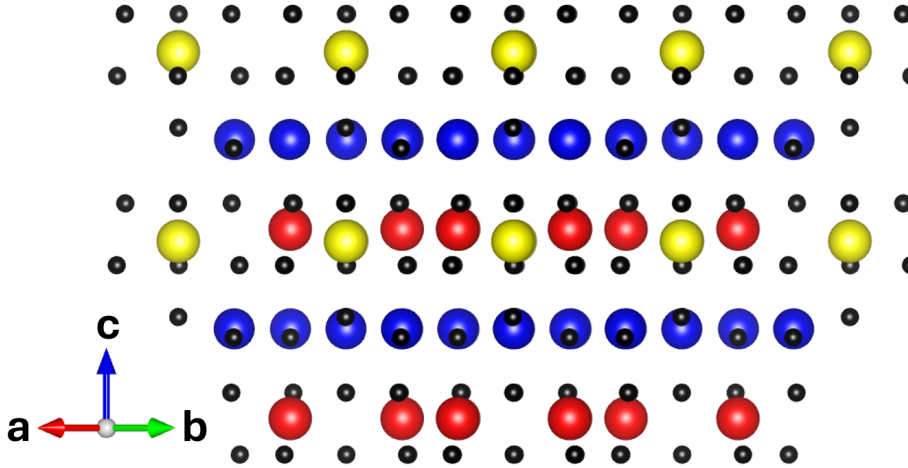
Figure 4.3 shows that $\chi^{-1}(T) \propto T$ for $T > 100 \text{ K}$ for the ab and c axes and the powder average. The latter two appear to deviate from the linear behavior at $T \lesssim 30 \text{ K}$, while the onset for the deviation for $B||c$ appears to be at $T \approx 75 \text{ K}$.

A Curie-Weiss fit, see eq. (2.48), with an additional constant term χ_0 is fitted to the single-crystal data and to the powder average at $T \geq 100 \text{ K}$:

$$\chi(T) = \frac{M(T)}{B} = \frac{C}{T - \theta_W} + \chi_0 \quad (4.2)$$



(a) Crystal lattice of TbInO_3 projected onto the ab plane. The green parallelogram marks the unit cell.



(b) Crystal lattice of TbInO_3 projected along the c axis. The c shift between the Tb1 and Tb2 sites is visible.

Figure 4.1: Crystal lattice of TbInO_3 . Tb1 sites are marked in yellow, Tb2 in red, In sites are blue, and O sites are black. The green rhombus at the top right of a marks the unit cell. Rendered in VESTA [72] based on data provided in [64].

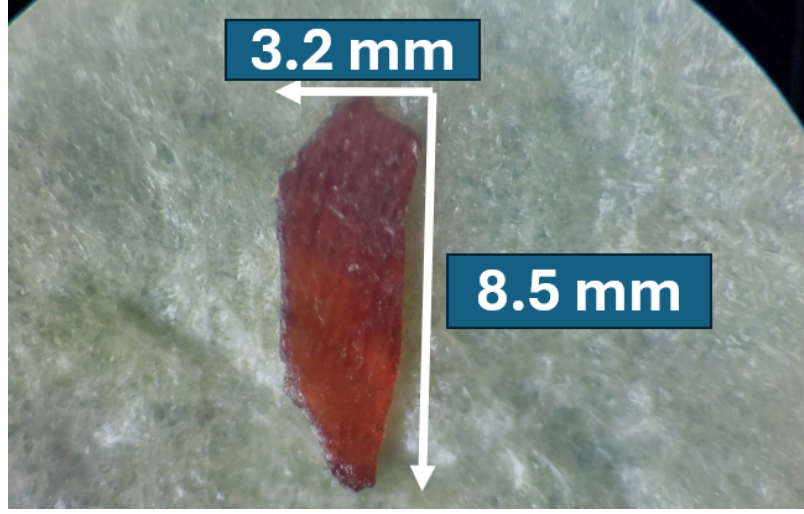


Figure 4.2: TbInO_3 single-crystal sample at hand.

This results in the following parameters:

$$\begin{aligned} c \text{ axis : } & \theta_W = -44(4) \text{ K} \quad \mu_{\text{eff}} = 5.8(2) \mu_B/\text{Tb} \\ ab \text{ axes : } & \theta_W = -12(2) \text{ K} \quad \mu_{\text{eff}} = 10.5(3) \mu_B/\text{Tb} \\ \text{powder : } & \theta_W = -15(4) \text{ K} \quad \mu_{\text{eff}} = 9.2(4) \mu_B/\text{Tb} \end{aligned}$$

Here, the effective moment μ_{eff} was determined according to eq. (2.45). A pronounced anisotropy between the c axis and the ab plane is evident, the in-plane magnetic susceptibility is higher than along the c axis by a factor of approximately 3. Apart from the deviations away from a Curie-Weiss like behavior, which are expected at low temperatures, no anomalies are visible in $\chi(T)$.

Figure 4.4 shows the quotient between the two crystallographic orientations probed χ_{ab}/χ_c at $B = 0.2$ T. It shows the magnetic anisotropy of the system and in particular the easy plane behavior through the enhanced magnetization in the ab plane. The ratio between these two approaches a maximum at $T \approx 15$ K, which is comparable to the Weiss temperatures $|\theta_W|$ for both the powder as well as the ab plane. Coming from lower temperatures, the increase is rather steep, coming from $\chi_{ab}/\chi_c \approx 2.4$ at 1.8 K to ≈ 5.1 at the maximum. Increasing T further yields a decrease in anisotropy which is somewhat reminiscent of a $1/T$ behavior. The anisotropy at 300 K is ca. 2.5.

Figure 4.5a shows the results of the isothermal magnetization $M(B)$ at 1.8 K and at 300 K for fields up to 7 T. Subplot b shows its field derivative, the isothermal susceptibility $\chi(B) = \frac{dM}{dB}$. At both temperatures, the anisotropy through the easier magnetization in the ab plane are visible. The magnetization along both axes

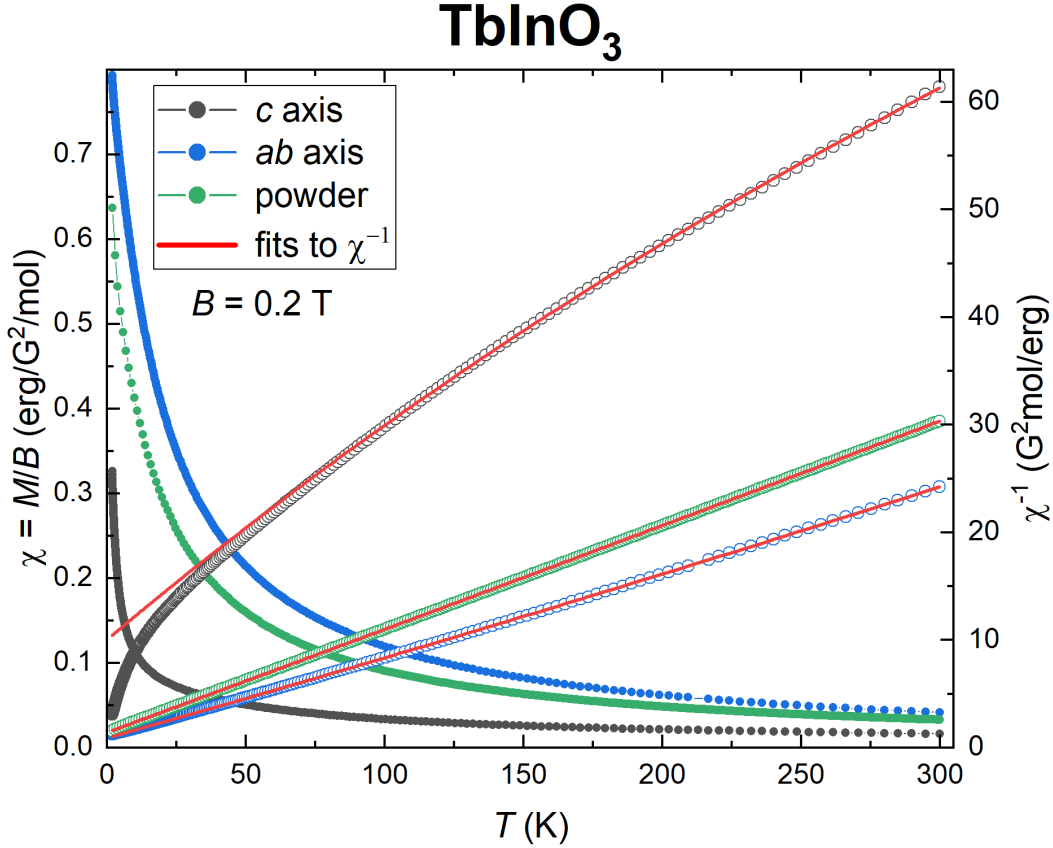


Figure 4.3: Temperature dependent static magnetic susceptibility $\chi(T) = M/B$ of single-crystal TbInO_3 between 2 K and 300 K measured at a field of $B = 0.2$ T parallel to the c axis and the ab plane respectively. Furthermore, a powder average is given. Empty markers show the inverse susceptibility and Curie-Weiss fits are marked by red lines (see the text for more details).

at 300 K is linear, along the c axis the slope is $\chi_c(B) \approx 0.015$ erg/G²/mol, it is $\chi_{ab}(B) \approx 0.04$ erg/G²/mol in the ab plane. This ratio agrees with the findings from the $\chi(T)$ measurements. At low temperatures, $T = 1.8$ K, the magnetization is much larger. An initial high slope can be seen in both directions, although the ab plane shows larger magnetizations. Along the c axis, a right bending of $M(B)$ appears at very low fields, which gradually turns into an almost linear magnetization at high fields. At 7 T, the magnetization reaches $M_c = 1 \mu_B/\text{Tb}$. The right bending for M_{ab} occurs only at ca. 1.5 T, no constant slope can be observed up to 7 T, where $M_c(7 \text{ T}) \approx 5 \mu_B/\text{Tb}$. A further anisotropic effect is that in the plane, the field deriva-

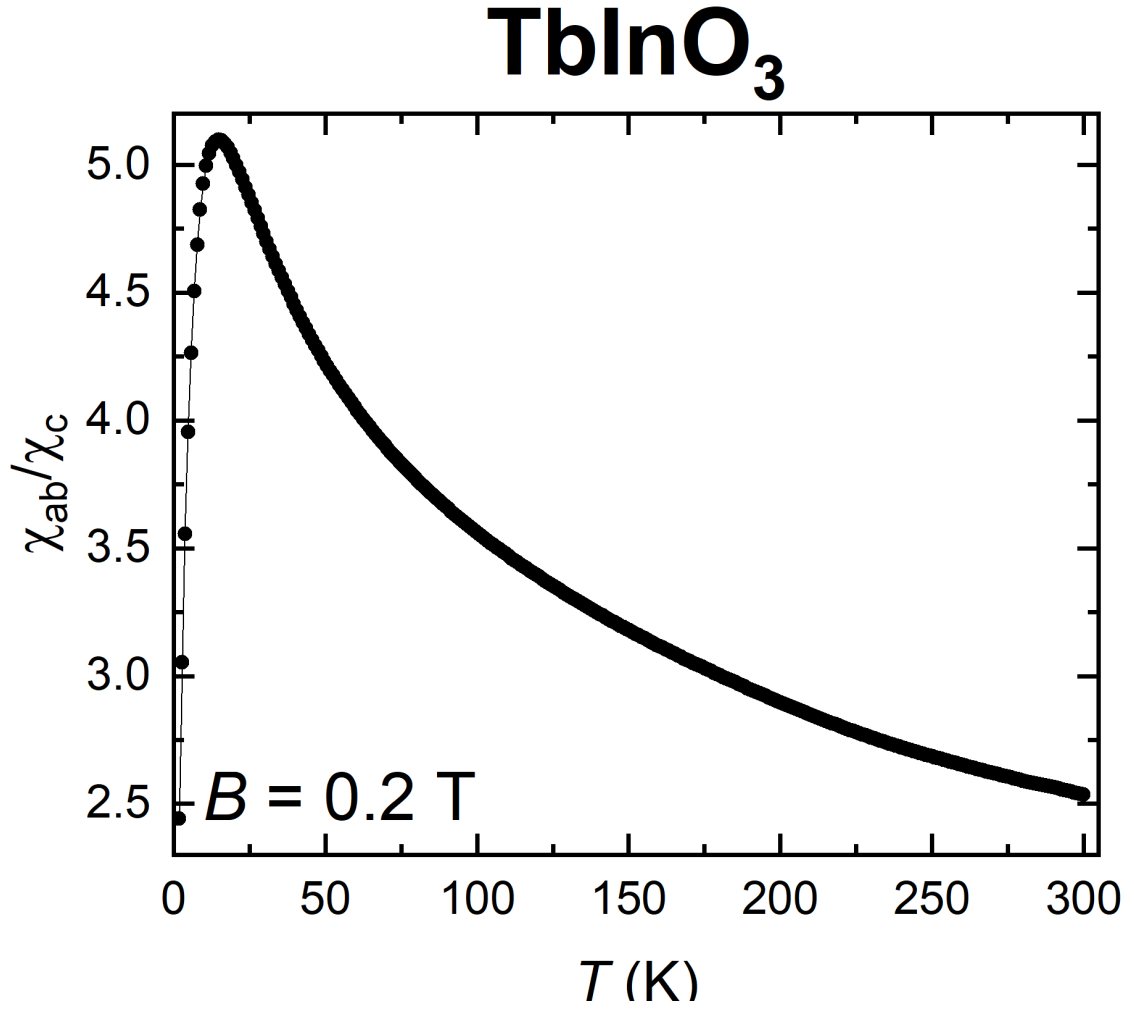


Figure 4.4: Anisotropy between the ab plane and the c axis in the form of the quotient χ_{ab}/χ_c as a function of temperature between 1.8 K and 300 K. The data used are the static magnetic susceptibilities measured at $B = 0.2 \text{ T}$.

tive $\chi_{ab}(B) = \frac{dM_{ab}(B)}{dB_{ab}}$ initially drops between 0 T and 0.5 T and then stabilizes at ca. $0.78 \text{ erg/G}^2/\text{mol}$ for $0.5 \text{ T} \leq B \leq 1 \text{ T}$. This hump in $\chi(B)$ is not seen for $B||c$.

4.3 Dilatometry

The thermal expansion and magnetostriction of TbInO_3 was investigated in a magnetic field $B||c$ in the PPMS using the dilatometric cell described in section 3.3. For

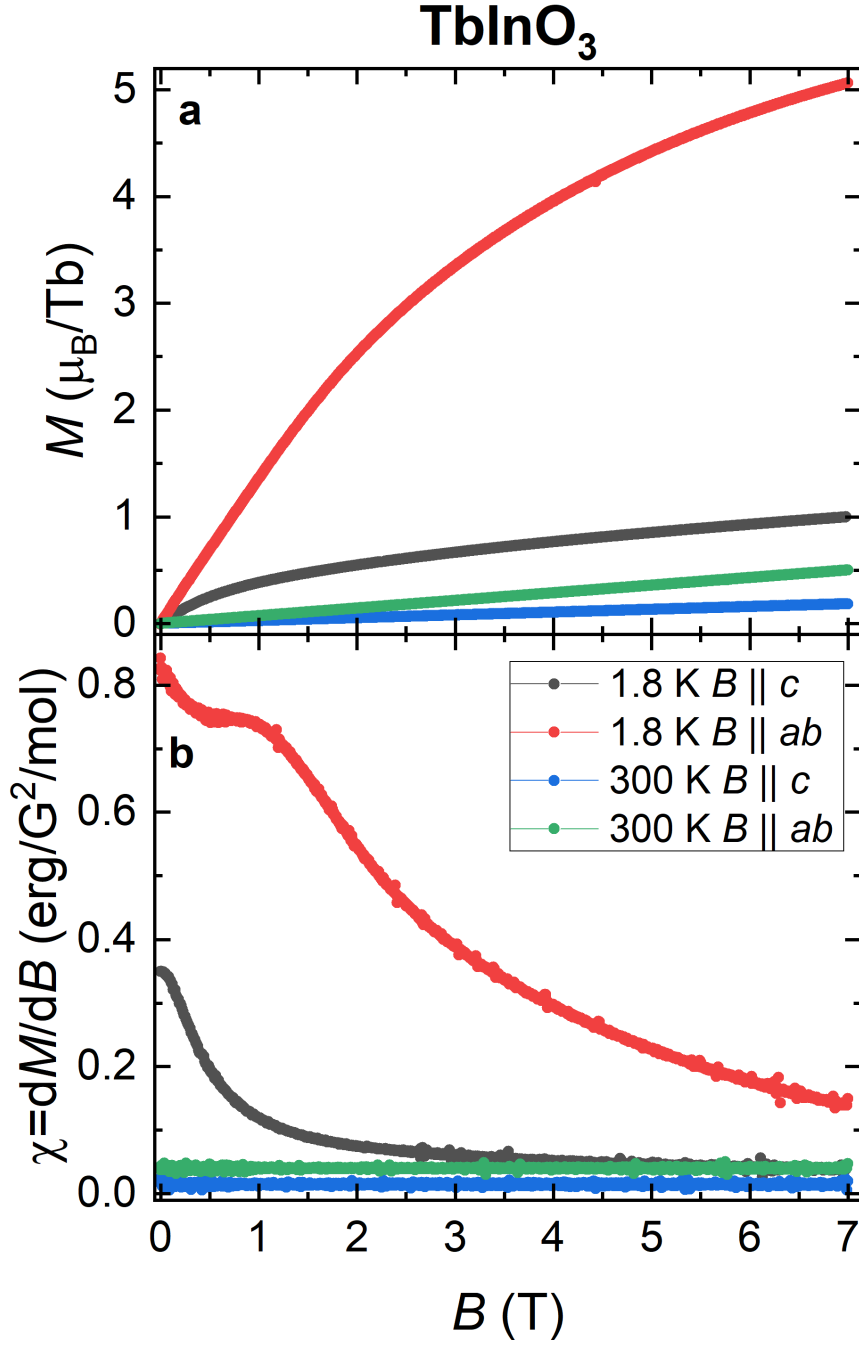


Figure 4.5: (a) Isothermal magnetization $M(B)$ at $T = 1.8$ K and 300 K measured up to 7 T. Data are presented both in parallel to the c axis as well as perpendicularly to it. Furthermore, a powder average is given. (b) is the field derivative $\chi(B) = \frac{dM}{dB}$ of the data in (a).

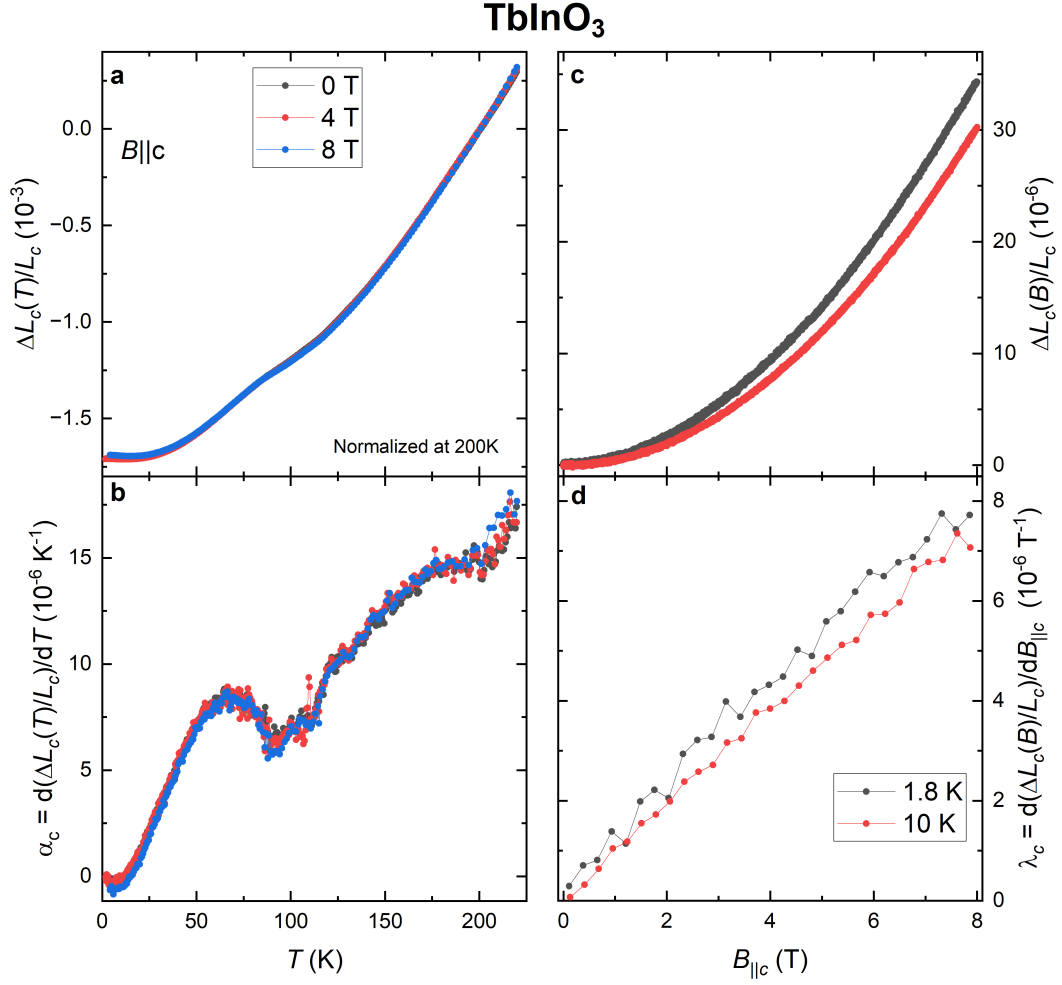


Figure 4.6: Dilatometric data for TbInO_3 with $B \parallel c$. a shows the thermal expansion data along the c axis as a function of temperature at magnetic field of $B = 0, 4, 8$ T normalized to coincide at $T = 200$ K. b are the respective thermal expansion coefficients $\alpha_c = \frac{d(\Delta L_c/L_c)}{dT}$. c is the magnetostriction as a function of applied magnetic field up to 8 T at $T = 1.8$ K and 10 K. d are the respective magnetostriction coefficients $\lambda_c = \frac{d(\Delta L_c/L_c)}{dB_{\parallel c}}$.

the thermal expansion measurements, the sample was field cooled to 1.8 K, including a brief reheating to release cooling induced stresses. The thermal expansion was then measured during the heating of the sample to 300 K. The reference length for strain normalization is the sample thickness at room temperature, $L_c = 0.172$ mm.

Furthermore, the magnetostriction was measured for fields up to 8 T at $T = 1.8$ K and 10 K.

Results of the thermal expansion measurements are shown in figure 4.6a & b. Subfigure a shows the thermally induced strain $\frac{\Delta L_c(T)}{L_c}$ for the three magnetic fields, 0 - 8 T. Subfigure b displays the respective thermal expansion coefficients $\alpha_c = \frac{d(\Delta L_c/L_c)}{dT}$. The thermal expansion at the three magnetic field strengths $B = 0, 4, 8$ T is qualitatively similar. Between 2 K and 15 K, L_c stays approximately constant in T . At higher temperatures this is no longer the case, the strain increases monotonically, albeit at a decreased rate between 85 K and 115 K. This could be construed as a hump overlaying $\frac{\Delta L_c(T)}{L_c}$. Subfigure b reveals that α_c shows a corresponding localized maximum at ~ 70 K which is followed by a decrease in α_c between 70 K and 100 K. Apart from this temperature regime, α_c grows monotonically. It appears that the thermal expansion data for 8 T are slightly shifted with respect to 0 T and 4 T. This might be a consequence of the standardization of the thermal strain (subplot a) to coincide at $T = 200$ K. Subplot c of figure 4.6 shows the magnetostriction of TbInO_3 at 1.8 K and at 10 K, subfigure d below plots the magnetostriction coefficient λ_c . The magnetostriction reveals a quadratic relationship between the field $B_{||c}$ and the strain $\frac{\Delta L_c}{L_c}$, the quadratic nature is established by the apparent linearity in $\lambda_c(B) = \frac{1}{L_c} \frac{d\Delta L_c}{dB}$. It is larger at 1.8 K than at 10 K as expected from eq. (2.25). λ_c at 1.8 K is ca. 15% larger than 10 K.

It was so far not possible to perform dilatometric measurements on TbInO_3 in the ab plane. This is because the sample broke into two smaller pieces during handling before these measurements could be conducted. Furthermore, the thin, plate like shape of the sample complicates measurements because a certain stress along the measurement axis is necessary which will very likely shatter the thin sample further.

In order to evaluate the effect of the dilatometer cage's thermal expansion, a cell effect was recorded with a copper sample of width $L = 0.236$ mm. The resulting strain and thermal expansion coefficient are shown in figure 4.7. In the cell effect, the strain as a function of temperature shows kinks in the thermal expansion coefficient α_c at 75 K and at 120 K.

4.4 Discussion

The magnetization of TbInO_3 was measured both isothermally and as a function of temperature. Thereby, trends reported in the literature regarding its behavior were confirmed. A Curie-Weiss fit (figure 4.3) yielded Weiss temperatures for both possible orientations (parallel to the c axis and perpendicular to it). θ_W for the powder average

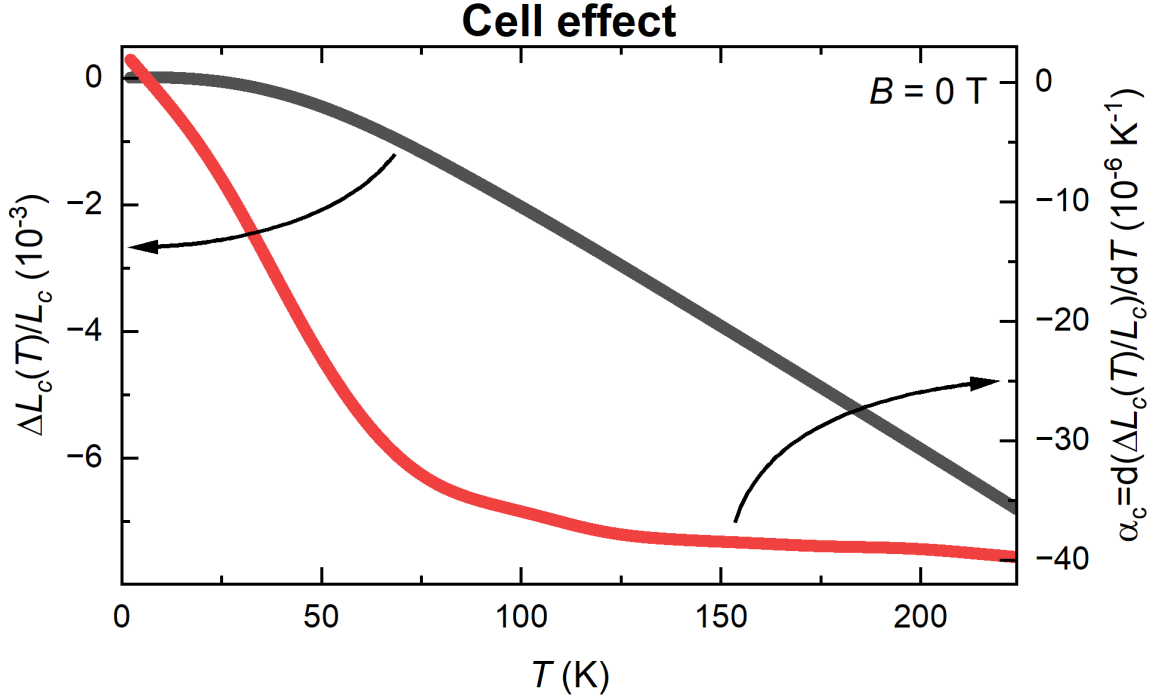


Figure 4.7: Thermal expansion $\frac{\Delta L_c(T)}{L_c}$ and thermal expansion coefficient $\alpha_c(T)$ of the dilatometer cell containing a copper sample of width $L_c = 0.236$ mm measured at $B = 0$ T.

agrees well with previous reports [67]. The temperatures established here are not in agreement with [69], where a much larger θ_W^{ab} of -205 K was found. They furthermore obtained a value for θ_W^c of +12 K, which does not agree in sign with the value reported here. Their result for the polycrystalline case was -20.6 K which is again in somewhat of an agreement with the values reported here and with [68], insofar as experimental results vary between differently synthesized samples. On the other hand, [71] have found a value for $\theta_W^{ab} = -11$ K in a thin film sample, much closer to the value determined from figure 4.3. A possible explanation for the difference in values is also that in many cases, Curie-Weiss fits are sensitive to the fitting range, Kim *et al.* do not explicitly state their chosen fitting ranges [69], while the fits described here chose a cutoff temperature of 100 K. The data obtained here yield an effective magnetic moment for each of the three spatial cases ($B||c$, $B \perp c$ and powder). Powder values were previously reported for [67] [69], these agree on $\mu_{\text{eff}} \approx 9.6 \mu_B/\text{Tb}$. Here, the powder average of the axes yields a somewhat smaller value of $9.2 \mu_B/\text{Tb}$, however it must be noticed that powder averages and values for polycrystalline samples do not necessarily agree [67]. The anisotropic Weiss temperatures for the axes are in

quantitative agreement with previous reports [69] [71]. Isothermal magnetization measurements conducted here, c.f. figure 4.5, agree with literature both qualitatively as well as quantitatively [69] [70] [71]. The reported anisotropy, in the form of the quotient $\chi_{ac}/\chi_c(T)$ peaks at ca. 15 K, which confirms the result from [67] [68].

Magnetostriction studies on TbInO_3 , as shown in figure 4.6c & d, show the magnetoelastic behavior in the probed field range between 0 T and 8 T. The magnetically induced strain at both 1.8 K and 10 K can be well modeled as quadratic, which is expected from eq. (2.25). Differences between the two temperatures can be reasoned to stem from different stiffnesses and susceptibilities at these two temperatures. In particular the susceptibility shows a significant variation between these two temperatures as was seen in figure 4.3 and figure 4.5. In the thermal expansion data, figure 4.6a & b only one feature is seen. A field independent hump can be made out which overlays an otherwise monotonous strain and thermal expansion coefficient (subplots a and b, respectively). This feature is located between 50 K and 90 K.

A possible explanation for the hump is that this is an effect due to the thermal expansion of the dilatometer cage or due to the correction for the cell effect. As can be seen in figure 4.7, the cell effect shows two kinks at $T \approx 75$ K and 120 K. Equation (3.8) describes how the thermal expansion is extracted from the cell strain. This part of the analysis is performed using programs available in the group. The formula implicitly assumes that the room temperature sizes of the chosen Cu reference and the sample are comparable. Due to the small sample size of TbInO_3 which was only approximately $170 \mu\text{m}$, the copper reference closest in size had a thickness of $236 \mu\text{m}$. A new, smaller reference could not practically be manufactured. As a result of this size mismatch of ca. 25%, eq. (3.8) becomes more susceptible to artifacts of the cell effect measurement. The observed feature for TbInO_3 is more prominent than what was observed in the cell effect, where the observed anomaly at the same temperature is only visible in the temperature derivative of the thermal expansion. Nonetheless it needs to be noted that the cell effect is overall larger, the cell effect showed $\frac{\Delta L_c(T=200 \text{ K})}{L_c} \approx 7 \times 10^{-3}$ while the corrected strain in the TbInO_3 sample was 1.7×10^{-3} . Combining this with the 25% size mismatch means that the strain of the cell is larger than the sample strain by a factor of more than 5. Any artifacts in the recorded cell effect is then magnified by a factor of 5 in the final data. This could explain the observed feature. Furthermore, it is known [73] that the mini dilatometer is sensitive to the orientation of the piston, c.f. figure 3.5. While the greatest care was taken to ensure a correct alignment, this factor cannot be completely ruled out.

Another explanation could be that the observed anomaly is of a physical origin and reflects the behavior of TbInO_3 . This argument is disfavored for the following reasons: Only one feature was found in the magnetization measurements, and that was the maximum in the ratio of the two anisotropic susceptibilities at 15 K. This is likely not

connected to the hump in α_c because it occurs at a different temperature. The feature is independent of the applied magnetic field, which was varied between 0 T and 8 T. This dissuades a field cause. Additionally, no anomalies are found in the relaxation rate of muon spins close to that temperature [68]. Kim *et al.* [69] measured the heat capacity of TbInO_3 at magnetic fields ranging from 0 T to 13 T and did not report any anomalies close to the hump at 70-100 K. This can serve as evidence that there is likely no crystallographic process underlying it, either, since this would be noticeable in calorimetric data. The only differences between the measurements for the three applied field strengths is visible in the low temperature region below $T = 30$ K, where $\left| \frac{\Delta L_c(T)}{L_c} \right|$ is smaller for $B = 8$ T than for the lower fields. Since the magnetostriction in figure 4.6c & d is featureless up to 8 T, this difference in the thermal expansions is likely not physical.

5 $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$

5.1 Introduction

$\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ can be considered to be part of the broad family of $R_2^{3+}M_2^{4+}\text{O}_7^{2-}$ compounds [40], where R^{3+} is a trivalent rare earth ion (or Y) and M^{4+} is a tetravalent (non-rare earth) metal ion. Of particular interest for the following investigation is the restriction of $M = \text{Ti}, \text{Zr}, \text{Hf}$; their tetravalent ions have only fully filled electron shells, in this case their electronic configuration is that of the noble gases, and they are thus non-magnetic. This means that the only magnetic ion species in $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ are the trivalent Tb^{3+} ions.

The crystal structures of $R_2M_2\text{O}_7$ ($M = \text{Ti}, \text{Zr}$) have previously been investigated for various rare earth ions [40] [74]. Their crystal structure is dependent on the ratio of the cationic radii r_R/r_M . Three particular cases for this distortion factor are described: For $r_R/r_M \gtrsim 1.78$, the oxide will crystallize in a perovskite-type lattice. For $1.46 \lesssim r_R/r_M \lesssim 1.78$, the crystal structure is of the pyrochlore-type. For a choice of ions with values in-between these cases, the lattice takes on a defect fluorite structure, which is characterized by structural disorder on the cation sites between the R and M ions. A defect fluorite structure is an anion deficient fluorite lattice, as shown in figure 5.1. Pyrochlore lattices can be characterized as a defect fluorite lattice that has undergone an anionic reordering [40] [75]. The structural disorder between the two cation species in $R_2\text{Zr}_2\text{O}_7$ was investigated in $\text{Tb}_2\text{Zr}_2\text{O}_7$ in [74] [76] [77]. A similar disordering is observed in $\text{Gd}_2\text{Zr}_2\text{O}_7$ [78] [74] and $\text{Ho}_2\text{Zr}_2\text{O}_7$ [79] [80]. Rare-earth zirconates with a defect fluorite structure are structurally disordered through mixing between their anion lattice sites, in this case between the R and Zr sites [40]. The disorder is accompanied by an observed connection between the ionic conductivity in the defect fluoride lattice and the ratio of the ionic radii [81] [82]. This increased mobility can be understood by considering that as r_R/r_M approaches 1, the ions on the R and M sites converge in radius which reduces the energy cost of the hopping [83]. It also influences the spin dynamics and through that also the magnetic structure of the system itself [84]. Members of the class $R_2M_2\text{O}_7$ are reported to take on a manifold of magnetic ground states, exhibiting long-range ordered phases, spin-glass, spin-ice and spin-liquid behavior [41]. Various rare-earth zirconates $R_2\text{Zr}_2\text{O}_7$ have been investigated by magnetometry in different temperature regimes and dominantly

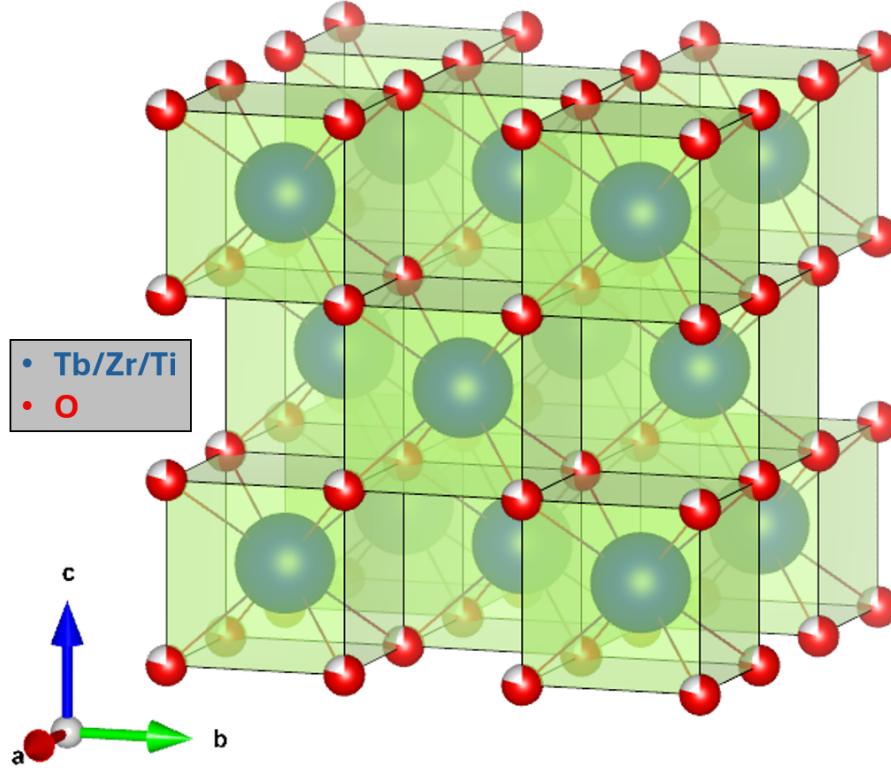


Figure 5.1: VESTA Rendering of the defect fluorite crystal structure of $Tb_2Zr_2O_7$. The Tb and Zr cations, colored in blue, are cubically coordinated by O anions (red). The structure has an anion deficiency of ca 12.5%.

show antiferromagnetic interactions [78] [84] [85] [86] [87].

In this work, $Tb_2Zr_2O_7$ and $Tb_2Zr_{1.5}Ti_{0.5}O_7$ were investigated in particular. The ionic radii of the un-titanated sample $Tb_2Zr_2O_7$ yield a ratio of $r_{Tb}/r_{Zr} \approx 1.4 - 1.5$ which places it right at the border between adapting a fluorite or a pyrochlore structure [40] [79] [88]. This agrees with previous investigations [76]. For $Tb_2Zr_{1.5}Ti_{0.5}O_7$, the quotient can be obtained by assuming an approximately random population of the two M ions and calculating it using the weighted harmonic mean

$$r_{Tb}/\langle r_{Zr_{1.5}Ti_{0.5}} \rangle = r_{Tb} \frac{\frac{1.5}{r_{Zr}} + \frac{0.5}{r_{Ti}}}{2} \approx 1.51. \quad (5.1)$$

This larger value suggests a tendency towards a pyrochlore lattice assuming the validity of the model described in [40]. No experimental work on $Tb_2Zr_{1.5}Ti_{0.5}O_7$ has been published to date so the crystal structure cannot be compared to other structural experiments.

Previous works have found $\text{Tb}_2\text{Zr}_2\text{O}_7$ and $\text{Tb}_2\text{Hf}_2\text{O}_7$ to exhibit a glassy magnetic behavior [76] [89]. The same is true for $\text{Ho}_2\text{Zr}_2\text{O}_7$ [84] [87], where Ho^{3+} has an even larger ionic radius than Tb^{3+} and thus r_R/r_M is increased. $\text{Tb}_2\text{Ti}_2\text{O}_7$, the member of the $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ family with $x = 2$, is speculated to be a quantum spin liquid [90] [91]. Other works expect to see a crossover between the reported glassy properties of $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Zr}_2\text{O}_7$ at some Ti concentration while tuning the value of x from 0 to 2 [76]. The influence of tuning the ionic radii ratio was investigated in the related compounds $\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ [92], $\text{Gd}_{2-x}\text{Ti}_x\text{Zr}_2\text{O}_7$ [74], $\text{Ho}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ [79] [93] and $\text{Nd}_{2-x}\text{Zr}_{2+x}\text{O}_{7+x/2}$ [94] showing an enhancement of the disordered defect fluorite structure. Ordering of $\text{R}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ solid solutions away from the defect fluorite phase is to be expected only at higher Titanium levels [79].

5.2 Magnetometry

Samples of $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ with $x = 0$ and $x = 0.5$ were investigated regarding their magnetic behavior, in particular at low temperatures. Both samples are polycrystalline. They were provided by the group of C. S. Yadav of IIT Mandi, India. The samples have the masses 14.61(2) mg and 33.69(2) mg for $\text{Tb}_2\text{Zr}_2\text{O}_7$ and $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$, respectively. After some initial measurements, it was determined that the sample size was too large because the magnetic moment at high fields exceeded the measurement range of the magnetometer. In order to overcome this, both samples were broken down into smaller pieces with mass 6.97(2) mg and 5.38(2) mg ($\text{Tb}_2\text{Zr}_2\text{O}_7$ and $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$).

The magnetization of both samples was measured at $B = 0.1$ T in the temperature range from 1.8 K to 350 K. For this, the MPMS3 was used with the brass and straw sample holders for measurements with $T = 1.8 - 300$ K and for sub-Kelvin measurements, respectively. During all the measurements, the samples were stored in a plastic capsule. Its magnetic signature can be neglected in the following as the $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ samples have a very large moment themselves. Figure 5.2 shows the results of these measurement as well as the respective inverse susceptibility $\chi^{-1}(T)$. For $T \gtrsim 40$ K, a $\chi \propto 1/T$ behavior can be observed. Below this, the susceptibility increases faster than $1/T$ during cooling. This is especially visible in χ^{-1} which is approximately linear down to 40 K where it starts to curve into a stronger decrease. A modified Curie-Weiss law is fitted to the data. The modification assumes a temperature independent susceptibility term added to eq. (2.48):

$$\chi(T) = \frac{C}{T - \theta_W} + \chi_0. \quad (5.2)$$

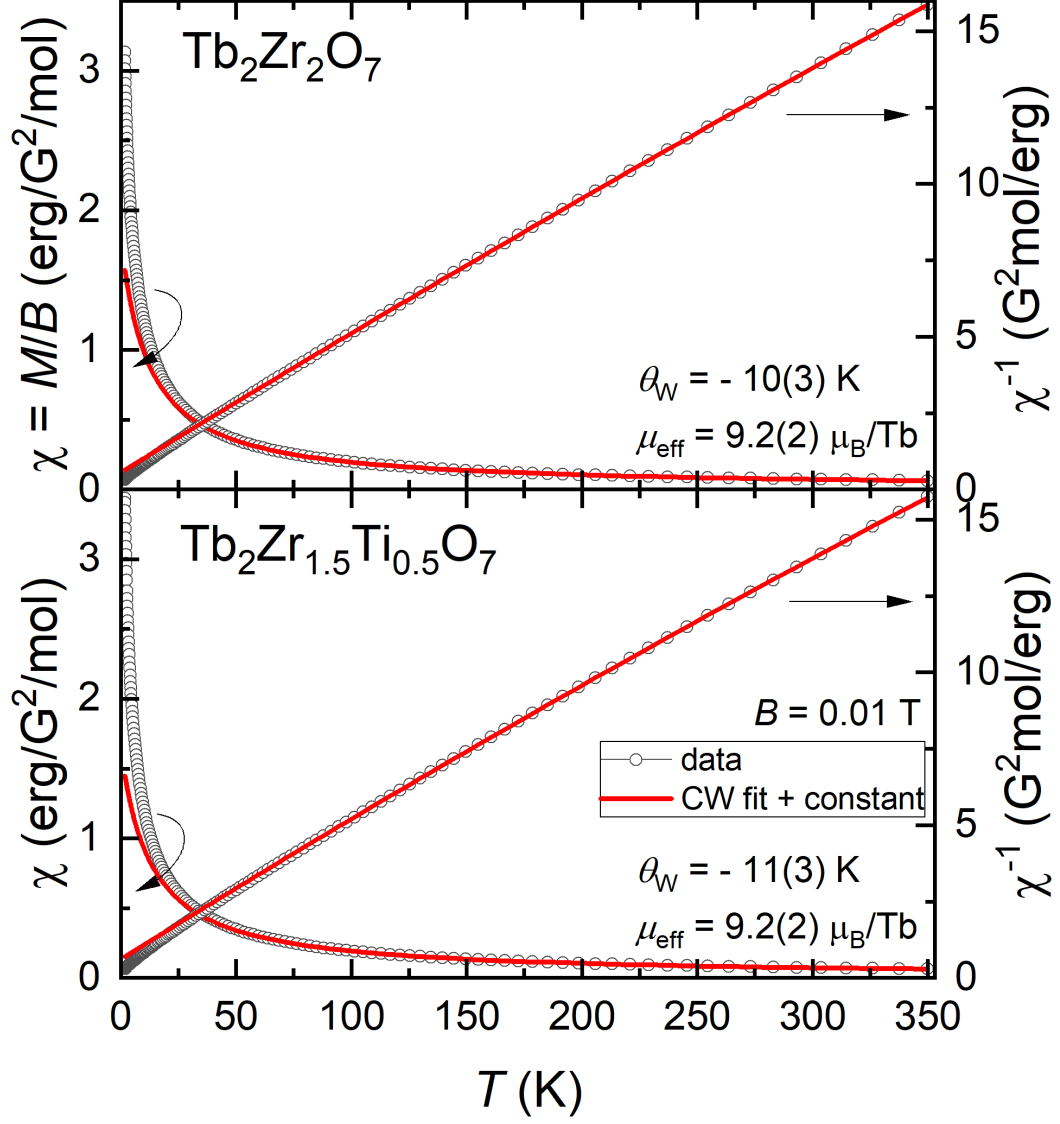


Figure 5.2: Static magnetic susceptibilities $\chi(T)$ and χ^{-1} of polycrystalline $Tb_2Zr_2O_7$ and $Tb_2Zr_{1.5}Ti_{0.5}O_7$ between 1.8 K and 350 K at 0.01 T. The red lines mark a Curie Weiss fit. The Weiss temperature θ_W and effective magnetic moment μ_{eff} are derived from the data. For details regarding the fitting, refer to the text.

The derived Weiss temperature θ_W and effective magnetic moment μ_{eff} are

$$\begin{aligned}\theta_W &= -10(3) \text{ K} & \mu_{\text{eff}} &= 9.2(2) \mu_B/\text{Tb} & \text{for Tb}_2\text{Zr}_2\text{O}_7, \\ \theta_W &= -11(3) \text{ K} & \mu_{\text{eff}} &= 9.2(2) \mu_B/\text{Tb} & \text{for Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7.\end{aligned}$$

μ_{eff} is obtained from C with the help of eq. (2.45). These values are in accordance with expectations as crystal field effects become significant in the low temperature regime [87]. The $\text{Tb}_2\text{Zr}_2\text{O}_7$ values of μ_{eff} and θ_W are in agreement with previous works [76].

5.2.1 Sub-Kelvin DC Magnetometry

DC magnetization in the temperature regime above 1.8 K reveals no ordering phenomena, however the presence of interactions between the magnetic moments are hinted at by the non-zero Weiss temperature determined in the previous section. Lower temperatures are probed in the dilution refrigerator option of the iQuantum 3. For this the brass sample holder were substituted for plastic straw holders. This was done by recording $\chi(T)$ and $M(B)$ curves. Results from the former for both $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ samples at multiple applied static magnetic fields are shown in figure 5.3a & d. Both zero field cooled (ZFC) and field cooled (FC) measurements were performed. Furthermore, the temperature derivative $\frac{d\chi}{dT}$ of the ZFC measurements (panels b & e) and the difference between the FC and the ZFC data are also shown (panels c & f). Figure 5.4a & d show the magnetization for both materials. Added into the insets of these subplots are the same data zoomed into the lower field regime. The first and second field derivatives as a function of the magnetic field for both materials are shown in subplots b & e and c & f, respectively.

The T -dependent susceptibilities of $\text{Tb}_2\text{Zr}_2\text{O}_7$ and $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ (as shown in subplots a & d of figure 5.3) exhibit a qualitatively similar behavior of both systems at all probed fields except at $B = 0.1$ T. In fields up to and including 0.5 T, a maximum in $\chi(T)$ is seen in the ZFC measurements at temperatures ranging from ca. 1.4 K at 0.01 T to 0.5 K at 0.5 T, they are marked with purple triangles. The shift is monotonous in both materials. Below the peak temperature of the ZFC curves, the FC susceptibility $\chi = M/B$ is quasi constant with only a small positive slope with decreasing T . The onset of the bifurcation between FC and ZFC at the maximum of $\chi(T)$ is shifted to higher temperatures in $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ compared to $\text{Tb}_2\text{Zr}_2\text{O}_7$. These temperatures are marked with purple triangles in the plots. A further shoulder in $\chi(T)$ is visible at 0.4-0.45 K after field cooling at $B < 0.1$ T without a clear correlation to the magnetic field. It is massively enhanced in $\text{Tb}_2\text{Zr}_2\text{O}_7$ at 0.1 T where it occurs at 450 mK and has the same size as the main peak, these are also marked with

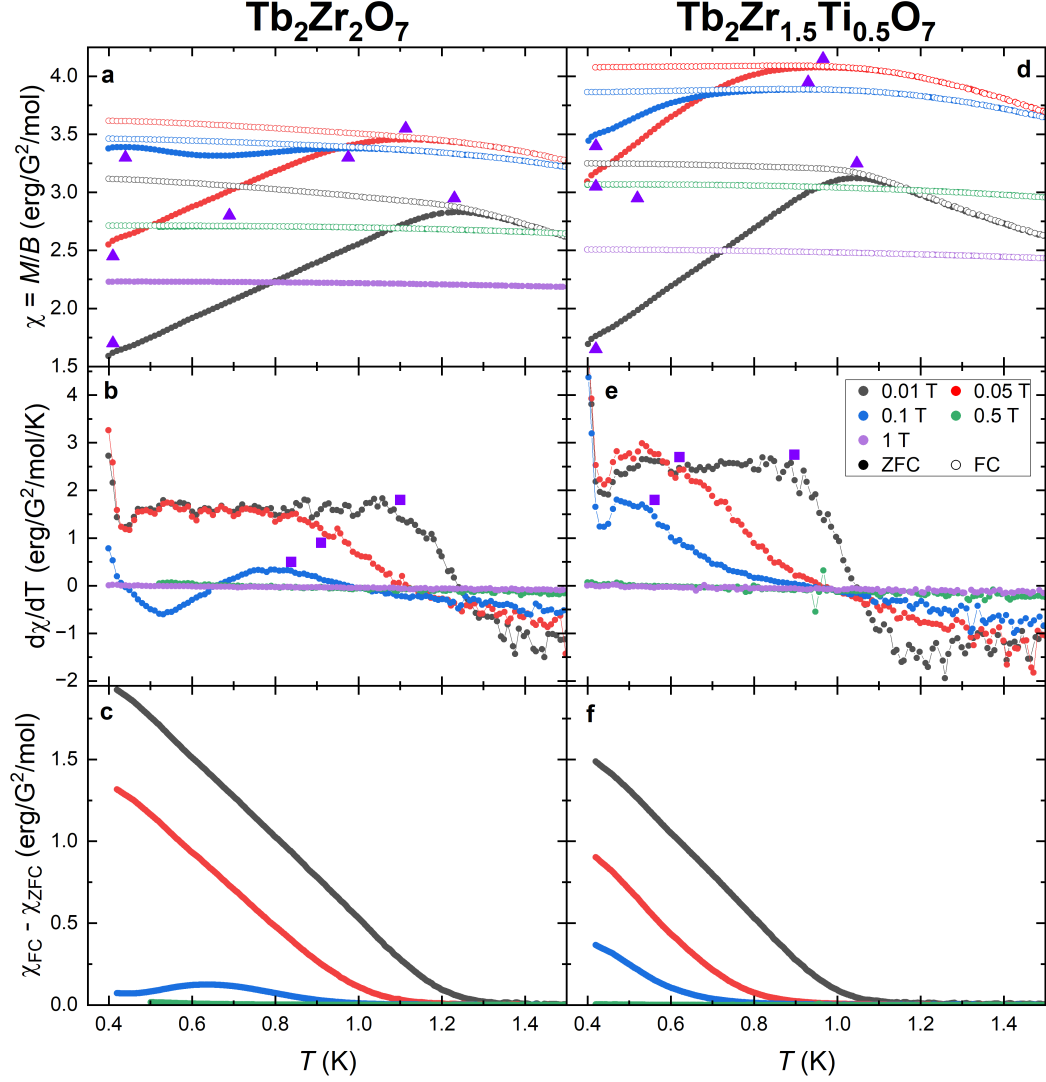


Figure 5.3: Low temperature magnetic susceptibility $\chi(T) = M(T)/B$ of polycrystalline $Tb_2Zr_2O_7$ and $Tb_2Zr_{1.5}Ti_{0.5}O_7$ at different external applied fields for zero-field cooled (ZFC) and field cooled (FC) measurements in a&c. b&e show the derivative of the ZFC susceptibility $d\chi_{ZFC}/dT$. c&f are the difference $\Delta\chi = \chi_{FC} - \chi_{ZFC}$. The purple triangles mark maxima and shoulders in $\chi(T)$, the squares mark shoulders in its derivative.

purple triangles. As further evidenced by the temperature derivatives of the susceptibility in figure 5.3b & e, the slope of the ZFC susceptibility at temperatures below the maximum in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ is larger in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ than in $\text{Tb}_2\text{Zr}_2\text{O}_7$. A shoulder (marked with purple squares) is seen in these data corresponding to a stabilization of the slope of χ_{ZFC} . It shifts with increased field to lower temperatures, from 1.1 K to 0.8 K in $\text{Tb}_2\text{Zr}_2\text{O}_7$ and from 0.9 K to 0.6 K in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ (for fields going from 0.01 T to 0.1 T). The difference between ZFC and FC in 0.5 T is too small to evaluate this feature.

Subplots figure 5.3c & f compare the difference between ZFC and FC, $\Delta\chi(T) = \chi_{\text{FC}}(T) - \chi_{\text{ZFC}}(T)$, across the four fields for both materials separately against temperature with a shared axis scaling for $\Delta\chi$. The difference appears systematically shifted to lower temperatures in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ (except at 0.1 T where the enhanced hump at 450 mK in $\text{Tb}_2\text{Zr}_2\text{O}_7$ suppresses the split).

Figure 5.4 shows the $M(B)$ magnetization behavior of both $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ at various temperatures spanning an order of magnitude between 0.4 K and 4 K in subplots a and d. For better visibility, curves of different temperatures are shifted vertically by $0.25 \mu_{\text{B}}/\text{Tb}$. The measurements include an up and down sweep of the field. All shown magnetization curves follow a broadly similar behavior, reminiscent of a Brillouin function (eq. (2.40)) with an overlaid linear behavior, i.e they initially increase steeply up to a right bending into a saturated and sloped field regime above approximately 2 T. At 7 T, the 1.2 K measurements show a maximum magnetization of roughly $\mu_{\text{plateau}} \approx 4.6(4.3) \mu_{\text{B}}/\text{Tb}^{3+}$ for $\text{Tb}_2\text{Zr}_2\text{O}_7$ ($\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$). This is ca. 50% of the free ion value of $\mu_{\text{sat}} = 9 \mu_{\text{B}}/\text{Tb}^{3+}$ for a Tb^{3+} ion with $S = L = 3$, $J = 6$. A change with T is not visible. The linear high field behavior can be linearly extrapolated and yields a plateau value of $3.5(3) \mu_{\text{B}}/\text{Tb}^{3+}$ for both systems. The discrepancy between measured values and free ion values can be explained by crystal field effects [95]. If the measured μ_{plateau} is assumed to be the saturation magnetization of the respective crystal field level, then the extrapolated values would correspond to a magnetic state of the free ion with a quantum number $m_J \approx 2 - 3$, and not $m_J = 6$ as predicted by Hund's rules for a free ion. The isothermal magnetization data barely exhibit any temperature dependence in their plateau field. At sub-Kelvin temperatures, particularly at 0.4 K - 0.8 K, the samples show a minute field hysteresis of $\Delta H \lesssim 20$ mT at 0.4 K and even smaller at 0.8 K. $\text{Tb}_2\text{Zr}_2\text{O}_7$ shows this at both 400 and 800 mK, while it is no longer visible at 800 mK in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$. This data can be compared to figure 5.3c & f: As predicted from the analysis of the FC/ZFC split, a hysteretic behavior should end at ca. 0.5 T. This is confirmed by the field dependent magnetization. As described above, the hysteresis is larger in $\text{Tb}_2\text{Zr}_2\text{O}_7$.

Further notable features here are not readily apparent from the $M(B)$ data but they become visible when examining the first and second field derivatives, as seen

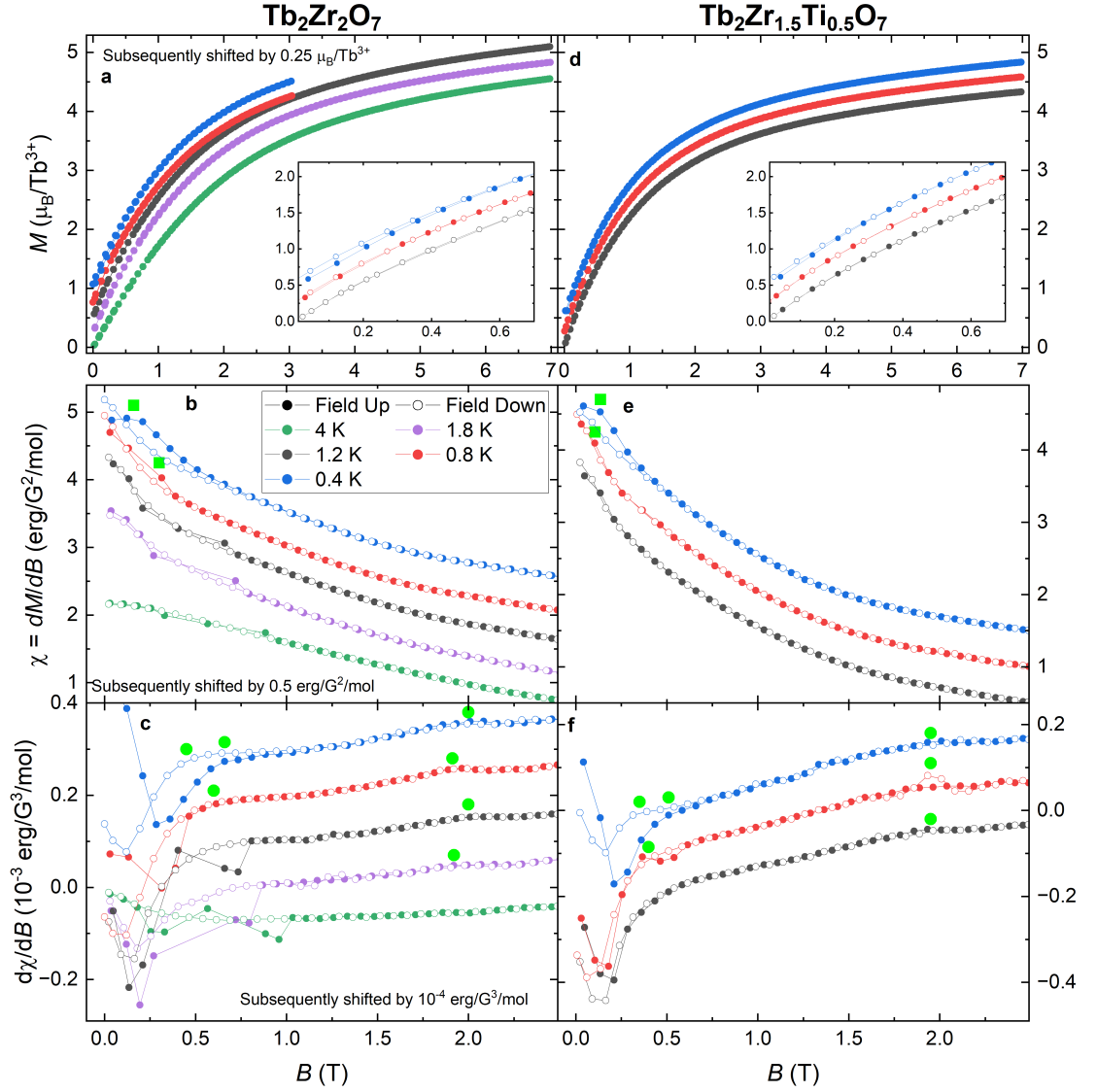


Figure 5.4: Low temperature isothermal magnetization data plotted against the magnetic field B for polycrystalline $Tb_2Zr_2O_7$ and $Tb_2Zr_{1.5}Ti_{0.5}O_7$ at multiple temperatures. Downsweeps are marked with empty circles. Subplots a & c show the magnetization $M(B)$ with zoomed in copy in the insets. b & e show the B derivative $\chi = dM/dB$, c & f show the second derivative. Curves for different temperatures are shifted relative to each other for better visibility. The green squares in subplots (b) & (e) mark shoulders in $\frac{dM}{dB}$, the green dots in subplots (c) & (f) mark maxima in and shoulders in the second derivative $\frac{dM^2}{dB^2}$.

in figure 5.4b-c & e-f. Points of interest are marked by green squares and circles in the plots. No constant regime in $\chi(B)$ is observed, i.e. $M(B)$ does not increase linearly over any observed field regime. The isothermal susceptibility shows subtle shoulders (green squares) in the initial magnetization regime at fields of 0.1 – 1 T for $T \leq 0.8$ K. At 0.4 K the shoulder is visible at 0.16 T in $\text{Tb}_2\text{Zr}_2\text{O}_7$ and 0.135 T in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$, this is shifted to 0.30 T and 0.10 T at 0.8 K in $\text{Tb}_2\text{Zr}_2\text{O}_7$ and $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ with increased temperature. They vanish in the down sweeps and are marked with squares. Relating to $M(B)$, the shoulders in its derivative correspond to an initial left bending of the magnetization curve at small field before reaching an inflection point, where it turns into the dominant right bending, similar to an S shape. The second field derivatives (subfigures c and f) reveal further anomalies: At temperatures $T < 4$ K, d^2M/dB^2 shows a peak around 1.9 T, the exact positions do not exhibit a consistent trend with temperature and are the same for both materials. Furthermore, there appears to be an additional shoulder in the field range between 0.4 T and 0.8 T in both materials, shifting to higher fields with T and with lower Ti content. It is suppressed above 0.8 K and barely visible at 0.8 K. The shoulder shows a hysteresis in position only at 0.4 K where it splits into two at 0.45 T and 0.66 T in $\text{Tb}_2\text{Zr}_2\text{O}_7$ and 0.35 T and 0.51 T in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$. Both the peak at 1.9 T and the shoulders are marked with green circles. At temperatures between 0.8 K and 1.8 K, there persists a mostly temperature independent shoulder in $\frac{d^2M(B)}{dB^2}$, onto which the aforementioned hump is overlaid.

5.2.2 AC Magnetometry

Furthermore the response behavior of the two samples was also probed with alternating magnetic fields at multiple frequencies and static field biases in the temperature range 1.8 K - 40 K. An excitation amplitude of $B_{ac} = 8$ Oe was chosen for all measurements. For stability reasons, it was decided to use a brass sample holder. An exemplary measurement at $B_{dc} = 0.5$ T, $f = 3$ Hz in the straw holder revealed that the signal quality was only degraded in brass but not to an extent which would hint at suppression of features. This is shown in appendix A. The results for $\text{Tb}_2\text{Zr}_2\text{O}_7$ are shown in figure 5.5 for $f = 3$ Hz, 113 Hz, 531 Hz. In particular, the reactive components χ' are shown in subplots a,d,g, its temperature derivative is in subplots b,e,h and the absorptive component χ'' is in c,f,i. For $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$, no workable results could be obtained at 531 Hz, for the other frequencies results are shown in figure 5.6 with the same subplot scheme as $\text{Tb}_2\text{Zr}_2\text{O}_7$. Measurements in some fields were only performed on one sample or on specific frequencies. Not all fields were applied in for both materials and frequencies. Furthermore, the ac susceptibility of $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ has also been measured in the absence of a static field, see figure 5.7

at various frequencies between 3 Hz and 931 Hz.

Subplots a,d,g of figure 5.5 and 5.6 show the reactive components of the ac susceptibility for both samples. Above 20 K, all curves show a $1/T$ like behavior. At lower temperatures, a B_{dc} -dependent deviation appears. In the lowest dc fields (≤ 0.1 T), only small deviations in the form of a subtle left bending of χ' are registered at the lowest temperatures around 2 K in both systems alike. A shoulder forms in higher B_{dc} , at ca. 4.5 T in 0.5 T in both $Tb_2Zr_{2-x}Ti_xO_7$, which shifts to lower T with increased field strength, going to 2.5 K at 2 T in $Tb_2Zr_{2-x}Ti_xO_7$. Differences between the two materials are not registered with this feature. Additionally to this, a second, rather broad peak in χ' appears at 10.5 K in $Tb_2Zr_2O_7$ and at 12 K in $Tb_2Zr_{1.5}Ti_{0.5}O_7$ at 1 T and at 15 K at 2 T in $Tb_2Zr_2O_7$. No significant frequency dependence is seen when comparing 3 Hz with 113 Hz. The derivative $d\chi'/dT$ in subplots b,e,f is used to more accurately localize these anomalies.

In fields above 0.1 T, a visible peak or kink in the absorption χ'' appears, see figure 5.5 and figure 5.6 c,f,i. In 0.1 T at 3 Hz, this is located at 7 K and shifts steadily to higher temperatures with increased fields at a rate of approximately 1 T/K. The feature's height is correlated with the bias field, its width relative to the height increases with B_{dc} . At the highest probed field, 2 T in $Tb_2Zr_2O_7$, this is visible at 10 K. The location and field dependence of the high temperature (relative to the other) feature suggests that the absorption peak is field induced. As becomes visible in figure 5.5 for $Tb_2Zr_2O_7$, the peak temperature in χ'' shifts slightly with increased field. The height of the absorption peak visibly decreases with increased frequency and static field in both systems, it tends to be slightly larger in $Tb_2Zr_2O_7$ (see both figure 5.5 and figure 5.6).

Figure 5.7 displays the dynamic susceptibility of $Tb_2Zr_{1.5}Ti_{0.5}O_7$ measured without bias magnetic field and at a wider range of frequencies ranging from $f = 3$ Hz to 931 Hz. No significant frequency dependence in χ' and $d\chi'/dT$ is visible, see subplots a&b. The χ'' data in subplot c reveal a slight kink at $T = 6 \pm 1$ K. This is in agreement with an extrapolation of the previously presented χ'' in a static field. A small tendency for the peak in absorption to shift down with temperature with an increased frequency is possible, although this is cannot be clearly established due to the small signal size and the rather high noise level in 531 Hz.

5.3 Discussion

The reported data on $Tb_2Zr_{1-x}Ti_xO_7$ appear to corroborate the expectation that both systems do not exhibit magnetic long range order in the full probed temperature range down to $T = 400$ mK. Main characteristics of a glassy system are laid out in

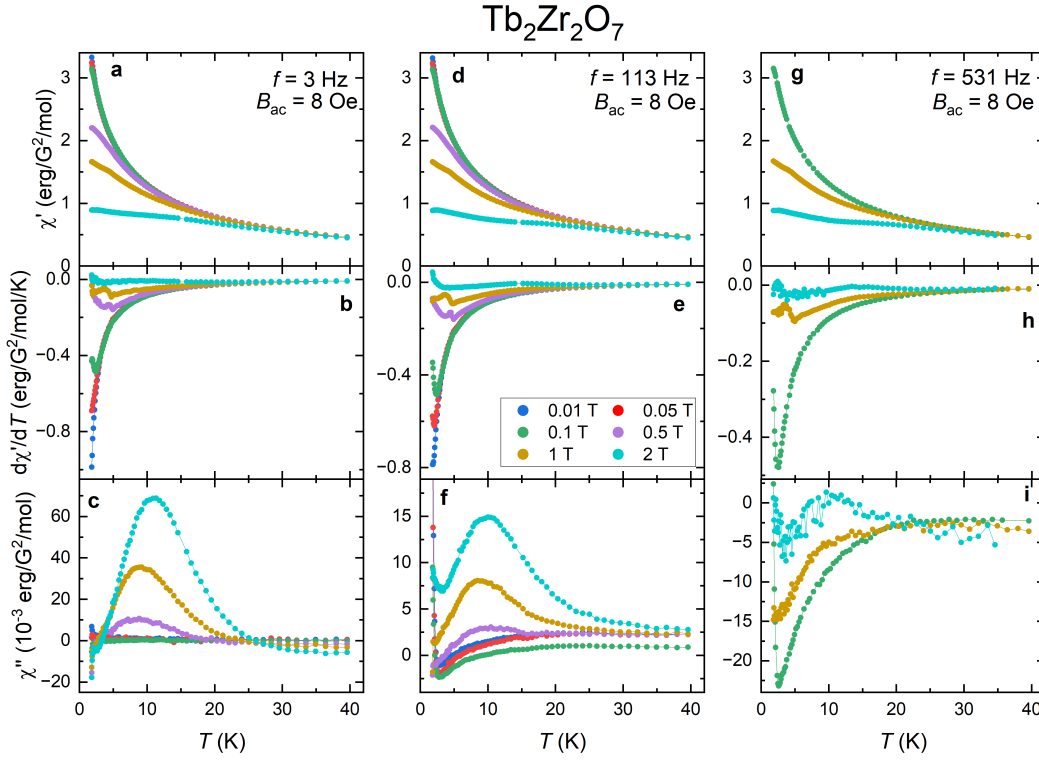


Figure 5.5: Dynamic susceptibility data of polycrystalline $\text{Tb}_2\text{Zr}_2\text{O}_7$ after zero field cooling as a function of sample temperature $1.8 \text{ K} \leq T \leq 40 \text{ K}$ at various applied fields $0.01 \text{ T} \leq B \leq 2 \text{ T}$ and excitation frequencies $3 \text{ Hz} \leq f \leq 531 \text{ Hz}$. The excitation field had an amplitude of $B_{ac} = 8 \text{ Oe}$. Subplots a, d, g show the reactive component χ' . b, e, h are temperature derivative of the previous plots $\frac{d\chi'}{dT}$. c, f, i show the absorptive components χ'' .

section 2.2.4. The $M(T)$ data shown in figure 5.2 imply dominant antiferromagnetic interactions, which is necessary for the frustration crucial to glassiness. Investigating the magnetization behavior further, into the sub-Kelvin range, reveals a bifurcation depending on the cooling protocol (FC/ZFC split), see figure 5.3a & d. This is indicative of the underlying blocking process in which the zero field cooled system is frozen into a spin configuration which it can only exit to follow the applied field on very long timescales. Since the mechanism counteracting the frozen-in state is a polarization of the spins, it must be expected that the bifurcation temperatures are shifting to lower temperatures with increased fields. The bifurcation temperatures as a function of the applied field are plotted as pink squares in figure 5.10. A linear

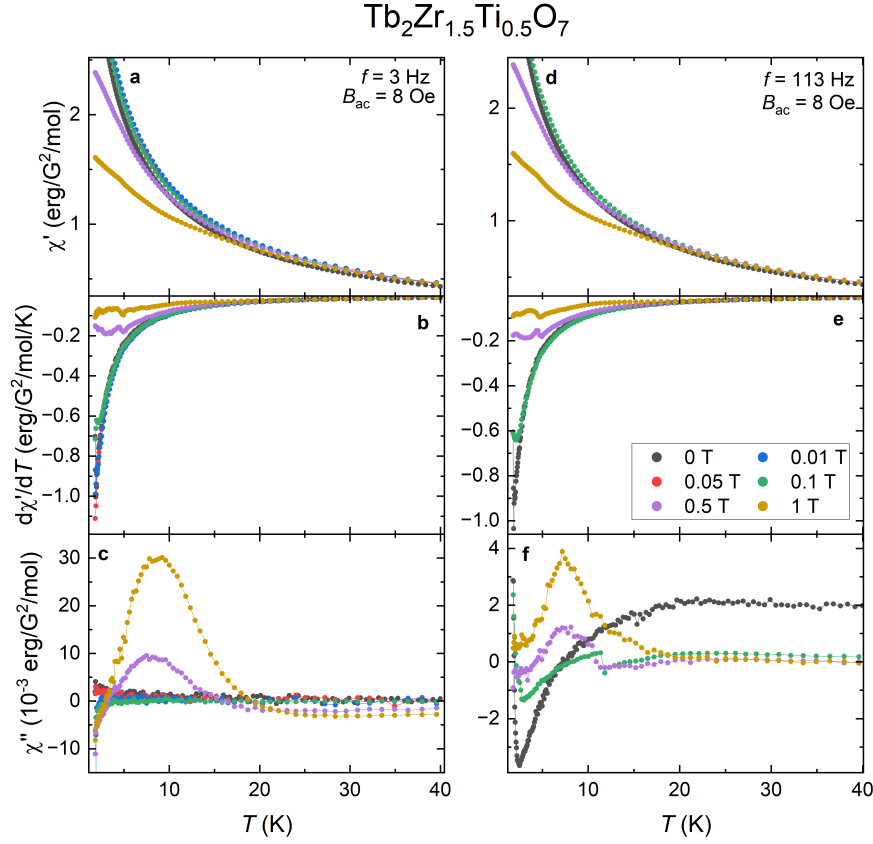


Figure 5.6: Dynamic susceptibility data of polycrystalline $Tb_2Zr_{1.5}Ti_{0.5}O_7$ after zero field cooling as a function of sample temperature $1.8 \text{ K} \leq T \leq 40 \text{ K}$ at various applied fields $0 \text{ T} \leq B \leq 1 \text{ T}$ and excitation frequencies $3 \text{ Hz} \leq f \leq 113 \text{ Hz}$. The excitation field had an amplitude of $B_{ac} = 8 \text{ Oe}$. Subplots a, d show the reactive component χ' . b, e are its temperature derivative $\frac{d\chi'}{dT}$. c, f show the absorptive component χ'' .

extrapolation of these points to higher fields suggests that the hysteresis would be suppressed to a temperature below 400 mK, which is not accessible with the available setup, at fields above 1 T. Directly comparing the two compounds shows that the blocking is reduced in $Tb_2Zr_{1.5}Ti_{0.5}O_7$. Due to the partially disordered distribution of the anions in the lattice and the 7/8 occupation of oxygen sites, the local environment around the Tb ions is statistically distributed. It is argued in [6] that such a glassy system exhibits a characteristic S-shape in its isothermal magnetization after being zero field cooled due to the environmental disorder. This phenomenon is hinted

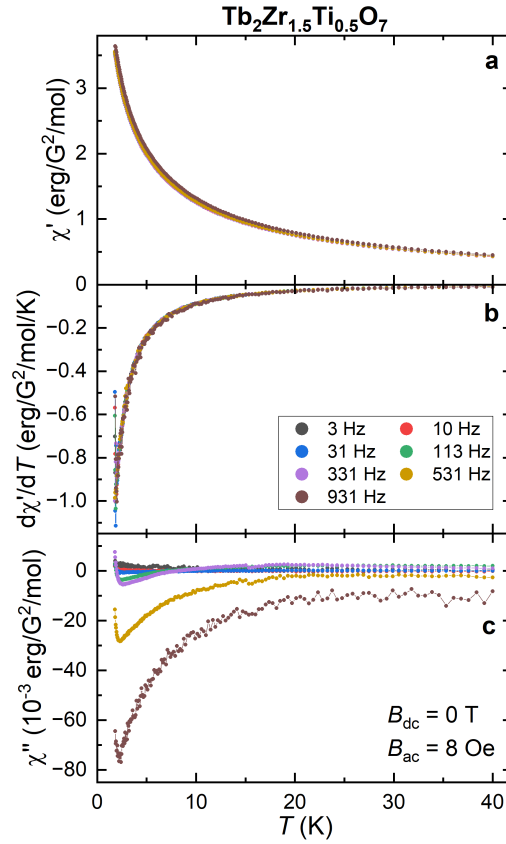


Figure 5.7: AC susceptibility data of polycrystalline $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ after zero field cooling as a function of sample temperature $1.8 \text{ K} \leq T \leq 40 \text{ K}$ without static magnetic field at excitation frequencies $3 \text{ Hz} \leq f \leq 931 \text{ Hz}$. The excitation field had the amplitude $B_{ac} = 8 \text{ Oe}$. Subplots a shows the reactive component χ' . b is the temperature derivative of the above $\frac{d\chi'}{dT}$. c shows the absorptive components χ'' .

at in $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ in the isothermal magnetic susceptibility $\chi(T) = dM(T)/dB$ (figure 5.4b & e) in the form of the previously mentioned shoulder like features which correspond to the inflection point of an S-shape, that may possibly be incorporated in the magnetization curve. Their temperature dependent field is marked with green squares in figure 5.10. The up sweeps can be contrasted with the field down sweeps, which do not exhibit this shape anymore and thus possess a smooth $\chi(B)$ curve. Arising from the difference between the field up and down sweeps, a hysteresis is visible in the insets of figure 5.4a & d. Its maximum width of less than 20 mT for

0.4 K in $Tb_2Zr_2O_7$ and the temperature range, in which it appears, are consistent with values reported for $Ho_2Zr_2O_7$ [84]. The field-temperature endpoints of the hysteresis are marked with pink dots in figure 5.10. It should be noted, however, that the hysteresis at 0.4 K continues far beyond the maximum in $\chi(B)$, at 0.8 K, the two features appear to occur at the same B .

There are two field regions resulting in maxima in the field derivative of $\chi(B)$, they are marked with green dots in figure 5.10. The 2 T hump is visible up to 1.8 K with no clear temperature dependence, at 4 K in $Tb_2Zr_2O_7$ its existence cannot be clearly determined. It corresponds roughly to the beginning of the plateau state which (as visible in figure 5.4) is rather independent of temperature. The kink at lower fields further helps located the underlying mechanism. Two observations about this should be noted however: Firstly, the analysis of $M(B)$ itself reveals a magnetic hysteresis only in temperatures below 1 K. An inflection in $M(B)$, which is possibly associated with an S-shaped magnetization process, would result in a maximum in the second field derivative $\frac{d^2M}{dB^2}$. This is only clearly visible in the upsweeps at 0.4 K in both materials, see figure 5.4c & f. The other curves show a strong right bending at similar fields but they cannot be definitively labeled as maxima. As seen in the insets in figure 5.4a & d, the hysteresis observed at 0.4 K it is already greatly suppressed at 0.8 K. The small hysteretic shift is not resolved above these temperatures. Due to the field ramping at finite rates, the systems might enter metastable states which decay only at timescales larger than the measurement, which might be a reason for the observed irreversibility. This would mean that the onset of the hysteresis in $M(B)$ is dependent on experimental parameters, such as the rate of field change. In the iHe3 setup, this cannot practically be modified. The same is true for the difference between the ZFC and FC magnetizations in the frozen state [39], only a relative comparison between them can be justified since the field change rate is constant across all presented measurements.

For a non-interacting paramagnetic system, the magnetization curves are described by a Brillouin function, eq. (2.40); a result of this is that the temperature dependence of the magnetic susceptibility $\chi(B)$ scales with T^{-1} . For $Tb_2Zr_{2-x}Ti_xO_7$ this is evidently not true, the $M(B)$ behavior below 4 K do not exhibit the temperature related differences expected from the change in temperatures. This comparison is illustrated in figure 5.8 which exemplarily shows the magnetization curves for $Tb_2Zr_{1.5}Ti_{0.5}O_7$ at 0.4 K and 1.2 K and compares these to Brillouin curves with a chosen total angular momentum of $J = 5/2$. The angular momentum for this plot is not the correct value as Tb^{3+} has an even number of electrons and thus will have an integer J . For illustrative purposes this is nonetheless chosen. As can be seen there and in figure 5.4, the experimental curves do not show a temperature dependence, in a stark contrast to the Brillouin curves. Figure 5.9 illustrates a further comparison of the

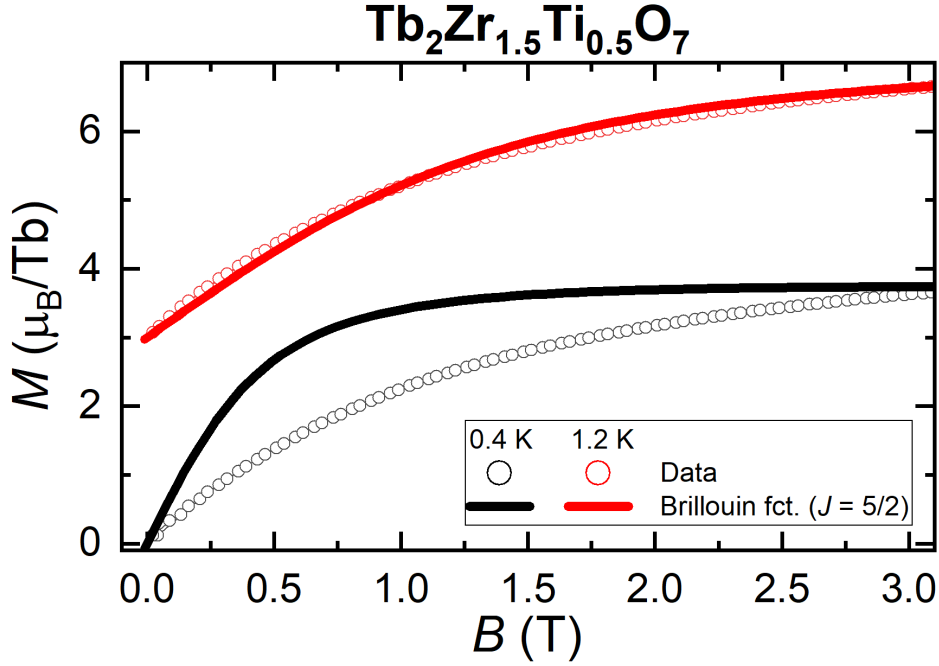


Figure 5.8: Comparison of magnetization data for polycrystalline $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ at 0.4 K and 1.2 K with Brillouin curves with $J = 5/2$ at the same temperatures. The curves for $T = 1.2$ K are shifted vertically by $3 \mu_B/\text{Tb}$.

0.4 K dataset with Brillouin curves for both $J = 6$ and also for $J = 5/2$ which causes a saturation magnetization of $\mu_{\text{eff}} \approx 3.75 \mu_B/\text{Tb}$ closer to the observed behavior. As becomes visible in this, and all other measurements below 4 K (which are not shown) for both $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$, the magnetization $M(B)$ is not well described by a Brillouin function with either saturation magnetization, confirming the previously found antiferromagnetic correlations. The plateau extracted by extrapolating the linear high field magnetization is in agreement with literature on $\text{Tb}_2\text{Zr}_2\text{O}_7$ [76] [95] and also with the related $R_2M_2\text{O}_7$ system $\text{Tb}_2\text{Hf}_2\text{O}_7$ [89]. This agreement between the zirconate and hafnate is similar for analogous compounds with other rare earth elements [78].

In the zero field cooled measurements at low temperatures (figure 5.3), both samples show small humps at the lowest measured temperatures (~ 0.4 K) for $B \leq 0.1$ T which are indicated in 5.10 by dark purple triangles. These might be indicative of a low temperature process almost out of measuring range. The broad 0.1 T peak in $\text{Tb}_2\text{Zr}_2\text{O}_7$, and in principle also the other low T ones, could be ascribed to a weak

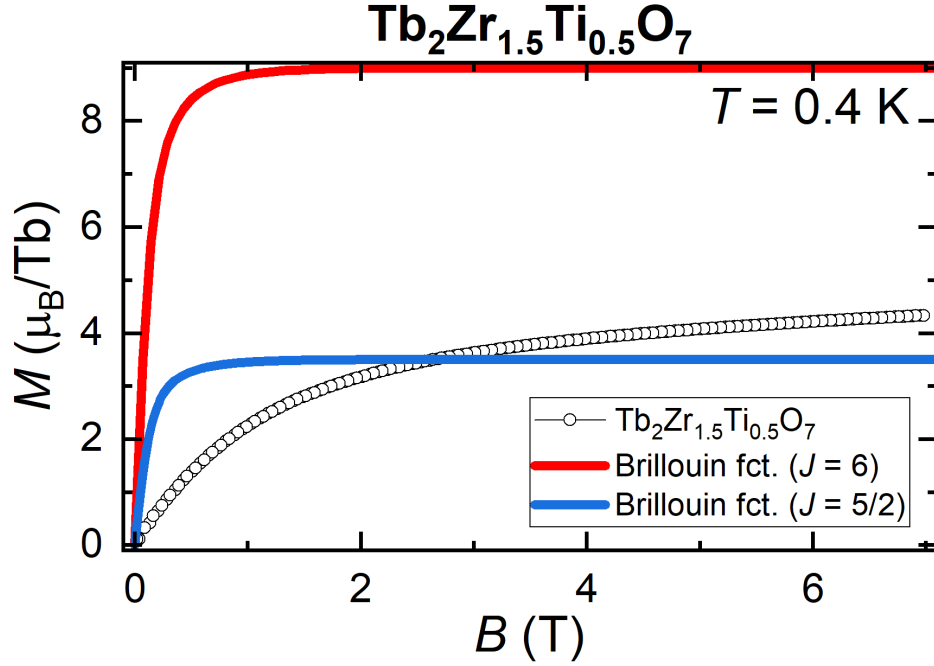


Figure 5.9: Comparison of magnetization data for polycrystalline $Tb_2Zr_{1.5}Ti_{0.5}O_7$ at 0.4 K with free ion expectations (Brillouin curves) with saturation values of $9 \mu_B$ and an extrapolated experimental saturation of $3.5 \mu_B$.

ferromagnetic interaction between clusters, which would only be significant below the freezing temperature and otherwise be suppressed by antiferromagnetic interactions. While not in the sub-Kelvin range, the ac magnetization still reveals a lot about the magnetic structure at hand. For static overlaid fields $B_{dc} < 0.1 \text{ T}$, no dissipation is seen in either system, i.e. the imaginary component $\chi''(T)$ does not exhibit any deviation from 0. The absorption process observed in larger fields has a B_{dc} dependence and slightly shifts to lower temperatures upon increasing the frequency. It is argued by Elghandour *et al.* [84] that such a field stabilized regime of ac anomalies is associated with slow spin relaxation and is common in pyrochlore and defect fluorite type systems. A maximum in the specific heat accompanies these absorptive dynamic processes [76] [87]. The same observations have already been made regarding the 2 K anomalies in χ_{ac} [76]. In $Tb_2Hf_2O_7$, for $B \geq 0.05 \text{ T}$, the $B - T$ trend of the low T anomaly is observed as initially increasing up from 0.8 K at $B = 0$ to $T = 1 \text{ K}$ at 0.05 T. At higher fields, this behavior reverses and the temperature shifts down with increased field to 0.5 K at 0.5 T [89]. This might also be the case

in $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ with the 2 K low B features and the ones at $T \leq 0.5$ K and higher fields being connected. However, a verification of this requires better low field ac measurements which are rather difficult to obtain because of a low signal strength. In applied static fields $B_{\text{dc}} \geq 1$ T, a shoulder in $\chi'(T)$ is recorded which shifts up with increased field and is analogously found in $\text{Tb}_2\text{Ti}_2\text{O}_7$ [96]. It can be interpreted as a consequence of a saturation in spin polarization [76] [96]. In $\text{Ho}_2\text{Ti}_2\text{O}_7$ this process was interpreted as being caused by thermal fluctuations in the population of the two ground states of Ho^{3+} [97] which can similarly be argued for Terbium. The fact that this sets in with $B_{\text{dc}} \geq 1$ T agrees with the observation that the $M(B)$ curves are (close to) saturated at $B = 1$ T.

Among the data presented here, there are only few qualitative differences between $\text{Tb}_2\text{Zr}_2\text{O}_7$ and $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$: Except the broad hump in the 0.1 T ZFC cooled $\chi(T)$ curve at 450 mK, the datasets only differ in magnitude. However, it seems that $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ exhibits faster initial magnetization, as seen by a larger low field susceptibility $\chi(B)$, while $\text{Tb}_2\text{Zr}_2\text{O}_7$ saturates at larger magnetic moments as indicated in figure 5.4. This is in accordance with the analysis of their susceptibilities up to room temperature, as shown in figure 5.2, where it was established that $\text{Tb}_2\text{Zr}_2\text{O}_7$ has a higher effective magnetic moment. Both systems contain the same magnetic ions, which means that the true saturation magnetization, assuming fully polarized magnetic ions, should be the same. The data of χ'' 0 T 113 Hz in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ are offset by $\sim 2 \times 10^{-3}$ erg/G²/mol. This can be explained as an experimental artifact as the three point read out of the MPMS3 ac option (see section 3.1.2) must have picked different points of the dipole curve, which can lead to a constant offset in the data. While this increases the uncertainty in the absolute data, this is of lesser concern for the analysis as it mostly neglects absolute magnitudes and can otherwise be simply scaled to compare.

As discussed in the introduction to this chapter, $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ takes on a defect fluorite structure while $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ tends towards pyrochlore. The reason for $\text{Tb}_2\text{Zr}_2\text{O}_7$ having a more disordered crystal structure is the similarity of ionic sizes between Tb^{3+} and Zr^{4+} which allows an increased ionic mobility on the cationic sites [74] [82] [92] [93] [98]. A partial substitution of Zr for Ti suppresses this disorder because the Ti mobility is much smaller than for Zr due to the larger ionic size. Only 25% of the M cationic sites are occupied by Titanium ions in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$, so a sizable amount of disorder is still to be expected. By introducing a more ordered pyrochlore structure into the crystal, the glassiness of the system is reduced and thus a decrease in the arising feature should be expected. This explains the suppressed hysteresis size with $x = 0.5$ and a later bifurcation of the ZFC and FC branches as observed. The earlier onset of the S-shape and smaller coercitive fields in the isothermal magnetization in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ and slightly decreased absorption χ'' are

due to the same factors. Maxima in χ'' are associated with the freezing process into a glassy configuration. These must be compared between the two systems for each frequency separately. The freezing temperatures under application of 3 Hz appear to only change very little. Meanwhile there is a non-negligible suppression of T_f in $Tb_2Zr_{1.5}Ti_{0.5}O_7$ at 113 Hz. A similar trend is observed in $Tb_2Zr_2O_7$ [76] but the opposite is true for related compounds. For a more quantitative and meaningful conclusion on this particular observation, this field induced absorption peak must be investigated systemically in a broader frequency range and ideally using complementary methods (such as neutron scattering).

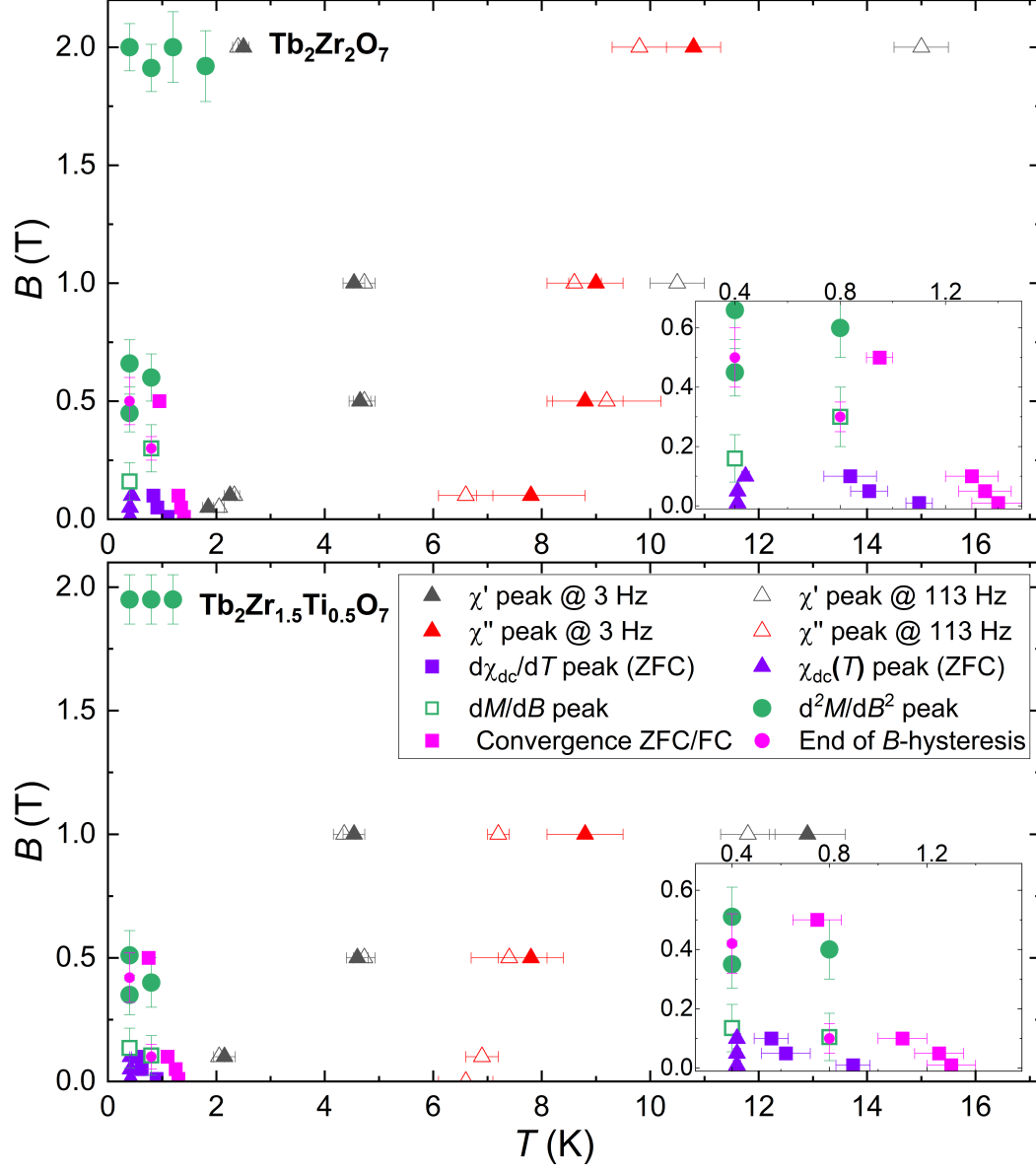


Figure 5.10: Summary of the features noted in figures 5.3 - 5.7 in the form of proposed phase diagrams for both systems.

6 $\text{Er}_2\text{Te}_4\text{O}_{11}$

6.1 Introduction

$\text{Er}_2\text{Te}_4\text{O}_{11}$ belongs to the class of rare earth oxo-tellurates $R_2\text{Te}_4\text{O}_{11}$ [99]. With $R = \text{La} - \text{Nd}, \text{Sm} - \text{Yb}$, they all adapt the same monoclinic crystallographic structure with space group $C2/c$ (No. 15). The lattice for $R = \text{Er}$ is shown in figure 6.1. Inside the lattice, the Er^{3+} ions are part of a low-symmetry distorted square antiprism arrangement of eight O^{2-} anions [99]. They are ordered in a buckled honeycomb lattice in the ab plane. Neighboring planes are shifted relative to one another resulting in an ABAB order. The honeycomb cells in $\text{Er}_2\text{Te}_4\text{O}_{11}$ are slightly disordered: The Er-Er distance along the a direction is $3.73\text{\AA}$, while the other directional distances are slightly longer at $3.80\text{\AA}$. The inter-plane distance is $7.683\text{\AA}$. In-between the Erbium planes, Te^{4+} ions take on two non-equivalent sites, Te1 and Te2, with the former located closer to the Er ions. This description of the lattice is only one of multiple discussed in [99] but it is the most practical considering the magnetic properties of $\text{Er}_2\text{Te}_4\text{O}_{11}$ since it focuses on the configuration of the magnetic ions.

The interest in $R_2\text{Te}_4\text{O}_{11}$ arises due to the 4f honeycomb lattice: A two-dimensional honeycomb lattice may host a Kitaev system if the magnetic ions can be described with an effective moment of $J_{\text{eff}} = 1/2$ [100]. Kitaev materials may host a quantum spin liquid phase [101]. The necessary $J_{\text{eff}} = 1/2$ requires a Kramers ion, i.e. an ion with an odd number of electrons resulting in a half integer spin and total angular momentum [34] [101].

The magnetic properties of polycrystalline $R_2\text{Te}_4\text{O}_{11}$ have been investigated experimentally down to 2 K for $R = \text{Ce} - \text{Nd}, \text{Sm} - \text{Er}, \text{Yb}$. For many of the measured magnetization curves, Curie-Weiss fits were performed, whose fit parameters can be compared. They are tabulated in table 6.1. These fits resulted in Weiss temperatures which are in many cases not consistent across different sources. In many sources, it was found that $\theta_W < 0$ and that they are of order 10^1 K, however in particular Huang *et al.* [102] report also positive Weiss temperatures for some systems. For $\text{Er}_2\text{Te}_4\text{O}_{11}$ only [102] reports results, the Weiss temperature there is -4.38 K. In contrast to θ_W , the reported values for μ_{eff} are consistent and agree with the expectation of the value for a free ion with charge state $3+$, as determined by Hund's rules [2] and eq. (2.40). To date, no measurements of the magnetic properties of $\text{Er}_2\text{Te}_4\text{O}_{11}$ at

R	θ_W (K)	$\mu_{\text{eff}}(\mu_B)$	Source
Ce	-64.8	2.41	[103]
Pr	-30.2	3.46	
Tb	-2.8	9.72	
Nd	-25.2	3.98	[104]
Sm	-	1.55	
Eu	-	3.31	
Gd	-1.5	7.99	
Ho	-4.2×10^{-3}	10.65	
Pr	-34.1	3.38	[105]
Nd	-38.0	3.58	
Eu	-	3.24	
Pr	-15.2	3.59	[106]
Gd	5.36	7.53	[102]
Tb	2.66	9.83	
Dy	-7.36	10.72	
Ho	4.48	10.95	
Er	-4.38	9.60	
Yb	-39.20	4.69	

Table 6.1: Weiss temperatures θ_W for various $R_2Te_4O_{11}$ compounds from the literature. For more details, see the text.

temperatures below 1.8 K have been published. The same is true for the dynamic susceptibility in the frequency range between 1 Hz and 1 kHz. Theoretical considerations on the crystal field have yielded predictions on the static susceptibility for some members of the $R_2Te_4O_{11}$ group but not on $Er_2Te_4O_{11}$ itself.

6.2 Magnetometry

$Er_2Te_4O_{11}$ samples were provided by P. Khuntia of IIT Madras, India. The sample consisted of a pellet of pressed polycrystalline powder. Similar to $Tb_2Zr_{2-x}Ti_xO_7$, the mass was eventually reduced from 83.09(3) mg to 14.43(7) mg to ensure that the magnetization would remain in the measurement range. Due to the powdery consistency and the associated risk of loss of material and possible sample chamber contamination, the $Er_2Te_4O_{11}$ was placed inside a polymer capsule for all measurements after being weighed.

A T -dependent magnetization curve was recorded for $Er_2Te_4O_{11}$ between 1.8 K and

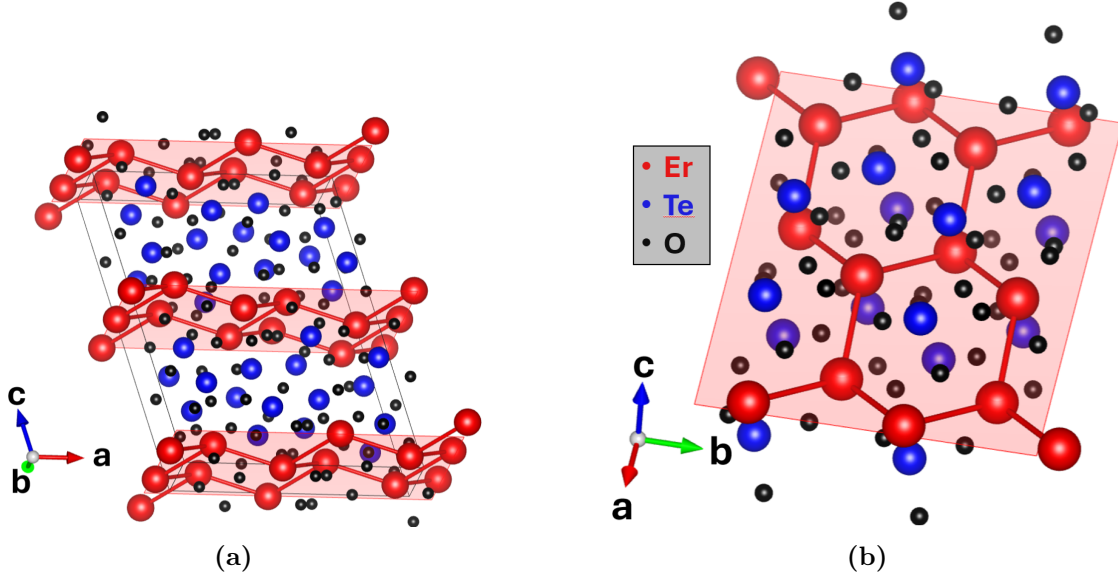


Figure 6.1: Crystal structure of $\text{Er}_2\text{Te}_4\text{O}_{11}$ rendered in VESTA [72] based on data provided in [107]. Er sites are marked in red, Te sites blue, and O sites black. The arrangement of the Er ions in a buckled honeycomb lattice is indicated by the red lines between nearest neighbor Erbium ions.

300 K at 0.1 T. The data are shown as $\chi^{-1}(T)$ in figure 6.2. Inset into this is $\chi(T)$. A Curie-Weiss law with an additional constant term is fitted to the data above 50 K and plotted as a red line. The Curie-Weiss like behavior persists to temperatures lower than 50 K. From this and eq. (2.40), an effective moment and Weiss temperature can be inferred:

$$\mu_{\text{eff}} = 9.5(3) \mu_{\text{B}}/\text{Er} \quad \theta_{\text{W}} = -7(3) \text{ K}.$$

μ_{eff} is in agreement with theoretical and experimental values for Er^{3+} [2]. A negative Weiss temperature might indicate dominant antiferromagnetic interactions between the Erbium ions. This result is in qualitative agreement with [102] but the value is larger by a factor of almost two. No further features are detected at temperatures above 1.8 K, as seen in the inset of figure 6.2.

Isothermal magnetization curves were recorded in Quantum Design's PPMS in the VSM mode [108] with a brass sample holder. Field sweeps were performed up to $B = 14$ T at $T = 1.8 - 10$ K. The magnetization curves are shown in figure 6.3. An initially steep magnetization is visible up to a temperature dependent right-bending point. It shifts from approximately 1.5 T at $T = 1.8$ K to 4 T at 10 K. At higher field strengths, the magnetization only shows a weak right-bending. The magnetization values at $B = 14$ T coincide at approximately $6.2 \mu_{\text{B}}/\text{Er}$ at all three temperatures.

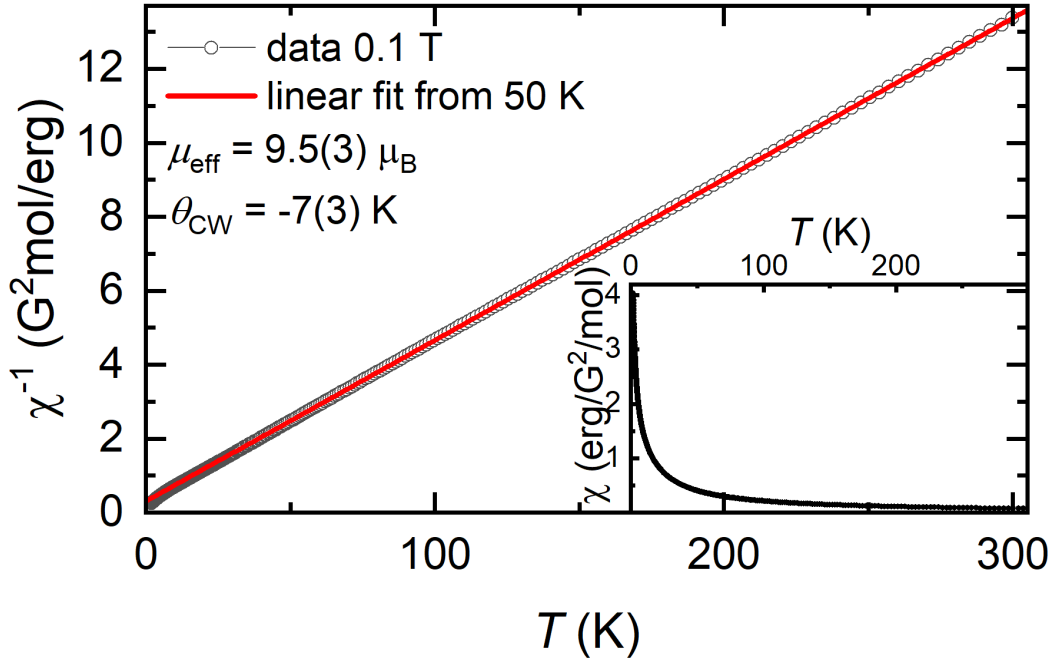


Figure 6.2: Inverse magnetic susceptibility χ^{-1} vs temperature T of $\text{Er}_2\text{Te}_4\text{O}_{11}$ measured between 1.8 K and 300 K at 0.1 T. The red line is a modified Curie-Weiss fit as described in the text. The inset shows the corresponding $\chi(T)$.

6.2.1 Sub-Kelvin DC Magnetometry

More measurements were performed probing the magnetic response of the samples in a lower temperature regime. The results of various $\chi(T)$ sweeps at magnetic fields ranging from 0.02 T to 1 T are shown in figure 6.4a, the temperature derivative $\frac{d\chi}{dT}$ of the ZFC data is shown below in figure 6.4b and Fisher's specific heat $\frac{d(\chi T)}{dT}$ in subplot c. Up to $B = 0.2$ T, all presented sub-Kelvin $\chi(T)$ measurements exhibit the same qualitative behavior. Coming from low temperatures, the susceptibility starts to increase in a left bending manner, which culminates in a point of maximum slope at ca. 470 mK. This is followed by a broad maximum in χ . Upon increasing B , the initial increase gets suppressed, at $B = 1$ T it is no longer visible. The inflection point of the susceptibility is most clearly identifiable in its derivative $\frac{d\chi}{dT}$ (figure 6.4b) as peaks, marked with purple empty squares. Subplot c of figure 6.4 shows that the same features are also visible in Fisher's specific heat, at similar temperatures (where they are marked with filled purple squares). It could be argued that the peak

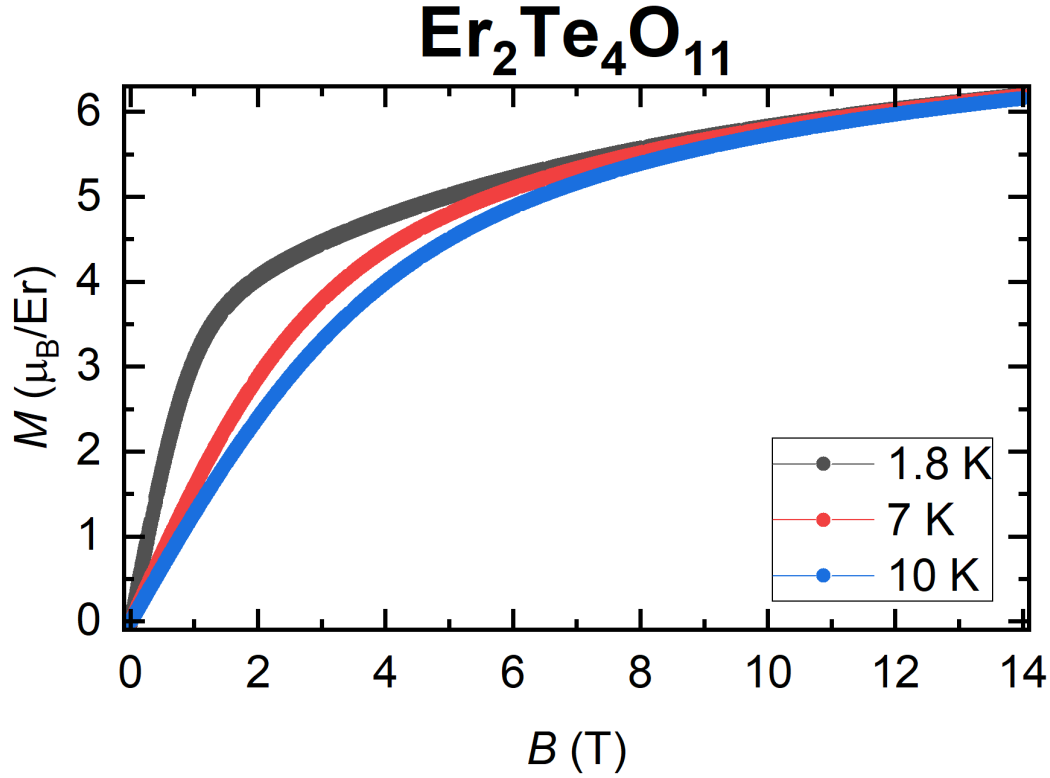


Figure 6.3: Isothermal magnetization as a function of applied field $M(B)$ of $\text{Er}_2\text{Te}_4\text{O}_{11}$ measured up to 14 T at temperatures between 1.8 K and 10 K K.

in Fisher's specific heat is reminiscent of a lambda λ transition. However in order to confirm this, more data points close to this would be necessary. With the given resolution, a symmetric anomaly cannot be ruled out. A further noteworthy feature is a difference between the zero field cooled (full circles) and field cooled (empty circles) magnetization curves. Both FC and ZFC measurements show a peak in χ , FC does not show a plateauing below the maximum. This thermal hysteresis in the low temperature susceptibility occurs in datasets with $B \leq 0.1$ T (above this field, no usable FC data was recorded). Lastly, the field cooled curves exhibit a small but visible peak at 420-450 mK prior to reaching the maximum slope, this is not visible in the ZFC data; a similar feature is also noticeable in the higher field ZFC curves.

Isothermal magnetization curves $M(B)$ were recorded in a similar manner, the results for four different temperatures $0.4 \text{ K} \leq T \leq 1.8 \text{ K}$ are presented in figure 6.5a with its

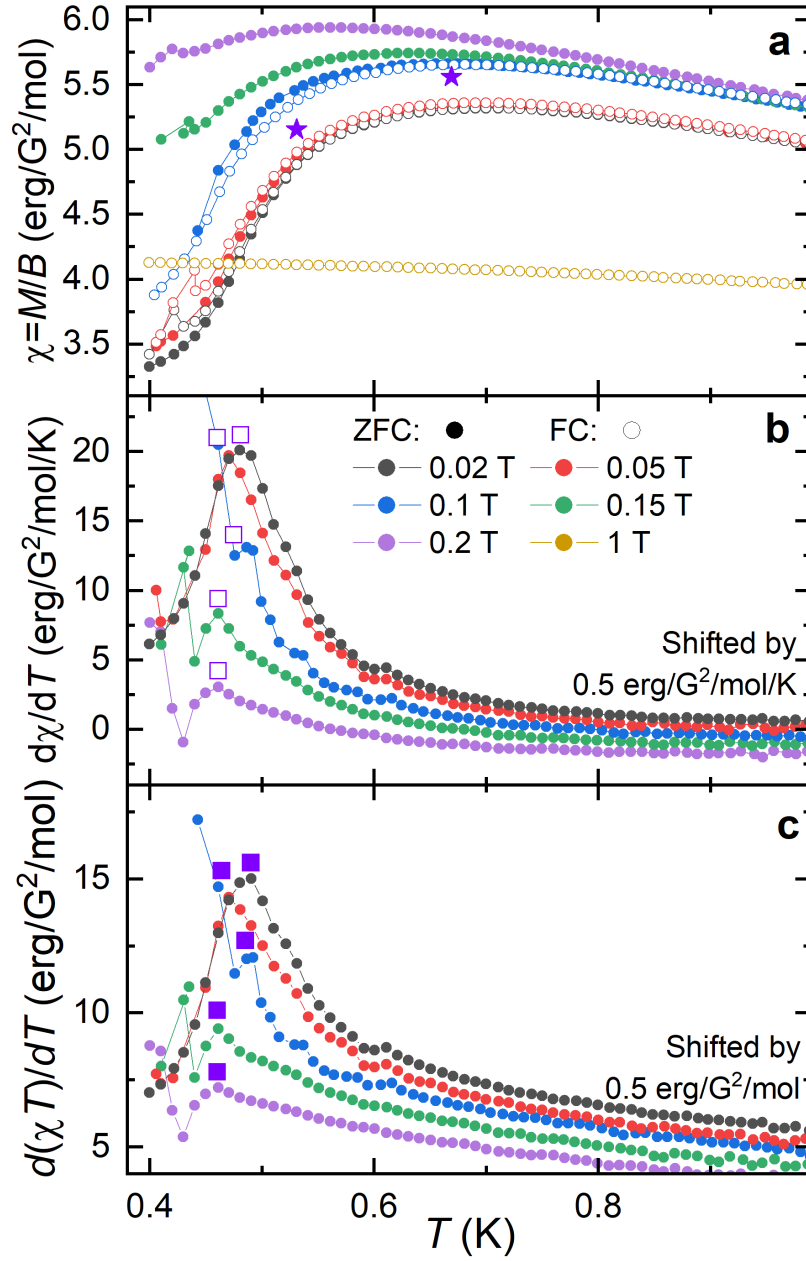


Figure 6.4: Magnetic susceptibility χ against the temperature T of $\text{Er}_2\text{Te}_4\text{O}_{11}$ between 0.4 K and 1 K at fields between 0.02 T and 1 T. (a) $\chi(T)$ both field cooled and zero field cooled, (b) Derivative $\frac{d\chi}{dT}$ of subplot (a) only for ZFC measurements and $B < 1$ T, (c) Fisher's specific heat $\frac{d(\chi T)}{dT}$. In (b) & (c) squares mark maxima in $\frac{d\chi}{dT}$ and $\frac{d(\chi T)}{dT}$. The curves are shifted for better visibility.

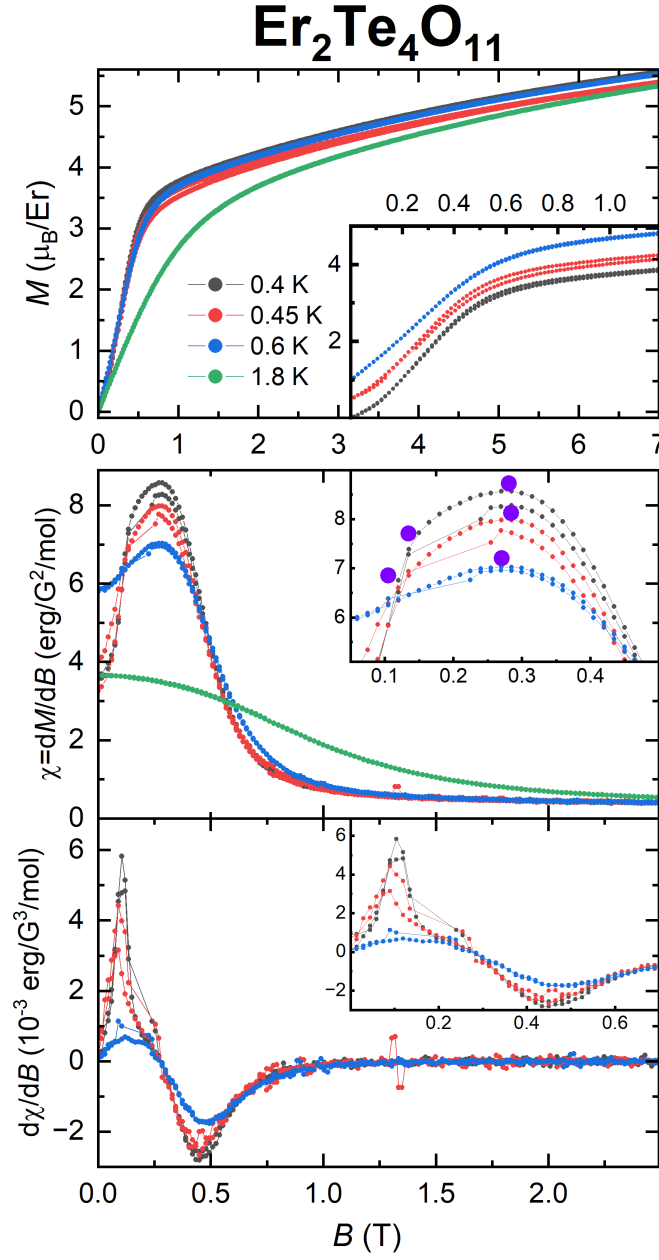


Figure 6.5: Isothermal magnetization as a function of applied field $M(B)$ of $\text{Er}_2\text{Te}_4\text{O}_{11}$ measured up to 7 T at temperatures between 400 mK and 1.8 K. (a) Magnetization curves, (b) Susceptibility $\chi = dM/dB$. The inset contains purple dots which mark maxima and shoulders in $\chi(B)$ (c) Derivative of the susceptibility. The insets are zoomed into the low field region.

first two field derivatives $\chi = \frac{dM}{dB}$ and $\frac{d\chi}{dB}$ shown in figure 6.5b & c. At 400-600 mK, the magnetization initially shows an increasing slope up to an inflection field, taking on an S-shape. This is not visible in the measurements with $T \geq 1.8$ K. Above ca. 0.5 T, M bends to the right and assumes a slope of $\frac{dM}{dB} \lesssim 0.1 \mu_B/\text{T}$, which is only slowly decreasing further. This becomes most apparent in the susceptibility $\chi(B) = \frac{dM}{dB}$ in figure 6.5b. The observed sub-Kelvin isothermal magnetization sweeps match the behavior of the sweeps with 1.8 – 10 K in the high field region, a slight right-bending is visible. In order to get a rough estimate on the saturation magnetization at high fields, a linear extrapolation of the plateau magnetization to $B = 0$ T is performed. This yields an approximate value of $3.8(1.0) \mu_B/\text{Er}$. An exact value for this is difficult to obtain for two reasons: The curve is not perfectly linear in the interval, and the individual curves appear to be scaled relative to each other. This can be explained by the fact that measurements in SQUID magnetometers like the MPMS3 are sensitive to the orientation of the same in the sample holder. Furthermore, the exact centering in the chamber influences the dipole fitting. The isothermal measurement at 450 mK was performed in a different measurement series than the 400 and 600 mK measurement. As a consequence of the sample removal and re-installation, it is realistic that the exact orientation and centering of the initial measurements could not be replicated and thus cause the described variations.

At $T = 0.4$ K and 0.45 K, a hysteresis is recorded in the $M(B)$ curves, see inset of figure 6.5a. It is not centered around 0 T but around 0.6 T and covers the largest field interval at 450 mK. The maximum size is temperature dependent: At 400 mK it starts at $0.07 \mu_B/\text{Er}$, at 450 mK it is maximally spread at a width of $0.15 \mu_B/\text{Er}$ and then shrinks back to $0.04 \mu_B/\text{Er}$. It is not visible at 1.8 K.

6.2.2 AC Magnetometry

Figure 6.6 shows the temperature dependence of the ac susceptibility for $\text{Er}_2\text{Te}_4\text{O}_{11}$ as probed at 600 Hz and static fields $B = 0 - 7$ T with an excitation field of $B_{\text{ac}} = 1$ & 2 Oe, divided into the real parts χ' in subplots a and d, their temperature derivatives $d\chi'/dT$ in subplots b & e, and the imaginary components χ'' in c and f. Some derivatives and imaginary components are omitted because of overwhelming noise.

Differences between the two driving fields are only quantitative. For $B_{\text{dc}} \leq 0.1$ T, the reactive susceptibilities χ' (upper panels in figure 6.6) exhibit a Curie-Weiss like behavior, i.e. a monotonous decrease with T . This is confirmed by the derivative $d\chi'/dT$ where no features are visible. In larger fields, a shoulder starts to form in $\chi'(T)$ which gains prominence with increasing static field. At 0.2 T, the maximum

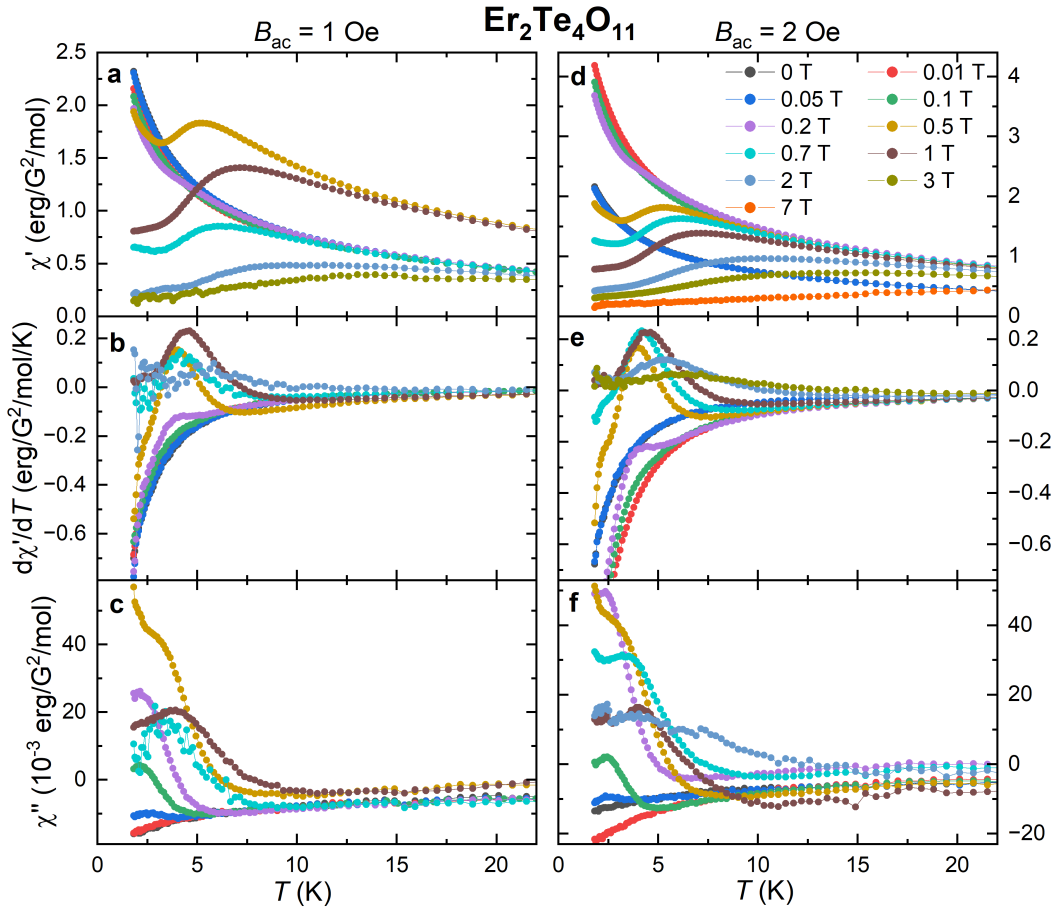


Figure 6.6: Ac susceptibility data of $\text{Er}_2\text{Te}_4\text{O}_{11}$ as a function of sample temperature T at various applied static fields. At the excitation frequency $f = 600$ Hz two excitation field strengths B_{ac} were applied. (a) Real part of the ac susceptibility χ' , (b) T derivative of a $d\chi'/dT$, (c) Imaginary component χ'' , (d)-(f) Same as a-c with $B_{ac} = 2$ Oe.

is located at 4.5 K, and shifts almost linearly to 14 K at 3 T. Accompanying this is an inflection point in temperature which leads to a shoulder/peak in the derivative $d\chi'/dT$, in the middle panels. Between 0.2 and 0.5 T, the shoulder turns into a peak that is most pronounced around 0.5-0.7 T. This feature shifts higher in T and gets broader with increasing B_{dc} . χ'' exhibits an anomaly close to the inflection points of χ' at 2.5 K and 0.05 T, which also shifts to higher temperatures (4.5 K at 3 T) and gets broader with B . Apart from this, no other features are seen in χ'' .

A comparison of the χ' between the two values of B_{ac} shows that for $B_{\text{ac}} = 1$ Oe the 0.5 T and the 1 T curves are shifted upwards by ~ 0.4 erg/G²/mol with respect to the others while with $B_{\text{ac}} = 2$ Oe the 0.05 T and 7 T curves are shifted downwards by the same value. $d\chi'/dT$ show no difference between the driving field strengths indicating that the observed difference truly is an offset and therefore a systematic error.

6.3 Discussion

Analyzing the dc magnetic susceptibility in the context of the Curie-Weiss model revealed dominant antiferromagnetic interactions in $\text{Er}_2\text{Te}_4\text{O}_{11}$, which agrees with previous works on $\text{Er}_2\text{Te}_4\text{O}_{11}$ and on chemically similar oxotellurates of the class $R_2\text{Te}_4\text{O}_{11}$, as summarized in table 6.1. The experimentally found Weiss temperature $\theta_{\text{W}} = -7$ K, see figure 6.2, agrees with the literature [102]. No magnetic ordering is observed down to at least 1 K, which indicates a frustration in the magnetic lattice. Indeed, honeycomb lattices are known as possible hosts for geometrically frustrated structures [109]. Huang *et al.* [102] found that the exchange between the Er planes is much larger than the interlayer exchange perpendicular to it. The interplane distance between the magnetic ions is 2.23 times larger than the intraplane distance. Since the dipolar interaction scales with $1/d^3$, the interaction within between the planes is suppressed by a factor of supposedly more than 11 compared to the interaction within the planes. This agrees with the approximation of two dimensional magnetism constrained to the layers on a broad energy scale (and subsequent suppression of possible ordering to low temperatures) [102]. The effective magnetic moment of $\mu_{\text{eff}}^{\text{exp}} = 9.5(3) \mu_{\text{B}}/\text{Er}$, as is extrapolated from the Curie-Weiss fit (see figure 6.2), is in excellent agreement with the value expected from a free ion picture for Er^{3+} which is $9.59 \mu_{\text{B}}/\text{Er}$ [2].

Deviations from the Curie-Weiss approximation in the magnetic susceptibility $\chi(T)$ are found in the sub Kelvin range as shown in figure 6.4. Only a small difference between the ZFC and FC measurements is visible in the susceptibility (subplot a). This approximate reversibility indicates a lack of metastable magnetized states and thus rules out the interpretation of a spin glass behavior. The visible maximum in $\chi(T)$ regardless of the magnetic history could indicate a crossover into a region dominated by antiferromagnetic interactions. In a temperature range, where AFM correlations dominate, the magnetization must decrease with lowering the temperature. At sufficiently high T thermal fluctuations favor a disordered paramagnetic state, which leads to a vanishing magnetization as $T \rightarrow \infty$. The correlation maximum in $\chi(T) = M/B$ is a consequence of a crossover between these two temperature regimes. A true phase

transition between two states would typically be accompanied by a more pronounced peak in the susceptibility or its derivative at T_N [33]. Fisher showed that the magnetic heat capacity in an antiferromagnet close to its phase transition behaves like $\frac{d(\chi T)}{dT}$ [110] [111]. If a lambda shape were confirmed in Fisher's specific heat, it could be associated with a second order phase transition [112]. Such a behavior would be in accordance with a phase transition between a paramagnetic and an antiferromagnetic phase [113]. Stronger arguments about the nature of the peaks in both $\chi(T)$ and $\frac{d(\chi T)}{dT}$ could only be made if higher resolution measurements of the temperature dependent magnetization were available. This might in particular allow a more definite statement on the shape of the peak like feature in Fisher's specific heat (see figure 6.4c) and rule out or confirm a λ -shape.

Figure 6.9 collects observed features in a phase diagram. It can be seen there and in figure 6.4 that the maxima in Fisher's specific heat and thus the inflection points in $\chi(T)$ shift to lower temperatures upon application of a larger magnetic field. A linear extrapolation of the trend yields a temperature of $T_{\text{inflection}}(1 \text{ T}) \approx 0.38 \text{ K}$, which lies below the measured temperature range and can be one explanation for why this transition is no longer observed in 1 T. Alternatively, this crossover could be suppressed at such field strengths as can be seen in figure 6.5a.

It might be argued based on the inset in figure 6.5b, that at 0.4 K and 0.45 K, the peak in the isothermal susceptibility $\chi(B) = \frac{dM}{dB}$ might consist of two peaks close together or of a main peak at 290 mT and a side peak at ca. 140 mT. If this had a genuine physical origin, it might be explained as being associated with a small jump in magnetization due to a further low temperature phase. The corresponding potential transition field at 0.45 K, 0.105 T, lies close to the line marked by the maxima in Fisher's specific heat described above. This is however highly speculative as it relies on only two data points and requires further measurements in the low temperature regime. Alternatively, it could also simply be due to systematic errors from the measurements. It was nonetheless marked and included into figure 6.9. The observed peaks in $\chi(T)$ at $T \lesssim 450 \text{ mK}$ could also be due to device artifacts.

In the isothermal magnetization $M(B)$ for $T \leq 0.6 \text{ K}$ in figure 6.5, an S-shape can be seen in the low field region. The maximum in the susceptibility $\chi(B) = dM/dB$ is associated with an inflection point in M . This field is marked with purple dots in both figure 6.5 and figure 6.9. Since glassiness is unlikely to occur in $\text{Er}_2\text{Te}_4\text{O}_{11}$, as was laid out above, another mechanism would have to be the cause for the inflection behavior. The underlying mechanism could possibly be a spin-flip or spin-flop process, as was reported for the related compound $\text{Tb}_2\text{Te}_4\text{O}_{11}$ [102] as well as other antiferromagnets [114]. These two phenomena occur in the isothermal magnetization of antiferromagnets when the magnetic field is being applied in parallel to the axis, along which the magnetic moments lie. Due to the AFM alignment and the anisotropy keeping the

magnetic moments rigidly oriented, no magnetization is induced by magnetic fields small compared to the anisotropy barrier. In sufficiently large fields, either a complete reversal of the antiparallel spins (spin-flip) or a rotation by 90° and subsequent canting of the magnetic moments (spin-flop) occurs. Both cases result in a jump in $M(B)$ at the field B_{sf} [2].

In figure 6.7a, the jump in magnetization ΔM_{sf} at $T = 0.4$ K is determined assuming a spin-flip at $B_{\text{sf}} = 0.28$ T by approximating two linear regimes at lower and higher fields, as indicated in the plot, and taking the difference between these two lines at the inflection point of $M(B)$. The jump size determined in this manner is $\Delta M_{\text{sf}} = 2.4 \mu_{\text{B}}/\text{Er}$. Since the $\text{Er}_2\text{Te}_4\text{O}_{11}$ sample is polycrystalline, its magnetization must be considered as a powder average over the possible directions:

$$M_{\text{powder}} = \sum_{i \in \text{axes}} M_i = \frac{1}{3}M_{\parallel} + \frac{2}{3}M_{\perp}. \quad (6.1)$$

This means that the hypothesized spin-flip jump in monocrystalline $\text{Er}_2\text{Te}_4\text{O}_{11}$ is three times that value, i.e. $\Delta M_{\text{sf}}^{\text{mono}} = 7.2 \mu_{\text{B}}/\text{Er}$. The value obtained for ΔM_{sf} from figure 6.7s must be assumed to have a rather high uncertainty because it relies on linear fits for two regions with only approximate linearity in the magnetization. In the AFM model underlying above considerations, the perpendicular axes do not exhibit any jumps in $M_{\perp}(B)$ but show a linear behavior up to saturation because they cant in field. There are two possible factors which could explain why a clear spin-flip associated jump is not visible in the isothermal magnetization even in the powder average. Thermal fluctuations cause a deviation from the uniaxial alignment of the spins even in fields smaller than B_{sf} which broadens the feature. The width in the presented data is ca. 0.5 T and thus rather large compared to the feature location. Furthermore, the simple model of an antiferromagnet is not generally accurate, especially when considering a frustrated system.

In figure 6.7a the saturation field B_{sf} is determined for $T = 0.4$ K is determined as the intersection of linear extrapolations of the high-field magnetization and the maximized slope around the inflection point. It is $B_{\text{sf}} = 0.52(5)$ T and is marked with a purple open circle. This is also done for the two other sub-Kelvin temperatures and included in the phase diagram 6.9. The saturation field strengths are located at or close to the loci where the curvature of $M(B)$ is maximized, thus they can also be seen in figure 6.5c. Both the inflection fields B_{sf} as well as the saturation fields B_{sat} do not show a pronounced T -dependence in the three measurements with $T \leq 0.6$ K. This is in agreement with the assumption that the spin flip condition is fulfilled when the energy due to the Zeeman interaction eq. (2.38) surpasses the energy barrier due to anisotropy, this is approximately independent of the temperature, which only broadens the effect [2]. A broadening with increased T is not observed. The same lack

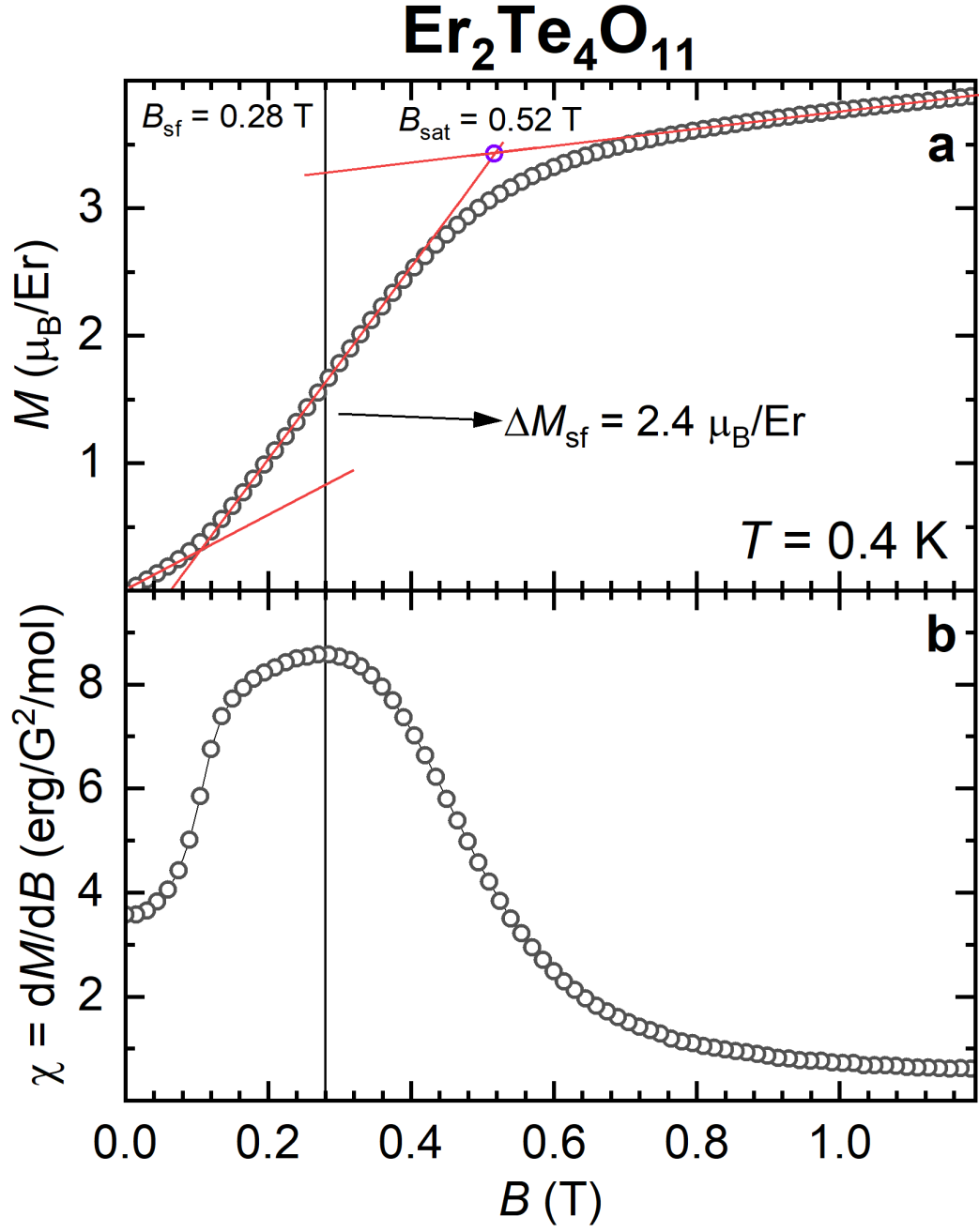


Figure 6.7: (a) Determination of the spin-flip-gap ΔM_{sf} in polycrystalline $\text{Er}_2\text{Te}_4\text{O}_{11}$ at $T = 0.4 \text{ K}$. The red lines show linear extrapolations of three sections of the data. The spin flip field is marked with a vertical line, the saturation field is marked with a purple circle. (b) Susceptibility $\chi(B) = \frac{dM}{dB}$ from (a).

of a pronounced T dependence in the spin-flip field is also reported for $\text{Tb}_2\text{Te}_4\text{O}_{11}$ [102]. From eq. (2.3), assuming $dG = 0$, the Maxwell relation

$$-\frac{\Delta S}{V\Delta M} = \frac{\partial B_{\text{crit}}}{\partial T}$$

can be derived. This implies that processes which show no temperature dependence in their critical fields B_{crit} are associated with a vanishing entropy change ΔS . The absence of a visible T -dependence in the process described here might indicate just that.

An alternative explanation for the observed magnetization shape can also be that the antiferromagnetic spin order breaks down at low magnetic fields due to a departure from an antiferromagnetically ordered phase. The Zeeman energy associated with the spin-flip field B_{sf} can be estimated using eq. (2.38) as

$$\Delta E_{\text{sf}} = g_J J \mu_B B_{\text{sf}} = 0.15 \text{ meV} \approx 1.7 \text{ K} \times k_B.$$

Herein, free Er ions were assumed, in order to obtain J and g_J . Considering that the extrapolated saturation value is not the free ion saturation but a moment reduced to approximately 42% of that, a correction to the energy barrier by the same factor can be applied. This yields a modified spin-flip energy of

$$\Delta E_{\text{sf}}^{\text{mod}} = \frac{\mu_{\text{sat}}}{\mu_{\text{sat}}^{\text{free ion}}} \Delta E_{\text{sf}} = 0.06 \text{ meV} \approx 0.7 \text{ K} \times k_B.$$

The energy barrier must only be taken as an estimate because the underlying process, i.e. whether it is truly a spin-flip, is not established. Furthermore, the feature is observed in a polycrystalline sample, so the assumption that this process is restricted to only one axis (as a spin-flip in an antiferromagnet would be), is not experimentally verified. It is nonetheless useful to notice that it is comparable in size to the temperatures where Fisher's specific heat peaks.

An Arrott plot [115] [116] [117] offers further insights on both the onset of the AFM-PM transition [118] as well as its order [102]. This analysis is shown in figure 6.8. The Arrott plot shows the squared magnetization M^2 against the inverse field specific magnetization B/M , its inset zooms in on the data with $M^2 < 0.3 \times 10^9 \text{ erg}^2/(\text{G mol})^2$. For the three lower temperatures, B/H shows a broad minimum between 0.2 and $1.2 \times 10^9 \text{ erg}^2/(\text{G mol})^2$ and otherwise a linear behavior, which can be extrapolated to cross the axis defined by $B/M = 0$ at values $M^2 > 0$ for all shown temperatures. At $T = 1.8 \text{ K}$, the extrapolation yields a value of $M^2 \approx 0.5 \times 10^9 \text{ (erg/G/mol)}^2$, which is noticeably smaller than the value for the lower temperatures, for which this is larger by a factor of 2. Even at 1.8 K , there is a minimum in the curve, however this is located between 0.01 and $0.02 \times 10^9 \text{ (erg/G/mol)}^2$ and is only very small. Huang *et al.*

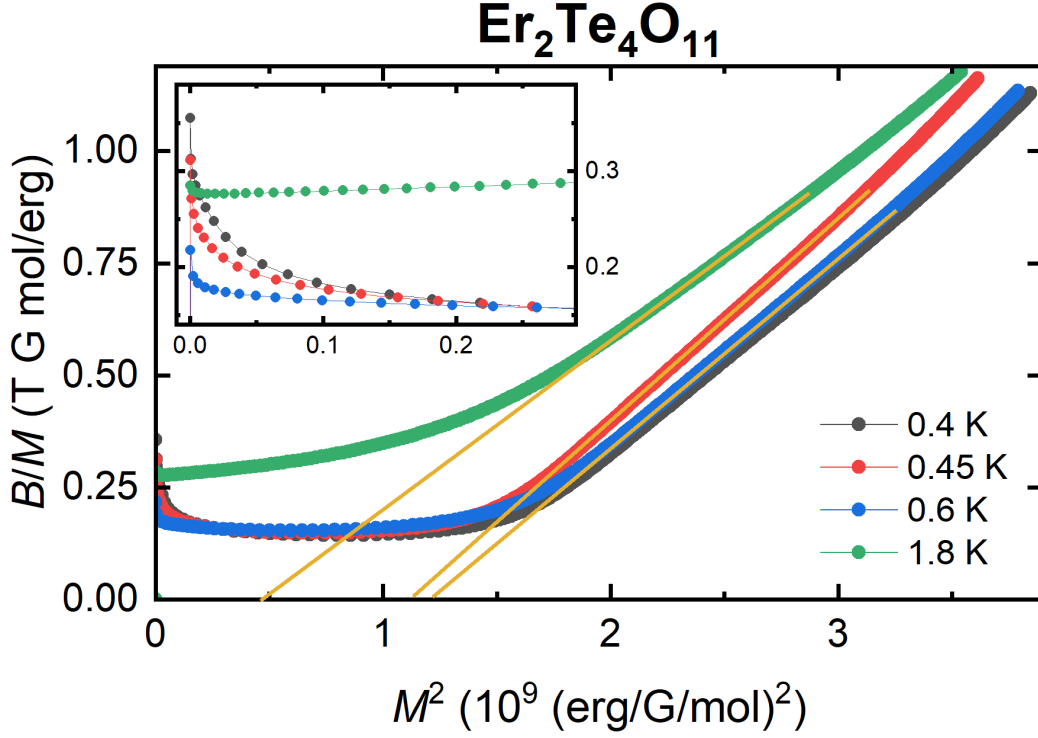


Figure 6.8: Arrott plot for $\text{Er}_2\text{Te}_4\text{O}_{11}$ at four temperatures. Only field up sweeps are included. The orange lines mark a linear extrapolation of the regions with higher M^2 to $B/M = 0$. The inset shows a zoom in of the low M^2 region.

[102] attribute the pronounced negative slope in the Arrott plot at low temperatures (as contrasted to the virtual lack of it at higher T) to a first order phase transition. This is presumably based on the Banerjee criterion which predicts a shift of the minimum in B/M to $M^2 = 0$ at $T = T_c$ and a broad minimum similar to the one observed at $M^2 > 0$ for $T > T_c$ [116] [119]. Furthermore it was observed in $\text{Tb}_2\text{Ti}_4\text{O}_{11}$ that the transition temperature suggested by the Arrott plot coincided with the broad maximum in $\chi(T)$ [102]. Applying this line of reasoning to $\text{Er}_2\text{Te}_4\text{O}_{11}$ would yield a similar conclusion that there might be a first order phase transition in temperature between 0.6 K and 1.8 K. However this interpretation seems tenuous as no discontinuity is observed in variable temperature measurements for $\text{Er}_2\text{Te}_4\text{O}_{11}$, as seen in figure 6.4. In order to be able to draw a conclusion better founded on empirical evidence, it would be beneficial to perform further isothermal magnetization measurements at temperatures below and above 1.8 K and analyzing them in Arrott plots. This might

reveal the temperature at which it predicts a phase transition and this could then be compared further to the measured $\chi(T)$. The axes intercepts could also be evaluated more systematically given these data.

In high field ($B > 1$ T), the extrapolated saturation value of $\mu_{\text{sat}} = 3.8 \mu_{\text{B}}/\text{Er}$ is approximately 42% of the free ion moment $\mu_{\text{sat}}^{\text{free ion}} = g_J J \mu_{\text{B}} = 9 \mu_{\text{B}}$. The value and general case of a measured saturation at 40-50% of the free ion value are in accordance with literature on the anisotropic members ($R=\text{Tb-Er, Yb}$) of the $R_2\text{Te}_4\text{O}_{11}$ class in which it arises due to an easy axis anisotropy. This is in accordance with the observation of a strong deviation from a mean-field behavior, as was already seen by the difference between $\chi(T)$ and a behavior in accordance with a Curie-Weiss law at low temperatures. Probing the behavior in higher fields, as was done with $T \geq 1.8$ K up to 14 T, revealed no further anomalies. The continued non-zero slope after saturation may be attributed to van Vleck paramagnetism [102]. An estimated value of this contribution can be obtained from figure 6.5, a linear extrapolation of the high field behavior yields a value of $\chi_{\text{vV}} \approx 0.25(5) \mu_{\text{B}}/\text{T}/\text{Er}$. As is visible for $T = 1.8$ K, the right-bending continues to at least 14 T without any further anomalies. The value for χ_{vV} is comparable to that found in $\text{Tb}_2\text{Ti}_4\text{O}_{11}$ [95] [102].

For $T = 0.4$ K and 0.45 K, the isothermal magnetic susceptibility $\chi(B) = \frac{dM}{dB}$ has a visible asymmetry around the field B_{sf} . A shoulder-like feature can be seen at $B \approx 0.1$ T, as shown in figure 6.5b and is particularly noticeable in figure 6.7b. The reproducibility of this feature rules out a statistical cause. An explanation for this could be that the low- B side consists of an additional underlying peak which causes the shoulder. This might be caused by a more mobile magnetization process. However, from the available data alone, no further conclusions can be drawn.

The recorded thermal hysteresis in the $\chi_{\text{dc}}(T)$ measurements is rather small compared to the total magnetization, as seen in figure 6.4a. At 0.02 T, the split between ZFC and FC is less than 5% of the total magnetization. In conjunction with the reported antiferromagnetic Weiss temperature, and lack of field hysteresis, this rules out a large ferromagnetic tendency in $\text{Er}_2\text{Te}_4\text{O}_{11}$. The relative shifting of the two curves is not constant, i.e. in 0.02 T and 0.05 T, the FC susceptibilities are larger while this is reversed in 0.1 T. Especially the observation, that the 0.1 T FC curve is smaller than the ZFC curve, is not physical. Because of this, it must be assumed that the observed difference between the curves is due to a systematic error of the magnetometer and not due to physical phenomena inherent to $\text{Er}_2\text{Te}_4\text{O}_{11}$.

The small peaks in $\chi(T)$, which are visible in the FC data for 20 mT and 50 mT, but not in the ZFC data of the respective magnetic fields, and in the ZFC data in 150 and 200 mT must also be understood as artifacts caused by the measurements with the iHe3 option and not as a physical process. This is in particular seen in the non-

monotonous choice of temperatures within the data of $B = 0.15$ T. This cannot easily be changed because the control software for this setup offers only limited flexibility in changing parameters.

Measurements of the ac susceptibility of $\text{Er}_2\text{Te}_4\text{O}_{11}$ under applied static magnetic fields, see figure 6.6, reveal field induced and stabilized processes. A behavior similar to the observed χ' data is reported for the frustrated pyrochlore systems $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Ti}_2\text{O}_7$ [96]. In the former, this anomaly was interpreted as a freezing into a glassy like state caused by the local frustrations [47]. Ueland *et al.* [96] explain the observed behavior rather as a field induced polarization of clusters of the Tb spins in high fields. These two works observe an onset of the anomalies in χ' only at (for the specific system) sufficiently high frequencies, which are comparable to the ones probed in this work. Just as the magnetic rare earth ions in the two previously mentioned $R_2\text{Ti}_2\text{O}_7$ compounds, the quasi two-dimensional honeycomb lattice of $\text{Er}_2\text{Te}_4\text{O}_{11}$ can lead to frustrated interactions between the Er ions. Er^{3+} is anisotropic and in particular possesses an easy axis anisotropy with respect to the lattice [102]. The field enhancing of the dynamic susceptibility anomalies suggests a connection to the polarization of the system.

For $\text{Er}_2\text{Te}_4\text{O}_{11}$, an analysis of the frequency has not yet been performed. Probing more frequencies, particularly lower ones, would help understand to gain an improved understanding of the underlying process and could allow evaluations in the context of spin dynamic models like comparing it to the Arrhenius or Vogel-Fulcher relationship, as performed in [47] [96] [120]. This could reveal whether disorder is indeed the cause of the observed freezing processes and if so, which dynamics the freezing process possesses.

Some of the χ' datasets in figure 6.6 are shifted above the others. This is indeed not a scaling but a shift as can be seen by the fact that this difference does not persist in the derivatives. An explanation for this can be found in the measurement technique as laid out in section 3.1.2 with a misidentification of characteristic points in the three point method. These datasets are kept in the analysis, nonetheless, because they retain the qualitative features that are needed for understanding the magnetic behavior of $\text{Er}_2\text{Te}_4\text{O}_{11}$.

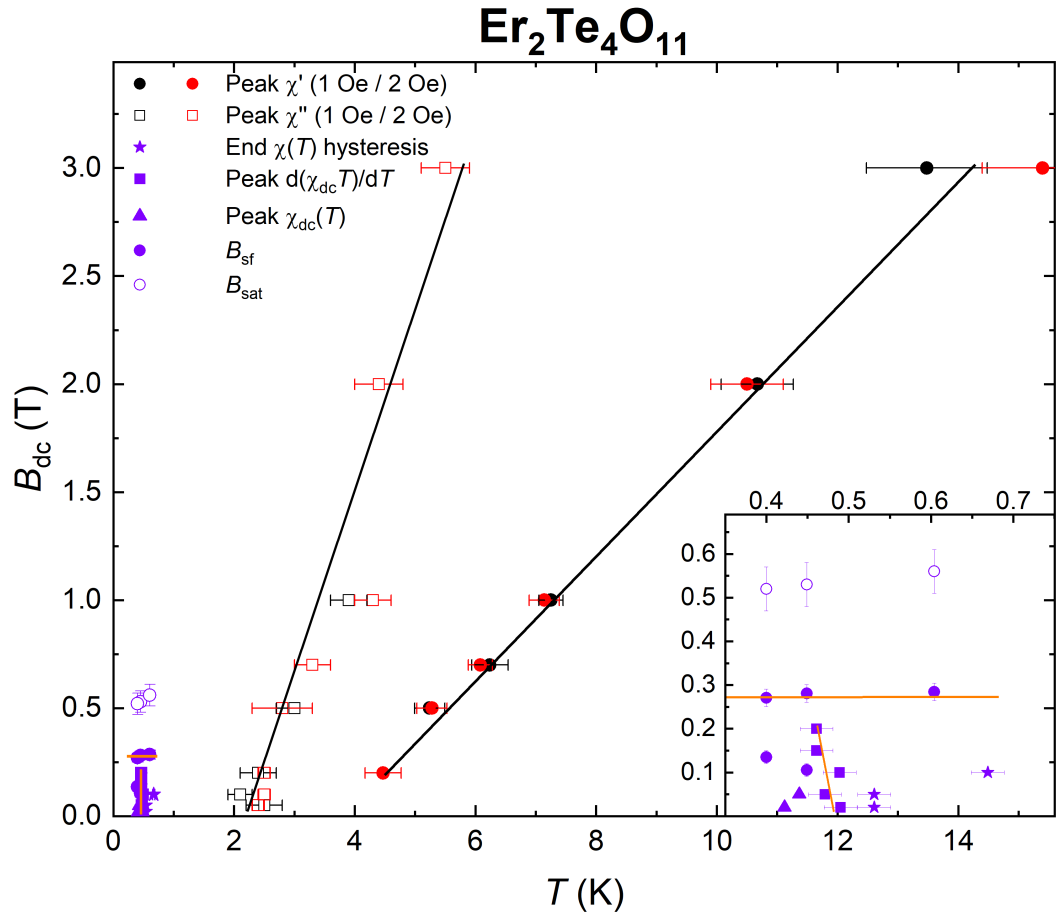


Figure 6.9: Summary of figure 6.4 - figure 6.6. Lines are guides to the eyes.

7 Fe_3GaTe_2

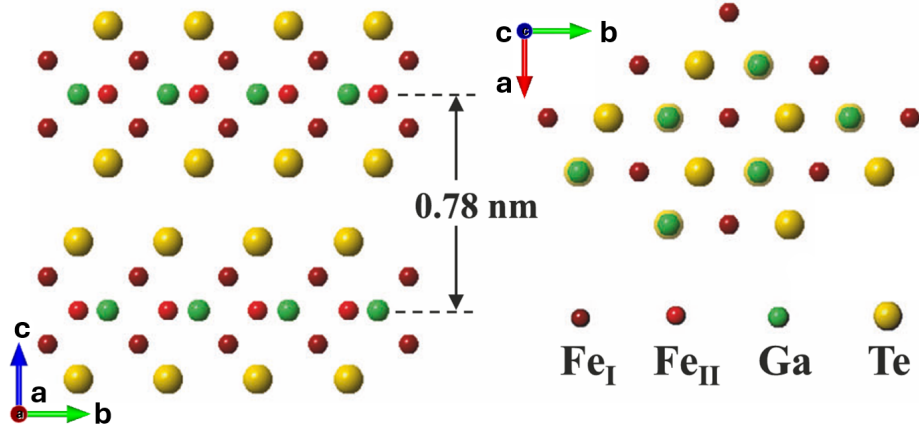


Figure 7.1: Crystal structure of Fe_3GaTe_2 , taken from [121]. As seen along the a axis (left) and along the c axis (right).

7.1 Introduction

Fe_3GaTe_2 crystallizes in a hexagonal lattice in the space group $P6_3/mmc$ (no. 194) with lattice constants $a = b = 3.986 \text{ \AA}$, $c = 16.229 \text{ \AA}$ [121] [122] [123]. Fe_3Ga layers are sandwiched between Te layers. The Fe ions are located in two inequivalent crystallographic positions of the lattice [122] [124] [125]. A rendering of Fe_3GaTe_2 's crystal structure, taken from [121] is shown in figure 7.1. The valences of the ions have been determined as Fe^0 , Fe^{3+} , Ga^{2-} , Te^{2-} , where the magnetic properties are attributable due to the two Fe ion species (the Fe^{3+} occurs in a high-spin state) [121]. Fe_3GaTe_2 is part of a broader family of systems sharing the composition Fe_nGTe_2 ($n = 3, 4, 5$; $G = \text{Ga}, \text{Ge}$), which contains multiple layered materials with high Curie temperatures [123] [124]. The van der Waals interaction between the Fe_3Ga layers is assumed to be significantly weaker than the in plane exchanges, making the material magnetically two-dimensional [121] [122] [126]. Previous magnetometrical studies [121] [122] [123] [124] have revealed a remanent magnetization which hints at ferromagnetic behavior, the field hysteresis was confirmed using Magnetic Force Microscopy [124]. The

magnetization is anisotropic and follows an easy axis behavior, this means that the magnetic moments preferably align along the c axis, perpendicular to the Fe_3Ga layers in the ab plane [121] [122] [124].

Fe_3GaTe_2 has attracted interest for two main reasons: It retains its highly anisotropic ferromagnetic spontaneous magnetization even at room temperature, due to its high Curie temperature $T_C = 350 - 380$ K [121]. Secondly, it is an electrical conductor with a conductivity of $641000 \text{ } \Omega\text{m}^{-1}$ [127]. This would point towards itinerant (Stoner) ferromagnetism. However, it is argued based on ARPES data that the ferromagnetic ordering above room temperature is at least partially caused by localized magnetic moments, in particular the $3d$ moments of the Fe ions [122] [126].

7.2 High Field Electron Spin Resonance

Samples of Fe_3GaTe_2 were provided by M. Abdel-Hafiez. They were grown in a platelet shape parallel to the crystallographic ab plane. Fe_3GaTe_2 was investigated in the high field-electron spin resonance setup at KIP with parallel magnetic fields and microwave incidence along its c axis. The material is air sensitive and contact with air must be limited to less than 30 min [128]. This increases the difficulty of handling it because in particular the sample preparation for the ESR has to be done in a protective Argon atmosphere.

Fe_3GaTe_2 was investigated using HF-ESR with $B||c$. Spectra were recorded at 2 K and at 220 K for fields up to 16 T and with microwave radiation in the frequency range between ~ 50 GHz and ~ 900 GHz. Measurements exceeding 800 GHz did not result in any usable spectra. Based on the longitudinal conductivity measured by [127], a skin depth can be determined using eq. (3.2), allowing an estimate on the penetration depth and thus the interaction volume of the microwave radiation with the magnetic moments. At $T = 2$ K, the skin depth δ in the relevant frequency range according to eq. (3.2) is plotted in figure 7.2. The interaction volume, which scales with δ , decreases with $1/\sqrt{f}$. Experimentally probed frequencies in the HF-ESR setup range from ca. 50 GHz to 900 GHz, correspondingly there is a change in skin depth from $2.81 \text{ } \mu\text{m}$ by a factor of 4 to $0.71 \text{ } \mu\text{m}$. The microwaves are not transmitted through the sample because of the aforementioned shielding. This and the fact that the attenuation of an electromagnetic wave is generally larger with increased frequency, explains why the signal vanishes at high frequencies.

The spectra at each frequency contain an up and a down sweep of the magnetic field. An exemplary spectrum of Fe_3GaTe_2 is shown in figure 7.3, which shows the transmittivity through the surface layers as a function of applied field $B_{||c}$ at $f = 331.4256$ GHz at a temperature of 2 K. The up and down sweeps are shown in one

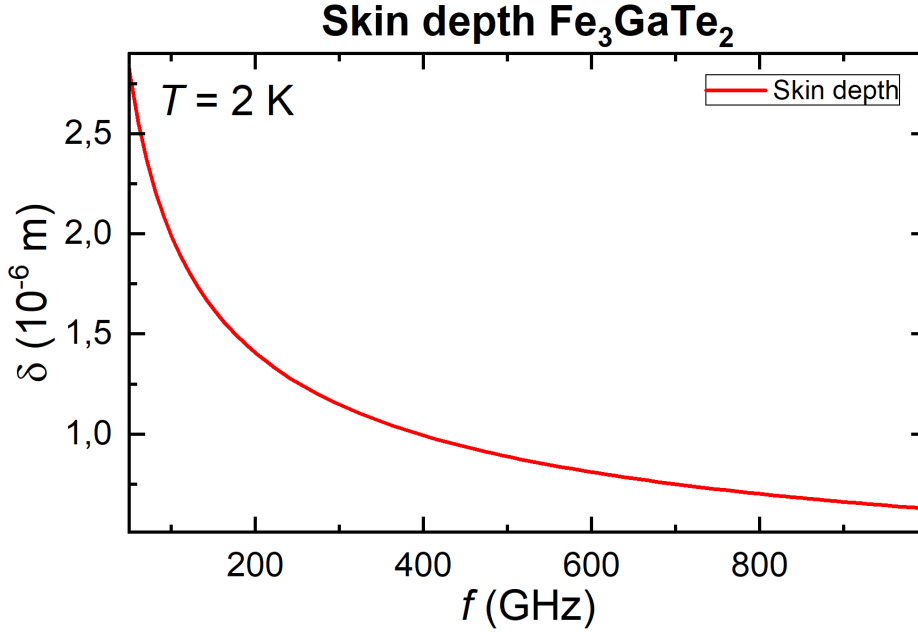


Figure 7.2: Calculated skin depth $\delta(f)$ at $T = 2$ K as a function of frequency f according to eq. (3.2) with conductivity given in [127].

plot, the curves are shifted along the vertical transmittivity axis to allow for better visibility. Already in the raw data, two features in the transmittivity can be seen. They are marked with vertical lines. A phase shift between the electric and magnetic components of the microwave can lead to them mixing, which needs to be corrected for [129]. In order to perform a quantitative analysis of spectra requires this to be corrected because due to the phase mixing, a shift in the resonance position of the absorptive component of the signal is possible.

Figure 7.4 shows the spectra obtained for $B \parallel c$ at 2 K for Fe_3GaTe_2 at a number of frequencies between 40 GHz and 900 GHz. Anomalies are marked for each sweep. The same is done for 220 K in figure 7.5. Anomalies were only marked if they appeared in both the up and the down sweep. These features can be interpreted as possible resonance positions. From the spectral datasets at both temperatures, the field-frequency loci can be collected in a $f - B$ diagram, see figure 7.6. It is possible to see at least two linear resonance branches of recorded positions in both measurement series. One appears gapless, i.e. it may reasonably be extrapolated to the origin of the plot. The other one appears gapped if assumed to be linear. Assuming a linear

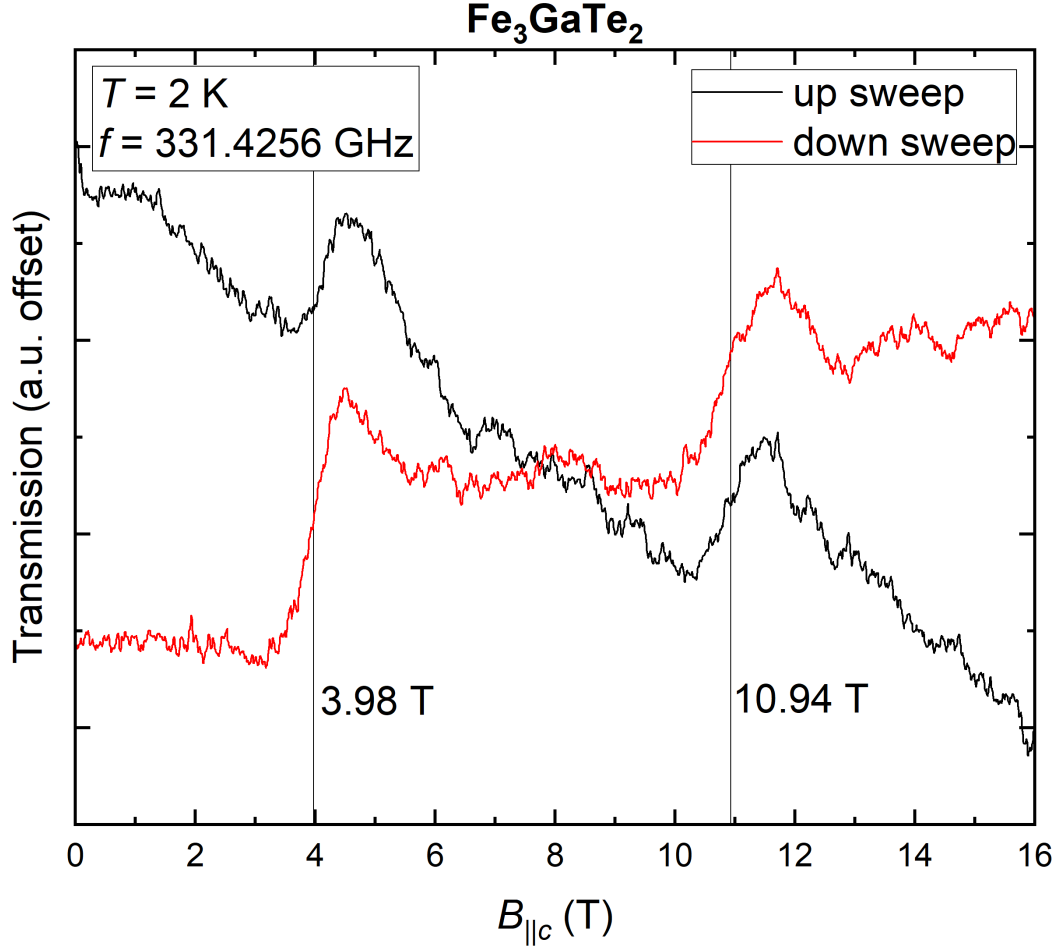


Figure 7.3: ESR spectrum of Fe_3GaTe_2 for $B_{||c}$ at 331.4256 GHz and $T = 2\text{K}$. Both sweeps (up and down) are shown but are shifted along the transmission axis for better visibility. The two lines mark the observed resonance features.

field behavior of the two resonance branches, a corresponding linear function can be fitted to the data:

$$f(B) = \frac{\mu_B}{h} g_{\text{eff}} B + f_{\text{gap}}. \quad (7.1)$$

g_{eff} is the effective g factor of the excitation. Performing such a fit yields two gaped modes with the corresponding effective g factors of 2.05(10) and 2.19(10) and gap sizes

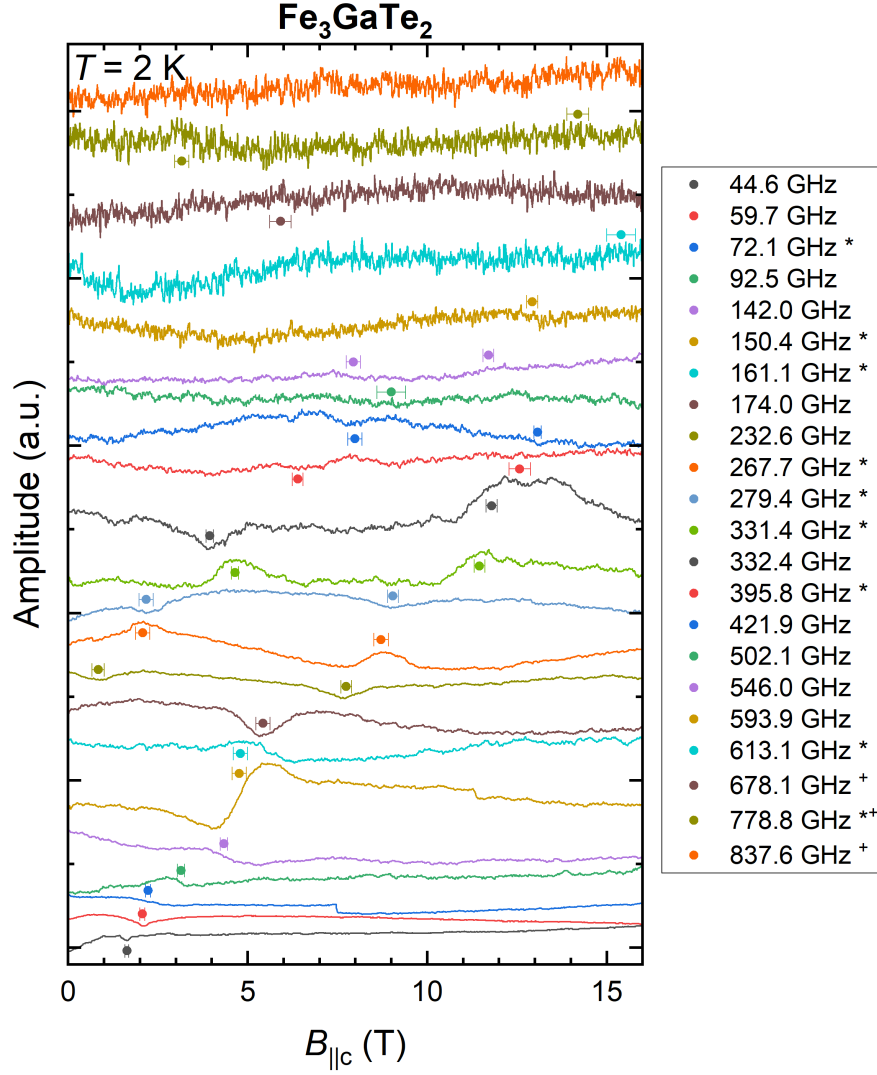


Figure 7.4: HF-ESR spectra for Fe₃GaTe₂ for $B_{\parallel c}$ at 2 K. Various microwave frequencies were probed. The color coded markers indicate inferred resonance positions in the corresponding sweep. In the legend, some frequencies are marked with *, which indicates that a linear term was subtracted as a background from the spectrum, while the + signifies that the spectrum's amplitude was scaled.

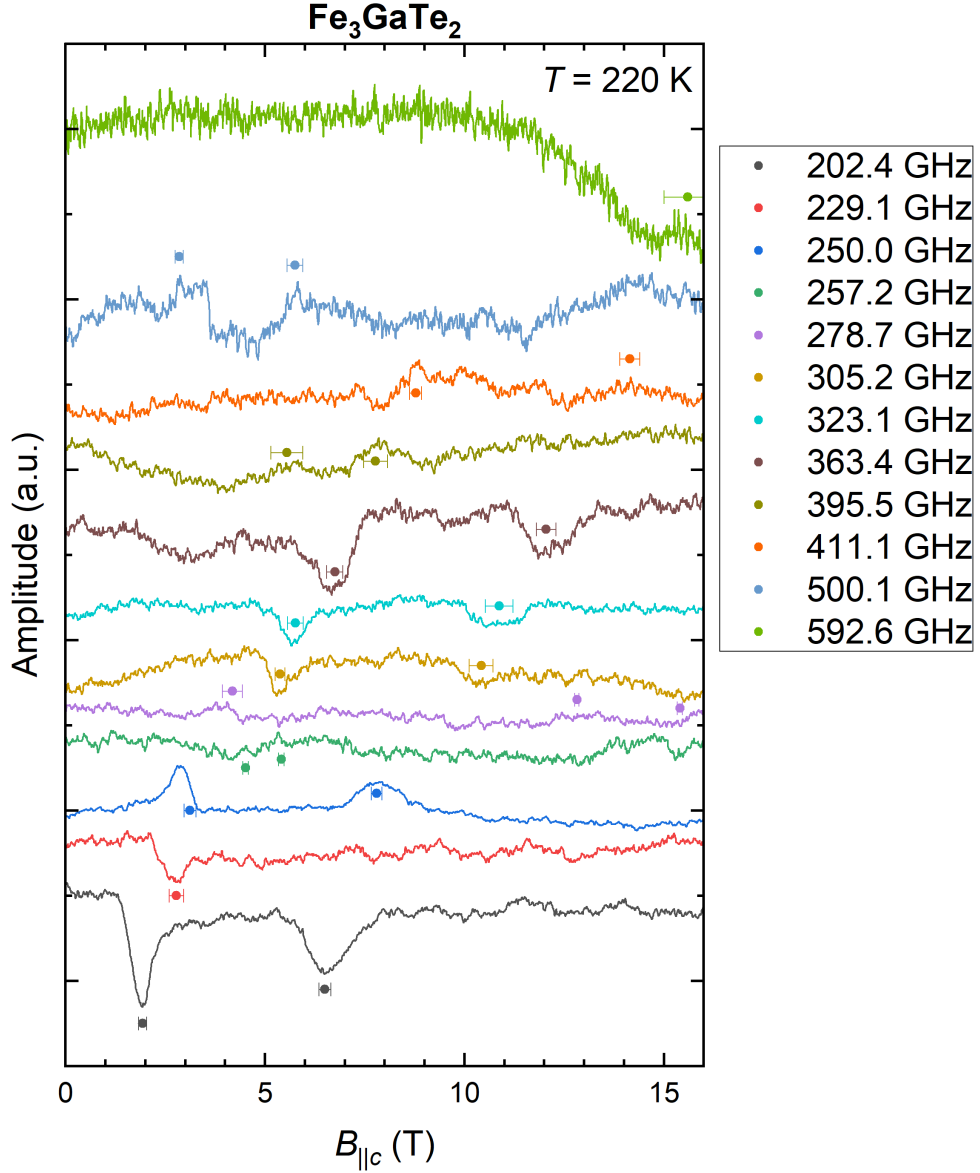


Figure 7.5: HF-ESR spectra for Fe_3GaTe_2 with $B \parallel c$ at 220 K. Various microwave frequencies were probed. The color coded markers indicate inferred resonance positions in the corresponding sweep.

$E_{\text{gap}} = h \times 210(10) \text{ GHz} = 0.87(4) \text{ meV}$ and $E_{\text{gap}} = h \times 144(10) \text{ GHz} = 0.60(4) \text{ meV}$ respectively for 2 K and 220 K. The lower lying modes are assumed to be gapless ($f_{\text{gap}} = 0$) and yield $g = 2.22(10)$ and $g = 2.20(15)$, respectively. Allowing a gap as a

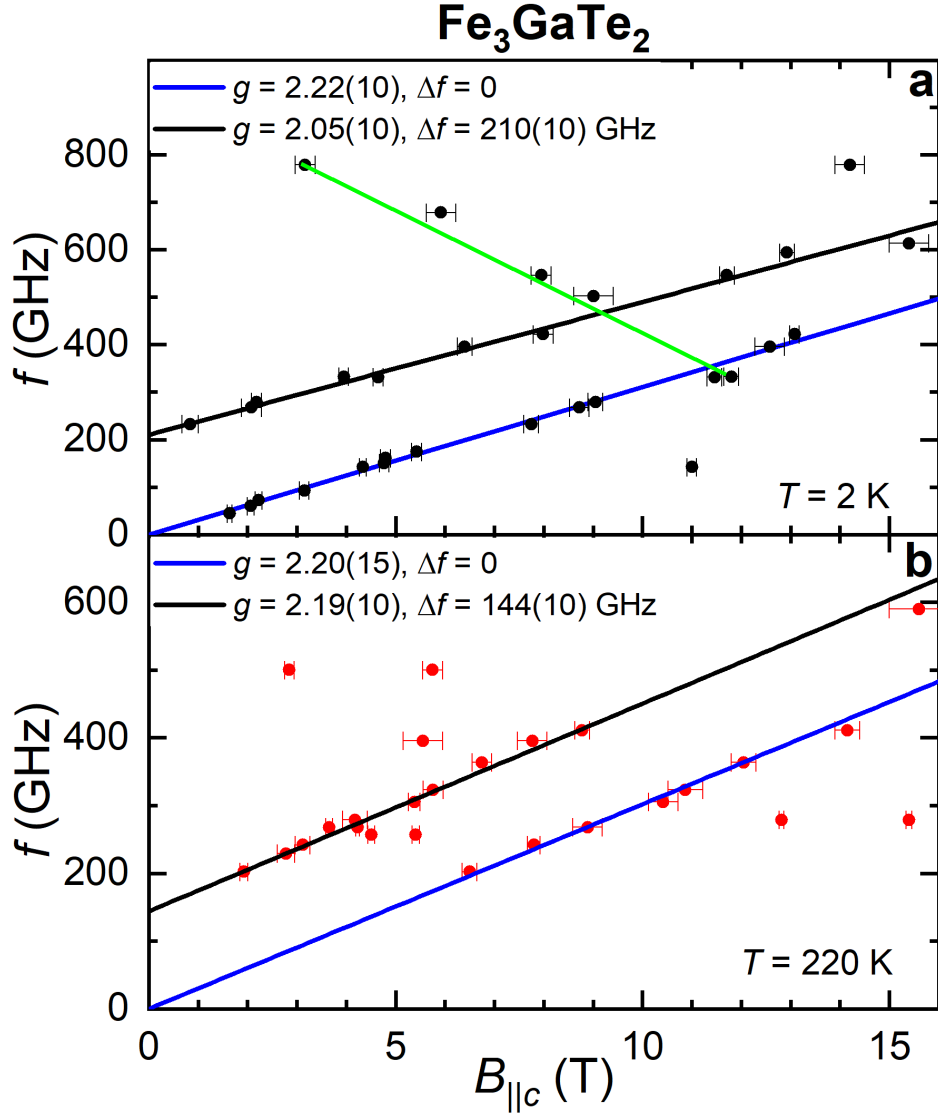


Figure 7.6: Resonance-frequency-magnetic-field diagram of Fe₃GaTe₂ at 2 K (a) and 220 K (b) for $B_{||c}$. The lines are explained in the text.

fit parameter, does not result in significantly differing results with a deviation smaller than 3σ compared to a fit without the gap as a degree of freedom.

There is a further possible line in the 2 K data of figure 7.6, which is marked in green. Fitting a linear function to these points yields a negative slope in the $f(B)$ branch. The value for g is approximately $g \approx 3.9$ with a gap of $f_{\text{gap}} \approx 970$ GHz. However, this line is speculative because no resonances on this line were found in-between the two more established ones and half of the defining anomalies could also be part of the other two more established branches.

At the microwave frequency $f = 267.8$ GHz, spectra were measured for a number of temperatures ranging from 2 K to 260 K. These data are shown in figure 7.7. Two features can be seen in the measurement at 2 K at 2 T and at 9 T. These resonance positions are marked in the plot and their resonance field position is followed with increasing temperature. It appears that the 2 T resonance moves towards higher fields with increasing temperature; at $T = 260$ K, it is located at approximately 4.7 T. The second feature lacks such a clear trend. Figure 7.8 shows the resonance fields as a function of sample temperature. It can be seen that the 9 T feature indeed does not exhibit a clearly established trend with temperature except at temperatures $T \leq 10$ K, where a decrease in B can be noticed, albeit within the margin of error as marked by the error bars. The low field feature shows a clear increase in field strength with sample temperature. Shifting from 2 T to 4.5 T at 260 K in a monotonous fashion.

All available Fe_3GaTe_2 crystals have a plate like shape where the ab plane coincides with the plate. In order to get data with $B \perp c$, measurements with a sample installation perpendicular to the c axis were necessary. This was initially attempted by clamping the crystal between two Teflon blocks (as seen in figure 3.4a). Experimentally it turned out that the sample was not stabilized enough in this approach as sudden jerks of the crystal were observed. An alternative approach tried was fixing the sample in an upright position using molten icosane. The amount of icosane required to stabilize the crystal in an upright position was also sufficient to absorb all the microwave radiation and thus no signal was recorded in these measurements. This is described in more detail in appendix B.

In the future, approaches to measure the same sample should therefore rely on another fixing agent. This could be a stronger glue which requires less material than the previously utilized icosane and thus circumvent the observed absorption bottleneck. However, special care must taken to not damage the delicate material.

The magnetization of Fe_3GaTe_2 was measured both isothermally and as a function of temperature. Due to reasons discussed in appendix C, these data cannot be used for further quantitative analysis.

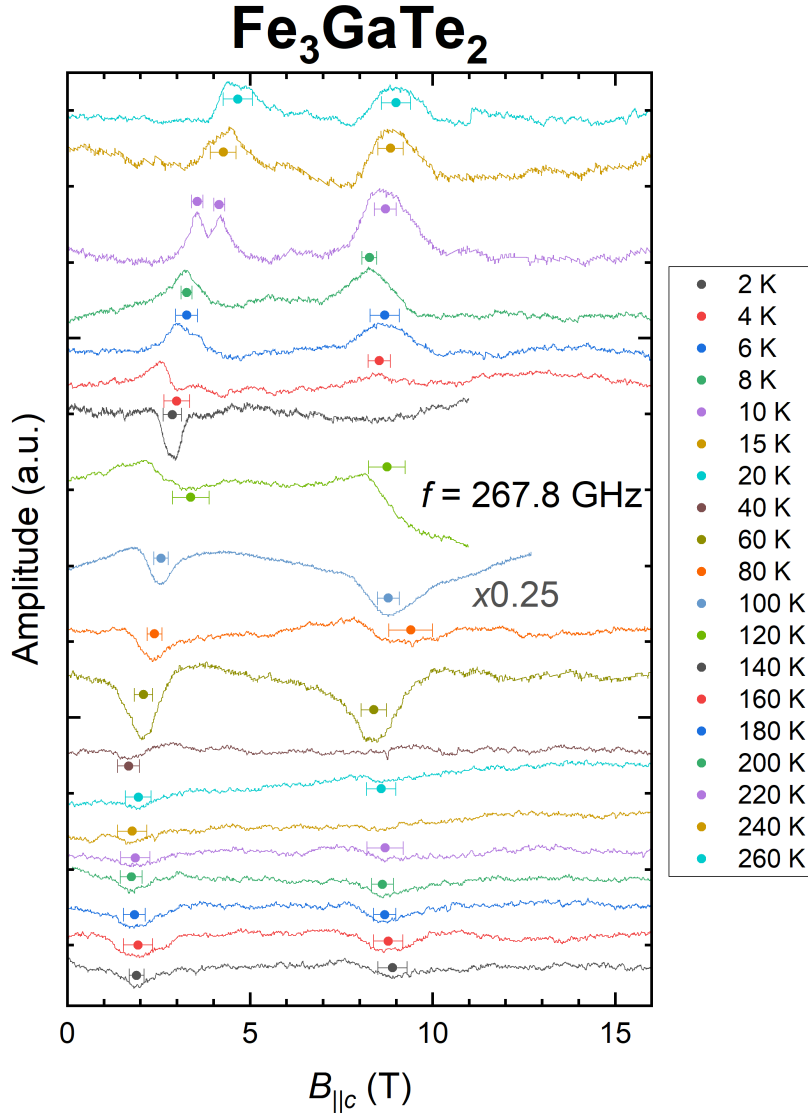


Figure 7.7: HF-ESR spectra for Fe_3GaTe_2 with $B \parallel c$ at the fixed frequency $f = 267.8$ GHz. The temperature was varied between 2 K and 260 K. The color coded markers indicate inferred resonance positions in the corresponding sweep. For better visibility, a third order polynomial background was removed with some spectra. Between 100 K and 140 K, the sweeps were cut off at either 11 T or 12.7 T because the amplitudes were running away, no features are expected in the removed field regions.

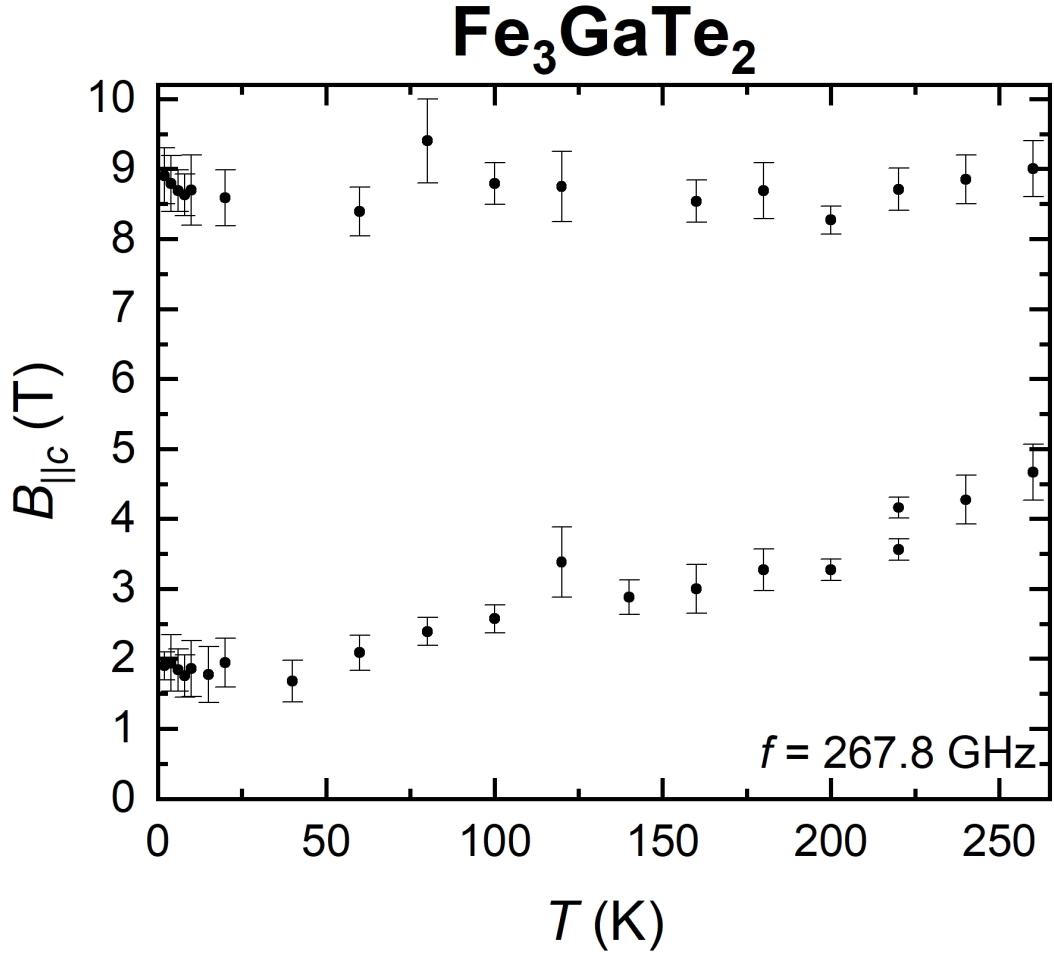


Figure 7.8: Summary of the resonance positions of Fe_3GaTe_2 determined in figure 7.7 as a function of temperature T .

7.3 Discussion

HF-ESR spectra were recorded of Fe_3GaTe_2 at 2 K and at 220 K for $B_{||c}$. The resonance fields determined from the spectra shown in figure 7.4 & figure 7.5 are summarized in the resonance-frequency-magnetic-field diagram in figure 7.6. Most of these features can be grouped into two resonance branches with approximately linear $f(B)$ behavior. By performing linear fits for both branches, an effective g -factor can be extracted from the corresponding slopes according to eq. (7.1). At

both temperatures, the lower energy branch is gapless, i.e. $f(B = 0) = 0$, and yields $g > 2$. At higher microwave frequencies, a gapped branch with $g = 2$ becomes visible. The zero field gap separating the two branches from one another is about 210 GHz at 2 K and decreases to 144 GHz at 220 K. It is expected that the zero field excitation gap decreases with increased temperature due to thermal fluctuations. The reported Curie temperature for Fe_3GaTe_2 is $T_C = 350$ K, which is in accordance with a non-zero excitation gap at 220 K. In the related two-dimensional van der Waals ferromagnets Fe_3GeTe_2 , Fe_4GeTe_3 and CrI_3 [130] [131] [132], a similarly gapped branch for the out-of-plane direction was found which also increased its resonance fields with temperature. In these systems an in-plane resonance branch was observed, whose resonance fields showed an opposite shifting with increasing temperature. The zero field excitation gap and the shift of the resonance field of the branches for the two different B field directions as reported in [130] [131] [132] approaches zero only above T_C . A similar analysis cannot be performed here, both due to a lack of in-plane data and because the Curie temperature of Fe_3GaTe_2 lies beyond the temperature regime accessible with the available HF-ESR setup

In order to get a more complete understanding of the magnetic qualities of Fe_3GaTe_2 , more measurements are needed. These include in particular probing the in plane behavior of the crystal to complete the $f(B)$ diagram. This would allow a quantitative comparison to other two-dimensional vdW ferromagnets and potentially simulations of the field dependence of the energy dispersion of the magnon modes as was done in [133]. Further data that will give more insights into the evolution of e.g the g -factor and the zero field excitation gap with temperature T , are $f(B)$ diagrams (like figure 7.6) at further temperatures, both between 2 K and 220 K and at higher temperatures, as was performed for the related compound Fe_3GeTe_2 [130]. Ideally, this would be done even beyond the Curie temperature, which is not possible with the HF-ESR setup at KIP, as it only allows measurements at temperatures up to 300 K. Probing the resonance behavior beyond the ordering temperature allows a determination of the onset of magnetic ordering on timescales comparable to the HF-ESR timescales and would enable a more complete picture on the ordering mechanism itself if combined with simulations of the magnon branches.

8 Summary and Outlook

This thesis reports on investigations regarding the magnetic and magnetoelastic properties of four strongly correlated systems. AC magnetometry was performed in a temperature range between 1.8 K and 300 K in static fields up to 7 T, the excitation fields were chosen between 1 and 8 Oe and driven at various frequencies between 3 and 930 Hz. DC magnetometric measurements were performed with magnetic fields up to 7 T with temperatures down to 400 mK. Furthermore, high precision capacitance dilatometry was employed in fields $B \leq 8$ T between 1.8 and 300 K. High field electron spin resonance (HF-ESR) was performed with sample temperatures in the same range, the available magnetic field range was up to 16 T in conjunction with microwave frequencies of up to 900 GHz.

Single-crystalline TbInO_3 (see chapter 4) was investigated with SQUID magnetometry parallel and perpendicular to the c axis as well as by high-resolution capacitance dilatometry parallel to the crystallographic c axis for temperatures between 1.8 K and 300 K in magnetic fields $B||c$ up to 8 T. The magnetization data only agreed with the literature when a powder average is applied, individual axes show deviating behavior. A pronounced anisotropy in the magnetization was confirmed to peak with $\chi_{ab}/\chi_c \approx 5$ at 15 K. A limiting factor to the capacitance dilatometry was the small sample size with a thickness of 0.17 mm. Magnetostriction data at 1.8 K and 10 K revealed a featureless behavior. In the thermal expansion measurements, a broad field-independent hump was found, which can reasonably be attributed to irregularities in the dilatometer cell independent of TbInO_3 . These results, particularly the absence of ordering, further support the hypothesis of Quantum Spin Liquid behavior in TbInO_3 . Further investigations will have to repeat the dilatometry measurements for both axes in an improved setup in order to avoid device artifacts.

$\text{Tb}_2\text{Zr}_2\text{O}_7$ was previously reported to exhibit glassy behavior. These features were investigated further using DC magnetometry between 400 mK and 300 K as well as AC magnetometry down to 1.8 K with driving frequencies between 3 Hz and 930 Hz. The same methods were applied to the related system $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ which is assumed to be closer in behavior to the Quantum Spin Liquid candidate $\text{Tb}_2\text{Ti}_2\text{O}_7$ but has not been investigated so far. Signs of glassiness were recovered in both systems, however a visible suppression of them could be established in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ compared to $\text{Tb}_2\text{Zr}_2\text{O}_7$. In particular, temperatures and fields associated with freezing processes

were reduced upon substitution of Zr for Ti. Examples for these processes are bifurcation between field cooled and zero field cooled susceptibilities and magnetic hysteresis in the isothermal magnetization. The glassy behavior can be attributed to the fact that the larger relative ionic radius of the Terbium ions in $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ leads to a suppressed cationic disorder, which in turn reduces frustrations and glassiness [40]. Furthermore, a field stabilized phase of slow spin relaxation was found in both systems between 7 K and 15 K in the AC magnetization data, which appears to be a characteristic feature of this class of materials. The findings from the aforementioned measurements are summed up in a B vs. T phase diagram for $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ with $x = 0$ & 0.5, respectively. Ac susceptometry needs to be performed more systematically as a function of frequency in order to analyze the results more quantitatively as done in [76]. Furthermore, the same behavior needs to be probed at lower temperatures because some of the observed features shift outside of the measurement range to $T < 2$ K.

AC & DC magnetometry on polycrystalline $\text{Er}_2\text{Te}_4\text{O}_{11}$ did not conclusively reveal any clear magnetic ordering transitions. Antiferromagnetic interactions were found in the paramagnetic phase in higher temperatures via a Curie-Weiss fit. At temperatures of $T \approx 600$ mK, a broad maximum in the temperature dependent magnetization shows the onset of an antiferromagnetically dominated behavior. A peak in Fisher's specific heat is taken as a delimiter for this region in a suggested phase diagram. Inflection points in the isothermal magnetization can be interpreted as spin flop processes that appear to extend beyond the region marked by Fisher's specific heat. From an Arrott plot, a possible first order phase transition could be assumed, however the evidence for this is not definite. In conclusion with the lack of clear ordering signatures, this suggests a crossover into an antiferromagnetically dominated region without a distinct phase transition. Frustrations stemming from the trigonal crystal structure, as indicated by the lack of ordering beyond the purported Weiss temperature, cause the isothermal magnetization to saturate into a moment which is reduced by a factor of more than two relative to the free ion value in agreement with reports on the related $\text{Tb}_2\text{Zr}_4\text{O}_{11}$. At higher temperatures, beginning at 2 K, a field stabilized region of increased absorption was found by ac magnetic susceptibility measurements, which is possibly connected to the aforementioned frustration. An analysis of the frequency dependence of this process requires further measurements of the ac susceptibility in a broader frequency range.

In Fe_3GaTe_2 , high-frequency electron spin resonance spectroscopy with $B||c$ revealed two resonance branches, of which one is gapped and the other one gapless. The gapless branch possesses an effective g -factor of 2, while the gapped one exhibits a g factor significantly differing from 2. It could be shown that the resonance fields in the gapped branch follow a behavior consistent with other two-dimensional van der

Waals ferromagnets. The gapless branch's slope does not change with temperature dependence. Measurements of the in plane behavior need to be performed in order to evaluate the anisotropy of the modes and compare them to related compounds. The development of the gap size needs to be probed to temperatures beyond the Curie temperature $T_C = 350$ K.

Bibliography

- ¹P. W. Anderson, “Spin Glass I: A Scaling Law Rescued”, en, [Physics Today](#) **41**, 9–11 (1988).
- ²S. Blundell, *Magnetism in condensed matter*, eng, Oxford master series in condensed matter physics (Oxford university press, Oxford New York, 2001).
- ³L. Balents, “Spin liquids in frustrated magnets”, en, [Nature](#) **464**, 199–208 (2010).
- ⁴G. H. Wannier, “Antiferromagnetism. The Triangular Ising Net”, en, [Physical Review](#) **79**, 357–364 (1950).
- ⁵P. J. Ford, “Spin glasses”, en, [Contemporary Physics](#) **23**, 141–168 (1982).
- ⁶K. Binder and A. P. Young, “Spin glasses: Experimental facts, theoretical concepts, and open questions”, en, [Reviews of Modern Physics](#) **58**, 801–976 (1986).
- ⁷J. A. Mydosh, *Spin Glasses: An Experimental Introduction*, en, 1st ed. (CRC Press, Apr. 2014).
- ⁸P. Anderson, “Resonating valence bonds: A new kind of insulator?”, en, [Materials Research Bulletin](#) **8**, 153–160 (1973).
- ⁹Y. Zhou, K. Kanoda, and T.-K. Ng, “Quantum spin liquid states”, en, [Reviews of Modern Physics](#) **89**, 025003 (2017).
- ¹⁰Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, “Spin Liquid State in an Organic Mott Insulator with a Triangular Lattice”, en, [Physical Review Letters](#) **91**, 107001 (2003).
- ¹¹A. Pustogow, “Thirty-Year Anniversary of $-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3$: Reconciling the Spin Gap in a Spin-Liquid Candidate”, en, [Solids](#) **3**, 93–110 (2022).
- ¹²T. Itou, A. Oyamada, S. Maegawa, M. Tamura, and R. Kato, “Quantum spin liquid in the spin- $\frac{1}{2}$ triangular antiferromagnet $\text{Et Me}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ ”, en, [Physical Review B](#) **77**, 104413 (2008).
- ¹³M. Yoshida, K. Nawa, H. Ishikawa, M. Takigawa, M. Jeong, S. Krämer, M. Horvatić, C. Berthier, K. Matsui, T. Goto, S. Kimura, T. Sasaki, J. Yamaura, H. Yoshida, Y. Okamoto, and Z. Hiroi, “Spin dynamics in the high-field phases of volborthite”, en, [Physical Review B](#) **96**, 180413 (2017).

- ¹⁴M. R. Norman, “*Colloquium* : Herbertsmithite and the search for the quantum spin liquid”, en, [Reviews of Modern Physics](#) **88**, 041002 (2016).
- ¹⁵Y. Okamoto, H. Yoshida, and Z. Hiroi, “Vesignieite $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$ as a Candidate Spin-1/2 Kagome Antiferromagnet”, en, [Journal of the Physical Society of Japan](#) **78**, 033701 (2009).
- ¹⁶Y. Singh, Y. Tokiwa, J. Dong, and P. Gegenwart, “Spin liquid close to a quantum critical point in $\text{Na}_4\text{Ir}_3\text{O}_8$ ”, en, [Physical Review B](#) **88**, 220413 (2013).
- ¹⁷S.-H. Baek, S.-H. Do, K.-Y. Choi, Y. S. Kwon, A. U. B. Wolter, S. Nishimoto, J. Van Den Brink, and B. Büchner, “Evidence for a Field-Induced Quantum Spin Liquid in RuCl_3 ”, en, [Physical Review Letters](#) **119**, 037201 (2017).
- ¹⁸A. Banerjee, C. A. Bridges, J.-Q. Yan, A. A. Aczel, L. Li, M. B. Stone, G. E. Granroth, M. D. Lumsden, Y. Yiu, J. Knolle, S. Bhattacharjee, D. L. Kovrizhin, R. Moessner, D. A. Tennant, D. G. Mandrus, and S. E. Nagler, “Proximate Kitaev quantum spin liquid behaviour in a honeycomb magnet”, en, [Nature Materials](#) **15**, 733–740 (2016).
- ¹⁹V. Cannella and J. A. Mydosh, “Magnetic Ordering in Gold-Iron Alloys”, en, [Physical Review B](#) **6**, 4220–4237 (1972).
- ²⁰J. B. Goodenough, “Theory of the Role of Covalence in the Perovskite-Type Manganites $[\text{La}, \text{M}(\text{II})]\text{MnO}_3$ ”, en, [Physical Review](#) **100**, 564–573 (1955).
- ²¹J. Kanamori, “Theory of the Magnetic Properties of Ferrous and Cobaltous Oxides, I”, en, [Progress of Theoretical Physics](#) **17**, 177–196 (1957).
- ²²K. Westerholt and H. Bach, “Magnetic ordering in $\text{Eu}_x\text{Sr}_{1-x}\text{Se}_2$ ”, en, [Journal of Magnetism and Magnetic Materials](#) **24**, 191–196 (1981).
- ²³P. Anderson, “Localisation theory and the CuMn problem: Spin glasses”, en, [Materials Research Bulletin](#) **5**, 549–554 (1970).
- ²⁴<https://arxiv.org/abs/2412.08381>E. D. Dahlberg, I. G.-A. Pemartín, E. Marinari, V. Martin-Mayor, J. Moreno-Gordo, R. L. Orbach, I. Paga, G. Parisi, F. Ricci-Tersenghi, J. J. Ruiz-Lorenzo, and D. Yllanes, *Spin-glass dynamics: experiment, theory and simulation*, 2024.
- ²⁵D. Sherrington and S. Kirkpatrick, “Solvable Model of a Spin-Glass”, en, [Physical Review Letters](#) **35**, 1792–1796 (1975).
- ²⁶S. F. Edwards and P. W. Anderson, “Theory of spin glasses”, [Journal of Physics F: Metal Physics](#) **5**, 965–974 (1975).
- ²⁷G. Parisi, “Nobel Lecture: Multiple equilibria”, en, [Reviews of Modern Physics](#) **95**, 030501 (2023).

-
- ²⁸W. Nolting, *Grundkurs Theoretische Physik 4/2*, Springer-Lehrbuch (Springer Berlin Heidelberg, Berlin, Heidelberg, 2016).
- ²⁹T. Fließbach, *Statistische Physik: Lehrbuch zur Theoretischen Physik IV*, de (Springer Berlin Heidelberg, Berlin, Heidelberg, 2018).
- ³⁰É. d. Trémolet de Lacheisserie, *Magnetostriction: theory and applications of magnetoelasticity*, eng (CRC Press, Boca Raton, 1993).
- ³¹R. Gross and A. Marx, *Festkörperphysik*, ger, 4., aktualisierte Auflage, De Gruyter Studium (De Gruyter, Berlin Boston, 2023).
- ³²A. S. Borovik-romanov, “Piezomagnetism, linear magnetostriction and magneto-optic effect”, en, [Ferroelectrics](#) **162**, 153–159 (1994).
- ³³J. M. D. Coey, *Magnetism and Magnetic Materials*, 1st ed. (Cambridge University Press, Jan. 2001).
- ³⁴S. Mugiraneza and A. M. Hallas, “Tutorial: a beginner’s guide to interpreting magnetic susceptibility data with the Curie-Weiss law”, en, [Communications Physics](#) **5**, 95 (2022).
- ³⁵V. Franco and B. Dodrill, eds., *Magnetic Measurement Techniques for Materials Characterization*, en (Springer International Publishing, Cham, 2021).
- ³⁶M. Bałanda, “AC Susceptibility Studies of Phase Transitions and Magnetic Relaxation: Conventional, Molecular and Low-Dimensional Magnets”, en, [Acta Physica Polonica A](#) **124**, 964–976 (2013).
- ³⁷S. Hunklinger and C. Enss, *Festkörperphysik*, 6th ed., De Gruyter Studium (De Gruyter Oldenbourg, Boston, 2023).
- ³⁸A. P. Ramirez, “Strongly Geometrically Frustrated Magnets”, en, [Annual Review of Materials Science](#) **24**, 453–480 (1994).
- ³⁹O. A. Petrenko, M. R. Lees, and G. Balakrishnan, “Titanium pyrochlore magnets: how much can be learned from magnetization measurements?”, [Journal of Physics: Condensed Matter](#) **23**, 164218 (2011).
- ⁴⁰A. F. Fuentes, E. C. O’Quinn, S. M. Montemayor, H. Zhou, M. Lang, and R. C. Ewing, “Pyrochlore-type lanthanide titanates and zirconates: Synthesis, structural peculiarities, and properties”, en, [Applied Physics Reviews](#) **11**, 021337 (2024).
- ⁴¹J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, “Magnetic pyrochlore oxides”, en, [Reviews of Modern Physics](#) **82**, 53–107 (2010).

- ⁴²J. A. Mydosh, “Recent experiments on spin glasses: An overview”, in *Heidelberg Colloquium on Glassy Dynamics*, Vol. 275, edited by H. Araki, J. Ehlers, K. Hepp, R. Kippenhahn, H. A. Weidenmüller, J. Wess, J. Zittartz, W. Beiglböck, J. L. Van Hemmen, and I. Morgenstern (Springer Berlin Heidelberg, Berlin, Heidelberg, 1987), pp. 23–39.
- ⁴³J. L. Van Hemmen, “Classical Spin-Glass Model”, en, *Physical Review Letters* **49**, 409–412 (1982).
- ⁴⁴J. L. Van Hemmen, A. C. D. Van Enter, and J. Canisius, “On a classical spin glass model”, en, *Zeitschrift für Physik B Condensed Matter* **50**, 311–336 (1983).
- ⁴⁵V. S. Zotev, G. G. Kenning, and R. Orbach, “From linear to nonlinear response in spin glasses: Importance of mean-field-theory predictions”, en, *Physical Review B* **66**, 014412 (2002).
- ⁴⁶R. Knitter and J. Kouvel, “Field-induced magnetic transition in a Cu-Mn spin-glass alloy”, en, *Journal of Magnetism and Magnetic Materials* **21**, L316–L319 (1980).
- ⁴⁷J. Snyder, J. S. Slusky, R. J. Cava, and P. Schiffer, “How ‘spin ice’ freezes”, en, *Nature* **413**, 48–51 (2001).
- ⁴⁸<https://www.mrl.ucsb.edu/sites/default/files/documents/instruments/1500-100%20Rev.%20F1%20MPMS%203%20Users%20Manual.pdf> *Magnetic Property Measurement System: MPMS3 User’s Manual*.
- ⁴⁹https://www.qd-latam.com/_libs/dwns/659.pdf *MPMS3 Product Description*.
- ⁵⁰J. Clarke, “SQUIDS: THEN AND NOW”, en, *International Journal of Modern Physics B* **24**, 3999–4038 (2010).
- ⁵¹<https://apiezon.com/products/vacuum-greases/apiezon-n-grease/> *Apiezon N Grease*.
- ⁵²M. J. Coak, C. Liu, D. M. Jarvis, S. Park, M. J. Cliffe, and P. A. Goddard, “SquidLab—A user-friendly program for background subtraction and fitting of magnetization data”, en, *Review of Scientific Instruments* **91**, 023901 (2020).
- ⁵³M. Buchner, K. Höfler, B. Henne, V. Ney, and A. Ney, “Tutorial: Basic principles, limits of detection, and pitfalls of highly sensitive SQUID magnetometry for nanomagnetism and spintronics”, en, *Journal of Applied Physics* **124**, 161101 (2018).
- ⁵⁴*Magnetic Property Measurement System: SQUID VSM AC Option User’s Manual*.
- ⁵⁵M. Jonák, “Low-Energy Magnetic Excitations and Magnetisation in Magnetoelectric Antiferromagnets MnTiO₃ and LiMnPO₄ and in van-der-Waals Ferromagnet CrI₃”, Doctoral Thesis (Heidelberg University, Heidelberg, Nov. 2022).

- ⁵⁶L. T. Tsymbal, V. I. Kamenev, Y. B. Bazaliy, D. A. Khara, and P. E. Wigen, “Structural properties of Er Fe O_3 in the spin-reorientation region”, en, [Physical Review B](#) **72**, 052413 (2005).
- ⁵⁷W. Sławiński, R. Przeniosło, I. Sosnowska, and E. Suard, “Spin reorientation and structural changes in NdFeO_3 ”, [Journal of Physics: Condensed Matter](#) **17**, 4605–4614 (2005).
- ⁵⁸W. Heywang, *Piezoelectricity: Evolution and Future of a Technology*, eng, Springer Series in Materials Science Ser v.114 (Springer Berlin / Heidelberg, Berlin, Heidelberg, 2008).
- ⁵⁹R. KÜchler, A. Wörl, P. Gegenwart, M. Berben, B. Bryant, and S. Wiedmann, “The world’s smallest capacitive dilatometer, for high-resolution thermal expansion and magnetostriction in high magnetic fields”, en, [Review of Scientific Instruments](#) **88**, 083903 (2017).
- ⁶⁰R. KÜchler, R. Wawrzyńczak, H. Dawczak-Dębicki, J. Gooth, and S. Galeski, “New applications for the world’s smallest high-precision capacitance dilatometer and its stress-implementing counterpart”, en, [Review of Scientific Instruments](#) **94**, 045108 (2023).
- ⁶¹R. Pott and R. Schefzyk, “Apparatus for measuring the thermal expansion of solids between 1.5 and 380K”, [Journal of Physics E: Scientific Instruments](#) **16**, 444–449 (1983).
- ⁶²<https://www.andeen-hagerling.com/ah2550a.htm> *AH 2550A Ultra-precision Capacitance Bridge*.
- ⁶³F. R. Kroeger and C. A. Swenson, “Absolute linear thermal-expansion measurements on copper and aluminum from 5 to 320 K”, en, [Journal of Applied Physics](#) **48**, 853–864 (1977).
- ⁶⁴C. Min, Y. Wu, Y. Li, C. Zhou, S.-W. Cheong, X. Lu, T. Zhou, and L. Zhang, “Structural and Improper Ferroelectric Properties of TbInO_3 Single Crystal Grown by Laser Floating Zone”, en, [Crystals](#) **13**, 287 (2023).
- ⁶⁵J. Sahoo, D. Kochkov, B. K. Clark, and R. Flint, “Classical phase diagram of the stuffed honeycomb lattice”, en, [Physical Review B](#) **98**, 134419 (2018).
- ⁶⁶M. G. Kim, B. Winn, S. Chi, A. T. Savici, J. A. Rodriguez-Rivera, W. C. Chen, X. Xu, Y. Li, J. W. Kim, S.-W. Cheong, and V. Kiryukhin, “Spin-liquid-like state in pure and Mn-doped TbInO_3 with a nearly triangular lattice”, en, [Physical Review B](#) **100**, 024405 (2019).
- ⁶⁷N. Yuan, “High-Pressure Single Crystal Growth and Magnetization Studies on Correlated Electron Systems”, Dissertation (Universität Heidelberg, 2024).

- ⁶⁸L. Clark, G. Sala, D. D. Maharaj, M. B. Stone, K. S. Knight, M. T. F. Telling, X. Wang, X. Xu, J. Kim, Y. Li, S.-W. Cheong, and B. D. Gaulin, “Two-dimensional spin liquid behaviour in the triangular-honeycomb antiferromagnet TbInO₃”, en, [Nature Physics](#) **15**, 262–268 (2019).
- ⁶⁹J. Kim, X. Wang, F.-T. Huang, Y. Wang, X. Fang, X. Luo, Y. Li, M. Wu, S. Mori, D. Kwok, E. D. Mun, V. S. Zapf, and S.-W. Cheong, “Spin Liquid State and Topological Structural Defects in Hexagonal TbInO₃”, en, [Physical Review X](#) **9**, 031005 (2019).
- ⁷⁰P. Chen, B. S. Holinsworth, K. R. O’Neal, T. V. Brinzari, D. Mazumdar, C. V. Topping, X. Luo, S.-W. Cheong, J. Singleton, S. McGill, and J. L. Musfeldt, “Magnetochromic effect in multiferroic R In_{1-x}Mn_xO₃ (R = Tb, Dy)”, en, [Physical Review B](#) **91**, 205130 (2015).
- ⁷¹J. Nordlander, M. A. Anderson, T. Chiang, A. Kaczmarek, N. Pokhrel, K. Talit, S. Doyle, E. Mercer, C. Tzschaschel, J.-H. Son, H. El-Sherif, C. M. Brooks, E.-A. Kim, A. De La Torre, I. El Baggari, E. A. Nowadnick, K. C. Nowack, J. T. Heron, and J. A. Mundy, “Signatures of quantum spin liquid state and unconventional transport in thin film TbInO₃”, en, [Nature Communications](#) **16**, 9469 (2025).
- ⁷²K. Momma and F. Izumi, “VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data”, [Journal of Applied Crystallography](#) **44**, 1272–1276 (2011).
- ⁷³L. Gries, *Personal communication*, Nov. 2025.
- ⁷⁴E. Reynolds, P. E. R. Blanchard, B. J. Kennedy, C. D. Ling, S. Liu, M. Avdeev, Z. Zhang, G. J. Cuello, A. Tadich, and L.-Y. Jang, “Anion Disorder in Lanthanoid Zirconates Gd_{2-x}Tb_xZr₂O₇”, en, [Inorganic Chemistry](#) **52**, 8409–8415 (2013).
- ⁷⁵A. F. Fuentes, S. M. Montemayor, M. Maczka, M. Lang, R. C. Ewing, and U. Amador, “A Critical Review of Existing Criteria for the Prediction of Pyrochlore Formation and Stability”, en, [Inorganic Chemistry](#) **57**, 12093–12105 (2018).
- ⁷⁶J. Ramon, P. Silva, J. Gardner, and R. Freitas, “Glassy correlated state induced by disorder in the frustrated antiferromagnet Tb₂Zr₂O₇”, en, [Journal of Magnetism and Magnetic Materials](#) **565**, 170215 (2023).
- ⁷⁷B. Mandal, A. Banerji, V. Sathe, S. Deb, and A. Tyagi, “Order–disorder transition in Nd₂yGdyZr₂O₇ pyrochlore solid solution: An X-ray diffraction and Raman spectroscopic study”, en, [Journal of Solid State Chemistry](#) **180**, 2643–2648 (2007).
- ⁷⁸J. Xu, “Magnetic Properties of Rare Earth Zirconates”, Doctoral Thesis (Technische Universität Berlin, Berlin, 2017).

- ⁷⁹E. C. O’Quinn, K. E. Sickafus, R. C. Ewing, G. Baldinozzi, J. C. Neuefeind, M. G. Tucker, A. F. Fuentes, D. Drey, and M. K. Lang, “Predicting short-range order and correlated phenomena in disordered crystalline materials”, en, *Science Advances* **6**, eabc2758 (2020).
- ⁸⁰P. E. Blanchard, R. Clements, B. J. Kennedy, C. D. Ling, E. Reynolds, M. Avdeev, A. P. Stampfl, Z. Zhang, and L.-Y. Jang, “Does Local Disorder Occur in the Pyrochlore Zirconates?”, en, *Inorganic Chemistry* **51**, 13237–13244 (2012).
- ⁸¹B. Wuensch, “Connection between oxygen-ion conductivity of pyrochlore fuel-cell materials and structural change with composition and temperature”, *Solid State Ionics* **129**, 111–133 (2000).
- ⁸²K. J. Moreno, M. A. Guevara-Liceaga, A. F. Fuentes, J. García-Barriocanal, C. León, and J. Santamaría, “Room-temperature synthesis and conductivity of the pyrochlore type $\text{Dy}_2(\text{Ti}_1\text{yZr}_2)\text{O}_7$ (0y1) solid solution”, en, *Journal of Solid State Chemistry* **179**, 928–934 (2006).
- ⁸³Y. Li, P. M. Kowalski, G. Beridze, A. R. Birnie, S. Finkeldei, and D. Bosbach, “Defect formation energies in $\text{A}_2\text{B}_2\text{O}_7$ pyrochlores”, en, *Scripta Materialia* **107**, 18–21 (2015).
- ⁸⁴A. Elghandour, Sheetal, C. S. Yadav, and R. Klingeler, “Slow spin relaxation and low-temperature spin freezing in the disordered fluorite $\text{Ho}_2\text{Zr}_2\text{O}_7$ ”, en, *Physical Review B* **110**, 064408 (2024).
- ⁸⁵P. Rani, S. Singh, and U. Singh, “Structural and Magnetic Properties of some Rare-Earth Zirconate”, *Indian Journal of Scientific Research* **5**, 101–107 (2014).
- ⁸⁶A. M. Durand, P. Klavins, and L. R. Corruccini, “Heat capacity of the frustrated magnetic pyrochlores $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ ”, *Journal of Physics: Condensed Matter* **20**, 235208 (2008).
- ⁸⁷Sheetal, A. Elghandour, R. Klingeler, and C. S. Yadav, “Field induced spin freezing and low temperature heat capacity of disordered pyrochlore oxide $\text{Ho}_2\text{Zr}_2\text{O}_7$ ”, *Journal of Physics: Condensed Matter* **34**, 245801 (2022).
- ⁸⁸K. E. Sickafus, L. Minervini, R. W. Grimes, J. A. Valdez, M. Ishimaru, F. Li, K. J. McClellan, and T. Hartmann, “Radiation Tolerance of Complex Oxides”, en, *Science* **289**, 748–751 (2000).
- ⁸⁹V. K. Anand, L. Opherden, J. Xu, D. T. Adroja, A. D. Hillier, P. K. Biswas, T. Herrmannsdörfer, M. Uhlarz, J. Hornung, J. Wosnitza, E. Canévet, and B. Lake, “Evidence for a dynamical ground state in the frustrated pyrohafnate $\text{Tb}_2\text{Hf}_2\text{O}_7$ ”, en, *Physical Review B* **97**, 094402 (2018).

- ⁹⁰H. R. Molavian, M. J. P. Gingras, and B. Canals, “Dynamically Induced Frustration as a Route to a Quantum Spin Ice State in $\text{Tb}_2\text{Ti}_2\text{O}_7$ via Virtual Crystal Field Excitations and Quantum Many-Body Effects”, en, [Physical Review Letters](#) **98**, 157204 (2007).
- ⁹¹J. S. Gardner and A. Hoser, “Neutron Scattering and a.c. Susceptibility Studies on the Geometrically Frustrated $\text{Tb}_2\text{Ti}_2\text{O}_7$ ”, [Hyperfine Interactions](#) **133**, 269–272 (2001).
- ⁹²A. Kumar, P. Kulriya, S. Sharma, V. Grover, A. Tyagi, and V. Shukla, “Structural and compositional effects on the electronic excitation induced phase transformations in $\text{Gd}_2\text{Ti}_{2-y}\text{Zr}_y\text{O}_7$ pyrochlore”, en, [Journal of Nuclear Materials](#) **539**, 152278 (2020).
- ⁹³D. L. Drey, E. C. O’Quinn, T. Subramani, K. Lilova, G. Baldinozzi, I. M. Gussev, A. F. Fuentes, J. C. Neuefeind, M. Everett, D. Sprouster, A. Navrotsky, R. C. Ewing, and M. Lang, “Disorder in $\text{Ho}_2\text{Ti}_{2x}\text{Zr}_x\text{O}_7$: pyrochlore to defect fluorite solid solution series”, en, [RSC Advances](#) **10**, 34632–34650 (2020).
- ⁹⁴S. K. Sahu, R. Shukla, V. Grover, R. Dawar, P. Patro, T. Vazhappilly, R. Urkude, and B. Ghosh, “Tuning thermophysical properties of zirconate pyrochlore systems: B-site driven non-stoichiometric approach”, en, [Journal of the European Ceramic Society](#) **45**, 117190 (2025).
- ⁹⁵A. V. Kuznetsov, O. A. Churkin, V. V. Popov, I. V. Shchetinin, A. A. Ivanov, A. A. Yastrebtsev, B. R. Gaynanov, A. A. Yaroslavl'tsev, O. V. Chernysheva, F. d’Acapito, A. Puri, P. A. Alekseev, and A. P. Menushenkov, “Magnetization of Crystalline and Amorphous Phases of $\text{R}_2\text{Ti}_2\text{O}_7$ and $\text{R}_2\text{Zr}_2\text{O}_7$ ($\text{R} = \text{Gd}, \text{Dy}, \text{Tb}$)”, en, [Journal of Superconductivity and Novel Magnetism](#) **33**, 2395–2404 (2020).
- ⁹⁶B. G. Ueland, G. C. Lau, R. J. Cava, J. R. O’Brien, and P. Schiffer, “Slow Spin Relaxation in a Highly Polarized Cooperative Paramagnet”, en, [Physical Review Letters](#) **96**, 027216 (2006).
- ⁹⁷G. Ehlers, A. L. Cornelius, T. Fennell, M. Koza, S. T. Bramwell, and J. S. Gardner, “Evidence for two distinct spin relaxation mechanisms in hot spin ice $\text{Ho}_2\text{Ti}_2\text{O}_7$ ”, [Journal of Physics: Condensed Matter](#) **16**, S635–S642 (2004).
- ⁹⁸J. G. Acosta Ramón, “Magnetismo geométricamente frustrado no pirocloro $\text{Er}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ e nas fluoritas desordenadas $\text{R}_2\text{Zr}_2\text{O}_7$ ($\text{R}=\text{Dy}, \text{Ho}, \text{Tb}$)”, Doctoral Thesis (Universidade de Sao Paulo, Sao Paulo, 2020).
- ⁹⁹S. F. Meier and T. Schleid, “Oxotellurate(IV) der Lanthanide: I. Die isotype Reihe $\text{M}_2\text{Te}_4\text{O}_{11}$ ($\text{M} = \text{La} - \text{Nd}, \text{Sm} - \text{Yb}$)”, en, [Zeitschrift für Naturforschung B](#) **59**, 881–888 (2004).

- ¹⁰⁰G. Jackeli and G. Khaliullin, “Mott Insulators in the Strong Spin-Orbit Coupling Limit: From Heisenberg to a Quantum Compass and Kitaev Models”, en, *Physical Review Letters* **102**, 017205 (2009).
- ¹⁰¹S. Trebst and C. Hickey, “Kitaev materials”, en, *Physics Reports* **950**, 1–37 (2022).
- ¹⁰²R. Huang, J. Zhou, Y. Yang, Q. Zeng, J. Li, L. Ling, W. Tong, and Z. Tian, “A Family of Quasi-Two-Dimensional Honeycomb Lattice Magnets $\text{RE}_2\text{Te}_4\text{O}_{11}$ ($\text{RE} = \text{Gd-Er}$ and Yb) with Large Interlayer Distances”, en, *Inorganic Chemistry* **64**, 19621–19631 (2025).
- ¹⁰³C. Parada, J. Alonso, and I. Rasines, “Preparation and study of the new oxides $\text{Ln}_2\text{Te}_4\text{O}_{11}$ ($\text{Ln} = \text{Ce, Pr, Tb}$)”, en, *Inorganica Chimica Acta* **111**, 197–199 (1986).
- ¹⁰⁴M. López, M. Veiga, F. Fernández, A. Jerez, and C. Pico, “Synthesis, characterization and magnetic properties of $\text{Ln}_2\text{Te}_4\text{O}_{11}$ ($\text{Ln} = \text{La, Nd, Sm, Eu, Gd, and Ho}$)”, en, *Journal of the Less Common Metals* **166**, 367–375 (1990).
- ¹⁰⁵C. Cascales, P. Porcher, and R. Sáez-Puche, “Crystal field effects on the magnetic susceptibility of rare earth tellurium oxides”, en, *Journal of Physics and Chemistry of Solids* **54**, 1471–1474 (1993).
- ¹⁰⁶I. Ijjaali, C. Flaschenriem, and J. A. Ibers, “Synthesis and characterization of the wide band-gap compound $\text{Pr}_2\text{Te}_4\text{O}_{11}$ ”, en, *Journal of Alloys and Compounds* **354**, 115–119 (2003).
- ¹⁰⁷Y.-L. Shen and J.-G. Mao, “Synthesis, crystal structure and luminescent properties of $\text{Er}_2\text{Te}_4\text{O}_{11}$ ”, en, *Journal of Alloys and Compounds* **385**, 86–89 (2004).
- ¹⁰⁸https://web.njit.edu/~tyson/PPMS_Documents/PPMS_Manual/1096-100%20Rev.%20A3%20VSM.pdf *Physical Property Measurement System: Vibrating Sample Magnetometer (VSM) Option User’s Manual*, Jan. 2008.
- ¹⁰⁹E. M. Wilson and J. T. Haraldsen, “Effects of frustration on the spin dynamics of the zigzag honeycomb lattice”, en, *Physical Review B* **110**, 064429 (2024).
- ¹¹⁰M. E. Fisher, “Relation between the specific heat and susceptibility of an antiferromagnet”, en, *Philosophical Magazine* **7**, 1731–1743 (1962).
- ¹¹¹P. Ramakrishnan, U. Varadaraju, J. Majhi, G. Subba Rao, A. Maignan, and B. Raveau, “Studies on Magnetic Properties of $\text{MnTi}_{1-x}\text{Nb}_x\text{O}_3$ System”, en, *Journal of Solid State Chemistry* **136**, 115–119 (1998).
- ¹¹²V. A. Drebuschak, “Lambda-peak in heat capacity II: solution to the problem”, en, *Journal of Thermal Analysis and Calorimetry* **150**, 16113–16122 (2025).

- ¹¹³A. Elghandour, L. Gries, L. Singer, M. Hoffmann, S. Spachmann, M. Uhlarz, K. Dey, and R. Klingeler, “Magnetic anisotropy, magnetoelastic coupling, and the magnetic phase diagram of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{TiO}_3$ ”, en, [Physical Review B](#) **108**, 014406 (2023).
- ¹¹⁴H. Nakotte, R. A. Robinson, A. Purwanto, Z. Tun, K. Prokeš, E. Brück, and F. R. De Boer, “Antiferromagnetism and domain effects in UPdSn”, en, [Physical Review B](#) **58**, 9269–9275 (1998).
- ¹¹⁵A. Arrott, “Criterion for Ferromagnetism from Observations of Magnetic Isotherms”, [Physical Review](#) **108**, 1394–1396 (1957).
- ¹¹⁶B. Banerjee, “On a generalised approach to first and second order magnetic transitions”, en, [Physics Letters](#) **12**, 16–17 (1964).
- ¹¹⁷I. Yeung, R. M. Roshko, and G. Williams, “Arrott-plot criterion for ferromagnetism in disordered systems”, [Physical Review B](#) **34**, 3456–3457 (1986).
- ¹¹⁸A. Galluzzi, D. Mancusi, C. Cirillo, C. Attanasio, S. Pace, and M. Polichetti, “Determination of the Transition Temperature of a Weak Ferromagnetic Thin Film by Means of an Evolution of the Method Based on the Arrott Plots”, en, [Journal of Superconductivity and Novel Magnetism](#) **31**, 1127–1132 (2018).
- ¹¹⁹S. Bustingorry, F. Pomiro, G. Aurelio, and J. Curiale, “Second-order magnetic critical points at finite magnetic fields: Revisiting Arrott plots”, [Physical Review B](#) **93**, 224429 (2016).
- ¹²⁰K. Matsuhira, Y. Hinatsu, and T. Sakakibara, “Novel dynamical magnetic properties in the spin ice compound $\text{Dy}_2\text{Ti}_2\text{O}_7$ ”, [Journal of Physics: Condensed Matter](#) **13**, L737–L746 (2001).
- ¹²¹G. Zhang, F. Guo, H. Wu, X. Wen, L. Yang, W. Jin, W. Zhang, and H. Chang, “Above-room-temperature strong intrinsic ferromagnetism in 2D van der Waals Fe_3GaTe_2 with large perpendicular magnetic anisotropy”, en, [Nature Communications](#) **13**, 5067 (2022).
- ¹²²H. Wu, C. Hu, Y. Xie, B. G. Jang, J. Huang, Y. Guo, S. Wu, C. Hu, Z. Yue, Y. Shi, R. Basak, Z. Ren, T. Yilmaz, E. Vescovo, C. Jozwiak, A. Bostwick, E. Rotenberg, A. Fedorov, J. D. Denlinger, C. Klewe, P. Shafer, D. Lu, M. Hashimoto, J. Kono, A. Frano, R. J. Birgeneau, X. Xu, J.-X. Zhu, P. Dai, J.-H. Chu, and M. Yi, “Spectral evidence for local-moment ferromagnetism in the van der Waals metals Fe_3GaTe_2 and Fe_3GeTe_2 ”, en, [Physical Review B](#) **109**, 104410 (2024).
- ¹²³M. Wang, B. Lei, K. Zhu, Y. Deng, M. Tian, Z. Xiang, T. Wu, and X. Chen, “Hard ferromagnetism in van der Waals Fe_3GaTe_2 nanoflake down to monolayer”, en, [npj 2D Materials and Applications](#) **8**, 22 (2024).

- ¹²⁴S. Jin, Y. Wang, H. Zheng, S. Dong, K. Han, Z. Wang, G. Wang, X. Jiang, X. Wang, J. Hong, H. Huang, Y. Zhang, T.-L. Xia, and X. Wang, “Thickness- and Field-Dependent Magnetic Domain Evolution in van der Waals Fe_3GaTe_2 ”, en, *Nano Letters* **24**, 5467–5473 (2024).
- ¹²⁵X. Li, M. Zhu, Y. Wang, F. Zheng, J. Dong, Y. Zhou, L. You, and J. Zhang, “Tremendous tunneling magnetoresistance effects based on van der Waals room-temperature ferromagnet Fe_3GaTe_2 with highly spin-polarized Fermi surfaces”, en, *Applied Physics Letters* **122**, 082404 (2023).
- ¹²⁶<https://www.researchsquare.com/article/rs-3674982/v1>Z. Zhang, A. Rahman, M. Rehman, D. Mai, Z. Muhammad, K. Ruan, R. Dai, Z. Wang, L. Zhang, and Z. Chen, *Emergent Magnetic Phases with Robust Two-Dimensional Spin Interactions and Electronic Transport in Above-Room Temperature Ferromagnet Fe_3GaTe_2* , Jan. 2024.
- ¹²⁷H. Algaidi, C. Zhang, C. Liu, Y. Ma, D. Zheng, P. Li, and X. Zhang, “Room-temperature unconventional topological Hall effect in a van der Waals ferromagnet Fe_3GaTe_2 ”, en, *APL Materials* **13**, 011108 (2025).
- ¹²⁸M. Abdel-Hafiez, *Personal communication*, Personal communication, June 2024.
- ¹²⁹H.-A. Krug von Nidda, “Elektronenspinresonanz an elektronisch hochkorrelierten Cer-Verbindungen”, German, PhDThesis (Technische Universität Darmstadt, Darmstadt, Nov. 1997).
- ¹³⁰B. G. Beier, E. S. Beier, J. Arneth, E. Brücher, R. K. Kremer, and R. Klingeler, “Elucidating the origin of long-range ferromagnetic order in Fe_3GeTe_2 by low-energy magnon excitation studies”, en, *Physical Review B* **112**, 214414 (2025).
- ¹³¹R. Pal, J. J. Abraham, A. Mistonov, S. Mishra, N. Stölkerich, S. Mondal, P. Mandal, A. N. Pal, J. Geck, B. Büchner, V. Kataev, and A. Alfonsov, “Disentangling the Unusual Magnetic Anisotropy of the Near-Room-Temperature Ferromagnet Fe_4GeTe_2 ”, en, *Advanced Functional Materials* **34**, 2402551 (2024).
- ¹³²M. Jonak, E. Walendy, J. Arneth, M. Abdel-Hafiez, and R. Klingeler, “Low-energy magnon excitations and emerging anisotropic nature of short-range order in CrI_3 ”, en, *Physical Review B* **106**, 214412 (2022).
- ¹³³L. Bischof, J. Arneth, R. Kalaivanan, R. Sankar, K.-Y. Choi, and R. Klingeler, “Spin waves in $\text{Na}_2\text{Co}_2\text{TeO}_6$ studied by high-frequency/high-field ESR: Successes and failures of the triple- q model”, en, *Physical Review B* **112**, 104406 (2025).

A Comparison sample holders in ac susceptometry

Exemplarily for $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$ with $B_{\text{dc}} = 0.5 \text{ T}$, $B_{\text{ac}} = 8 \text{ Oe}$, $f = 3 \text{ Hz}$, the ac susceptibility was measured using both the brass sample holder as well as in a straw. The resulting data are shown in figure A.1. As can be seen there, the real component $\chi'(T)$ (subfigure (a)) shows little differences between the two sample holders, an estimate is a reduction of magnitude by approximately 3%. The suppression of the absorptive component χ'' in subfigure (b) is more significant, exceeding 50% (assuming the values at $T = 30 \text{ K}$ to be the baseline). A reason for this is that the eddy currents in the metallic brass influence the phase shift underlying the absorptive processes in $\text{Tb}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$. The decision to continue using the brass sample holder was made in order to keep consistent datasets for all measurements as the initial measurements were already performed in brass.

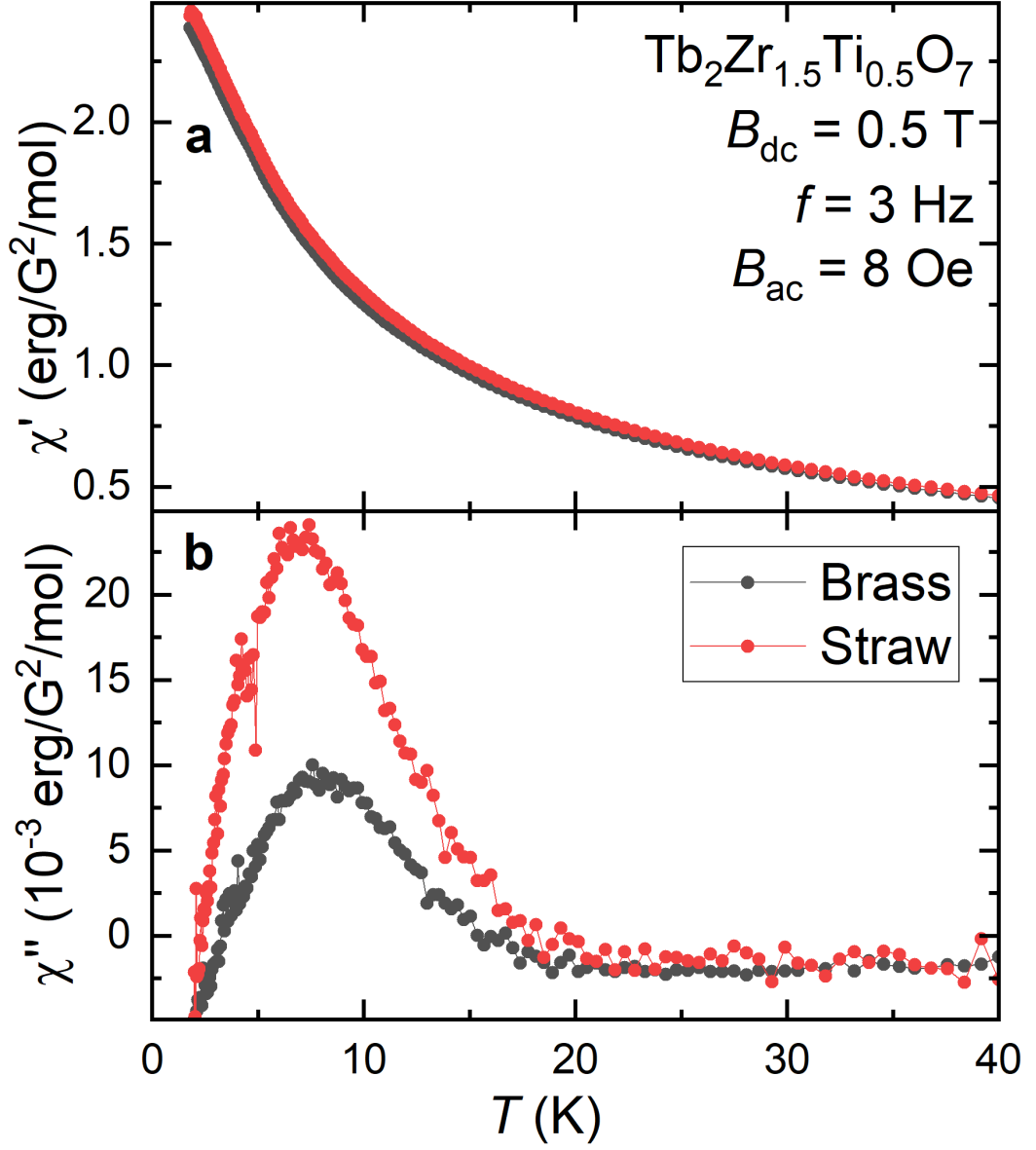


Figure A.1: Comparison of the brass sample holder with a straw. Subfigure (a) & (b) show the real and imaginary components, χ' and χ'' , of ac susceptibility measurements with varying temperature on polycrystalline $\text{Tb}_2\text{Zr}_{1.5}\text{Ti}_{0.5}\text{O}_7$. The chosen magnetic fields were $B_{\text{dc}} = 0.5 \text{ T}$, $B_{\text{ac}} = 8 \text{ Oe}$. The frequency was $f = 3 \text{ Hz}$.

B HF-ESR on Fe_3GaTe_2 in the ab plane

ESR-measurements of Fe_3GaTe_2 for B parallel to the ab plane did not yield usable results. An exemplary spectrum of the performed measurements is shown in figure B.1. Clear discontinuities in the signal can be seen at multiple fields. The magnetic field, at which they occur is not reproducible, as can be seen by comparing the up- and down sweep. Such jumps can be understood as physical jerks of the sample induced by an insufficiently strong fixation compared to the magnetically induced torque. A probable reason for lies in the sample fixing procedure: The thin Fe_3GaTe_2 platelet had to be stabilized in such a way that the magnetic field is parallel to the plane. This was achieved by manually fitting Teflon blocks to fill the ESR sample rings and only leave enough room to hold the sample stable in place, c.f figure 3.4a. It appears that the hand made Teflon clamps do not offer a sufficiently strong grip on the sample to fix it.

An alternative approach to the Teflon blocks was freezing the sample in an upright position using molten icosane. This is shown in figure 3.4b. Unfortunately, the amount of icosane required to keep the crystal in the desired position was also sufficient to absorb all of the microwaves and thus no signal was recorded. Only a singular frequency of $f \approx 18 \times 10.8$ GHz showed any transmission, which is insufficient for any further investigation.

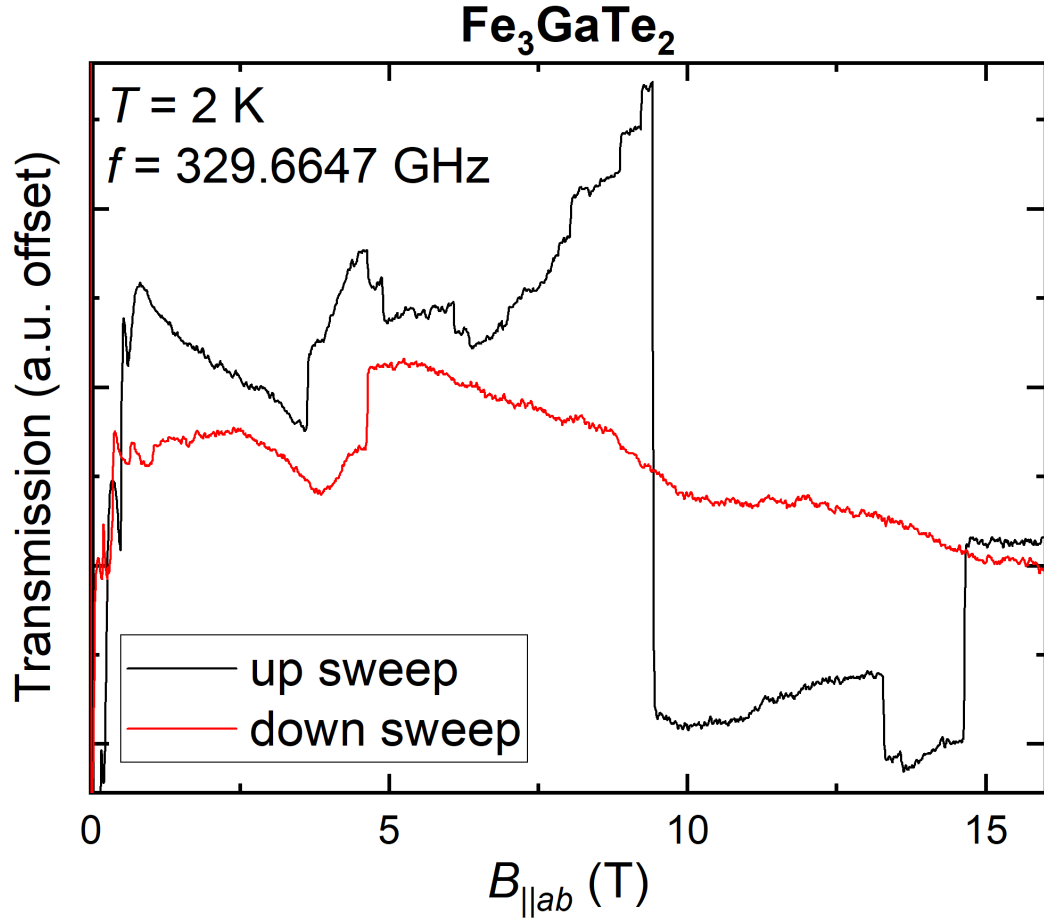


Figure B.1: HF-ESR spectrum of Fe_3GaTe_2 for $B \perp c$ at 329.6647 GHz in 2 K. Both sweeps (up and down) are shown, they are shifted along the transmission axis for better visibility.

C Magnetization of Fe_3GaTe_2

Isothermal and temperature dependent SQUID magnetization data for Fe_3GaTe_2 are shown in figure C.2 & figure C.1. While evaluating the underlying raw data, it turned out that fitting a dipole function to the raw SQUID signal, as explained in section 3.1.1, section 3.1.1 and a proper background subtraction could not be performed in a reproducible and satisfactory manner. In particular the signal shape of the sample used did not agree well with a dipole shape expected for fitting. Thus the inferred magnetization data can at most be taken as a qualitative result. The fact that the susceptibility in figure C.1 increases massively above 200 K is not in agreement with reported measurements [121] [124]. In figure C.2 two fields with a right bending in $M(B)$ are seen at approximately 0.5 T and at 6 T, which does not agree with pervious works [121], where the magnetization is saturated at field less than 1 T in comparable temperatures. Hence it must be expected that the magnetization measurements suffered from sub-par raw data.

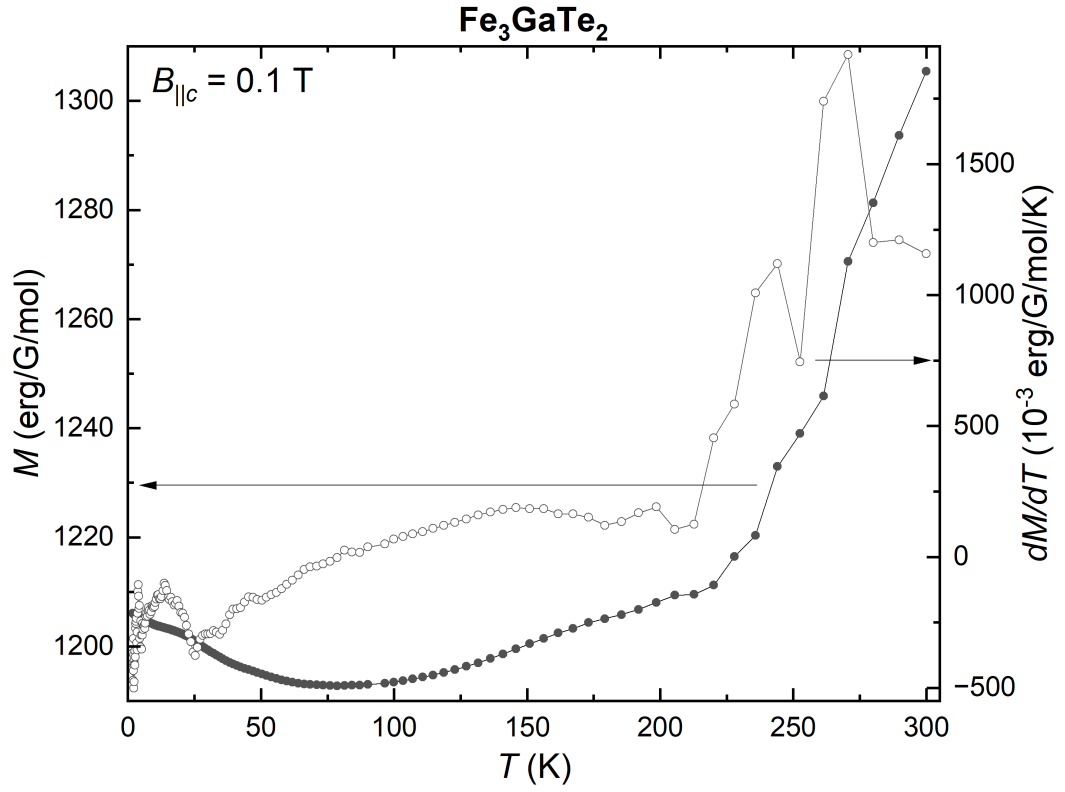


Figure C.1: Temperature dependent magnetization $M(T)$ along the c axis and its temperature derivative $\frac{dM}{dT}$.

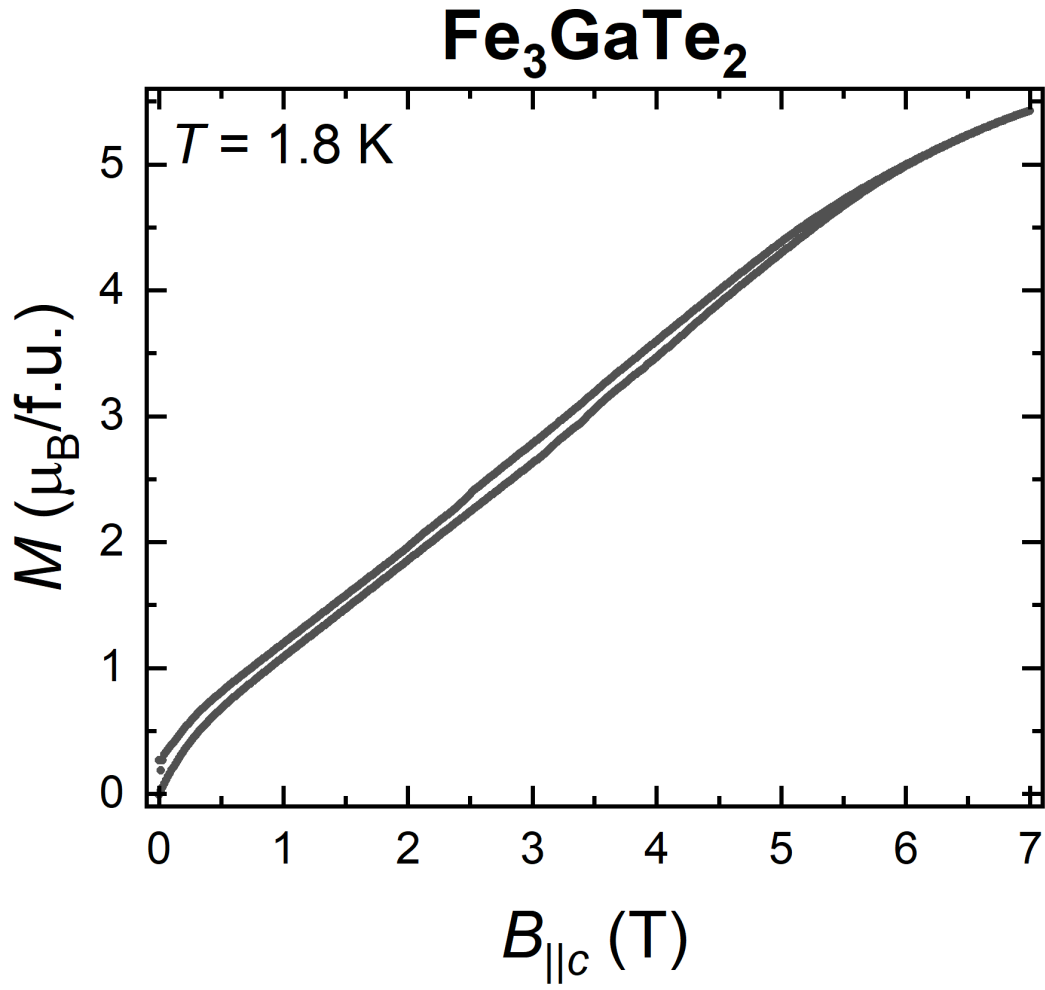


Figure C.2: Isothermal magnetization $M(B)$ of Fe_3GaTe_2 along the c axis as a function of the applied magnetic field B at $T = 1.8$ K.

Eigenständigkeitserklärung

Ich versichere, dass ich diese Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Heidelberg, 1. März 2026

Frederik Leon Carstens

