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Electron Spin Resonance Studies on Frustrated Low Dimensional $\text{PbCuSeO}_4(\text{OH})_2$ and GdInO_3

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Electron Spin Resonance Studies on Frustrated Low Dimensional $\text{PbCuSeO}_4(\text{OH})_2$ and GdInO_3

Electron spin resonance (ESR) studies on the frustrated and potentially low-dimensional magnets $\text{PbCuSeO}_4(\text{OH})_2$ and GdInO_3 are presented. For the 1D quantum spin chain system $\text{PbCuSeO}_4(\text{OH})_2$, which is isostructural to the well-studied multiferroic linarite, high field ESR (HF-ESR) studies on polycrystalline powder reveal that local magnetic fields already develop at about $15 \cdot T_N$, evidencing strong spin fluctuations. Furthermore, analysis of the spectroscopic data confirms the low dimensionality of the system and reveals a magnetic *easy*-axis anisotropy in the system. Four resonance branches occur in the ordered state, two of which exhibit zero field gaps of $\Delta_1 = 82.4(14)$ GHz and $\Delta_2 = 32.9(14)$ GHz. X-band ESR studies at varying angles of the external magnetic field with respect to the crystallographic *c*-axis of the filled honeycomb system GdInO_3 indicate that the resonance linewidth is dominated by crystal field anisotropy at high temperatures while dipole-dipole interactions seem to be the main contribution at low temperatures. Furthermore, the data allows to conclude that planar anisotropy develops with decreasing temperature. Additionally, the measurements reveal that short range correlations already set in at temperatures as high as $\sim 70 \cdot T_N$. In the magnetically ordered state HF-ESR measurements uncover at least three linear resonance branches with zero field excitation gaps in the order of 10 GHz.

Elektronenspinresonanz-Spektroskopie an frustriertem niederdimensionalem $\text{PbCuSeO}_4(\text{OH})_2$ und GdInO_3

In der vorliegenden Arbeit werden die frustrierten und potentiell niederdimensionalen Materialien $\text{PbCuSeO}_4(\text{OH})_2$ und GdInO_3 mittels Elektronenspinresonanz-Spektroskopie (ESR) untersucht. Hochfeld ESR (HF-ESR) Messungen an polykristallinem Pulver des 1D Quantumspinsystems $\text{PbCuSeO}_4(\text{OH})_2$, welches die gleiche Kristallstruktur wie das in der Literatur ausführlich untersuchte Linarit hat, zeigen, dass lokale magnetische Felder bereits bei ca. $15 \cdot T_N$ auftreten. Des Weiteren bestätigt die Analyse der spektroskopischen Daten die Niederdimensionalität des Systems und belegt axiale magnetische Anisotropie. Im geordneten Zustand werden vier Resonanzzweige beobachtet, von denen zwei eine Anregungslücke im Nullfeld von $\Delta_1 = 82.4(14)$ GHz und $\Delta_2 = 32.9(14)$ GHz zeigen. X-Band ESR Messungen bei variierendem Winkel zwischen dem externen magnetischen Feld und der kristallographischen c -Achse am gefüllten Honigwabengitter-Material GdInO_3 lassen erkennen, dass die Resonanzlinienbreite bei hohen Temperaturen von Kristallfeldanisotropie dominiert wird, während Dipol-Dipol Wechselwirkungen vermutlich den Hauptbeitrag bei tiefen Temperaturen bilden. Des Weiteren lässt sich aus den Daten schließen, dass sich mit abnehmenden Temperaturen eine planare Anisotropie entwickelt. Außerdem zeigen die Messungen, dass kurzreichweitige Korrelationen bereits bei $\sim 70 \cdot T_N$ einsetzen. Im magnetisch geordneten Zustand zeigen HF-ESR Messungen mindesten drei lineare Anregungszweige mit Anregungslücken im Nullfeld in der Größenordnung von 10 GHz.

Contents

1	Introduction	9
2	Theoretical Background	11
2.1	Electron Spin Resonance	11
2.2	Linewidth	14
2.3	Collective Magnetic Excitations	16
3	Experimental Methods	17
3.1	X-Band Electron-Spin-Resonance (X-band ESR)	17
3.1.1	Sample Preparation and Data Correction	17
3.2	High-Frequency/High-Field Electron Spin Resonance (HF-ESR)	18
3.2.1	Sample Preparation and Data Correction	19
4	Experimental Results	23
4.1	PbCuSeO ₄ (OH) ₂	23
4.1.1	Introduction	23
4.1.2	Results and Discussion	28
4.1.3	Conclusions	58
4.2	GdInO ₃	60
4.2.1	Introduction	60
4.2.2	Results and Discussion	63
4.2.3	Conclusions	98
5	Conclusions	101
6	Appendix	103
6.1	Comparison of Fit Routines on PbCuSeO ₄ (OH) ₂ Data	103
6.2	ESR-Data of GdInO ₃ at Different Temperatures	108
6.3	Original Data to the 3D Plots	116

1 Introduction

Physicists strive to understand physical systems and to predict their behavior by employing idealized models. As an experimentalist, seeking to investigate systems, which correspond to the theoretical framework as much as possible, does not only allow to describe the system in a conclusive manner but can also uncover the model's weaknesses and thus spark further understanding of the underlying concepts. A typical framework for understanding the interactions of electronic spins on an extended lattice is the idea of dimensionality. A system is called magnetically low-dimensional if the spin-spin interaction along at least one spatial direction is significantly weaker than along the other directions. In low-dimensional spin systems the enhanced quantum fluctuations tend to suppress magnetic long-range order, as can be seen from the expected absence of magnetic long-range order in 1D Ising [1], XY [2] and Heisenberg [3] models as well as 2D XY and Heisenberg systems at finite temperatures [2, 3, 4]. However, anisotropy may stabilize magnetic long-range order as in the 2D Ising model a magnetically ordered state will occur at finite temperatures [5]. Although there is no conventional magnetic long-range order expected for 2D XY spin-systems, Kosterlitz and Thouless predicted that a topological order, in which pairs of vortex and antivortex arrangements of spins may be found, emerges at sufficiently low temperatures [6]. Several other exotic spin states are assumed to exist for low dimensional systems, such as Bose-Einstein condensates [2], spin-liquids [7] or spin density waves [8, 9].

Another route towards rich phase diagrams and exotic phases is magnetic frustration [8]. The term frustration describes the phenomenon that for certain spatial spin arrangements the spin-spin interactions compete with each other, such that the ideal spin-arrangement for each interaction path can not be satisfied simultaneously. This leads to many degenerate energy levels possibly including the ground state. A simple example are antiferromagnetically coupled Ising spins on a triangular lattice, where each spin should be aligned antiparallel to its neighbour, which is not possible on a triangle. The existence of many degenerate energy levels due to frustration also tends to suppress magnetic long-range order, yet if long-range order eventually develops it is found to be highly susceptible to external tuning parameters such as pressure or magnetic field, often yielding complex phase diagrams [8, 10].

Similarly to magnetically ordered phases, where classically speaking the symmetry of

the magnetic dipoles is broken, electric order occurs when there is spontaneous symmetry breaking of electric dipoles. Materials exhibiting both magnetic and electric order are called multiferroics. One generally differentiates between type-I multiferroics, where the ferroelectricity sets in at higher temperatures than the magnetic order and type-II (improper) multiferroics where ferroelectricity is induced by the magnetic order [11, 12]. Multiferroics are not only interesting from a physical standpoint, as they elucidate on the interplay between magnetic and electronic degrees of freedom, but they also possess great potential for applications such as in non-volatile and easily writable memory devices [11, 13, 14, 15]

Although each of the aforementioned properties is fascinating on its own, there are materials, which combine all three, for example, as they may be intertwined. Such as the ones investigated in this thesis by means of electron spin resonance. $\text{PbCuSeO}_4(\text{OH})_2$ is isostructural to the well studied type-II multiferroic linarite [16] and is predicted to be a quasi-one-dimensional, frustrated quantum spin chain. The frustration parameter $\alpha = J_2/|J_1|$ (J_1 is the ferromagnetic nearest neighbour interaction and J_2 the antiferromagnetic next nearest neighbour interaction) lies above the critical value, such that it is reasonable to expect spiral order in this compound. Indeed, long range antiferromagnetic (afm) order sets in at $T_N = 4.8$ K and several antiferromagnetically ordered high field phases were found for $\text{PbCuSeO}_4(\text{OH})_2$ [17, 18]. GdInO_3 has the magnetically active Gd^{3+} ions arranged on a filled honeycomb lattice and is known to show geometric ferroelectricity. Due to the layered arrangement of the gadolinium ions, it is expected to behave like a quasi-2D system. Afm long range order sets in at $T_N = 2.1$ K and several in-field afm phases were found for GdInO_3 as well [19].

To elucidate on the interplay of frustration and anisotropy or the extent of the low dimensional character of the aforementioned compounds, electron spin resonance (ESR) is a very powerful tool to investigate the microscopic parameters. In the ordered regime, magnons are excited and their magnetic field dependence can be mapped out, which ideally provides information on the spin order and the anisotropy. Measurements at varying temperatures provide information on the development of short range order being linked to frustration and low dimensionality. The dependence of the data on the angle between the applied magnetic field and a unique axis of the investigated crystal allows to draw conclusions on the dominating spin interactions.

This thesis contains five main parts: Chapter 2 provides a very brief introduction to the theoretical concept of ESR, whereas chapter 3 describes the experimental setup and process. Chapter 4 discusses the experimental results of $\text{PbCuSeO}_4(\text{OH})_2$ and GdInO_3 . The last main chapter 5 gives a general conclusion, which is followed by an appendix, showing additional data.

2 Theoretical Background

2.1 Electron Spin Resonance

Electron Spin Resonance (ESR) is a form of spectroscopy where the oscillating magnetic field of microwaves is used to cause magnetic dipole transitions between electronic energy levels of a paramagnetic system or excitations of collective modes in a spin ordered state. Note, that the term electron paramagnetic resonance (EPR) is often used synonymously. Throughout this thesis the abbreviation ESR will be used to emphasise that collective spin excitations in the long range ordered state are probed. The term paramagnetic resonance is used to describe the quasi-independent electron spin excitations in the high temperature limit. The energy levels between which dipole transitions can occur are given by the Hamiltonian of the system. For paramagnetic centers interacting with other paramagnetic and non-magnetic centers in their environment the effective spin Hamiltonian neglecting nuclear Zeeman interaction, nuclear quadrupole interactions as well as hyperfine interaction, can be formulated as [20]:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_A + \mathcal{H}_E. \quad (2.1)$$

The three terms denote the electron Zeeman interaction, anisotropy including single-ion anisotropy and crystal field effects, and spin-spin interaction.

The electron Zeeman interaction describes the interaction of the electron spin with a static magnetic field. This interaction lifts the degeneracy of the electron spin energy levels with quantum number m_s . The splitting of the energy levels is proportional to the magnetic field. The corresponding spin Hamiltonian for a single electron is given as:

$$\mathcal{H}_Z^{\text{electron}} = \mu_B g_e \mathbf{H} \mathbf{S}, \quad (2.2)$$

where $\mu_B = \frac{e}{2m_e} \hbar$ (e : electron charge, m_e : electron mass, and $\hbar$: reduced Planck constant) is the Bohr magneton, g_e the electronic g -factor, $\mathbf{H}$ the applied magnetic field and $\mathbf{S}$ the spin-operator. The dipolar selection rules allow transitions with $\Delta m_s = \pm 1$ and $\Delta S = 0$, which gives the simple resonance condition [20, p. 114]

$$h\nu = \mu_B g_e H, \quad (2.3)$$

where the direction of $\mathbf{H}$ determines the z -direction of the spin-system, while h is the Planck constant and ν the applied microwave frequency.

When considering electrons in an ion, spin-orbit coupling needs to be taken into account if the orbital moment is non-zero. The combined spin-orbit coupling and Zeeman interaction Hamiltonian then reads [20, p. 105]:

$$\mathcal{H}_{\text{so}} = \lambda \mathbf{L} \mathbf{S} + \mu_B (\mathbf{L} + g_e \mathbf{S}) \mathbf{H}, \quad (2.4)$$

with λ being the spin-orbit coupling constant and $\mathbf{L}$ the orbital moment operator. If spin-orbit coupling is considered to be small a spin-only Hamiltonian can be recovered by perturbation theory yielding the combined Zeeman- and single-ion anisotropy term:

$$\mathcal{H}_Z + \mathcal{H}_A = \mu_B \mathbf{S} \mathbf{g} \mathbf{S} + \mathbf{S} \mathbf{D} \mathbf{S} \quad (2.5)$$

where the orbital contribution is absorbed by the tensors $\mathbf{g}$ and $\mathbf{D}$. Although the anisotropy tensor $\mathbf{D}$ was derived from spin-orbit coupling, it may in general describe the magnetic anisotropy in the system, which could also be due to crystal field effects.

The term crystal field effect refers to the phenomenon, that the electric field produced by the charged ions of the surrounding ligands, lifts the degeneracy of the orbital energy states of an electron in an environment of charged particles (often a lattice environment is considered). As the electric field is produced by ions on lattice sites it must have the same point symmetry as the considered ion site and its ligands. Thus, it is often possible to determine the correct electronic ground state of the electrons in the system simply by symmetry arguments. In $3d$ ions the crystal field effect is often more dominant than the spin-orbit coupling. This renders Hund's rules for determining the ground state S , L , and J values invalid. Indeed experiments show, that the crystal field effect in such systems yields ground states where $L=0$ [8]. This phenomenon is called orbital quenching [8].

So far those terms of the effective spin Hamiltonian have been discussed which do not involve spin-spin interactions. The interaction between two spins can be described as [21, p. 21 f]:

$$\mathcal{H}_E = \mathbf{S}_i \mathbf{J}_{ij} \mathbf{S}_j \quad (2.6)$$

where $\mathbf{J}_{ij}$ is a tensor containing all interaction parameters. $\mathbf{J}_{ij}$ can be decomposed into a scalar, a polar vector and a symmetric traceless tensor, such that $\mathcal{H}_E$ can be written as:

$$\mathcal{H}_E = J_{ij} \mathbf{S}_i \mathbf{S}_j + \mathbf{d}_{ij} \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \mathbf{D}_{ij} \mathbf{S}_j. \quad (2.7)$$

The first term describes isotropic, the second antisymmetric or Dzyaloshinskii-Moriya (DM) and the third anisotropic spin-spin interactions. In this notation, if J_{ij} is nega-

tive, the spins tend to align ferromagnetically, while they tend towards antiferromagnetic order when J_{ij} is positive. Due to symmetry reasons, the antisymmetric tensor $\mathbf{d}_{ij}$ must be zero if there is an inversion center between interacting spins. Depending on the mechanism responsible for the interaction, i.e. whether it is dipole-dipole or exchange interaction, the aforementioned tensors will contain different expressions. For example, the dipole-dipole interaction can be described by the Hamiltonian [21, p. 137]:

$$\mathcal{H}_{\text{dip}} = g^2 \mu_B^2 (\mathbf{S}_i \mathbf{S}_j / r_{ij}^3 - 3(\mathbf{S}_i \mathbf{r}_{ij})(\mathbf{S}_j \mathbf{r}_{ji}) / r_{ij}^5) \quad (2.8)$$

with $\mathbf{r}_{ij}$ being the vector between interacting paramagnetic centers and r_{ij} the distance between them, such that the dipolar anisotropy D_{dip} can be estimated as $D_{\text{dip}} = E_{\text{dip}} / S^2 = \mu_B^2 \mu_{\text{eff}}^2 \mu_0 / 4\pi r^3 S^2$. In the case of exchange interaction the antisymmetric and anisotropic components of the interaction arise due to the admixture of excited states to the ground state caused by spin-orbit coupling [21]. The symmetric anisotropy parameter is often estimated as $D \sim (\Delta g / g)^2 J$ [21], where Δg is the difference between the average g -factor and two and g is the average g -factor. J is the dominant exchange interaction in the system, which can be determined by experiments. However, J may by no means be the same as the exchange interaction between the ground state of one ion interacting with the excited state of another ion, which is at the origin of the anisotropic exchange interaction but is not readily accessible by experiments. Thus, the above estimate can be completely wrong in some cases. The magnitude of the polar vector determining the antisymmetric exchange is usually estimated as $d \sim \Delta g / g J$. Due to the linear dependence on $\Delta g / g$, if DM interaction exists, it can cause quite large anisotropies in comparison to the symmetric anisotropy.

The discussed interactions complicate the simple resonance condition for a free electron given above (eq. 2.3). The g -factor becomes a tensor so that the resonance energy will vary for different directions of applied magnetic field. At the same time the anisotropy tensor $\mathbf{D}$ lifts the degeneracy of the m_s spin states, which adds a constant to the resonance condition. Since this splitting occurs independent of the applied magnetic field, it is called zero field splitting. Fig. 2.1 shows a schematic diagram of the energy levels and the corresponding resonance field positions and frequency-field diagram for a $S=1$ system with and without anisotropy.

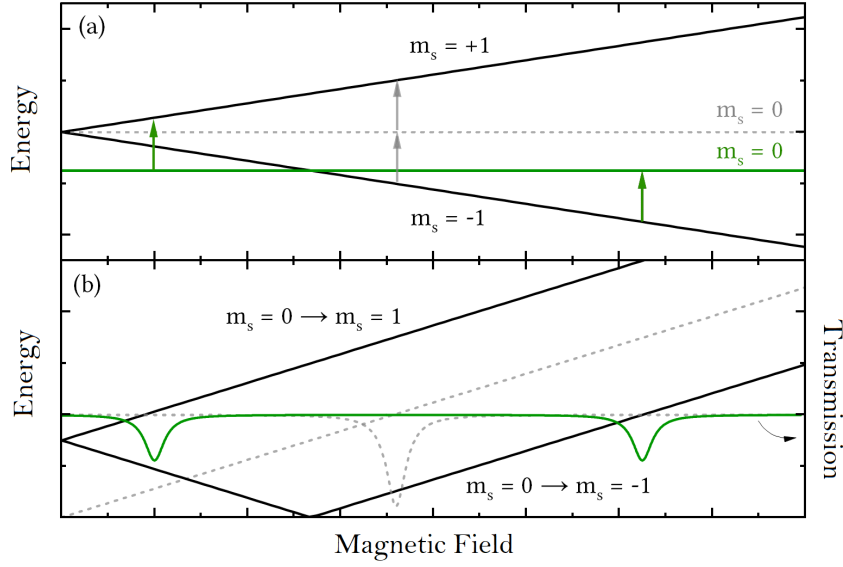


Figure 2.1: (a) Energy levels of an effective spin $S=1$ system with an applied magnetic field $H||z$. In grey for $\mathbf{D} = 0$ and green for $\mathbf{D} = \text{diag}(0, 0, D_z)$. Possible dipole transitions are indicated with arrows. (b) Resonance-frequency-field-diagram for the transitions in (a) and one corresponding transmission spectrum. From [22].

2.2 Linewidth

So far the lifetime of an electron in an excited spin state and thus the finite width of the absorption signal has not been considered. In resonance spectroscopy experiments one often distinguishes between homogeneous and inhomogeneous line broadening. If the broadening is due to relaxation processes, e. g., due to spin-spin or spin-lattice interactions, it is called homogeneous. If it is caused by different Larmor frequencies of the spins distributed in the sample it is called inhomogeneous. The difference in Larmor frequency can be caused by several effects, such as inhomogeneities in the applied magnetic field, different gyromagnetic factors [23, p. 110 f] or inhomogeneous local magnetic fields, caused e.g. by neighbouring paramagnetic ions [23, p. 110 f]. Not only the linewidth but also the lineshape of the resonance absorption feature is influenced by the spin interactions in a paramagnetic system. So far the effective spin Hamiltonian has been discussed for electrons in a single ion in an environment of charged and/or paramagnetic ions on fixed sites, taking only into account the interaction to one other ion. In an extended lattice the Hamiltonian consists of a sum over all single ion terms and all interaction terms. The sum of the interaction terms is often truncated such that only nearest neighbours are considered. Exact diagonalization of such a Hamiltonian is cumbersome and instead the method of "moments" is used to gain information about the width and shape of the absorption

curve [23]. The n th moment of an absorption line is defined as [23, p. 515]:

$$\langle \Delta\nu^n \rangle = \frac{\int (\nu - \nu_0)^n f(\nu) d\nu}{\int f(\nu) d\nu} \quad (2.9)$$

with $f(\nu)$ the normalized shape factor, which describes the distribution of energy levels between which the transition is taking place, and ν_0 the resonance frequency if there were not any interactions. Usually the lineshape is estimated by just the second moment, as the calculation of moments is still difficult and higher moments mainly contribute to the wings of the absorption line [23], which in experiments are often effected by noise. In the absence of exchange interaction the shape function is assumed to be gaussian, as an exact form of the shape function is not readily available [23]. In fact, this holds true for any slow interaction but is often attributed to the dipolar interaction. The isotropic exchange does not contribute to the second moment, hence one might think that it does not contribute to the lineshape. However, it contributes to the fourth moment, which causes the absorption line to be narrowed in the center and extended in the wings, which is known as exchange narrowing. This is the reason why the lineshape of the resonance changes to lorentzian for sufficiently strong exchange interaction. This effect can be understood in a simple picture if one assumes spin fluctuations due to exchange interaction to be at a rate of about $\nu \approx J/h$. These fast spin flops average out the local fields produced by neighbouring ions thereby reducing the line broadening [20, 21, 23]. Other mechanisms causing line broadening are the anisotropic and antisymmetric exchange interaction as well as single ion anisotropy and crystal field effects.

In most X-band ESR setups (setups using microwave frequencies of about 10 GHz) the externally applied magnetic field is modulated to improve the signal to noise ratio [24]. Thus, instead of the absorption the derivative of the absorption is measured. Additionally, most setups use linearly polarized light, which can be understood as the superposition of two circularly polarized components, rotating in opposite direction, where only the one rotating in the same sense as the Larmor precession of the magnetic moment of the investigated system is responsible for the resonance. For sufficiently narrow lines, the other component can be neglected. To fully describe the lineshape for a setup using linearly polarized light and a spectrum exhibiting broad linewidths however, not only the resonance but also the counter resonance at $-H_{\text{res}}$ must be taken into account [25]. Furthermore, admixture of dispersion to the absorption signal may occur, especially in metallic samples [25]. Thus the function to describe X-band data amounts to [25, 24]:

$$\frac{dP_{\text{abs}}}{dH} = G \cdot \left(\frac{-2x + \alpha(1 - x^2)}{(1 + x^2)^2} + \frac{-2y - \alpha(1 - y^2)}{(1 + y^2)^2} \right) + a + bH \quad (2.10)$$

with $x = (H - H_{\text{res}})/\Delta H$ and $y = (H + H_{\text{res}})/\Delta H$ and the inclusion of a linear background. With H_{res} being the resonance field, ΔH the linewidth at full width half maximum (FWHM), G a variable prefactor, α the ratio of absorption and dispersion, and a and b parameters for the linear background.

2.3 Collective Magnetic Excitations

In long-range ordered magnets instead of exciting isolated paramagnetic ions the microwave energy is absorbed by collective excitations, which are semi-classically known as spin waves or quantum mechanically called magnons. There are several ways to calculate the field dependence of the resonance frequency of magnon modes in antiferromagnets, such as molecular field theory [26] or the exchange symmetry based hydrodynamic description [27, 28]. Depending on the magnetic order and the anisotropy of a spin system, different resonance-frequency-field-dependencies will result. Such that conclusions on the magnetic order and anisotropy can be drawn by the shape of the resonance branches with respect to the applied external magnetic field. The strength and sign of the anisotropies for example is related to the excitation gap of the magnon modes in zero external magnetic field. Or in other words, if there was no or only a very small excitation gap at zero applied magnetic field, there is also no or only very little anisotropy in the system.

This is why it is desirable to do ESR measurements at varying microwave frequencies, as it allows to map out the excitation gaps in zero applied magnetic field and the shape of the resonance branches with respect to the applied field. X-band ESR can not provide such information as the frequency is too low to excite collective modes of energy higher than 10 GHz. In high-field ESR (HF-ESR) setups microwave frequencies between 10 GHz and 1000 GHz can often be employed, which makes them a great tool to gain information about the anisotropy and interactions in a spin system. The higher frequencies in HF-ESR also make larger energy level splittings accessible yielding in principle a better resolution. In order to tune the investigated spin system into resonance the microwave frequency is kept fixed, while the magnetic field is slowly varied. Although one could theoretically also keep the field fixed and vary the frequency the first approach is much easier to realize experimentally.

The preceding chapter is meant as a very brief introduction to the concept of ESR and is mainly based on the very comprehensive books by Bencini and Gatteschi [21] on EPR in exchange coupled systems, Pake and Estle [20] giving an introduction to EPR and Abragam and Bleaney [23] on EPR of transition ions. These volumes are recommended to the interested reader.

3 Experimental Methods

3.1 X-Band Electron-Spin-Resonance (X-band ESR)

Measurements at varying angles of the applied magnetic field with respect to the crystallographic c -axis of a single crystal of GdInO_3 (Sample 2 batch nr. GIO 1.1) at room temperature were performed at the Institute for molecular systems engineering and advanced materials (IMSEAM) with help of the research group of Prof. Dr. Frauke Gräters. A commercial X-band spectrometer EMXmicro-6/1/P/L (SN: EMM 2311) by *Bruker* equipped with an ER 070 magnet was used. It provides a frequency of $f = 9.84$ GHz and magnetic fields up to $B = 0.645$ T. The external magnetic field is modulated such that the derivative of the absorption power is measured. The angle was measured by a self-made protractor with a precision of 5° .

Measurements at varying angles of the applied magnetic field with respect to the crystallographic c -axis at temperatures lower than room temperature as well as measurements at varying temperatures were performed at the Institute for Physics at Augsburg University, in the research group of Priv.-Doz. Hans-Albrecht Krug von Nidda. Measurements down to 4 K were carried out on a commercial X-band spectrometer Elexsys-II E500 by *Bruker*, equipped with an ER 4102ST resonator (*Bruker*), a flow cryostat ESR900 (*Oxford Instruments*), an automatic temperature controller (ITC 503 *Oxford Instruments*) and controllabe goniometer (*Bruker*). This setup provides magnetic fields of up to 1.4 T and a frequency of $f = 9.34$ GHz. Because the external magnetic field is modulated during the measurement, the derivative of the absorption power is measured. Measurements at varying temperature below 4.2 K were done with a second Elexsys II E500 spectrometer, equipped with a helium bath glass cryostate with liquid nitrogen shielding. Temperatures below 4.2 K were reached by reducing the pressure in the cryostate. In this setup measurements were performed in magnetic fields up to 1.2 T.

3.1.1 Sample Preparation and Data Correction

For the measurements at the IMSEAM the single crystal was fixed on a wooden rod using non-magnetic GE varnish. The rod was then inserted into a wilmad quartz tube, which fits into the cavity of the spectrometer. However, the wooden rod turned out

to have a distinct ESR feature consisting of one main resonance with six hyperfine lines. This background was subtracted from all measurements performed with the wooden sample holder.

For X-band measurements at Augsburg University single crystals were placed inside a quartz tube, such that the flat side of the crystal came to lie on the side wall of the tube. The samples were fixed with parafin, which was molten and subsequently frozen for that purpose. The polycrystalline powder was fixed by melting parafin, which seeped into the powder and glued it together. Measurements down to 4 K were done on sample 2 (GIO 1.1), while measurements below 4.2 K were done on sample 1 (GIO 1.3).

The background and possible admixture of dispersion was accounted for by the Lorentz derivative fit given in the previous chapter including a linear background term and a variable parameter for the admixture of dispersion (compare eq. 2.10).

3.2 High-Frequency/High-Field Electron Spin Resonance (HF-ESR)

For the HF-ESR spectrometer the microwaves are produced by Yttrium-Iron-Garnet (YIG) oscillators in a Millimeter Vector Network Analyzer (MVNA) by *AB millimeter Paris*, which provide frequencies between 8 GHz and 18 GHz. This source frequency is stabilized by an EP 575B Source Locking Microwave Counter by *Phase Matrix*. The source frequency is tuned to multiples of itself up to 1200 GHz by Schottky-diodes, called harmonic generators (HG). After transmission through the sample the output frequency is reduced to its original frequency by another set of Schottky-diodes (harmonic mixers (HM)). This reduced frequency is detected by the MVNA. The MVNA-signal is read out by a lock-in amplifier (SR 830 DSP Lock-In Amplifier by *Stanford Research Systems*), which decomposes the transmitted frequency into its amplitude and phase, while simultaneously amplifying the signal. Figure 3.1 shows a schematic diagram of the HF-ESR setup.

The sample is mounted in a sample rod, which can be inserted into a magnetocryostat (*Oxford Instruments*). The rod contains two circular waveguides, leading the microwaves to the bottom of the sample rod, where the sample is mounted and back up. The sample is placed at the bottom of the input waveguide, such that it is positioned in the middle of the magnetic field produced by the magnetocryostat. Gold coated mirrors guide the microwaves from the diodes into the waveguides and around the corners at the bottom of the sample rod. Because of the width of the wave guides, frequencies below ~ 30 GHz can not be used for the measurements, as their wavelength is larger than the diameter of the waveguides [29]. A Cernox CX-1040 thermometer

and a resistance heater controlled by *340 Lake Shore* enable temperature control at the sample. The wave guides are surrounded by a cylindrical tube, which is filled with 250 mbar of helium gas at room temperature prior to initial cool-down. The tube is mainly made from stainless steel, only the bottom is made from copper for better thermal conductivity in the vicinity of the sample. The magnetocryostat contains a Nb₃Sn superconducting cylindrical coil magnet, providing vertical magnetic fields up to 16 T. The superconducting coil is kept at a temperature of 4.2 K by a liquid helium bath. The magnetic field is controlled by a Mercury intelligent power supply (Mercury iPS *Oxford Instruments*). A Variable Temperature Insert (VTI) allows to control the temperature in the sample chamber: The insert is continuously pumped to create low pressure. With a needle valve the inflow of helium can be controlled, which allows evaporative cooling down to stable temperatures of 1.8 K. A resistive heater enables to heat the insert to 300 K. The temperature is controlled by a Mercury intelligent temperature controller (Mercury iTC *Oxford Instruments*). All control units as well as the lock-in amplifier are connected to a measurement computer, which allows to control the temperature and magnetic field and records the spectra. During the measurements the frequency is kept constant while the magnetic field is swept at a rate of 1T/min. If not stated otherwise, only downsweeps are shown in this thesis, as it can be assured that all powder grains of a loose powder sample are maximally aligned with the applied external field after the up-sweep. For measurements at varying temperatures, the sample was warmed up from the lowest temperature.

3.2.1 Sample Preparation and Data Correction

Samples were prepared by enclosing them in a brass ring 3.2, which was sealed at the bottom and on top with ESR inactive and microwave transmissive Kapton tape. For measurements on fixed powder samples, Eicosan powder (ESR inactive) was melted, such that it seeped into the powder sample and fixed it in position after freezing. For GdInO₃ two sets of measurements were performed on the loose powder, because coupling of the microwaves to the spin system was so good, that the system oversaturated in the first attempt. In the second setup a reduced amount of powder was used. This reduced amount of powder was later fixed.

The single crystal of GdInO₃ was glued to the bottom Kapton tape using GE varnish for measurements with magnetic fields along the *c*-axis, while it was glued between two teflon blocks for fields applied within the *ab*-plane. For measurements with the external magnetic field applied along the *c*-axis several attempts were needed because the crystal was repeatedly torn off and aligned itself in the applied external magnetic field such that its *ab*-plane was parallel to the external magnetic field. This was evident by sharp jumps or peaks in the microwave transmission at low applied

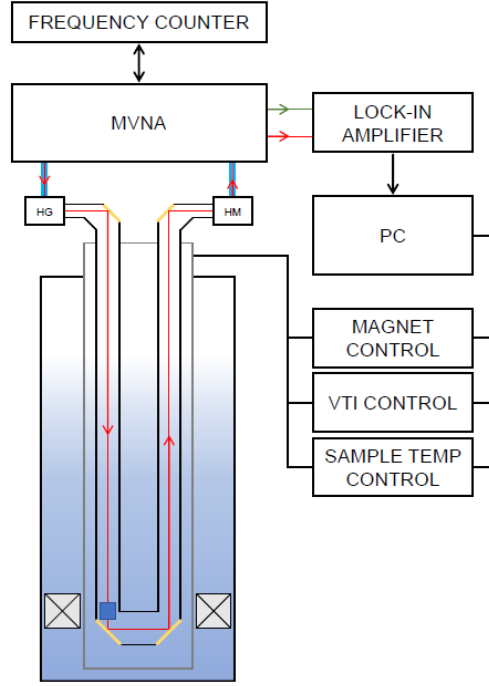


Figure 3.1: Schematic diagram of the HF-ESR experimental setup. The grey squares symbolize the superconducting coil, the blue square the sample, and the shaded blue area the liquid helium (see the text for further details). The figure is taken from [30].

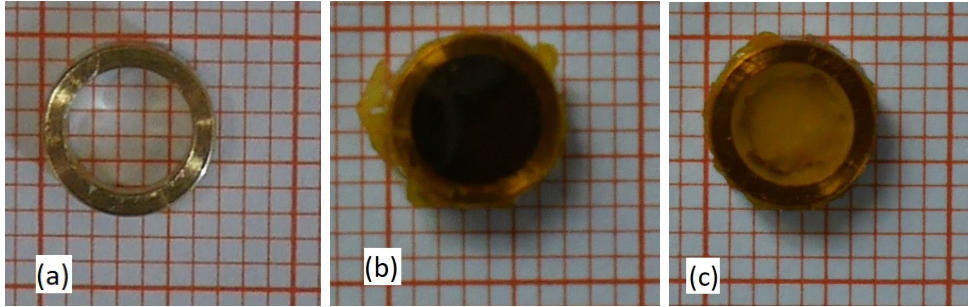


Figure 3.2: Photographs of (a) the brass ring, (b) the fixed powder of $\text{PbCuSeO}_4(\text{OH})_2$, and (c) the fixed powder of GdInO_3 . The bold square in the background corresponds to 1cm.

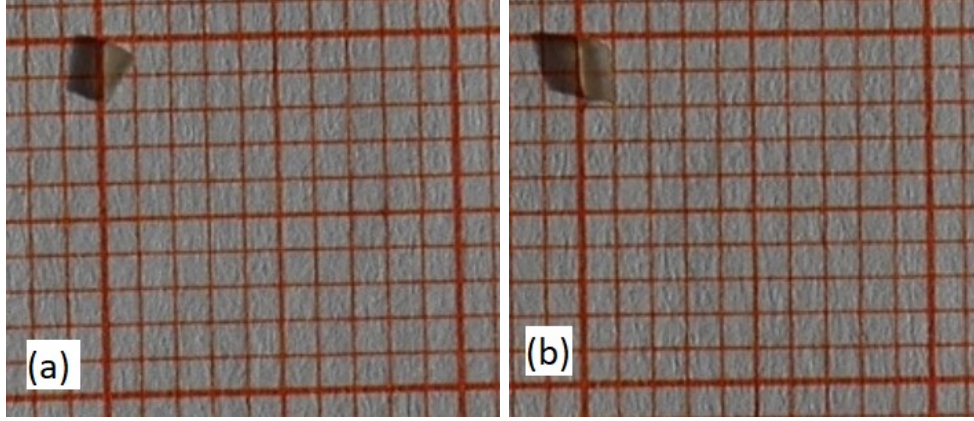


Figure 3.3: Photographs of the two single crystal GdInO_3 samples. (a) Sample 2 (GIO 1.1) and (b) sample 1 (GIO 1.3). The bold square in the background corresponds to 1cm.

magnetic fields in each field sweep and by the fact that the crystal had changed position towards being aligned with the formerly applied magnetic field after being taken out of the measurement setup. Finally, a combination of GE-varnish and Kapton tape on top of the flat crystal was sufficient to hold the crystal in place. This behavior already suggests a strong magnetic anisotropy in the system, which, at low temperatures, is supported by the experimental data, as will be shown in chapter 4.

Measurements on the single crystal were started with sample 1 (GIO 1.3), which has parallel surfaces (fig. 3.3). This sample showed numerous resonance features at high frequencies. In order to rule out the possibility of them being walker modes, a second crystal (sample 2, GIO 1.1) was cut in an acute angle (fig. 3.3). If not stated otherwise, all data in this thesis is extracted from measurements on sample 2.

HF-ESR spectra were background corrected either by subtracting a linear background or by subtracting a fully phenomenological background obtained by setting several data points along the spectrum and interpolating between them. In the HF-ESR setup an experimentally induced phase shift between the transmitted signal and the reference signal can lead to an admixture of dispersion (D) to the absorption (A). If there was a pure absorption signal in the investigated exchange coupled systems, Lorentz-shaped absorption features would be expected. Thus, experimentally, admixture of dispersion is evident from the deviation of the lineshape from a Lorentz-shape. Unfortunately, mixture of absorption and dispersion does not only change the lineshape but also the resonance position, making it crucial to correct for this effect. It is corrected for by adding a fraction of the dispersion to the absorption such that the real signal is $T_{real} = A + \epsilon D$, with $|\epsilon| < 1$ [31]. ϵ is found empirically by varying

the parameter until the signal appears Lorentz-like. If the so-called phase-mixing is strong, it can not always be fully corrected, introducing an additional error to the resonance field position. The correction of phase-mixing also changes the intensity of the absorption signal. This is relevant for measurements at varying temperatures, where the intensity, which is related to the susceptibility, is often used for a comparison to the static magnetic susceptibility. Thus, ESR susceptibilities obtained from HF-ESR measurements often suffer from poor accuracy.

4 Experimental Results

4.1 $\text{PbCuSeO}_4(\text{OH})_2$

4.1.1 Introduction

Since the early nineties [32] materials exhibiting quasi-1D spin-1/2 chains with ferromagnetic (fm) nearest neighbour (NN) interaction J_1 and antiferromagnetic (afm) next nearest neighbour (NNN) interaction J_2 have received ongoing attention due to the prediction of them showing exotic spin structures such as chiral spin liquids, spin density waves, magnon bound states, nematic or other multipolar phases [33, 34, 35]. Different ground states are predicted depending on the ratio between the coupling constants, $\alpha = |J_2/J_1|$. For $\alpha < 0.25$ ferromagnetic order is expected, for $\alpha > 0.25$ the ground state is formed by a helix [36, 37, 38]. However real materials often have non-zero interchain couplings which lead to a change in the pitch angle in the ground state [39, 40, 38]. There is already a substantial list of materials thought to exhibit quasi-1D spin-1/2 chains: Li_2CuO_2 [32, 41], $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ [42], LiCuVO_4 [43, 44], NaCu_2O_2 [45, 46], LiCu_2O_2 [47, 46], $\text{PbCuSO}_4(\text{OH})_2$, CuGeO_3 [48], Sr_2CuO_2 [49, 50], $\text{Li}_2\text{ZrCuO}_4$ [38, 51, 52, 53], and LiCuSbO_4 [54]. Many of them are edge-sharing chain cuprates. A prime candidate for experimental studies is linarite ($\text{PbCuSO}_4(\text{OH})_2$), which has an α of about 0.3 ($J_1 = -168$ K, $J_2 = 46$ K from INS [55]) and is thus close to the critical value of $\alpha = 0.25$. It has saturation fields not exceeding 10.5 T (a -axis: 7.6 T, b -axis: 10.5 T, and c -axis: 8.5 T) and occurs naturally as a single crystal [40]. Its space group is $\text{P2}_1/\text{m}$ with the lattice parameters $a = 9.7$ Å, $b = 5.65$ Å, $c = 4.69$ Å and $\beta = 102.7^\circ$ [56]. Buckled chains of edge sharing $\text{Cu}(\text{OH})_2$ units are aligned along the b -axis forming the quasi-1D chain (fig. 4.1). The chains are separated by lead and sulphur ions enclosed in oxygen octahedra [56]. The fm NN exchange between the copper moments is probably caused by superexchange mediated by the oxygen ions. They form an angle of 91.3° or 94.3° close to 90° suggesting fm superexchange according to Goodenough-Kanamori-Anderson rules [58, 59]. At $T_N = 2.8$ K linarite develops an incommensurate elliptical helical ground state with propagation vector $\mathbf{q} = (0 \ 0.186 \ 0.5)$ [16]. One spin component lies in the ac -plane, 27° away from the a -axis, while the other lies along b [60]. Ferroelectric polarisation develops simultaneously in the same phase, which is common for spiral spin order and renders linarite a multiferroic [16].

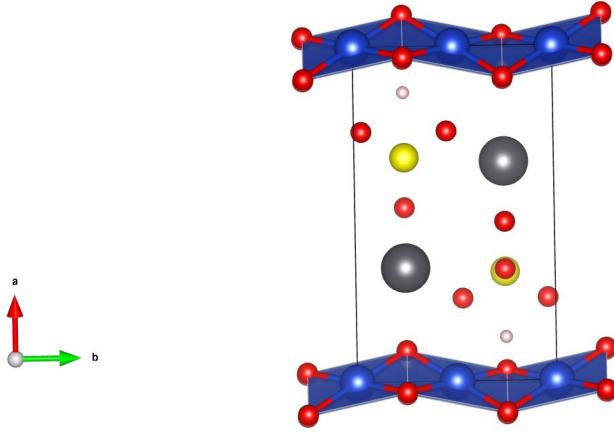


Figure 4.1: Crystal structure of $\text{PbCuSeO}_4(\text{OH})_2$ (isostructural to linarite): Blue spheres: Cu, red: O, white: H, yellow: Se, grey: Pb [57].

The magnetic phase diagram of linarite is highly anisotropic (fig. 4.2(a)). For fields applied along the chain direction (b -axis) five phases have been observed consistently [62, 63, 64, 60, 61, 65, 66]. The field-induced phase II is considered a hysteretic region between phase I (ground state) and the field-induced phase IV [60, 61]. On the other hand the field-induced phase III is supposed to be a mixed phase where the commensurate afm order of phase IV and a spiral spin structure coexist. The spiral in phase III is tilted with respect to the spiral in the ground state and the circular helix lies within the bc -plane [61]. Both phase II and III also exhibit ferroelectric ordering [63, 66]. Phase IV has a commensurate afm order with propagation vector $\mathbf{q}=(0\ 0\ 0.5)$. This might be due to the fact that a classical spin-flop is prohibited by the monoclinic angle β [61]. Phase V is framing the other phases and its exact structure is still under debate. Some argue it to be a spin-density wave (SDW) state [61] while others suggest an ordinary fan phase, which is also supported by symmetry arguments [55, 28]. For fields applied away from the chain direction most studies only report the phase transition into the spiral ground state and into phase V. However a spin-flop into a cone state is predicted and observed by angle resolved magnetic torque measurements as well as by ESR studies [28, 64]. The torque measurements show hardly any anisotropy of the phase transition at 2.8 T, which is the transition into the commensurate phase IV for fields applied along the b -axis and a spin-flop transition for fields applied along the easy axis (an axis within the spiral plane close to the a -axis). ESR studies reveal orthorhombic anisotropy with the g -values $g_a=2.34$, $g_b=2.1$, and $g_c=2.28$ [40]. Thus, g -tensor anisotropy suggests the easy axis along the a -direction while it seems to be along the b -axis when looking at fits to the susceptibility [40]. Other authors predict it to be along one of the directions lying within

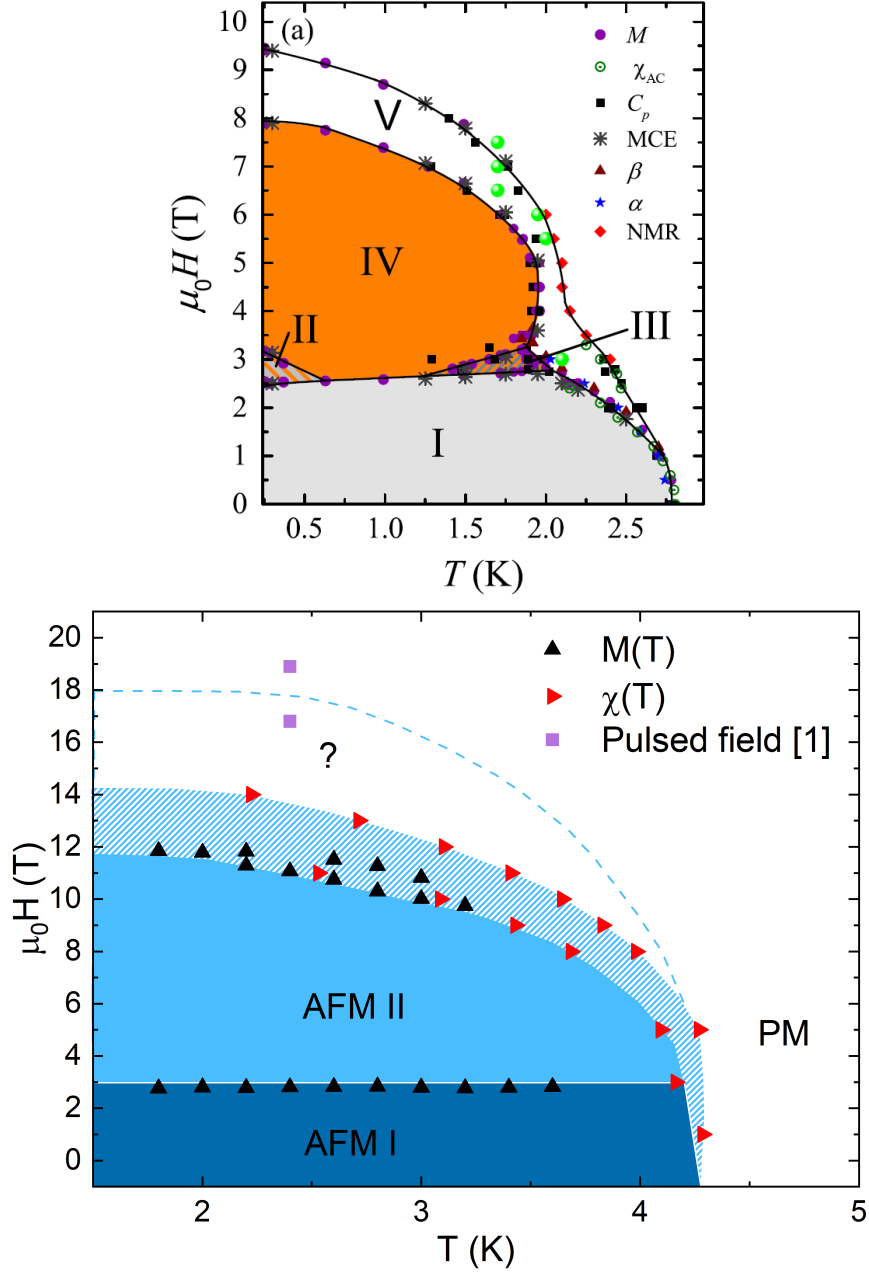


Figure 4.2: Phase diagrams for (a) linarite for magnetic fields applied along the b-axis (from [61]) and (b) $\text{PbCuSeO}_4(\text{OH})_2$: The diagram was constructed from magnetisation measurements obtained at varying external magnetic fields and varying temperatures (by Daniel Knauer [18]) as well as pulsed field magnetisation data (A. Vasiliev [17]) on a powder sample. The dashed area marks a phase transition regime and the dashed line marks a suggested boundary towards saturation. PM marks the paramagnetic region while AFM I (dark blue) corresponds to the antiferromagnetic ground state and AFM II (light blue) to the field-induced antiferromagnetic state. All lines are guides to the eye.

the spiral plane of the ground state order [28]. The magnetic phenomena linarite exhibits have been described with many similar models, which however slightly differ in their specific assumptions. The foundation for these models is always a simple Hamiltonian, including the dominant fm NN and afm NNN exchange interactions and a Zeeman term [62, 28, 55, 67, 61, 68]:

$$H = J_1 \sum_i^N \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \sum_i^N \vec{S}_i \cdot \vec{S}_{i+2} - h \sum_i^N S_i^z \quad (4.1)$$

where h is the external magnetic field along the z direction. However, they all have in common, that some kind of anisotropy and/or interchain coupling has to be included in order to properly describe the experimental results. Despite 20 years of research on this material, clearly open questions remain. Most importantly, there is yet no conclusive theoretical model successfully describing this seemingly simple frustrated 1D chain-system.

In this following chapter $\text{PbCuSeO}_4(\text{OH})_2$, a material isostructural to linarite will be investigated. This presents the opportunity to directly compare both materials and hopefully get some insight into what is characteristic to the quasi-1D chain in general and what is specific to linarite or $\text{PbCuSeO}_4(\text{OH})_2$. The sample under investigation is a synthetic powder provided by A. Vasiliev from Lomonosov Moscow State University. Recently, the material was found as a naturally occurring mineral and named franksousaite [69]. Preliminary magnetisation studies show $T_N = 4.8$ K and a spin-flop transition at 2.8 T [18]. The exchange couplings calculated from generalized gradient approximation including coulomb repulsion are $J_1 = -103$ K and $J_2 = 54$ K [17]. This predicts, $\alpha = 0.52$, making it reasonable to assume a spiral ground state. A preliminary phase diagram obtained from magnetisation measurements is shown in fig. 4.2. Qualitatively the phase diagram of franksousaite looks quite similar to the one of linarite.

Figure 4.3 shows the corresponding magnetisation data both in static and pulsed fields [17, 18]. The spin-flop transition is visible as a lambda-shaped peak in the magnetisation derivative with respect to the magnetic field for temperatures up to 4 K. There is an additional phase transition at about 11.5 T visible as a broad maximum and saturation sets in at about 17 T. Already at 10 K the magnetisation derivative does not show any distinct features anylonger. The pulsed field data at 2.4 K deviates from the 2.4 K data in static fields. This may be explained by a generally large uncertainty when scaling the pulsed field data to the static magnetisation.

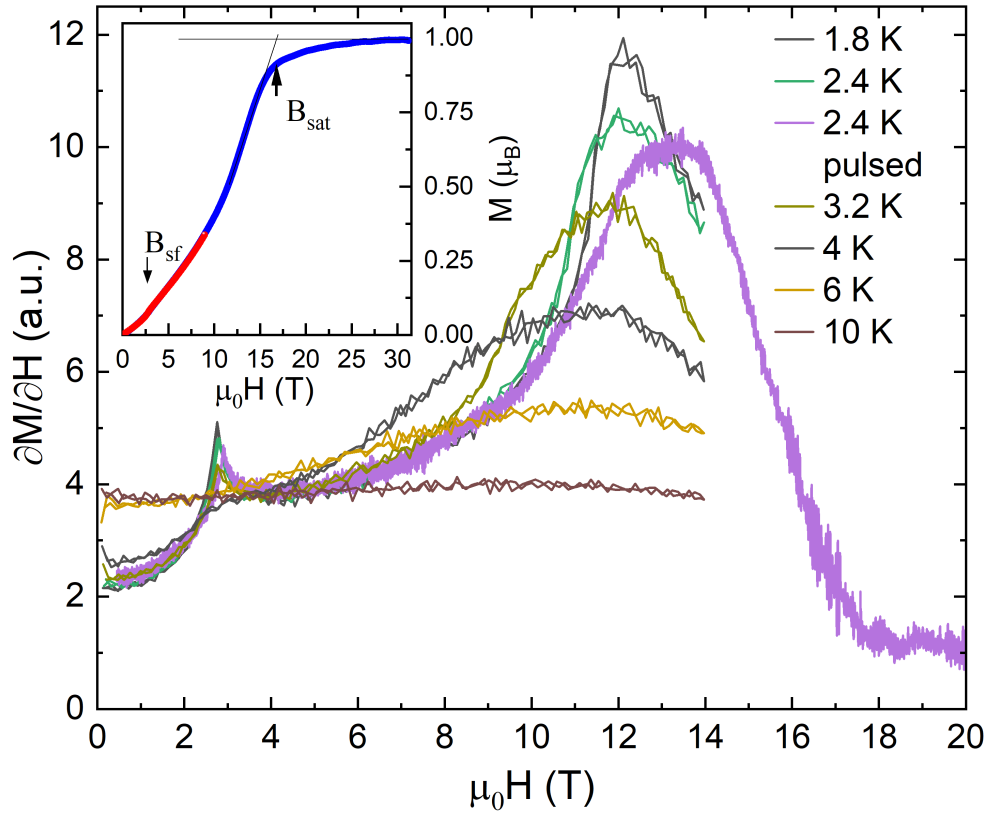


Figure 4.3: Magnetisation derivatives with respect to H at different temperatures measured by Daniel Knauer [18]. Pulsed field magnetisation data is provided by A. Vasiliev [17]. The inset shows the magnetisation in pulsed fields up to 31 T normalized to magnetisation data from a continuous field measurement. Both data sets are from A. Vasiliev [17].

4.1.2 Results and Discussion

ESR-Data at Different Microwave Frequencies

Figures 4.4(a) and 4.4(b) show the HF-ESR spectra obtained at different frequencies on a loose powder sample of franksousaite. Pronounced changes of transmission observed for all spectra at fields below 1 T are likely due to the alignment of the powder grains in field, as they appear for up- and down-sweeps of the applied magnetic field but not in the fixed powder sample of $\text{PbCuSeO}_4(\text{OH})_2$. For higher fields the grains of the powder are expected to be aligned with their magnetic *easy*-axis parallel to the field. In the range of 3 T to 4 T a change in transmission of varying magnitude is observed in all spectra. This change in transmission is attributed to the field-induced phase transition expected at 2.8 T, as will be discussed later. For frequencies of 129.4 GHz and above a clear resonance peak is visible (fig. 4.4(a)). It shifts to higher fields with increasing frequency and splits into two signals at 156.7 GHz and three signals at 210.5 GHz.

In fig. 4.5 spectra obtained on the fixed powder sample are shown for low frequencies of 48 GHz to 100.1 GHz. For the shown spectra, phase mixing was corrected as described in section 3 and a phenomenological background (either linear or individually drawn data points) was subtracted where possible. A weak resonance peak is visible at 1.6 T for lowest frequencies. Field position and intensity increase with frequency. This peak corresponds to the main feature also visible at higher frequencies. At 64 GHz a broad feature appears at roughly 1 T. Its intensity remains weak up to 89.9 GHz, which makes it hard to trace but it seems to move towards higher fields up to a frequency of 80 GHz. At 89.9 GHz the same or a new feature is clearly visible at about 1.3 T, which increases its field position with increasing frequency. These additional features are marked with a pink bar in the graph as it is difficult to determine their exact field positions. They are not visible for frequencies higher than 100 GHz (fig. 4.6(a)).

For frequencies of 129.8 GHz and above the main feature already observed at lower frequencies can be traced all the way up to 438.5 GHz. At 159.9 GHz it first splits into two and at 190.1 GHz into three signals, forming a broad shoulder on the left and the right of the main peak. With increasing frequency the resonance bunch broadens assuming a form typical for fixed powder samples. Such a broad feature in a fixed powder sample is caused by randomly oriented grains of the powder showing resonances at different magnetic fields according to the orientation of the corresponding magnetic axes with respect to the field. At 438.5 GHz the three signals single out to three independent peaks, whereas the right most is already outside the accessible field range. Powder spectrum simulations with fixed linewidth and three varying g-values were successfully fitted to the spectra for frequencies between

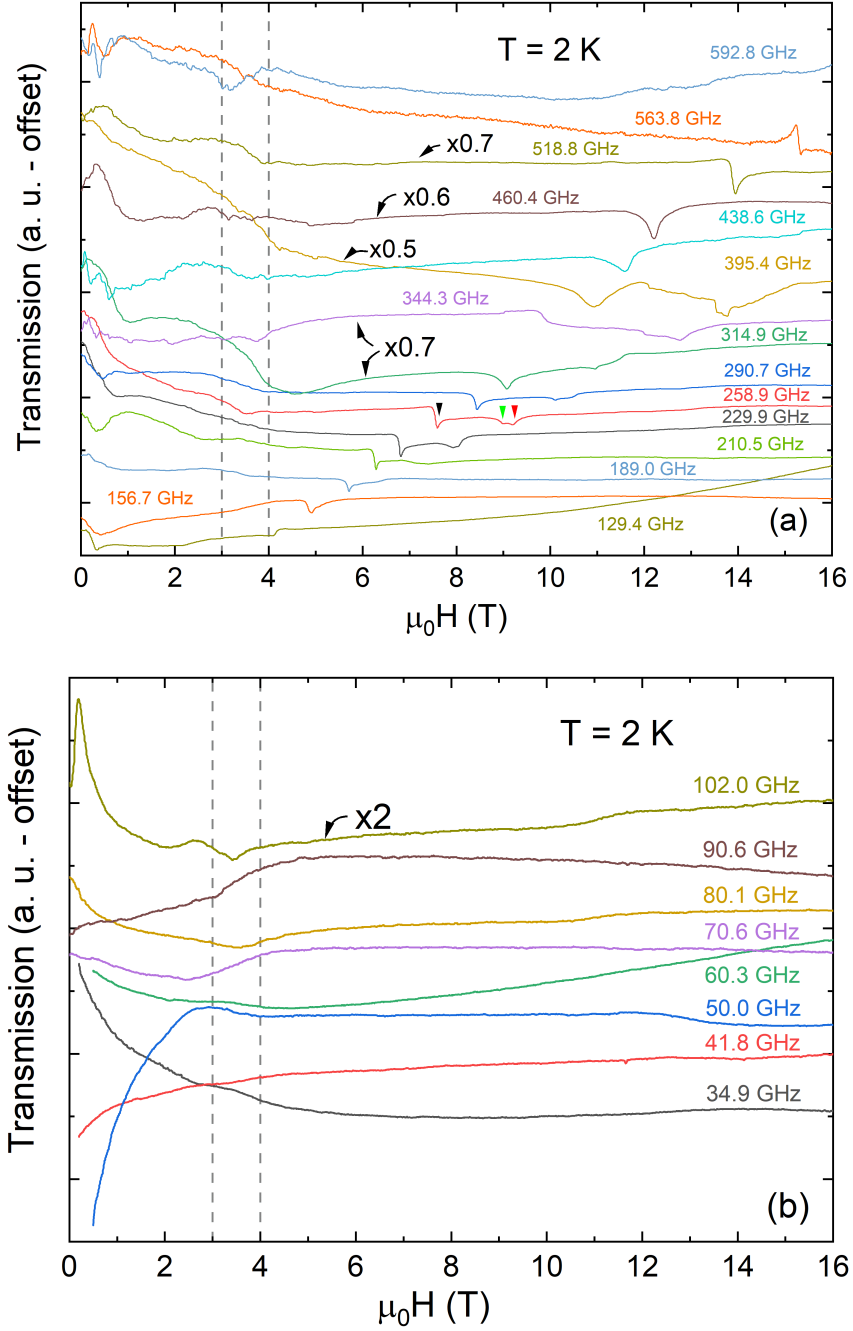


Figure 4.4: HF-ESR spectra obtained on a loose powder sample of franksousaite at 2 K and different frequencies ((a): 129.4 GHz - 592.8 GHz, (b): 34.9 GHz - 102.0 GHz) in fields between 0 T and 16 T. The curves are vertically shifted and partially scaled for better visibility. Vertical dashed lines enclose the field-range of the field driven phase transition. Small black, green, and red arrows indicate the position of the resonance belonging to the black, green and red branch in fig. 4.7.

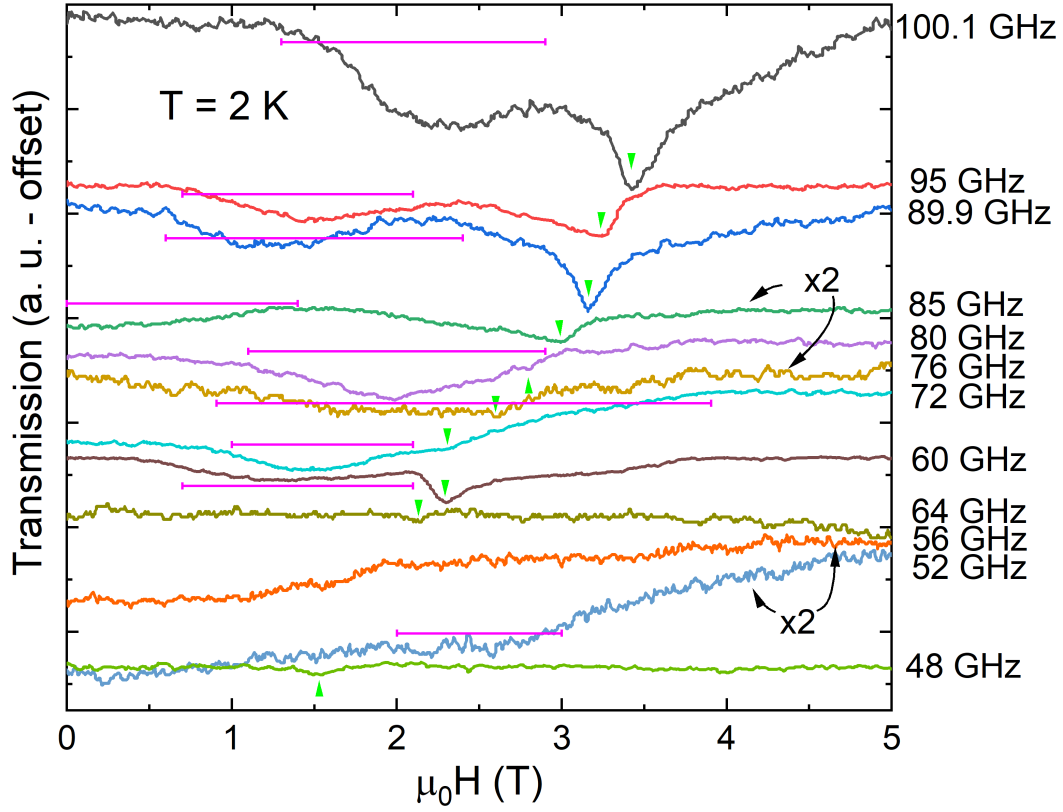


Figure 4.5: HF-ESR spectra obtained on a fixed powder sample of frankousaite at 2 K and different frequencies (48 GHz - 100.1 GHz) in fields between 0 T and 6 T. Where possible phase mixing was corrected and a phenomenological background subtracted (see the text). The curves are vertically shifted and partially scaled for better visibility. Main resonance features are marked with a small green arrow and additional features with a pink bar.

129.8 GHz and 394.3 GHz by means of EasySpin. An example is shown in the inset of figure 4.6(a). This fit assumes a diagonal anisotropic g -tensor and a paramagnetic resonance. One would thus not expect such a fit to be successful in the magnetically ordered regime, where collective excitations are expected instead of single ion paramagnetic resonances. The success of the fit merely suggests, that the observed magnon branches appear like an anisotropic paramagnetic signal. In other words, the fit is a phenomenological description of the data. The fact, that the resonance feature splits up into three distinct features at higher frequencies already shows, that this is not actually paramagnetic behavior. If it was, spectral weight would remain between the main transmission minima even at highest frequencies. Additionally, when looking at the g -values extracted from the fit, one would expect them to be constant with frequency, if it was indeed a paramagnetic signal. This is clearly not the case (see fig. 4.6(b)) and will be discussed in more detail later.

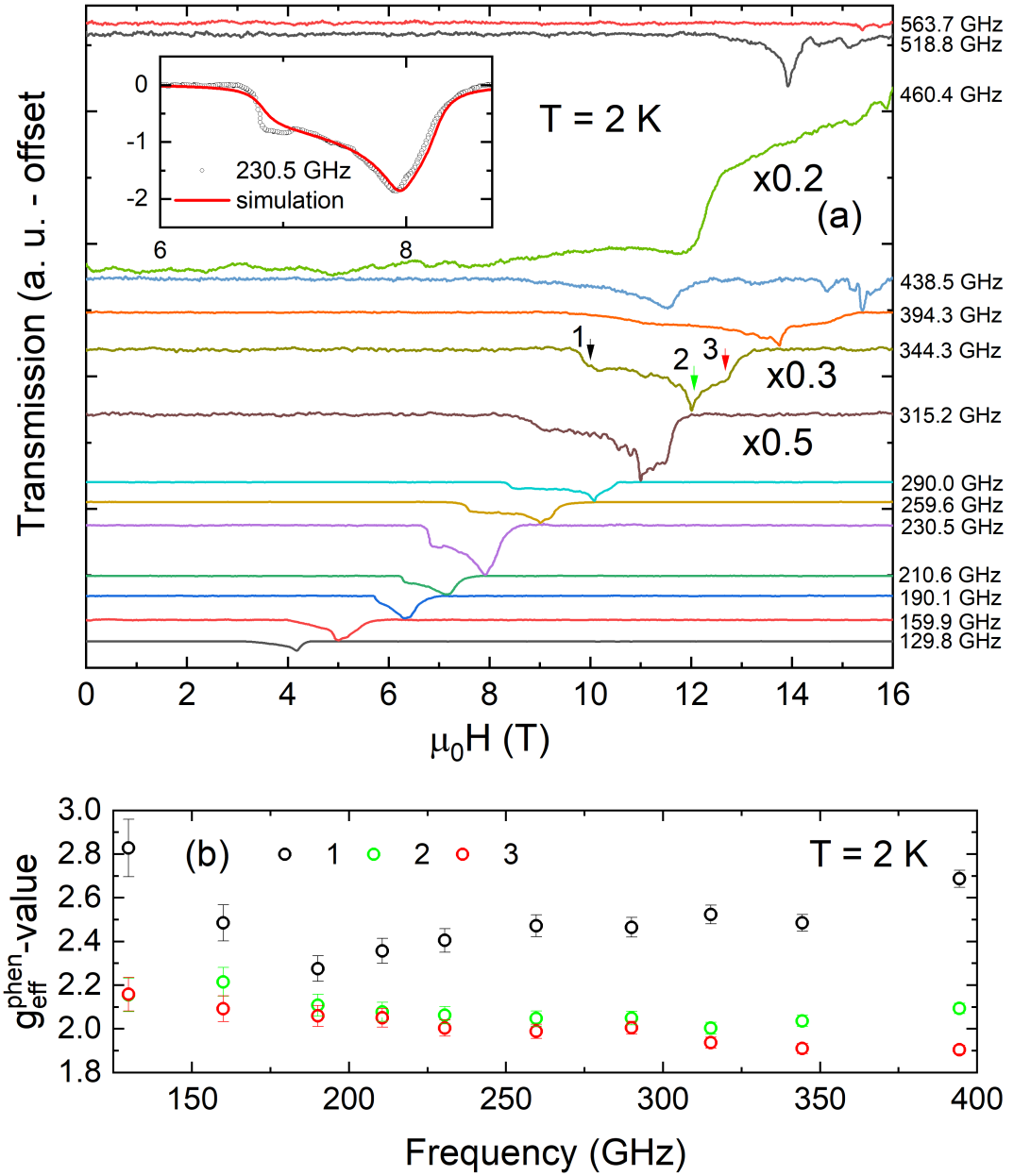


Figure 4.6: HF-ESR spectra obtained on a fixed powder sample of franksousaite at 2 K and different frequencies (129.8 GHz - 563.7 GHz) in fields between 0 T and 16 T. Where possible phase mixing was corrected and a phenomenological background subtracted (see the text). The curves are vertically shifted and partially scaled for better visibility. The inset shows a powder spectrum simulation phenomenologically fitted to the resonance at 230.5 GHz with EasySpin. Small black, green and red arrows with numbers correspond to the numbers and colours in (b): Effective g-values extracted from an phenomenological EasySpin fit to selected fixed powder spectra at different frequencies. See text for details.

The field position of the resonances and changes of transmission in the spectra for both the loose and the fixed powder sample are summarized in a frequency-field-phase diagram (fig. 4.7(b)). Changes in transmission are marked with blue squares and are visible for all frequencies but only for the loose powder sample. The change in transmission is visible at each frequency both in the up and down sweep of the field and is often more pronounced for the down sweep (data not shown). They roughly coincide with the critical field at 2.8 T and could be caused by a change in the dielectric function at the phase boundary. The dielectric function indeed changes between 2 T and 7 T evidenced by direct measurements thereof [17]. However, in the fixed powder (fig. 4.6), no change in transmission is visible any longer. An explanation could be that the phase transition at $B = 2.8$ T is highly anisotropic. If it is indeed a spin-flop it would only be observable for external magnetic fields applied along the magnetic *easy*-axis of the crystallites and thus no changes are observable in the randomly aligned fixed powder. As the grains of the powder are all randomly oriented, each of them would have the phase transition at a different field strength. The corresponding change in transmission however would be weak as only a few grains would be affected at each magnetic field strength, thus rendering it undetectable within the fixed powder sample.

At fields below 3 T the pink bars in fig. 4.7 and fig. 4.8 indicate the region where additional spectral weight was observed in the fixed powder at low frequencies (see also fig. 4.5). While the bar at lowest frequencies lies in the region of the phase transition, the next higher four bars might correspond to the red magnon mode visible at higher fields above the phase transition. If so it would be an indication that this mode prevails down to fields below the spin-flop. The highest four bars might belong to a distinct ground state magnon mode with a zero field gap of 85 ± 10 GHz. Since for $\text{PbCuSeO}_4(\text{OH})_2$ the frustration is predicted as $\alpha > 0.25$ a spiral ground state is expected. For such a spiral ground state Gotovko *et al.* have calculated the expected resonance branches both for fields applied perpendicular to the spiral plane and the two directions parallel to it. In all three cases two resonance branches are expected (see fig. 4.10). If $\text{PbCuSeO}_4(\text{OH})_2$ orders in a spiral ground state one would thus expect to see six branches in a fixed powder sample. However, the experimental resolution might not be high enough to resolve all six branches or they might lie outside the experimentally accessible frequency range. Additionally, field independent horizontal branches are hardly observable in a field-swept ESR setup. The equations for the respective resonance branches for fields applied perpendicular to the spiral plane and biaxial anisotropy are [28]:

$$\frac{\omega_{1,2}^2}{\gamma^2} = \frac{1 + \eta^2}{2} H^2 + \frac{D}{\chi_{\parallel}} \pm \sqrt{\frac{E^2}{\chi_{\parallel}^2} + \frac{D}{\chi_{\parallel}} H^2 (1 - \eta)^2 + \frac{(1 - \eta^2)^2}{4} H^4} \quad (4.2)$$

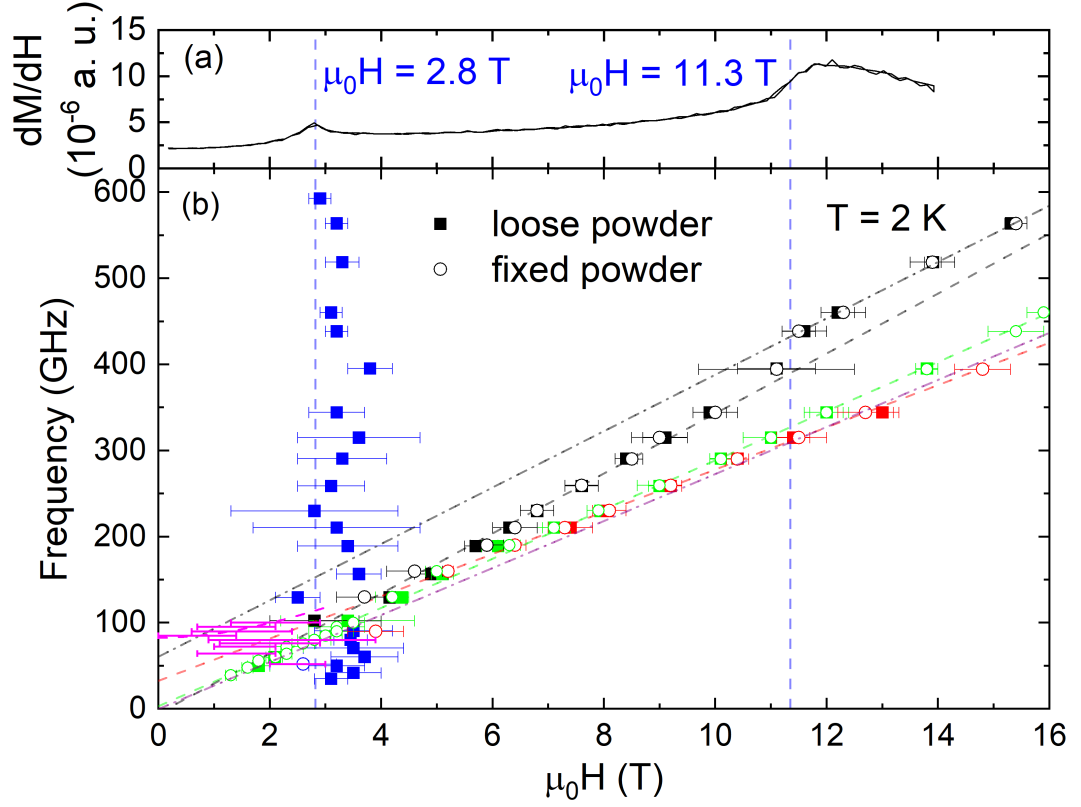


Figure 4.7: (a) Magnetisation derivative $\partial M/\partial H$ at $T = 2$ K. (b) Frequency-field diagram constructed from ESR measurements on the loose and fixed powder samples. Filled squares mark resonance positions and changes in transmission for the loose powder sample, open circles for the fixed powder. Pink bars indicate areas of additional spectral weight observed in the fixed powder studies. The vertical dashed blue line is a guide to the eye. Dashed black, green and red lines are linear fits to the data from the fixed sample and the pink dashed line is a theory fit to the upper most four pink bars. The violet line is an attempt on a non-gapped fit to the red data points (see text).

where D and E are anisotropy constants ($E=0$ for uniaxial anisotropy), $\chi_{\parallel}$ is the magnetic susceptibility for fields parallel to the spiral plane and $\eta = (\chi_{\perp} - \chi_{\parallel})/\chi_{\parallel}$. For fields parallel to the spiral plane one gets [28]:

$$\frac{\omega_1^2}{\gamma^2} = \frac{D \mp E}{\chi_{\parallel}}, \quad \frac{\omega_2^2}{\gamma^2} = \frac{D \pm E}{\chi_{\parallel}} + H^2 \quad (4.3)$$

where upper and lower signs correspond to $H \parallel x$ and $H \parallel y$ respectively. X and y are orthogonal directions within the spiral plane. As the observed resonance branch in $\text{PbCuSeO}_4(\text{OH})_2$ is clearly not field independent, if any, only branches 1 and 2 for fields applied perpendicular to the spiral plane or branches 2 for fields applied parallel to the spiral plane could match the observed result. Equation 4.2 has four independent parameters and since there are only four data points it is not reasonable to fit it to the data. When fitting the second equation in eq. 4.3 with only one free parameter a zero field gap of 82.5(14) GHz is obtained. The fit is shown as a pink dashed line in figures 4.7(b) and 4.8(a). Although the fit describes the data well, it is not very reliable due to the small number of data points and their large error bars. Additionally, the green resonance branch also observable in the ground state can not be described by the spiral phase model as it does not include any zero gap linear branches. By no means one can thus conclude from the data that the ground state is a spiral state. The green resonance branch can be traced across both phase transitions up to highest available field. A linear fit to the data from the fixed powder spectra yields a zero field splitting of 3 ± 2 GHz, which is negligible. The effective g -factor obtained from the slope amounts to 2.040(14). The small zero field splitting and the fact that the resonance branch is observable in all three magnetic phases suggests that it is of paramagnetic origin. Usually a paramagnetic signal is not expected in ordered phases. However, contamination with a paramagnetic material or the crystal having paramagnetic impurities such as unoccupied or differently occupied lattice sites, might yield a small paramagnetic signal even when the bulk material is in its ordered state. As the peak corresponding to this resonance branch is the strongest in the fixed powder sample, both scenarios seem rather unlikely. Nevertheless, as will be seen later, this peak also shows typical paramagnetic behavior in its temperature dependence.

Both the paramagnetic-like linear branch (green) and the gapped branch (pink bars) in the ground state could be well described with a two lattice model of an easy plane antiferromagnet (fig. 4.9). However, as will later be seen in the discussion of the measurements performed at varying temperatures, the material shows properties of an *easy-axis* anisotropy instead. The green resonance branch is therefor most likely a zero gap magnon excitation of a spin order, which prevails across the field driven phase transitions.

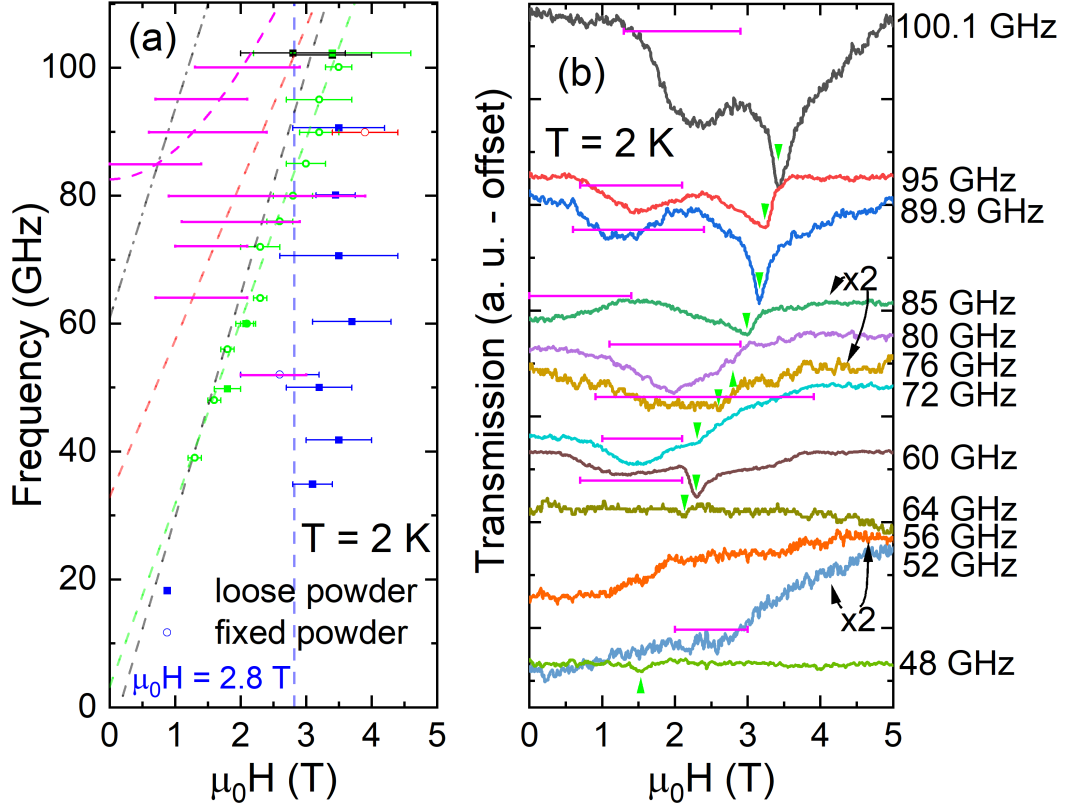


Figure 4.8: (a) Frequency-field diagram at low frequencies and fields. Additional spectral weight at low frequencies and fields are marked with pink bars. The vertical dashed blue line is a guide to the eye and marks the position of the spin-flop field. Dashed black, green and red lines are linear fits to the data from the fixed sample and the pink dashed line is a theory fit to the upper most four pink bars (see text). (b) HF-ESR spectra obtained on a fixed powder sample of franksousaite at 2 K and different frequencies (48 GHz - 100.1 GHz) in fields between 0 T and 6 T. Where possible phase mixing was corrected and a phenomenological background subtracted (see the text). The curves are vertically shifted and partially scaled for better visibility. Main resonance features are marked with a small green arrow and additional features with a pink bar.

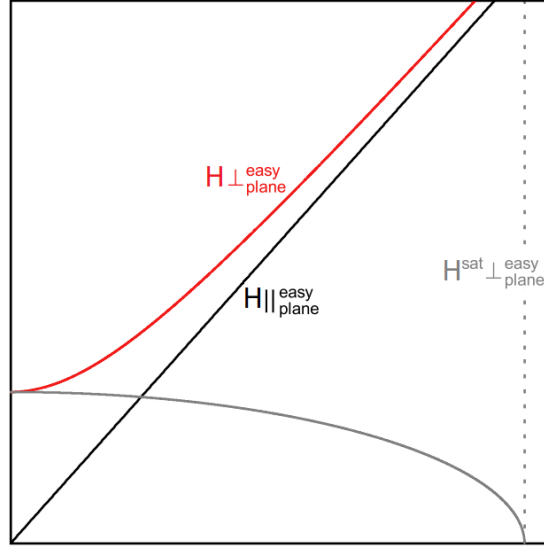


Figure 4.9: Schematic frequency-field diagram for an antiferromagnet with easy-plane anisotropy as predicted by a mean field model. From [30].

In the high-field phase above 4 T two more resonance branches occur, which diverge with increasing field. Linear fits to the fixed powder data yield a (phenomenological) zero field gap of -5 ± 8 GHz and 32.9 ± 1.4 GHz respectively (for the black branch low-field data up to 10 T was fitted). The former is negligible within its error. However, if the linear fit yielded a negative intercept with the ordinate this suggests softening of the magnon mode in the field range where the linear fit intercepts the abscissa. Effective g -factors obtained from the slope amount to $g_{\text{black}} = 2.48$ and $g_{\text{red}} = 1.75$. As discussed above, the g -values extracted from EasySpin fits to the fixed powder spectra change with frequency (fig. 4.6), suggesting that a linear model might not be completely sufficient to describe the data. This deviation from linear behavior however must be small, as the linear fits already describe the data well.

The black resonance branch shows a step at about 11.3 T corresponding to the field position of a phase transition from phase II into a high-field phase seen in the magnetisation. The slope of the branch only changes slightly, while the corresponding zero field gap increases significantly (see fit to the high field data: $g_{\text{eff}} = 2.34$, ZFS $\Delta = 61 \pm 14$ GHz). One may conclude that the internal fields in this new high-field phase are quite similar to those in phase II, while the anisotropy of the system changes. The change in the effective g -value should also be visible in the effective g -factors extracted from the phenomenological EasySpin fits to spectra at different frequencies. However, the jump at the phase boundary occurs at the same frequency range, where the resonance feature splits up into individual resonances, rendering an EasySpin fit impossible.

Although the high field branches (black and red) might at the first glance look like anisotropic branches belonging to the main gapless linear branch (green), the zero field gap of the red branch and the step in the black branch, indicate that these branches are independent magnon modes. To illustrate this fact a violet dashed line going through the origin of the graph was drawn. It does not describe the red data points very well.

It is known, that linarite exhibits a collinear, incommensurate afm phase in finite fields applied along the copper chains [61]. If $\text{PbCuSeO}_4(\text{OH})_2$ exhibited a similar phase, one would expect to observe the corresponding resonance branches with ESR on a fixed powder, because all crystallographic directions are probed simultaneously in such a case. Gotovko *et al.* have also calculated the expected resonance modes for the incommensurate afm phase in linarite. The respective branches can be described with the following equations [28]:

$$\omega_1 = 2|J_1|S\sqrt{(2j_c + \delta + \epsilon)(2j_c \sin^2 \beta + \delta \cos^2 \beta)} \quad (4.4)$$

$$\omega_2 = 2|J_1|S\sqrt{(\delta + \epsilon)(2j_c + \delta))\cos \beta} \quad (4.5)$$

with $\beta = H/(2S|J_1|(\delta + 2j_c))$ and $j_c = J_c/|J_1|$. Here, J_c is the interchain coupling along the c -direction. Clearly these equations can not describe the linear modes observed in $\text{PbCuSeO}_4(\text{OH})_2$ (fig. 4.7). For comparison the frequency-field diagrams and resonance branches of linarite and the corresponding theoretical fits from ref. [28] are shown in fig. 4.10.

Linear resonance branches with significant zero field gap were also observed in the quasi-1D frustrated systems LiCuVO_4 [43] and $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ [42, 70]. In the former two linear branches were observed, one being quasi-paramagnetic (branch III in the diagram) and the other only appearing above a critical field H_c (branch V in the diagram) similar to the black resonance branch reported here (see fig. 4.11(a) and 4.11(b)). However, this critical field in LiCuVO_4 marks the onset of a spin-modulated phase and lies above the spin-flop field. The linear resonance branch (branch V in the diagram) appearing above this critical field is speculated to belong to soliton excitations [43]. The quasi-paramagnetic branch (branch III in the diagram) in LiCuVO_4 does not show any anomalies at the critical field or the spin flop field [71, 44], which is similar to the quasi-paramagnetic branch (green) observed here. This branch in LiCuVO_4 is attributed to longitudinal excitations in the spin modulated phase. In the latter compound ($\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$) two linear branches were observed as well (fig. 4.12). However, this material differs from the other known spin chains with fm NN exchange and afm NNN exchange as its ground state is a spin-gapped non-magnetic singlet and not a spiral [42, 70]. It is speculated that the field-induced long range ordered phase might be a spiral instead and the

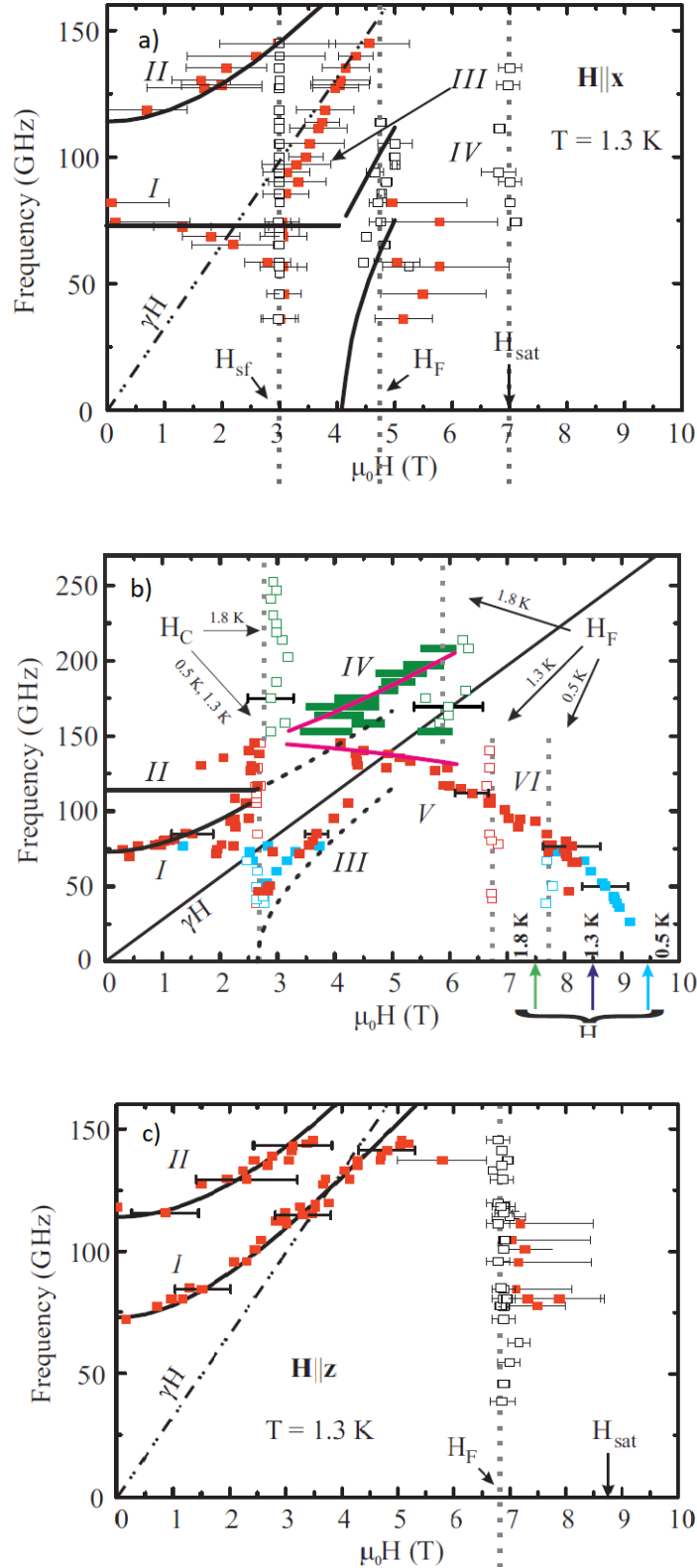


Figure 4.10: Frequency-field diagrams for linarite for magnetic fields applied along the directions (a) $x \perp b$, (b) $y = b$, and (c) $z \perp c$. Solid black lines are theoretical fits (except for the linear gapless line in (b), which shows the paramagnetic limit) and all other lines are guides to the eye. Taken from [28].

linear modes are assumed to be caused by fluctuations leading to spiral order [42]. In $\text{Li}_2\text{ZrCuO}_4$, which is also found to be a fm NN and afm NNN quantum spin chain Arango [72] has found a quasi-paramagnetic branch (fig. 4.13(c)) similar to what is observed here for $\text{PbCuSeO}_4(\text{OH})_2$. She attributes this branch to rotations of the spiral plane around the spiral vector (the vector pointing perpendicular to the plane). Such rotations do not change the energy of the system and, thus, are usually assumed to give a constant resonance branch at zero frequency [47], which is at odds with Arangos assumption. Additional ESR data from [53] on the same material do not show this branch (fig. 4.13(a)&(b)). In [53] the authors calculate the expected resonance branches of the spiral order above and below the spin-flop field by means of a molecular field model, assuming *easy*-plane anisotropy. The calculated branches above the spin-flop field look mostly linear and could also describe the branches observed on $\text{PbCuSeO}_4(\text{OH})_2$ except for the quasi-paramagnetic one. However, $\text{PbCuSeO}_4(\text{OH})_2$ does not show *easy*-plane-type anisotropy as will later be seen when discussing the temperature evolution of the spectra. Lastly, LiCu_2O_2 and NaCu_2O_2 are also compounds with fm NN and afm NNN exchange with a spiral ground state [47, 46]. Fig. 4.14 shows their resonance branches in the ordered phase. The branches in LiCu_2O_2 are described by the theory of exchange symmetry similar to the model used by Gotovko *et al.*. No linear branches are observed and the spin-flop field lies out of the accessible field range [47, 46]. However, Svistov et al. claim, that for weak anisotropy of the *ab*-plane (=spiral plane) and fields applied parallel to the *c*- or *b*-axis the resonance mode corresponding to a deviation of the spiral vector from the *bc*-plane is proportional to the applied field with the proportionality factor αg with $\alpha = \sqrt{\frac{\chi_{\parallel} - \chi_{\perp}}{\chi_{\perp}}}$. NaCu_2O_2 shows two nearly field independent branches and paramagnetic signals caused by impurities [45, 46].

ESR-Data at Different Temperatures

Both in the loose powder sample and in the fixed powder sample, the resonance features at fixed frequency were tracked to high temperatures: in each case for a low frequency corresponding to resonances in the ground state and a high frequency exhibiting resonances in the field range of the field-induced phase. In fig. 4.15 spectra obtained at 230 GHz on the loose powder sample between 2 K and 200 K are shown. In the spectra obtained at temperatures below $T_N = 4.5$ K the steep decrease in transmission at about 3-4 T occurs due to the field-induced phase transition (as was shown earlier in the frequency field diagram). For higher temperatures above T_N this phenomenon is no longer observed, which corroborates that it is indeed intrinsic to the field-induced phase transition. The resonance signal at 230 GHz shows two distinct peaks. The peak at lower fields is narrow and more pronounced than the one at higher fields. With increasing temperature but below T_N its intensity decreases, its

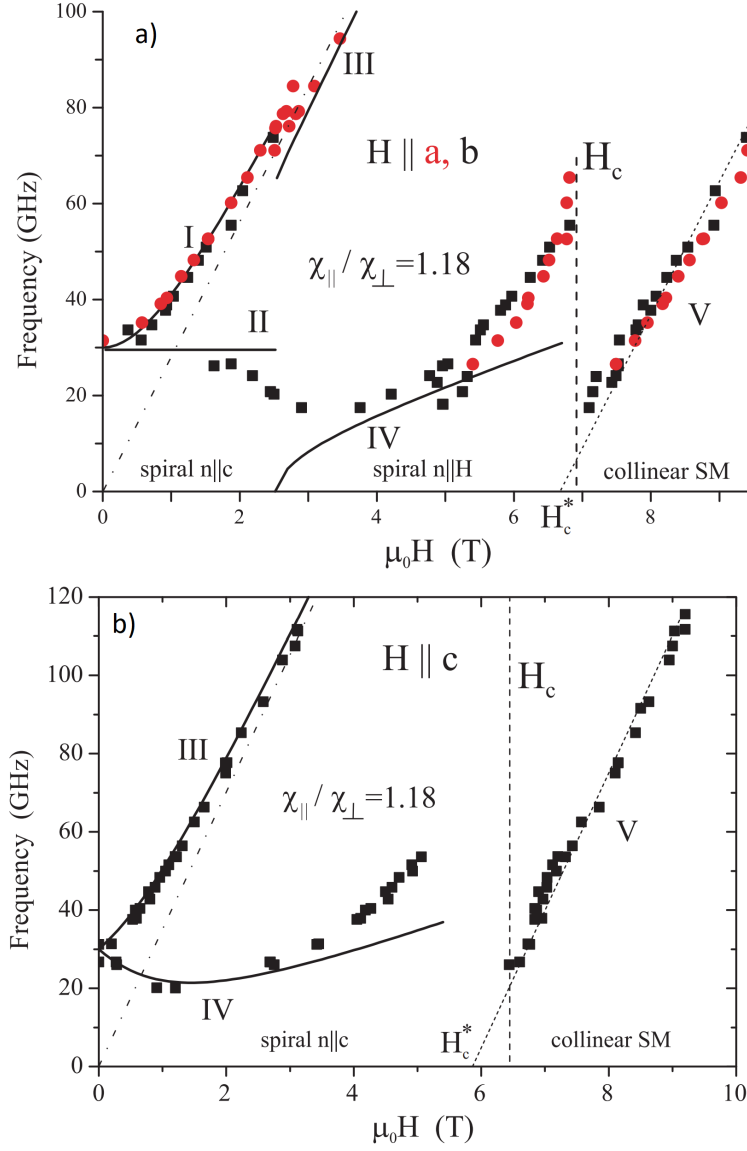


Figure 4.11: Frequency-field diagrams for LiCuVO_4 for magnetic fields applied along the directions (a) a , b and (c) c . Solid and dotted black lines are fits and dashed and dashed-dotted lines are guides to the eye. Taken from [43].

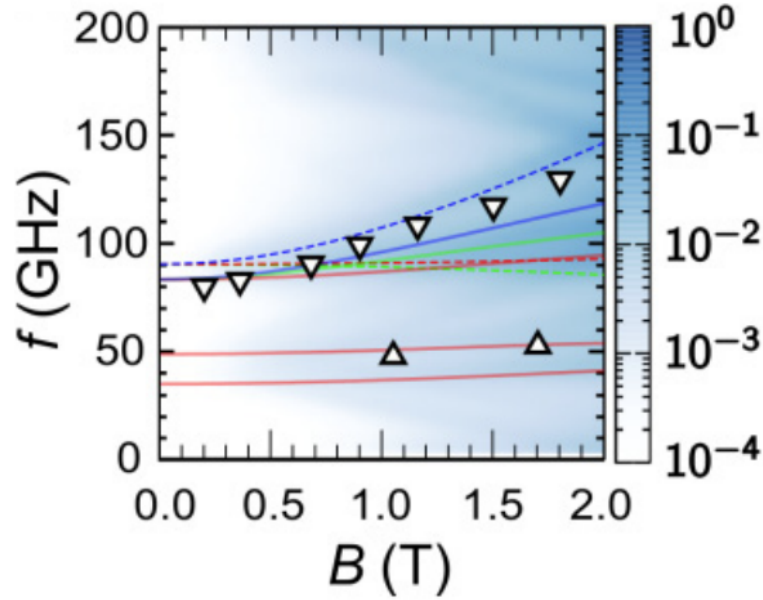
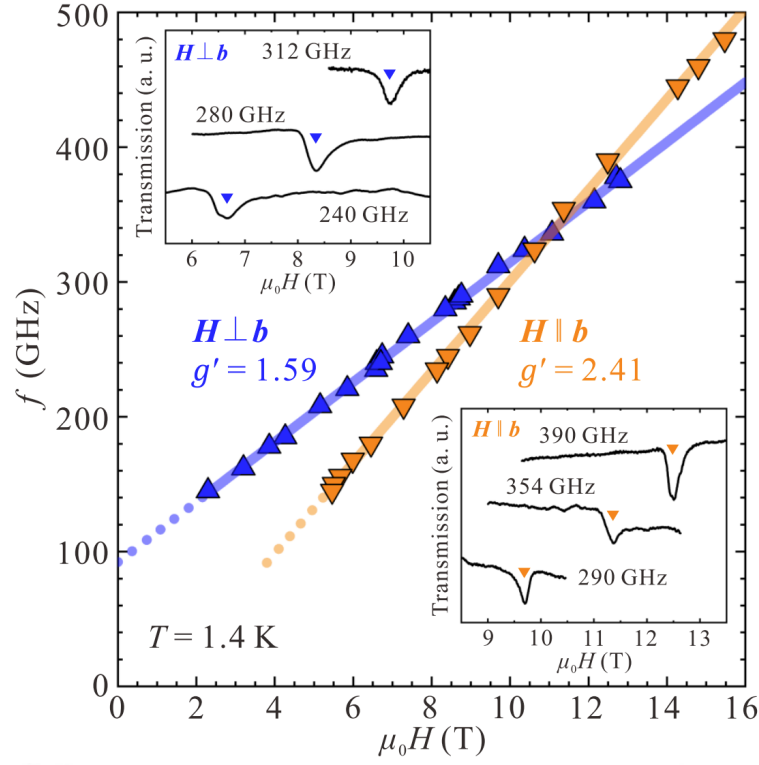


Figure 4.12: Frequency-field diagrams for $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ for temperatures ($T = 1.4$ K and 1.6 K respectively) above the field-induced ordered phase (see text). The colour scale indicates the theoretical optical absorption power. Linear lines are fits to the data, all other lines are theoretical models. Taken from [42, 70].

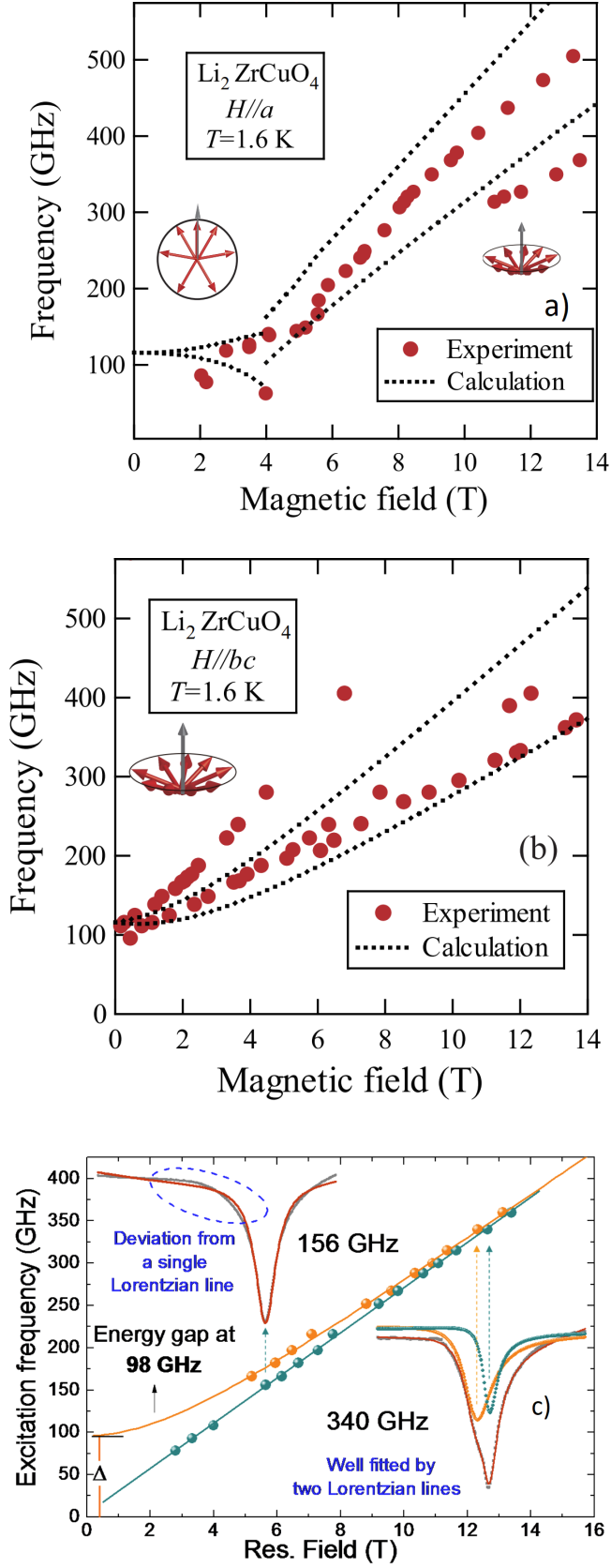


Figure 4.13: Frequency-field diagrams for $\text{Li}_2\text{ZrCuO}_4$ for magnetic fields applied along the directions (a) a , (b) bc , and (c) bc . Lines are theoretical fits to the data. Taken from [53, 72].

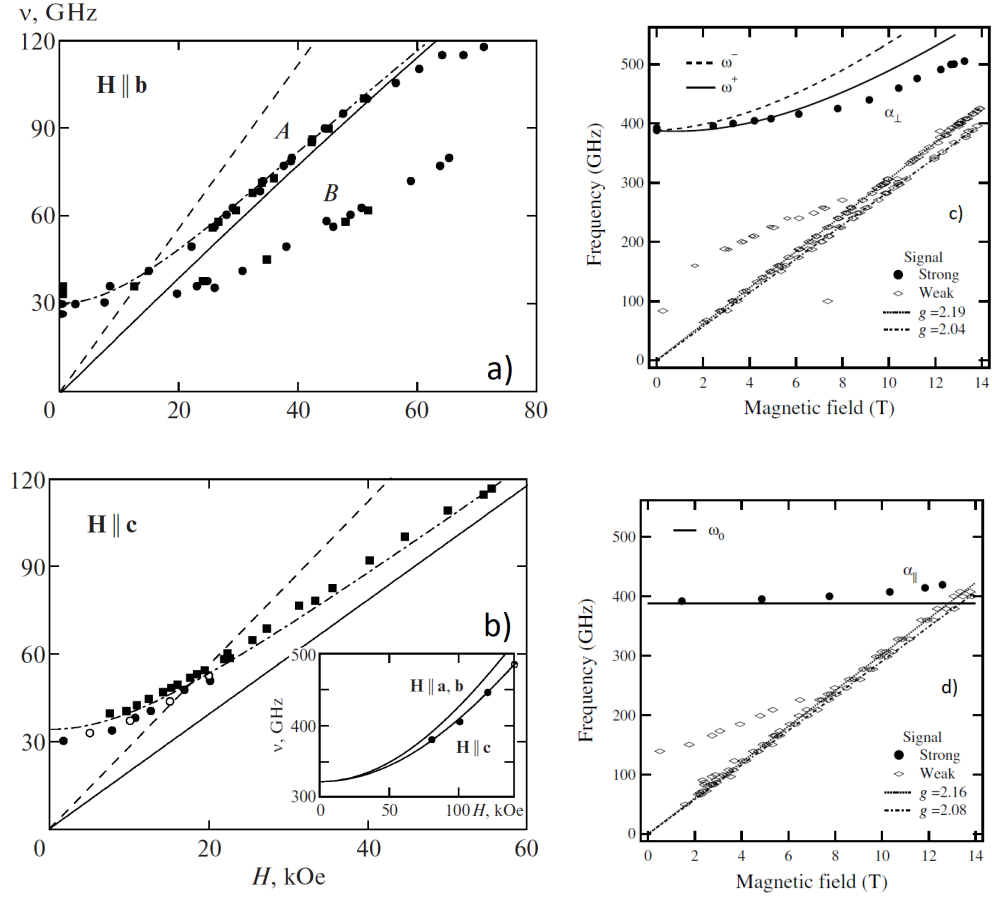


Figure 4.14: Frequency-field diagrams for LiCu_2O_2 for magnetic fields applied along the directions (a) b , (b) c , and NaCu_2O_2 for fields applied (c) perpendicular to the ab -plane and (d) parallel to it. Solid and dashed-dotted lines in a) and b) are fits to the data, in c) and d) solid and dashed lines are theoretical model fits and dash-dotted lines are linear fits to the paramagnetic impurity branches. From [45, 46, 47].

linewidth increases and it shifts towards lower fields. The field position of the second peak remains almost constant for the whole temperature range, while the intensity decreases and the linewidth first increases slightly up to T_N and then decreases. At the highest temperature of 200 K both peaks are still visible albeit with much smaller intensity than for low temperatures. Their resonance position corresponds to the paramagnetic g -factors $g_{\text{easy}} = 2.25 \pm 0.10$ and $g_{\text{hard}} = 2.08 \pm 0.10$. In a loose powder sample one expects to see only one paramagnetic resonance feature at high temperatures as the powder is supposed to be fully aligned with the external magnetic field, thus only the contribution of the *easy*-axis is probed. Temperature independent behavior of the resonance position down to 25 K suggests that the fully paramagnetic regime is reached at roughly 25 K corresponding to $5.6 \cdot T_N$. Merging of the peaks at higher temperature is thus not expected. This suggests that the powder is not fully aligned, showing still signals from at least two main axes. The temperature dependence in the resonance position of the left peak below 25 K and its increase in linewidth occurs due to the development of short range order changing the local fields of the copper moments. Thus, one may conclude that short range order sets in at the latest at 25 K = $5.6 \cdot T_N$.

Fig. 4.16 shows the temperature evolution of the loose powder spectrum at 60 GHz. The resonance feature is very weak and only slightly exceeds the noise level. The intensity decreases with temperature and the resonance is undetectable for temperatures higher than 60 K. The resonance field position is constant and corresponds to a g -value of 2.04 ± 0.10 , which matches within error to the value obtained at 230 GHz at high temperatures for the same resonance branch (namely 2.08(10)).

For the fixed powder sample the temperature evolution of the HF-ESR spectra at 315 GHz was traced up to 300 K (fig. 4.17). The total intensity of the broad powder spectrum decreases with rising temperature and the shoulders on the left and the right of the dominant peak shift towards it for temperature higher than T_N , decreasing the overall width of the feature. The right shoulder completely merges with the main peak for temperatures above 100 K. Below T_N the shoulders shift away from the main peak with increasing temperature, increasing the overall width of the feature. Compared to the resonance feature visible for the loose powder, the spectral weight is shifted more towards higher fields in the fixed powder feature in the whole temperature range. This is an indication for *easy*-axis anisotropy, as the axes with lower g -value coincide and cause more spectral weight at higher fields. For further analysis the spectra have been fitted for all temperatures using an EasySpin-simulation (three varying g -values, varying linewidth). The effective resonance field positions obtained from these fits are shown in fig. 4.18. For temperatures up to 8 K the resonance position corresponding to the right shoulder (open red circles) increases in value with increasing temperature and subsequently decreases to a constant value beyond 70 K,

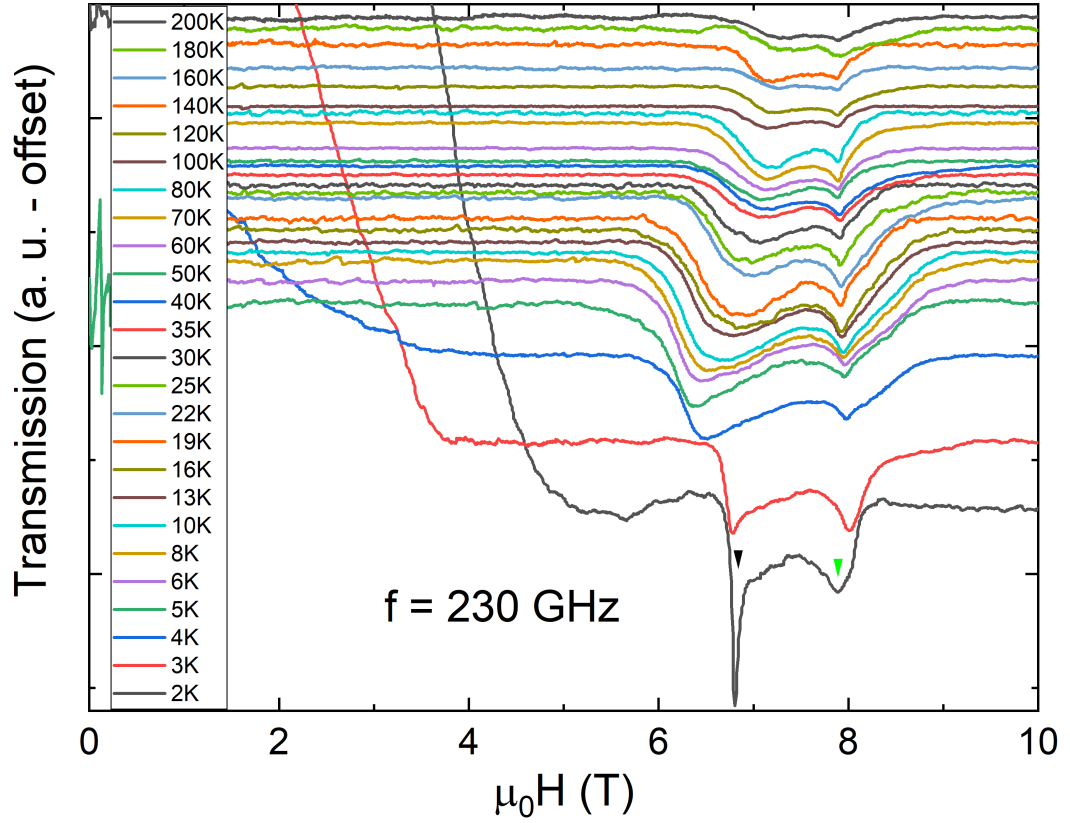


Figure 4.15: HF-ESR spectra obtained on a loose powder sample of franksousaite at 230 GHz and various temperatures in fields between 0.8 T and 10 T. Phase mixing was corrected and a phenomenological background subtracted. The curves are vertically shifted for better visibility. Small black and green arrows indicate the position of the resonance belonging to the black and green branch in fig. 4.7.

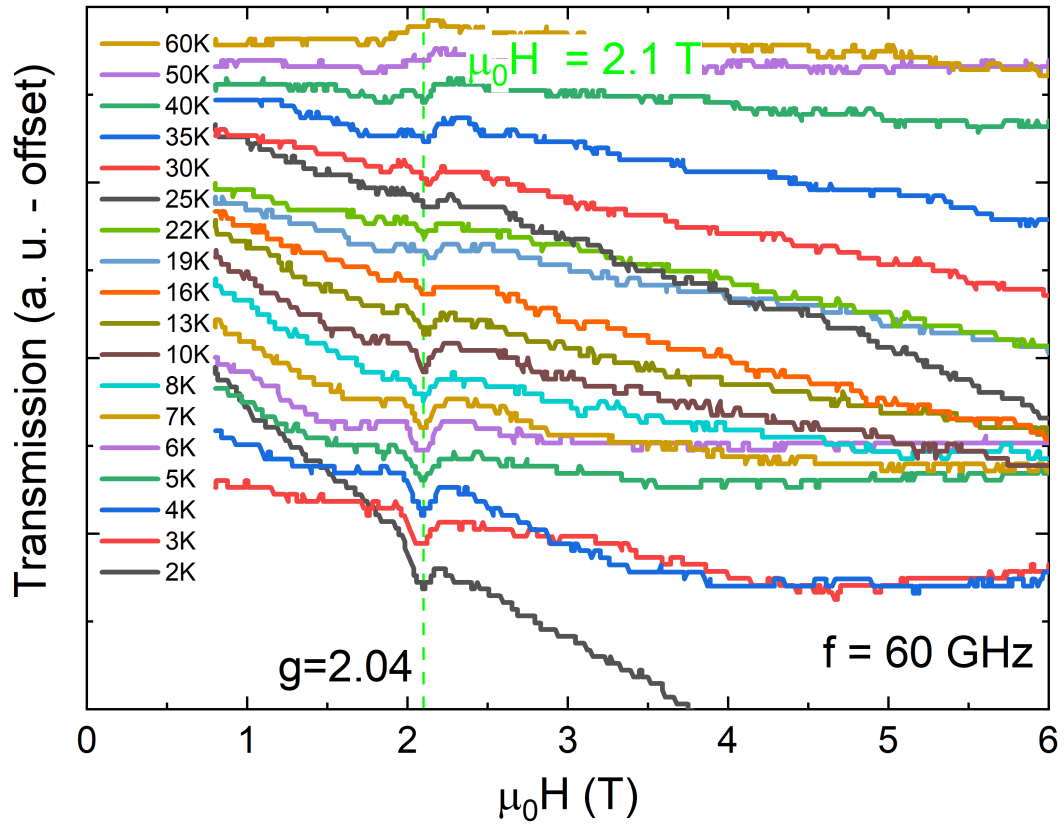


Figure 4.16: HF-ESR spectra obtained on a loose powder sample at 60 GHz and varying temperatures in fields between 0 T and 6 T. The curves are vertically shifted for better visibility. The dashed green line indicates the position of the resonance feature, which corresponds to the green branch in fig. 4.7.

corresponding to a paramagnetic g -factor of $g_{\text{hard}} = 2.06 \pm 0.05$. The resonance position corresponding to the main feature (open green circles) stays mainly constant throughout the whole temperature range and it corresponds to a high temperature paramagnetic g -factor of $g_{\text{hard}} = 2.05 \pm 0.05$. For the left shoulder (open black circles) the resonance position decreases with temperature for temperatures below T_N , while it increases for higher temperatures reaching a constant value for temperatures above 25 K, which corresponds to a g -factor of $g_{\text{easy}} = 2.33 \pm 0.10$. This behavior was already observed for the resonance position of the loose powder spectra. Since there are only two distinct g -factors observed for high temperatures, while the lower two coincide, it can be concluded that franksousaite exhibits *easy*-axis anisotropy in the paramagnetic regime. The divergence of the resonance positions from their high temperature values shows that short range correlations already develop at 70 K corresponding to $14.6 \cdot T_N$. These observations render the earlier suggested explanation of the resonance branches in the ground state by an *easy*-plane model unlikely to be true. Additionally, these results indicate a clear difference to linarite, where *easy*-plane or orthorhombic anisotropy is observed [40].

In order to trace the additional feature visible in the ground state for the fixed powder (indicated with pink bars in earlier figures) with temperature, the temperature evolution of the HF-ESR spectra at 90.2 GHz is shown in fig. 4.19. The additional feature shifts towards higher fields with temperature and starts merging with the gapless resonance branch at 4 K. At 5 K the left flank of the main resonance feature is slightly more pronounced and for higher temperatures the additional features is completely vanished. This corroborates that it is the signature of a collective spin-excitation in the ordered zero field phase. The feature corresponding to the gapless resonance branch can be traced all the way up to 200 K. It is fitted by an EasySpin-simulation (two varying g -values, varying linewidth) and the obtained two resonance positions making up the fixed powder feature are shown in fig. 4.20. At temperatures below T_N the fit is not very reliable because of the influence of the additional feature and, as mentioned before, the resonances are anyway attributed to collective excitations. For temperatures above T_N however, the simulation matches the data well. As before, the resonance position corresponding to the gapless branch (open green circles) stays mainly constant at a corresponding paramagnetic g -factor of $g_{\text{hard}} = 2.05 \pm 0.08$. The paramagnetic signal from the *easy*-axis has a g -value of $g_{\text{easy}} = 2.24 \pm 0.07$, matching the values obtained earlier. It starts to slightly deviate from the high temperature value at 40 K and below.

Averaging both high temperature g -values obtained at different frequencies gives $g_{\text{easy}} = 2.27(7)$ and $g_{\text{hard}} = 2.06(8)$, which is quite typical for copper in a square oxygen environment [40, 72, 73, 23]. Interestingly, g_{hard} corresponding to the signal constant in temperature and belonging to the quasi-paramagnetic branch (green) in

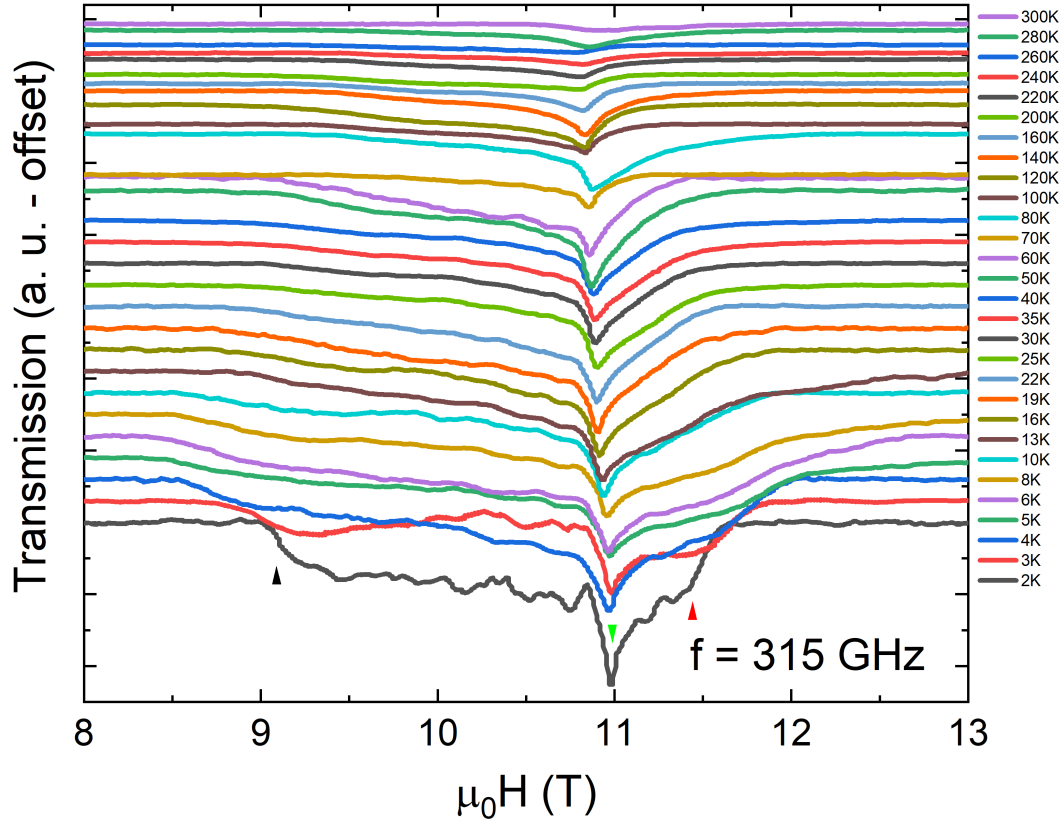


Figure 4.17: HF-ESR spectra obtained on a fixed powder sample of franksousaite at 315 GHz and varying temperatures in fields between 0 T and 16 T. Phase mixing was corrected and a phenomenological background subtracted. The curves are vertically shifted for better visibility. Small black, green and red arrows mark the resonance position and which branch the peaks belong to.

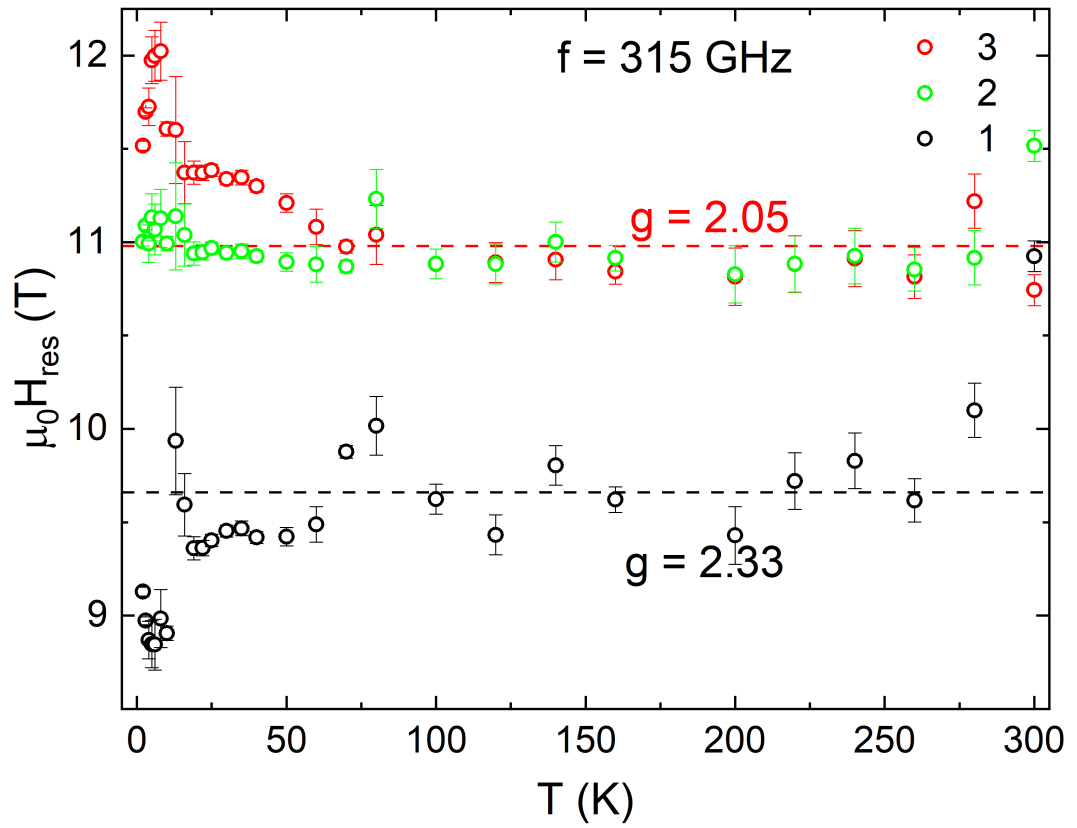


Figure 4.18: The temperature dependence of the resonance field positions obtained from an EasySpin-fit to the data at 315 GHz (see fig. 4.17). The colours correspond to the ones used in fig. 4.7. Horizontal lines are guides to the eye.

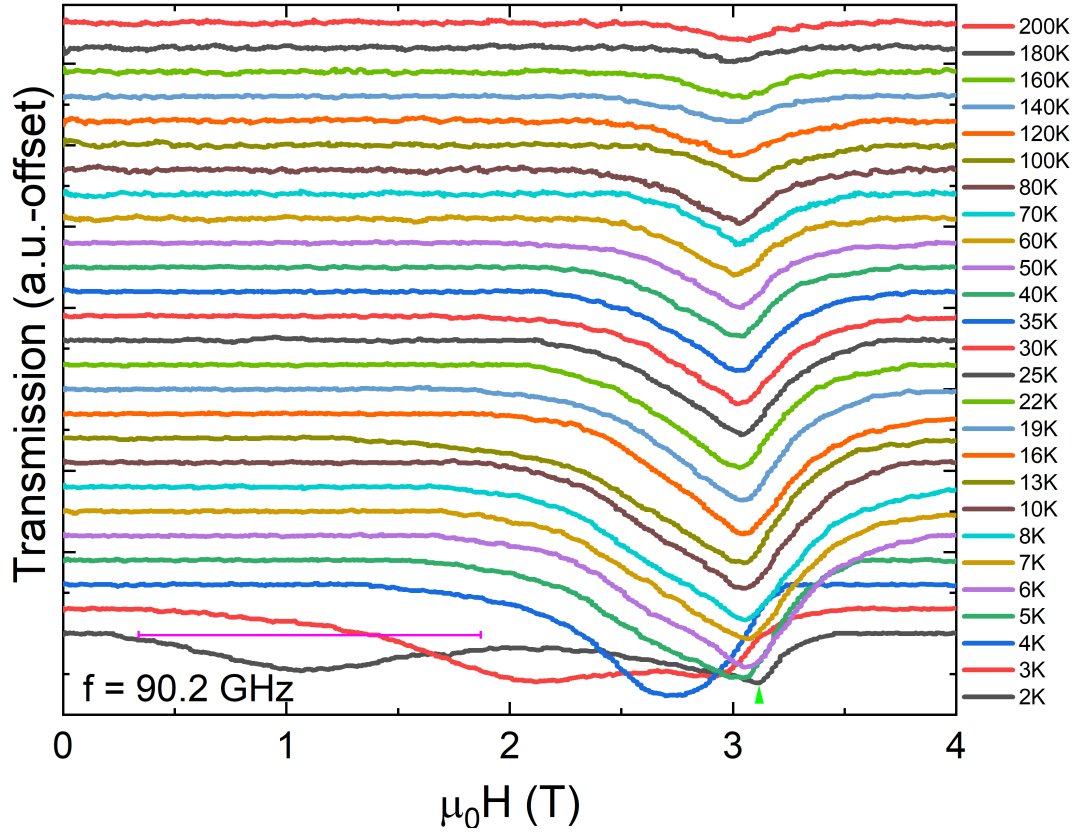


Figure 4.19: HF-ESR spectra obtained on a fixed powder sample of franksousaite at 90.2 GHz and varying temperatures in fields between 0 T and 6 T. Phase mixing was corrected and a phenomenological background subtracted. The curves are vertically shifted for better visibility. The pink bar and green arrows indicated the resonance position and the branch it belongs to.

the ordered state, matches to the effective g -value obtained from the slope of that branch. This match and the constant behavior in temperature strongly suggest this branch to be of paramagnetic origin. However, as pointed out earlier, paramagnetic branches are not expected in the ordered phase.

ESR Susceptibility: As ESR measures the response of the spins to a magnetic field (the magnetic component of the microwaves) the intensity of an ESR signal is directly related to the static magnetic susceptibility associated with the ESR-detected spins. When comparing the intensity evolution of the ESR signal in temperature with the susceptibility one can judge, whether all spins respond to the ESR or if there are excitations, which are unresponsive to the microwaves at this specific frequency (e.g. when a spin gap opens). If there is a good match it shows that (a) static magnetisation and ESR detect the same spins and (b) no information was lost during the processing of the ESR data (phase correction and background subtraction). Figure 4.21 shows a comparison of the ESR susceptibility (the temperature dependence

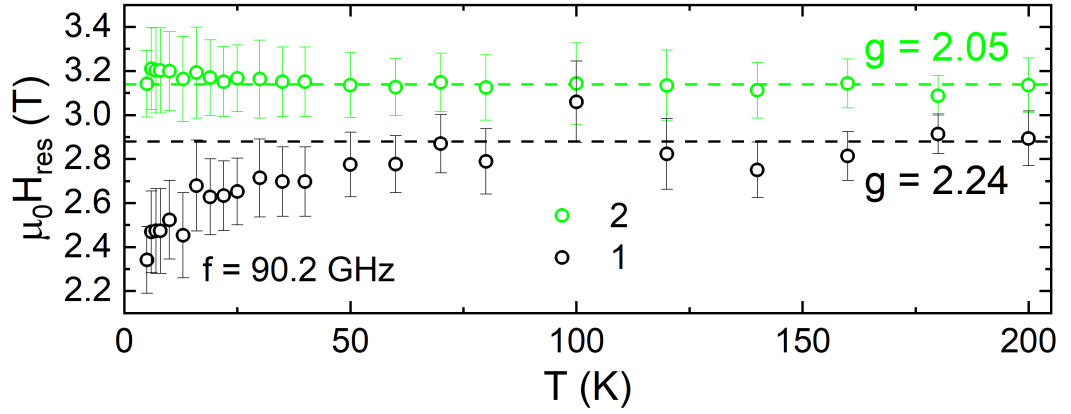


Figure 4.20: Temperature dependence of the resonance field positions obtained from an EasySpin-fit to the data at 90.2 GHz (see fig. 4.19). The colours correspond to the ones used in fig. 4.7. Horizontal lines are guides to the eye.

of the intensity of the resonance feature) and susceptibility from static magnetisation measurements. Temperature evolutions obtained at 230 GHz in loose powder (a) and at 90.2 GHz (b) and 315 GHz (c) in fixed powder are shown. In all three data sets there is a good qualitative agreement between ESR and static susceptibility. There is a broad maximum in the susceptibility at roughly $T_{\text{max}} = 8.3$ K, which is about $1.7 \cdot T_N$. Such a maximum at temperatures above T_N is typical for low dimensional materials and is indicative of short range order. In a uniform 1D antiferromagnet the static susceptibility can be described with the Bonner-Fisher model [74], which only takes one NN afm coupling parameter J along the chain direction into account. Fig. 4.21 shows such a fit to the static susceptibility data, where the Curie-constant, determining the high-temperature susceptibility value, was taken from a Curie-fit to the data [18]. As expected the Bonner-Fisher-fit can not reproduce the data at low temperatures. Drechsler *et al.* have collected data from other NN fm and NNN afm chains and done a model calculation, which predicts the maximum position of the susceptibility for different frustration ratios α [38]. The position of the maximum in susceptibility of $\text{PbCuSeO}_4(\text{OH})_2$ actually matches well with these predictions.

Linewidth Analysis: As introduced in section 2.2, the linewidth of a magnetic excitation feature is influenced by interactions of the spin with their environment. In $\text{PbCuSeO}_4(\text{OH})_2$ the most important contributions are through dipole-dipole interaction and symmetric and antisymmetric anisotropic exchange. When investigating the temperature dependence of the linewidth one hence may be able to draw conclusions on the underlying physical processes influencing the relaxation time perpendicular to the applied magnetic field. When approaching the Néel temperature, fluctuations of the staggered magnetic moment in the short range ordered regime enhance the

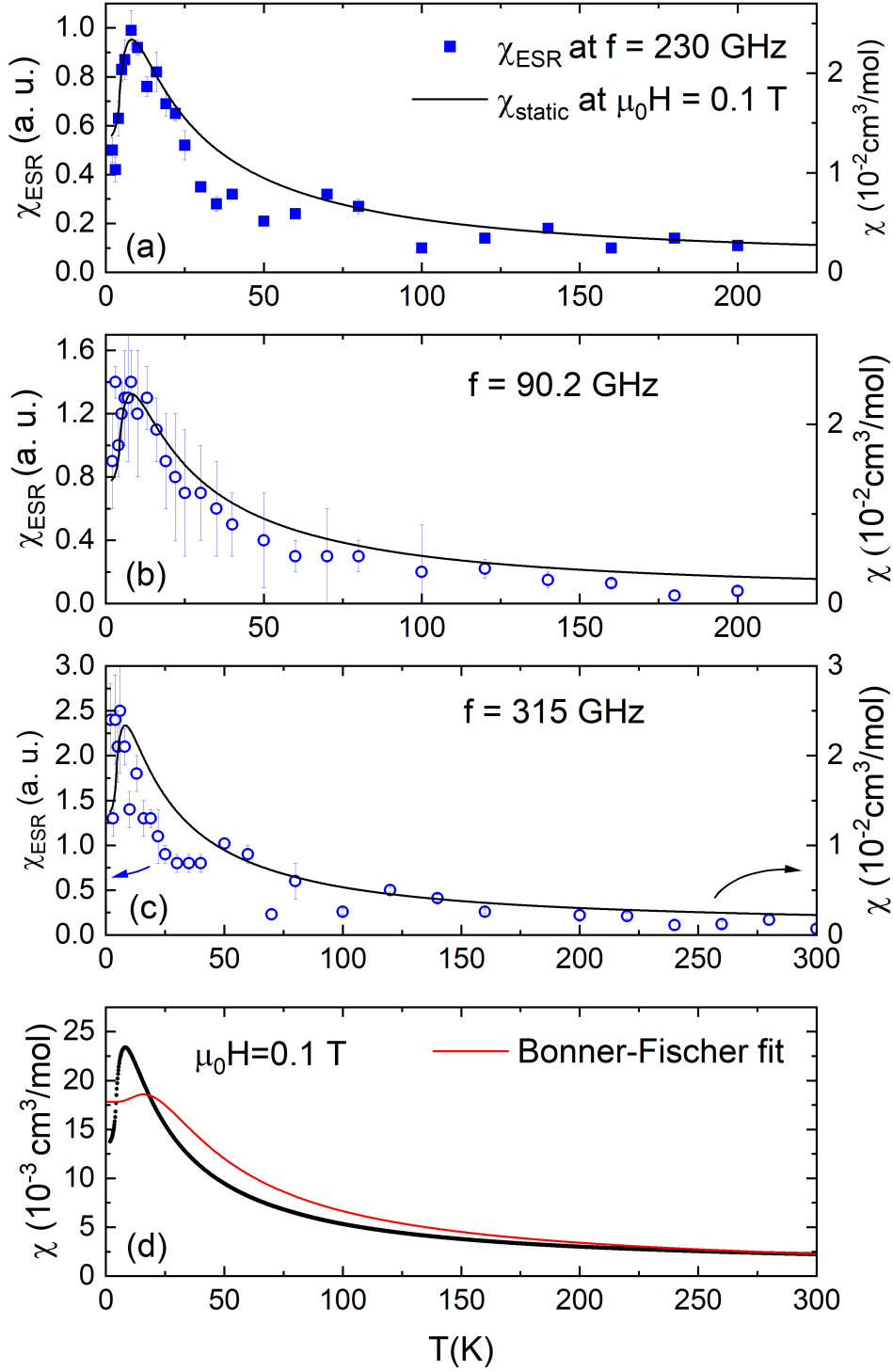


Figure 4.21: Comparison between ESR susceptibility for 230 GHz in the loose powder sample (a) and 90.2 GHz (b) and 315 GHz (c) in the fixed powder sample of $\text{PbCuSeO}_4(\text{OH})_2$ and static magnetic susceptibility at $B = 0.1$ T as well as a Bonner-Fisher fit to the static susceptibility (d). Static susceptibility data was obtained by Daniel Knauer [18].

relaxation time, which in turn increases the linewidth of the resonance feature [75]. Especially in 1D materials, quantum fluctuations are enhanced [76]. This broadening towards T_N can be analysed by:

$$\Delta H(T) = \Delta H_\infty + C[(T - T_N)/T_N]^{-p}, \quad (4.6)$$

which contains a temperature independent and a temperature dependent part [4, 75]. The exponent of this so called critical analysis ideally sheds light on the effective dimensionality of the system [40]. In the following an attempt on a critical analysis is made. Since X-band data obtained in a resonant cavity at different temperatures is missing for franksousaite, the data obtained in the high-field setup is used. This has the disadvantage that there is no cavity, which influences the linewidth determination. The linewidth of an absorption spectrum is extracted by a fit to the data. Different fit approaches to the datasets are described in detail in the appendix.

The temperature dependence of the linewidth obtained from the fit of two simple Lorentz curves and the EasySpin powder simulation to the 90.2 GHz data are shown in figure 4.22. The linewidth extracted from the EasySpin fit does not show any clear trend and seems to be roughly constant in temperature. The same holds true for the linewidth of the second peak in the Lorentz fit (corresponding to the green quasi-paramagnetic resonance branch in the frequency-field diagram). Only the first peak (black resonance branch) of the Lorentz fit shows linewidth broadening with decreasing temperature.

In figure 4.23 the extracted linewidth vs. temperature is shown for both peaks of the loose powder resonance at 230 GHz (see fig. 4.15). A clear trend in the temperature dependence of the linewidth of the second peak (green branch) can not be observed due to the strong variance of the data points. The first peak (black branch) shows increasing linewidth with decreasing temperature for temperatures above T_N . These trends are similar to what was observed at 90.2 GHz in the fixed powder, which is not surprising as the analysed features are the same but only the applied frequencies are different.

Thus, only peak one (the peak at lower magnetic field corresponding to the black branch) both at 90.2 GHz and 230 GHz shows a temperature dependence for the linewidth, which could be described by the critical equation. Was the linewidth completely constant with temperature, it would mean that the spin-spin interactions do not change significantly with temperature. This might be expected in a paramagnet. Despite it being unlikely to be true, the noncritical behavior of the linewidth of the main peak could thus be another indication for it to belong to a paramagnetic excitation. Critical behavior, which could be relevant for the linewidth of the first

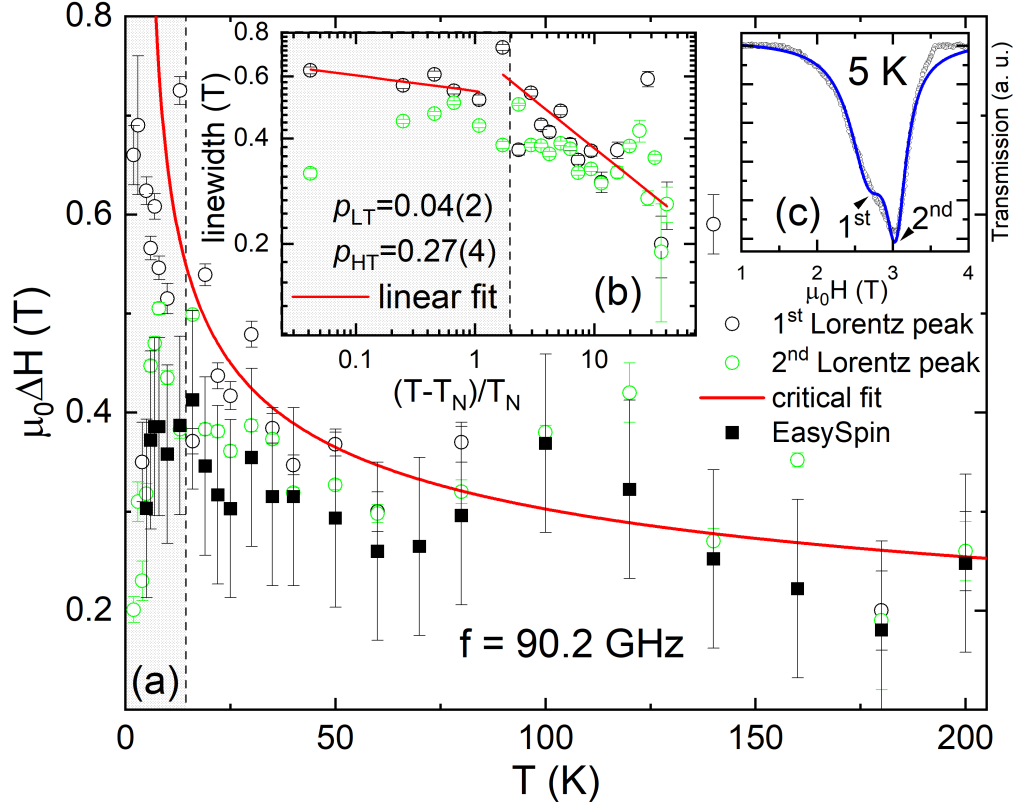


Figure 4.22: (a): FWHM linewidth vs. temperature obtained from two combined Lorentz curves and an EasySpin simulation fitted to the 90.2 GHz spectra and a critical fit (solid red line) to the first Lorentz peak above 13 K. The insets show (b) a log-log-plot with the reduced temperature on the x-axis ($T_N = 4.8$ K) and linear fits to the first Lorentz peak above and below 13 K and (c) the corresponding resonance feature at 5 K to point out the first and second resonance peak. p_{LT} and p_{HT} are the slope obtained from the linear fit in the low temperature range below 13 K and the high temperature range above 13 K. The slope of the linear fit corresponds to the exponent in the critical fit.

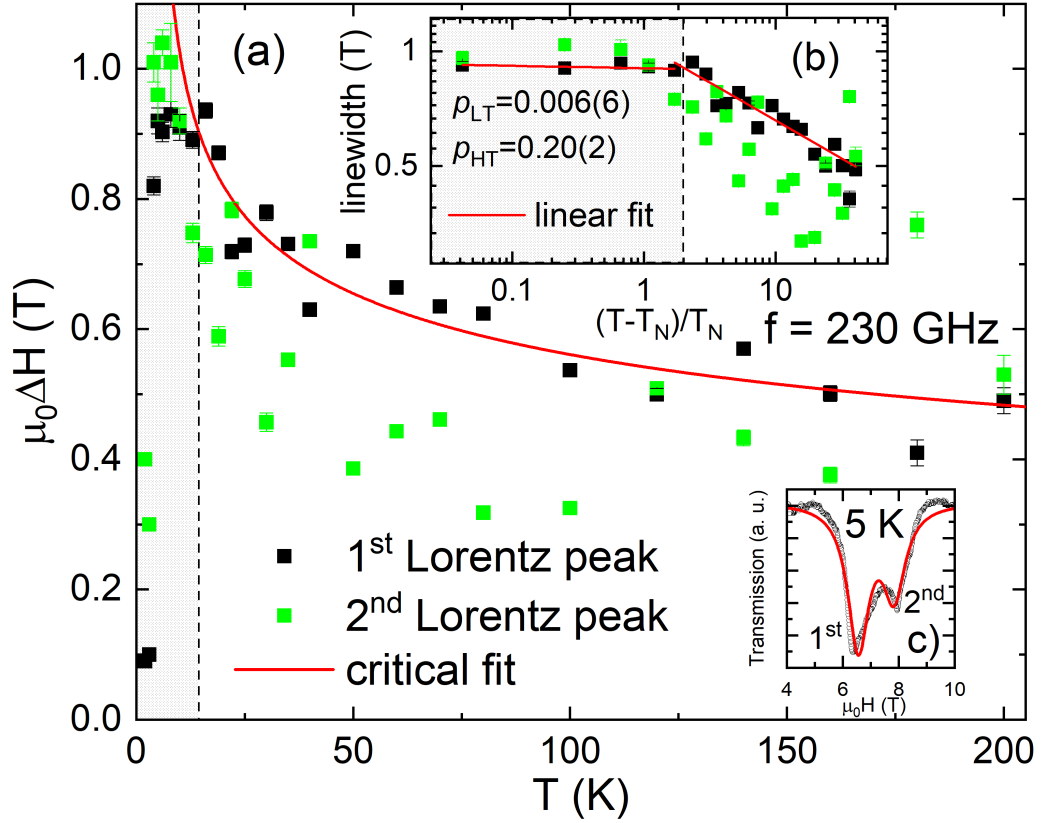


Figure 4.23: (a) FWHM linewidth vs. temperature obtained from Lorentz fits to the 230 GHz spectra and a critical fit (solid red line) to the data points of the first Lorentz peak for temperatures above 13 K. The insets show (b) a log-log-plot with the reduced temperature on the x-axis ($T_N = 4.8$ K) and linear fits to the data points of the first Lorentz peak for temperatures above and below 13 K and (c) the resonance feature at 5 K to point out the first and second resonance peak. p_{LT} and p_{HT} are the slope obtained from the linear fit in the low temperature range below 13 K and the high temperature range above 13 K. The slope of the linear fit corresponds to the exponent in the critical fit.

peak, is easier to see in a log-log-plot with the abscissa being the reduced temperature with $T_N = 4.8$ K, since a linear behavior would be expected. Such a plot is shown in the inset of figures 4.22 and 4.23 respectively. While two linear regimes are clearly observable at 230 GHz, the data at 90.2 GHz shows larger variance but seems to follow the same trend. A linear plot to both regimes (red lines) yields the p-values 0.04(2) and 0.27(4) at 90.2 GHz as well as 0.006(6) and 0.20(2) at 230 GHz for the low temperature and high temperature regime respectively. For a uniform Heisenberg chain with *easy*-axis anisotropy $p = 0.75$ is expected [77], while $p = 1$ holds for a quasi-1D chain where weak interchain interactions are also taken into account [78]. Values of $p = 0.5 - 0.8$ were observed in linarite [40] and $p = 0.55$ in LiCuVO_4 [79], while higher values of 1.2 and 2.5 were observed in other 1D spin-chains [80, 81]. Whereas a value of $p = 2.5$ is closer to the prediction made for classical spin chains, where $p=3$ is expected [81], than to the above mentioned predictions for quantum spin chains. Indeed the system of ref. [81] has a spin of $S = 5/2$, which is reasonable to be described classically. The very low p-value near the ordering temperature (below 13 K, shaded area in figs. 4.22 and 4.23) suggests that critical broadening slows down in this regime and thus the critical fit fails. This behavior was also observed in $\text{NaCuFe}_2(\text{VO}_4)_3$ and $\text{LiCuFe}_2(\text{VO}_4)_3$ [82] as well as in several 2D materials [4, 83]. In the latter case the lower p-value near the ordering temperature is attributed to the onset of 3D-correlations [4]. In the high temperature regime the p-values are still much smaller than theoretically expected but the power law fit seems to describe the data reasonably well. In 2D materials lower than expected p-values were observed for materials with competing interactions [83].

The critical power law fit describes the experimental data reasonably well even at very high temperatures. This suggests that short range correlations prevail up to these temperatures and mask spin-lattice relaxations, which would show up as a linear increase with temperature [84, 85]. Such high temperature behavior as seen here in franksousaite is untypical for quantum chains, which typically show linear dependence of the linewidth on temperature for $T < J$ (if anisotropic exchange or dipole-dipole interaction is dominant. For a staggered field $\Delta H \propto T^{-2}$) [86, 87, 76]. This would correspond to temperatures below ~ 100 K in franksousaite. Such linear behavior can not be observed in linarite either [40]. For spin chains such as franksousaite or linarite with fm NN and afm NNN exchange Krug von Nidda et al. have found an empirical equation to describe the linewidth with temperature [79]. However, this is based on experimental data also showing increasing linewidth with increasing temperature and thus can not be used here [79]. Since franksousaite is not showing any typical 1D behavior of the linewidth, this could be a further indication for significant interchain interactions.

At temperatures above the exchange energy one would expect the linewidth to assume

a constant value. This value is related to the exchange coupling and the anisotropy in the system. Possible contributions to the anisotropy are dipole-dipole interactions, anisotropic exchange or Dzyaloshinskii-Moriya (DM) interaction [85, 88]. The linewidth is given in cgs units as [88]

$$\Delta H \approx \frac{\hbar^2}{g\mu_B|J|}M \quad (4.7)$$

with M being the second moment. If the exchange energy is larger than the Zeeman energy the second moment for dipole-dipole interaction is given as:

$$M^{DD} = \frac{3g^4\mu_B^4}{2\hbar^2} \left(\sum_{i>j} \frac{1}{r_{ij}^3} \right)^2 S(S+1)(1+\cos^2(\theta)) \quad (4.8)$$

with r_{ij} the distance between neighbouring copper ions and θ the angle between the applied magnetic field and the chain axis. For anisotropic exchange the second moment is given as

$$M^{AE} = \frac{3}{2\hbar^2} A^2 S(S+1)(1+\cos^2(\theta)) \text{ with } |A| = \left(\frac{\Delta g}{g}\right)^2 |J| \quad (4.9)$$

and Δg being the difference between 2 and the average g -factor. For DM interaction the second moment is

$$M^{DM} = \frac{1}{6\hbar^2} |D|^2 S(S+1)(2+\sin^2(\theta)) \text{ with } |D| = \frac{\Delta g}{g} |J| \quad (4.10)$$

and the DM vector D perpendicular to the chain direction. The DM vector is perpendicular to the chain direction in linarite [62] and hence this holds true in franksousaite as well as both compounds are isostructural to each other. The DM interaction is allowed because of the monoclinic symmetry of the crystal [62]. The equations for A and D in eqs. 4.9 and 4.10 are order of magnitude estimates. The estimate for A only holds true if the ground state is an orbital singlet and when the spin-orbit coupling is small compared to the crystal field splitting of orbital states [23]. Since the sample studied here is a powder the angular part of eqs. 4.8, 4.9 and 4.10 with respect to the external field is averaged to 1.57 and 2.43 respectively. With the g -values $g_{easy} = 2.27(7)$ and $g_{hard} = 2.06(8)$ obtained earlier the average g -value is $\bar{g} = 2.17$ and the difference to two is roughly $\Delta g = 0.17$. The distance between two neighbouring copper ions is $r_{Cu-Cu} = 2.8727(15)$ Å [17]. Using the larger exchange coupling of $J_1 = -103$ K [17] one obtains for the dipole-dipole contribution $\Delta H^{DD} = 0.18(6)$ mT, for the anisotropic exchange $\Delta H^{AE} = 0.01(3)$ T and for the DM interaction $\Delta H^{DM} = 0.2(3)$ T. Clearly, only the DM interaction can be responsible for a linewidth with the same order of magnitude as observed in the ex-

perimental data at high temperatures (0.3 T and 0.5 T, respectively). Hence, one would be tempted to assume that the DM interaction is dominant in describing ΔH in this system. If it was, one would also expect a $1/T^2$ behavior in the linewidth at low temperatures, which the data however does not show. Additionally, it was argued, that the rough estimate using $|D| = \frac{\Delta g}{g}|J|$ is not sufficient in 1D chains [89]. On the contrary theory predicts the DM contribution to be comparable to the symmetric exchange in 1D chains [89]. A different approach towards explaining the unusually large linewidth observed in copper oxide chains was taken by Kataev *et al.* [73]. They argue that the 90° Cu-O-Cu bonds suppress the isotropic exchange and enhance the anisotropic superexchange through ring exchange [73]. This ring exchange is ferromagnetic and favours out-of-plane *easy*-axis anisotropy. *Easy*-axis anisotropy is also observed here. Keeping this in mind, Krug von Nidda *et al.* have found a formalism to calculate the corresponding linewidth [79, 90]. Following their calculations a linewidth one order of magnitude smaller even (0.002(3) T) than for the conventional estimate was found for franksousaite. The corresponding equation however is reciprocally proportional to the exchange interaction, which so far has only been calculated for franksousaite and, thus, might differ in reality. Nevertheless, when calculating the anisotropy parameter from the high-temperature linewidth (0.3 T), one gets an anisotropy parameter of roughly 5 K, which is five times larger than the estimate given above (ca. 1 K) and corresponds to about 100 GHz, which is not far of the zero field gaps observed in the frequency-field diagram (fig.4.7). One can conclude, that anisotropy plays a major role in franksousaite and standard symmetric anisotropic exchange might not suffice to explain this large contribution. Note however, that all quantitative values in this discussion need to be treated with caution, as the setup without resonance cavity influences the linewidth.

4.1.3 Conclusions

Powder samples of franksousaite, a quasi-1D quantum spin-chain closely related to the well studied linarite, was investigated by means of high-frequency, high-field ESR. The system orders antiferromagnetically at 4.8 K and undergoes a spin-flop transition at 2.8 T. The magnetic phase diagram is complex, showing at least three phases. The temperature evolution of the resonance position shows that local fields develop already at about 70 K, which is roughly $15 \cdot T_N$. Spin fluctuations prevailing up to such high temperatures are typical for low dimensional or frustrated systems. The shift of the spectral weight to higher fields in the fixed powder as compared to the loose powder as well as the temperature evolution of the *g*-value imply *easy*-axis anisotropy. In the ordered phase four resonance branches can be observed. In the low field phase one resonance branch exhibits a gap of 82.5(14) GHz and the other branch is gapless and linear. It prevails in all field-induced phases and its

effective g -value of 2.04 corresponds to the high temperature paramagnetic value of the same feature. Altogether this branch behaves like a paramagnetic branch in all aspects except for its strong signal in the ordered states. In the field-induced phase two more linear resonance branches occur. One has a negligible zero-field gap and the other amounts to 32.9(14) GHz. The gapless branch shows a significant change in resonance position (concomitant with the appearance of a zero field gap) at the high-field phase boundary, indicating a change in anisotropy. Overall, the frequency-field diagram does not resemble the diagram expected for a spiral ground state. This observation and the *easy*-axis anisotropy are in strong contrast to the related linarite.

The ESR susceptibility shows typical low dimensional behavior while the linewidth vs. temperature does not. The broad linewidth at high temperature is attributed to unusually large symmetric anisotropy.

Future studies should include elastic and inelastic neutron scattering to gain information about the spin structure in the ordered states and the magnitude and sign of the exchange interaction. With this information an attempt on a theoretical model describing the observed magnon excitations could be made.

4.2 GdInO₃

4.2.1 Introduction

Multiferroic materials are of high interest in current research, as they are promising candidates for technological applications, e.g. in magnetoelectric memory and storage devices [13, 14]. Furthermore, studying their physical properties allows to elucidate on the interplay of magnetic and electronic behavior. Materials in the RInO₃ family (R represents a rare earth ion) have recently been found to show geometric ferroelectricity [91]. For R = Eu, Gd, Tb, Dy, Ho, and Y the lattice assumes a hexagonal structure in the P6₃cm space group isostructural to LuMnO₃ [92] (fig. 4.24). In this structure the R ions occupy two distinct positions, which have a noncentrosymmetric distortion, causing geometric ferroelectricity [91]. In GdInO₃ at temperatures above 1573 K the structure changes to the high-symmetry P6₃mmc space group, which is paraelectric [91]. Although ferroelectricity could not be confirmed experimentally in GdInO₃ at first [93, 94], a Z₆ vortex domain structure observed in a GdInO₃ single crystal implies the ferroelectric nature of this material [95].

GdInO₃, which is the subject of this thesis is unique among the RInO₃ because of its half-filled 4f shell with zero orbital momentum and a large single ion spin of $S = 7/2$. This renders GdInO₃ a prime candidate to study semiclassical spins on a 2D frustrated lattice. The Gd ions are arranged on two sublattices, where one sublattice forms hexagons while ions of the other sublattice occupy the centre of each hexagon of the first sublattice (fig. 4.24). This structure is often referred to as a filled honeycomb lattice but can also be described as a distorted triangular lattice. Due to its geometry, there exist two main exchange interaction paths within the filled honeycomb lattice J_1 and J_2 (fig. 4.24). Both are assumed to be antiferromagnetic and thus the material is the more frustrated the closer the exchange parameters are in value [96], as both afm interactions on the triangle can not be satisfied simultaneously. From DFT+U calculations it is assumed that $J_2/J_1 \approx 3$ [96], however, a more recent study taking into account a small *easy*-axis anisotropy assumes that $J_1 > J_2$ and that both values are similar [97]. The observation of *easy*-axis anisotropy would be in line with a 1/3 magnetisation plateau at roughly 3 T for magnetic fields applied along the *c*-axis [97, 98, 19]. Thermodynamic measurements reveal a magnetic phase transition between 2.3 K and 1.8 K, below which the spins order antiferromagnetically [99, 96, 95, 97, 98, 19]. This is shown by the negative Weiß (Θ) temperature obtained from the inverse susceptibility. An overview of different Θ obtained so far is given in table 4.1. The ratio of $|\Theta|/T_N > 3.5$ is indicative of frustration in GdInO₃. Very similar saturation magnetisation values for magnetic fields along the *c*-axis and the *ab*-plane suggest a very small *g*-factor anisotropy, while magnetisation measurements at lower fields suggest planar anisotropy within

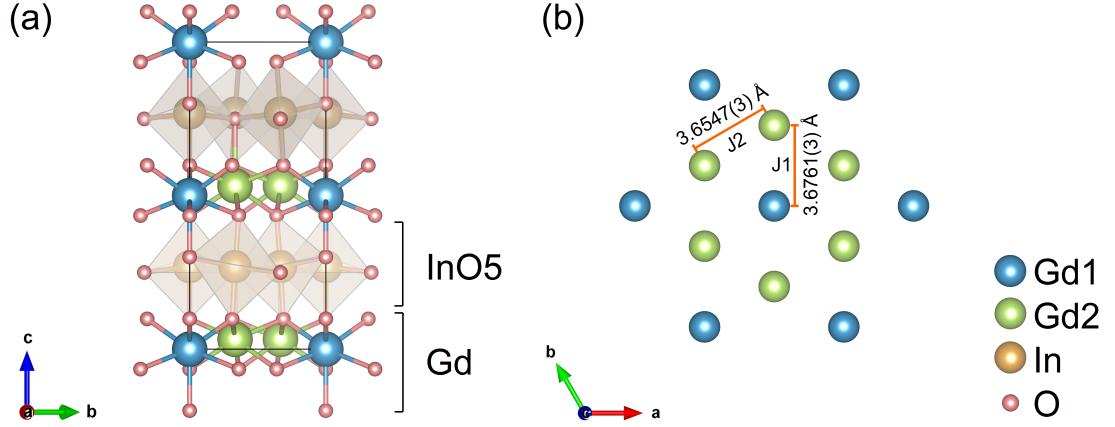


Figure 4.24: (a) Schematic of the crystal structure of GdInO₃ along the [100] projection. (b) In-plane filled-honeycomb arrangement of two inequivalent atomic sites of Gd³⁺ ions. J_1 and J_2 represent two magnetic exchange interactions that are distinguished by symmetry. Taken from [19].

the *ab*-plane [19]. A 1/3 magnetisation plateau is consistent with an up-up-down phase, which is common in triangular lattices [19]. Fig. 4.25 shows a preliminary phase diagram of GdInO₃ for fields applied within the plane and perpendicular to it.

In the following chapters ESR data obtained from measurements performed with varying angle between the applied magnetic field and the crystallographic *c*-axis of GdInO₃ as well as from measurements obtained at varying temperatures and frequencies both on single crystals and polycrystalline powder of GdInO₃ are shown and discussed. The samples were provided by Ning Yuan [19].

	T_N (K)	θ (K)	$ \theta /T_N$	Source
polycrystalline	<1.8	-50	>28	[99]
	0.475	-11.8(6)	26	[100]
	2.1	-7.41	3.5	[98]
computational	<1.8	-11 to -22	>12	[96]
single crystal average	2.1	-11	5	[19]
single crystal $\mu_0 H \parallel c$	-	-15.14	>8	[95]
	2.3	-13.06	5.7	[97]
single crystal $\mu_0 H \perp c$	-	-11.7	-	[95]
	2.3	-9.66	4.2	[97]

Table 4.1: Comparison of the Néel- and Weiß-temperature for GdInO₃ as reported in the literature.

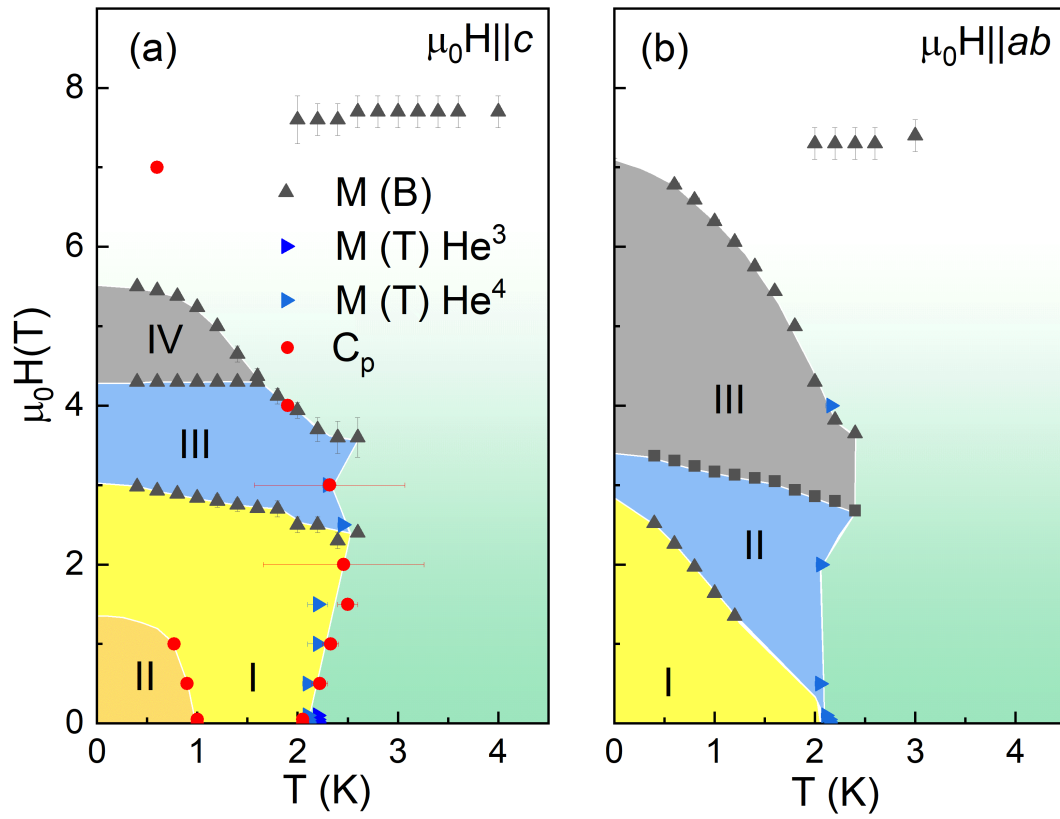


Figure 4.25: Phase diagrams of GdInO_3 constructed from magnetisation and specific heat measurements (a) for magnetic fields applied perpendicular to the ab -plane and (b) for magnetic fields applied within the ab -plane. From [19].

4.2.2 Results and Discussion

ESR Data at Different Angles of the Applied Magnetic Field

In order to investigate the magnetic anisotropy and its physical origins in the GdInO_3 system, the dependence of X-band ESR spectra on the angle between the applied magnetic field and the crystallographic c -axis of GdInO_3 single crystals was studied at different temperatures. Fig 4.26 shows the angle-dependence of the spectra at 4 K and 150 K. Already at a first glance one can see variations in the linewidths and amplitudes of the spectra with the angle of the applied magnetic field, which are different at 4 K and 150 K. To extract the variation of the linewidth with angle, Lorentz derivatives were fitted to the spectra. Due to the large linewidth, which is of the order of the resonance field, the counter resonance is taken into account as well as admixture of dispersion when fitting the spectra (see section 2.2 for details). Fig. 4.27 shows exemplary fits to the spectra for three different temperatures (4 K, 15 K and 150 K) as well as different angles corresponding to the applied magnetic field being along the c -axis, ab -plane and the magic angle. The magic angle refers to the angle where the linewidth is smallest, which in this case is 55° away from the c -axis, and will be discussed in more detail later. The fits describe the data perfectly.

The angle-dependence of the linewidth is extracted from the fits and shown in fig. 4.28. The data at 300 K was obtained in a different setup and fitted by a Lorentz derivative without considering a counter resonance but with admixture of dispersion, because this routine gave better fit results. The value of Θ was chosen such that 0° corresponds to the external field being aligned with the c -axis. From now on - unless stated otherwise - given angles will always correspond to the angle between the c -axis and the applied magnetic field. At high temperatures the linewidth is maximal at 0° , minimal at about 55° and exhibits another local maximum at 90° . With decreasing temperature down to 30 K the global maximum decreases, the local maximum increases and the minimum gets less pronounced. The same qualitative angle dependence is still visible but it seems to be slightly shifted towards higher angles at 20 K. At 15 K no periodicity can be observed. Below 15 K the qualitative behavior changes drastically, such that the linewidth is minimal at 0° and maximal at 90° . The overall linewidth increases down to 4 K and the angle-dependence becomes more pronounced. At about 115° there is a slight drop in linewidth visible both for 10 K and 4 K. A similar drop is observable at -35° and 4 K. At 4 K the two-fold rotational symmetry of the linewidth is slightly broken, as the amplitude of the curve describing the linewidth with respect to the angle of the applied magnetic field is more pronounced for angles higher than 50° . Possible explanations could be that the sample was slightly tilted or tensions were build up in the sample due to the ferroelectricity or the different environments at opposite crystal sides (the glass

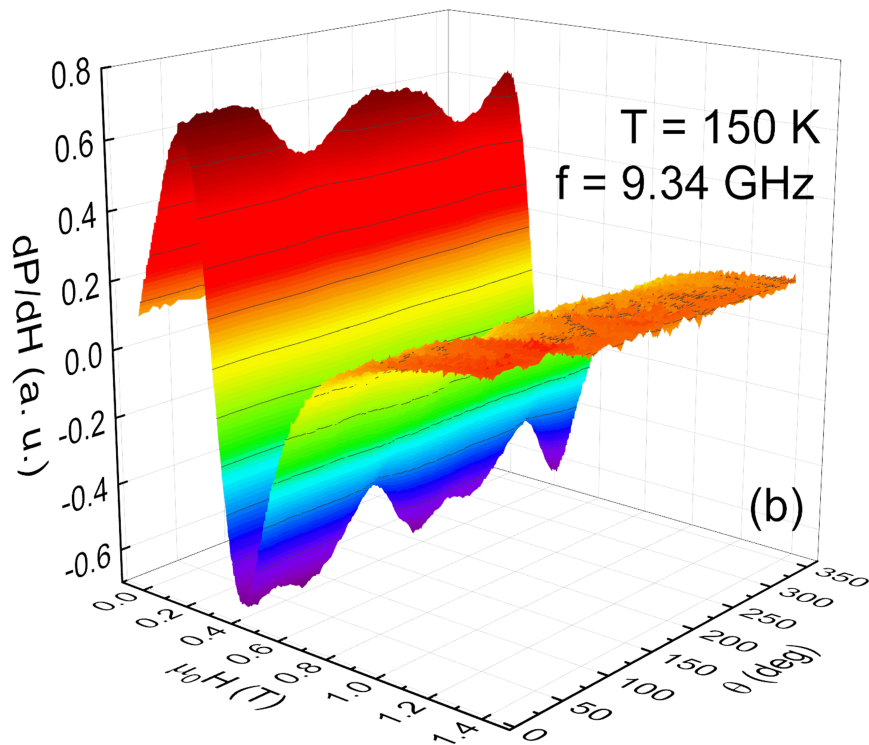
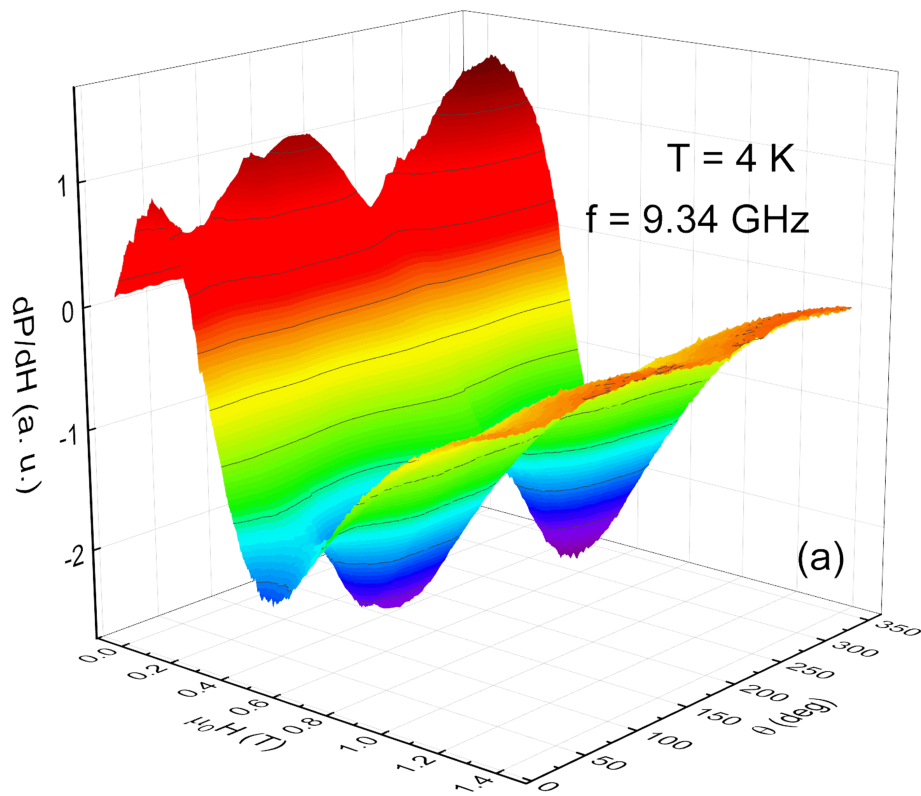


Figure 4.26: Angle-dependence of the X-band ESR spectra measured at (a) $T = 4$ K and (b) $T = 150$ K. An angle of 125° corresponds to the applied magnetic field along the c -axis and 35° correspond to the applied magnetic field along the ab -plane. Corresponding individual spectra can be found in the appendix (fig. 6.13).

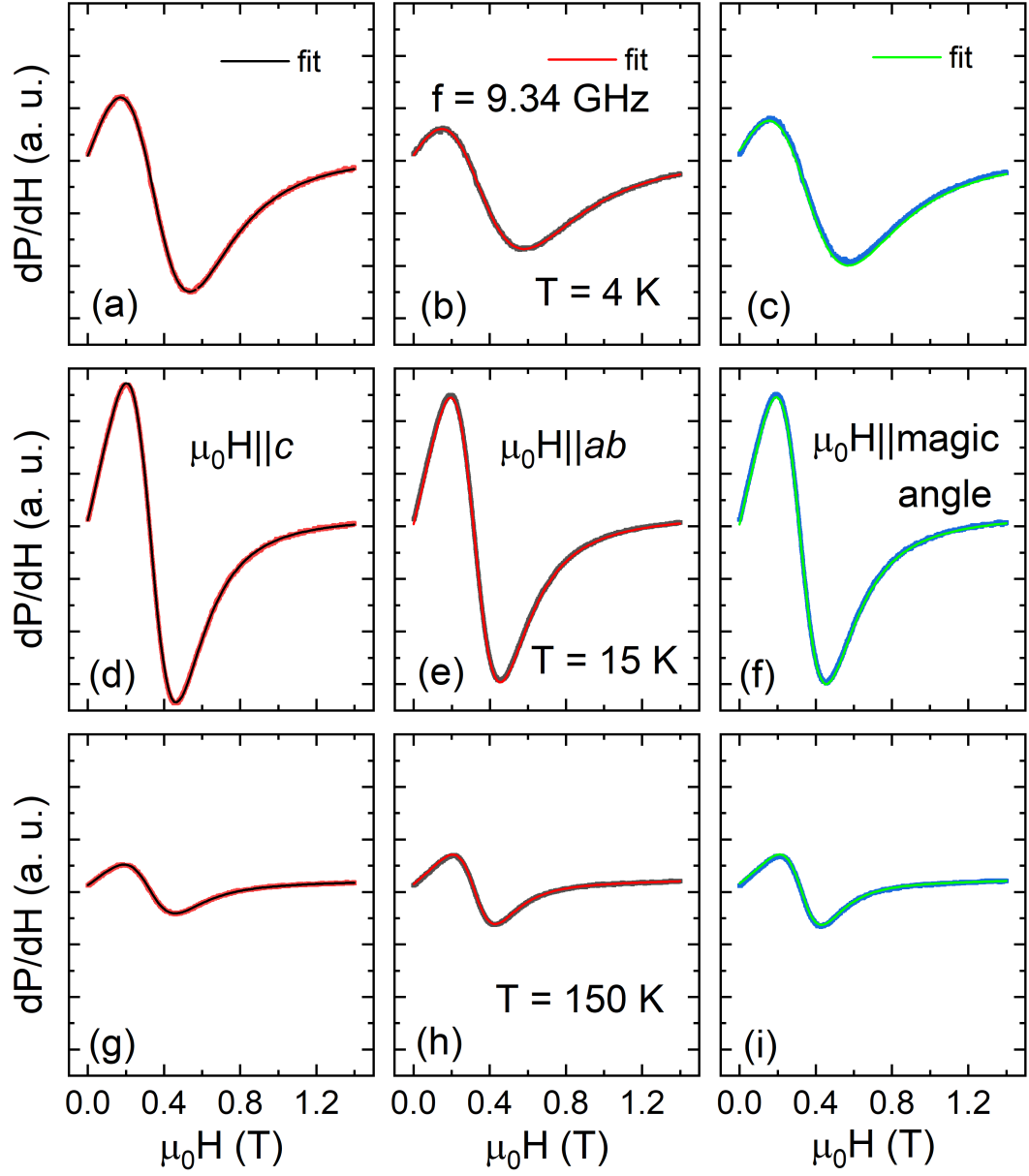


Figure 4.27: X-band ESR spectra at 4 K (a, b, c), 15 K (d, e, f) and 150 K (g, h, i) and for different directions of the applied magnetic field with respect to the crystallographic axes. Solid lines are Lorentz derivative fits taking counter resonance and admixture of dispersion into account.

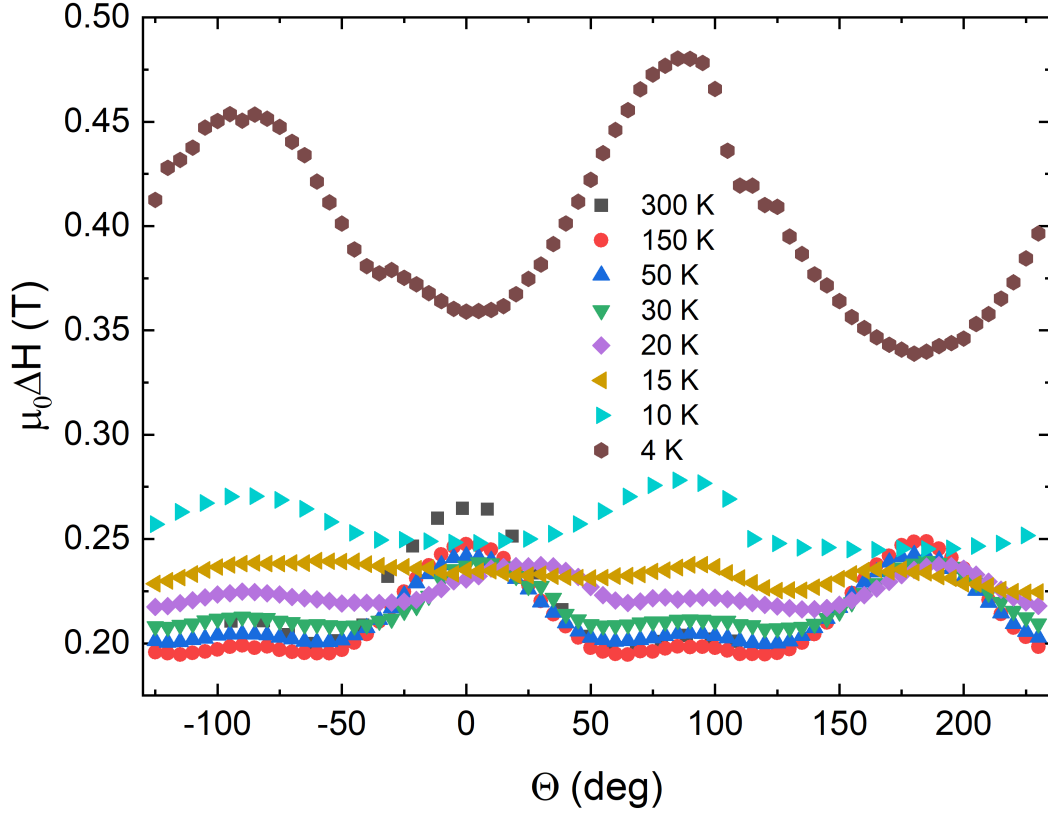


Figure 4.28: Angle-dependence of the FWHM linewidth of the X-band ESR resonance feature at different temperatures. Θ is the angle between the c -axis and the external magnetic field.

tube on the one side and the more pliable parafin on the other side).

The appearance of a minimum in the linewidth at 55° - as can be observed in GdInO_3 at temperatures between 300 K and 30 K - is typical for 2D materials [4]. In 2D materials this behavior is caused by the dominating spin diffusion, which yields an angle-dependence of the resonance linewidth of $\Delta H \propto (3\cos^2(\Theta) - 1)^2$, which is zero at 54.7° [4]. However, spin diffusion also causes the resonance to have a non lorentzian shape [101], which is clearly not the case in GdInO_3 , as the Lorentz fits perfectly agree with the experimental data. Additionally, Gordon *et al.* have calculated the in-plane and out-of-plane exchange interactions for GdInO_3 with DFT+U and DFT+U+SOC, for different values of U [96]. When averaging the calculated values for the different approaches one obtains, $J_1 = -0.3(1)$ K, $J_2 = -0.9(4)$ K, $J_3 = 0.012(1)$ K and $J_4 = 0.019(12)$ K, where J_3 and J_4 are inter-plane exchange energies. Thus, according to these numerical studies the exchange coupling within the planes is at most 75 times larger than the coupling between the planes. As in-plane and interplane couplings can have a difference of four orders of magnitude in some 2D materials [102], the difference predicted for GdInO_3 is on the smaller side.

In the following it is shown that the contributions to the linewidth both from dipole-dipole interactions as well as from anisotropy due to crystal field effects also yield a $\Delta H \propto (3\cos^2(\Theta) - 1)^2$ angle-dependence of the linewidth in specific cases.

At high enough temperatures where the linewidth is constant with respect to temperature it is given by the second moment of the resonance [103]:

$$\Delta H = \frac{h^2 M}{g\mu_B \sqrt{zS(S+1)}|J|} \quad (4.11)$$

with z being the number of nearest neighbours and J the dominant exchange coupling in the system. Any anisotropy in the system could contribute to this linewidth and the second moment for each contribution is given by a different expression. The linewidth contribution of the anisotropic exchange (both symmetric and antisymmetric) is roughly dependent on the anisotropy of the g -factor and the exchange coupling (compare eqs. 4.9 and 4.10 and the section on the theoretical background). Since Gd^{3+} has zero orbital moment and relatively small exchange coupling this contribution is expected to be small. Indeed taking $g = 2.06$ as obtained from the X-band data of measurements performed at different temperatures discussed in the next section and the weighted average of the in-plane exchange interactions $J_{\text{ave}} = (2J_1 + J_2)/3 = -0.5(2)$ one gets with $\Delta g = 0.06$: $\Delta H^{AE} = 0.7(3) \times 10^{-3}$ mT and $\Delta H^{DM} = 0.09(4)$ mT, being negligibly small. This leaves anisotropy due to dipole-dipole interactions or crystal field effects as possible contributions. Since Gd^{3+} has a half-filled shell and, thus, quenched orbital moment, crystal field splitting is expected to be a second order effect. This means that small admixtures of excited states with non-zero orbital moment to the ground state can still cause weak spin-orbit coupling. Thus, the crystal field could cause anisotropy for Gd^{3+} in a crystalline environment. Indeed, single-ion *easy*-plane anisotropy of Gd^{3+} ions in a trigonal point symmetry has been found to be of the order of 0.25 K in $(\text{Y}_{1-x}\text{Gd}_x)_2\text{Ti}_2\text{O}_7$ [104], which was of similar magnitude as the exchange interaction and one order of magnitude larger than the dipole-dipole interactions in the respective compound. Hence, such an anisotropy can lift the degeneracy of the eight spin states of Gd^{3+} . This causes the resonance between the eight levels to be at slightly different magnetic fields. Thus, provided sufficient experimental resolution one would expect to observe several independent resonance features as long as all levels are at least partially populated. For systems with strong enough exchange coupling, only one feature will be observed due to exchange narrowing. However, since the spacing depends on the $\mathbf{g}$ - and $\mathbf{D}$ -tensor and the angle between the c -axis and the applied magnetic field, both the resonance position as well as the linewidth show angle-dependence. This angle-dependence is different for cases where the exchange anisotropy is larger than the Zeeman energy at the resonance field strength and cases where it is smaller than the respective Zeeman

energy. In the latter case for axial, hexagonal, tetragonal, or trigonal symmetry the resonance field position can be described as: $H = \frac{h\nu}{g\mu_B} - \frac{1}{2} \frac{D}{g\mu_B} (3\cos^2(\Theta) - 1)(2m_s - 1)$ with m_s the z-component of the spin and g assumed to be isotropic. At the magic angle, the energy levels cross over, such that their splitting is minimal at this angle (see [20] for more details). The angle-dependence of the linewidth can again be described by $\Delta H \propto (3\cos^2(\Theta) - 1)^2$. Similarly, the second moment due to dipole-dipole interaction in the case of dominating Zeeman energy is given as [20]:

$$M_Z^{DD} = \frac{3S(S+1)g^4\mu_B^4}{4h^2} \sum_{i \neq j} \frac{3\cos^2(\Theta_{ij}) - 1^2}{r_{ij}^6}, \quad (4.12)$$

where r_{ij} is the distance between nearest neighbours and Θ_{ij} is the angle between the external field and the direction of r_{ij} ; g is assumed to be isotropic.

In the opposite case where the exchange energy dominates over the Zeeman energy the second moment arising from the anisotropy caused by the crystal field is [105]:

$$M^A = \frac{4S(S+1) - 3}{10} D^2 (1 + \cos^2\Theta) \quad (4.13)$$

where D is the axial anisotropy parameter. While for the dipole-dipole interaction the second moment is given as [106]:

$$M^{DD} = \frac{3g^4\mu_B^4S(S+1)}{2h^2} \sum_{i \neq j} \frac{1 + \cos^2\Theta_{ij}}{r_{ij}^6}. \quad (4.14)$$

With the help of some simple algebra one can obtain the angle-dependence with respect to Θ , the angle between the c -axis and the applied magnetic field, which gives a sine-like dependence. In order to decide which of the two scenarios holds true in GdInO_3 the exchange energy and Zeeman energy at resonance are estimated. With J_{ave} as estimated above the exchange energy is $JS^2 = 5(2)$ K while the Zeeman energy amounts to $g\mu_B\mu_0H_{\text{res}}/k_B = 0,4$ K with $\mu_0H_{\text{res}} \approx 0.32$ T. Hence, the exchange energy is about one order of magnitude larger and the second set of equations should be used for the analysis.

Although quantitatively the angle-dependence at low temperatures is different to the one at high temperatures, one can expect the same qualitative behavior. At low temperatures the linewidth seems to follow a sine-like behavior, as predicted by dominant dipole-dipole interactions. Thus the dipole-dipole contribution to the linewidth at high temperatures is estimated by combining eq. 4.14 with eq. 4.11. The weighted average distance $r_{ave} = (2r_1 + r_2)/3 = 3.6690(3)$ is calculated by taking the distances $r_1 = 3.6761(3)$ and $r_2 = 3.6547(3)$ from [19]. With $g = 2$ and $J_{ave} = 0.5(2)$ K from above the contribution of the dipole-dipole interaction at high

temperatures is thus found to be:

$$\Delta H = 0.0280(110)(2 + \sin^2\Theta) \text{ T} \quad (4.15)$$

with Θ being the angle between the external field and the c -axis. This contribution is subtracted from the linewidth vs. the angle of the applied magnetic field at all measured temperatures. The resulting linewidths are shown in fig. 4.29. The local maximum at 90° is nearly completely vanished after subtraction of the dipolar contribution, which means that the data might not have to be described by an angle-dependence recovering the magic angle. Such an angle-dependence would not be expected for systems with dominating exchange interaction, as was discussed above. The resulting linewidths at high temperatures seem to follow a rough cosine-dependence. This could be reproduced by the angle-dependence due to the anisotropy caused by crystal field effects (eq. 4.13). The magnitude of D can be estimated by the ratio between the linewidth for external fields applied along the c -axis and the ab -plane

$$\frac{\Delta H_c}{\Delta H_{ab}} = \frac{M^{DD}(0^\circ) + M^A(0^\circ)}{M^{DD}(90^\circ) + M^A(90^\circ)} = 1.25(2). \quad (4.16)$$

The numerical value was taken from fig. 4.34. Using the above equation D is calculated to be $D = 5.5 \text{ GHz} \hat{=} 0.26 \text{ K}$, agreeing well to literature values of $4f^7$ ions in different compounds [104, 103]. Using this value the linewidth contribution was calculated and plotted in red in fig. 4.30. It shows that this contribution alone can not reproduce the data. A contribution $\Delta H \propto (3\cos^2(\Theta) - 1)^2$ can not reproduce the data either, as can be seen from the blue curve in fig. 4.30. Consequently a mixture of both models with an additional constant and phase was plotted to the dataset corrected by the dipole contribution:

$$\Delta H_{\text{fit}}(\Theta) = \Delta H_A(1 + \cos^2(\Theta + \phi)) + \Delta H_{\text{magic}}(3\cos^2\Theta - 1)^2 + \Delta H_0 \quad (4.17)$$

As can be seen in fig. 4.29, this fits the data reasonably well, especially at high temperatures. This result suggests that the assumption of dominating exchange energy does not fully hold true and there is still a finite contribution as would be expected in the case of dominating Zeeman energy.

The fit parameters resulting from the fit of eq. 4.17 to the data in fig. 4.29 are listed in table 4.2. The obtained constant offset ΔH_0 is increasing with decreasing temperature. Both ΔH_A and ΔH_{magic} decrease down to $T = 15 \text{ K}$. While ΔH_A decreases further at $T = 10 \text{ K}$ and then increases drastically at $T = 4 \text{ K}$, ΔH_{magic} increases slightly both at $T = 10 \text{ K}$ and $T = 4 \text{ K}$. The ratio between both contributions is more meaningful than the individual values. It stays roughly constant with decreasing temperature down to $T = 30 \text{ K}$. Upon further cooling the crystal

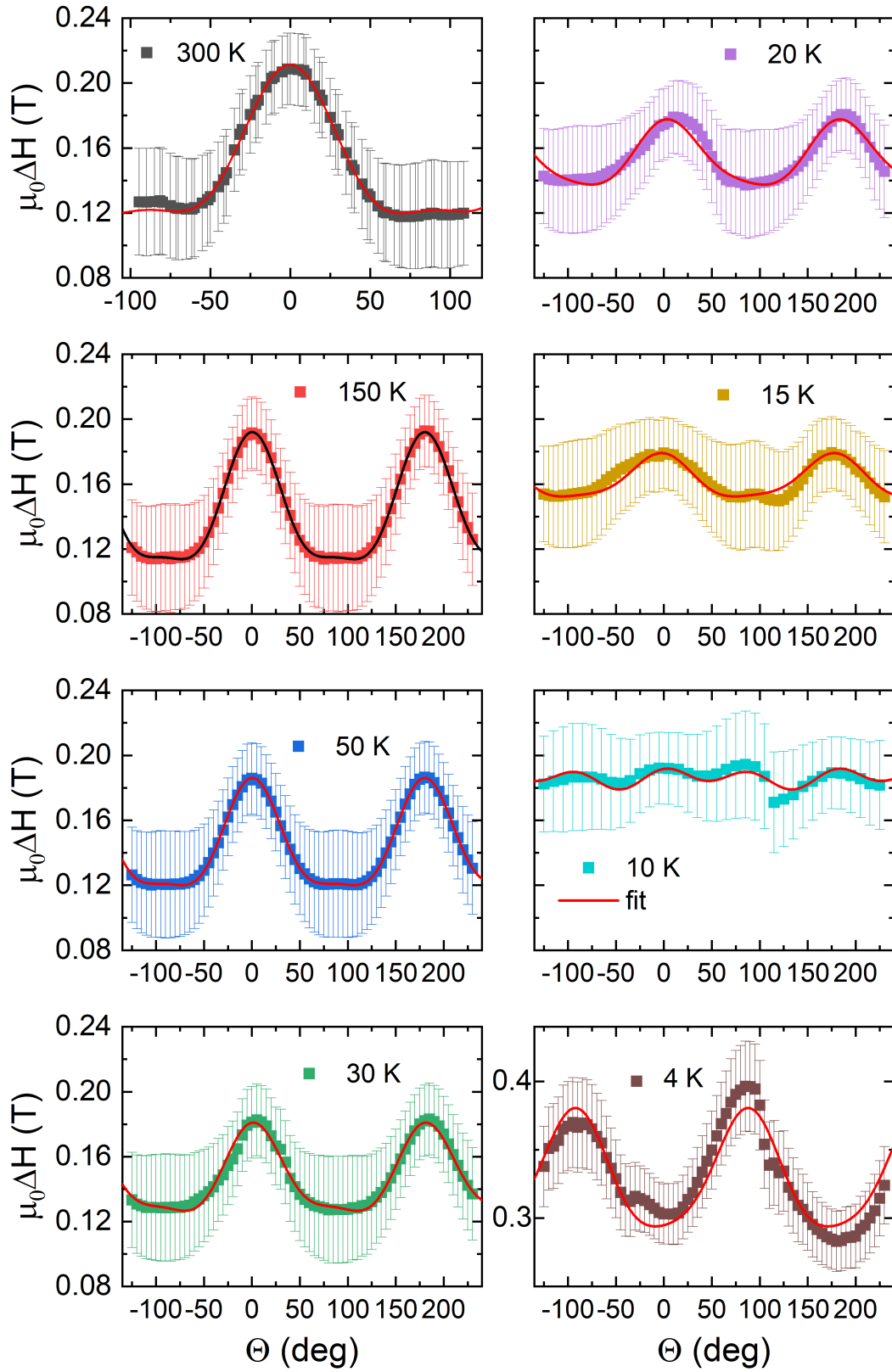


Figure 4.29: Angle-dependence of the FWHM linewidth of the X-band ESR spectra at different temperatures corrected by the high-temperature dipole-dipole contribution (see text for details). Θ is the angle between the c -axis and the external magnetic field. Solid lines are fits to the data (see text for details).

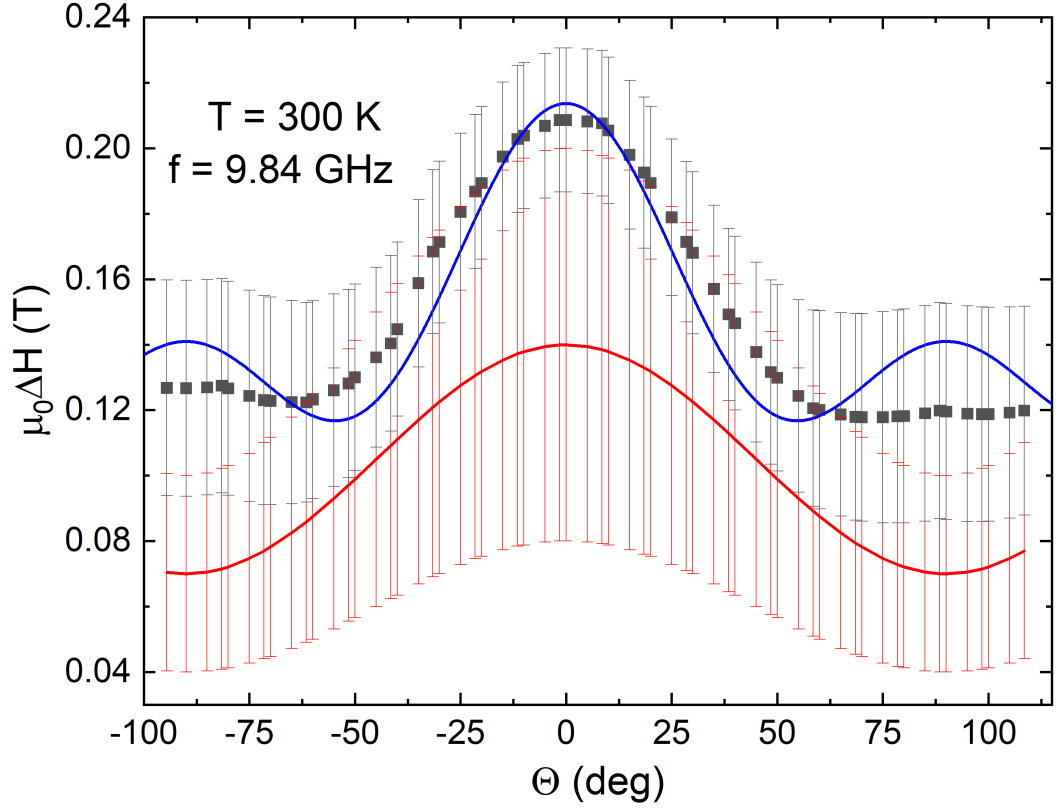


Figure 4.30: Angle-dependence of the FWHM linewidth of the resonance feature at X-band frequency and $T = 300$ K corrected by the high-temperature dipole-dipole contribution. Θ is the angle between the c -axis and the external magnetic field. Solid lines are a fit/model, blue: fit of a $\Delta H \propto (3\cos^2(\Theta) - 1)^2$ contribution only, red: calculated anisotropy contribution due to crystal field effects for dominating exchange coupling (see text for details).

field contribution becomes more dominant at $T = 20$ K, decreases again and becomes seemingly significantly more dominant at the lowest temperature of 4 K. The phase ϕ is negligibly small for $T = 300$ K, 150 K and 50 K. Afterwards the curves seem to be shifted by a few degree in the order of 10. At the lowest temperature there is a phase shift of about 90° , which can easily be explained if one assumes that the dipole-dipole interactions dominantly influence the angle-dependence of the linewidth at low temperatures instead of the anisotropy due to crystal fields. Such a contribution would yield the observed sine-like instead of the cosine-like angle-dependence and was already suggested above. At an intermediate temperature of $T = 10$ K there is a phase shift of about 100° . This can be attributed to the onset of the aforementioned dipole-dipole contribution. The discrepancy to 90° , which would be expected for the sine-like contribution, is feasible considering the overall small variation of the linewidth with respect to the angle of the applied field at 10 K.

T (K)	ΔH_A (T)	ΔH_{magic} (T)	C (T)	ϕ ($^\circ$)	$\Delta H_A/\Delta H_{magic}$
300	0.0507(14)	0.0128(4)	0.0580(20)	1.0(5)	4.0(2)
150	0.0479(5)	0.0097.8(14)	0.0571(7)	-1.5(2)	4.90(12)
50	0.0402(3)	0.0083.3(8)	0.0724(4)	-1.38(11)	4.83(8)
30	0.0332(15)	0.0066(4)	0.0890(20)	-5.3(8)	5.0(5)
20	0.0310(20)	0.0030(6)	0.1040(30)	-8.0(11)	10(3)
15	0.0190(20)	0.0026(5)	0.1320(20)	6(2)	7(2)
10	0.0110(30)	0.0040(8)	0.1640(50)	104(5)	2.8(13)
4	0.1040(60)	0.0060(20)	0.1660(120)	92.8(1.1)	17(7)

Table 4.2: Fit parameters resulting from the fit by eq. 4.17 to the FWHM linewidth in fig. 4.29, showing data, for which the high-temperature dipole-dipole contribution to the linewidth was subtracted (see text for details).

From the fit parameter ΔH_A at $T = 300$ K the anisotropy parameter D can be calculated. It amounts to $D = 4.5(11)$ GHz, which equals to the previous estimate within error. With this result the anisotropy energy can be estimated by $DS^2 \approx 55 \text{ GHz} \cong 2.6 \text{ K}$. The data in the next sections extracted from measurements at varying temperatures and frequencies will show that an excitation gap at zero magnetic field in the ordered phase must have an energy between 10 GHz and 30 GHz. Considering that this gap is caused by both the dipole-dipole anisotropy as well as the anisotropy due to crystal fields, D seems to be overestimated or the anisotropy model was oversimplified. In comparison, the dipole-dipole energy amounts to $E^{\text{DD}} = \mu_B^2 \mu_{\text{eff}}^2 \mu_0 / 4\pi r^3 = 0.952(2) \text{ K} \approx 20 \text{ GHz}$, with the weighted average r_{ave} from before and $\mu_{\text{eff}} = 8.69(1) \mu_B$ [19]. As shown above the exchange energy is of the order $JS^2 \approx 5 \text{ K}$. Hence, anisotropy due to crystal field effects is the second most relevant interaction in GdInO_3 , and similar energy scales were found in literature for Gd^{3+} ions in $(\text{Y}_{1-x}\text{Gd}_x)_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$ [104, 107].

ESR Data at Different Temperatures and Constant Angles

Investigating the temperature-dependence of the spin resonance gives valuable insight into the magnetic anisotropy and spin-spin as well as spin-lattice interactions: The resonance position tends to be shifted by developing intrinsic fields, when crossing the Néel temperature the opening of a gap might be observed, and the temperature dependence of the linewidth allows to draw conclusions on the spin interactions.

Fig. 4.31 shows X-band ESR spectra measured at varying temperatures for external magnetic fields applied within the *ab*-plane and along the *c*-axis, respectively. As before the spectra are fitted with Lorentz derivatives including the counter resonance as well as admixture of dispersion (see eq. 2.10). From the fits, the resonance field, the linewidth and the intensity of the resonance feature are extracted.

In fig. 4.32 the temperature-dependence of the resonance field is shown for the three directions of the applied magnetic field. For fields applied at the magic angle the resonance position is roughly constant in the whole measured temperature range, which is predicted for anisotropic Heisenberg systems [108, 109, 110]. The resonance field for the magnetic field applied along the *ab*-plane is at 0.3240 T at high temperatures, which corresponds to $g_{ab} = 2.060(6)$. It starts to deviate from the high temperature value towards lower magnetic fields (0.3035 T at 5 K) at about $T = 75$ K. Such deviation from the high temperature value is usually attributed to the development of intrinsic magnetic fields. Since $75 \text{ K} \approx 36 \cdot T_N$, this implies the evolution of internal magnetic fields already far above T_N . For the magnetic field applied along the *c*-axis the resonance field at high temperature is $\mu_0 H_{\text{res}} = 0.3235 \text{ T}$, corresponding to $g_c = 2.063(6)$. It shifts towards higher magnetic fields below $T = 125 \text{ K} \approx 60 \cdot T_N$ and back towards lower fields for temperatures below $T = 7 \text{ K}$. For temperatures below T_N the resonance disappears, which is indicative of a spin gap opening (see fig. 6.4(b) and 6.7 in the appendix). Additionally, below the ordering temperature a steep drop appears in the derivative of the absorption power at about $\mu_0 H = 180 \text{ G}$ for the up sweep of the magnetic field. This drop shows a hysteresis of about 90 G and appears at about $\mu_0 H = 90 \text{ G}$ when ramping down the field (fig. 6.5 in the appendix). This feature is only visible for the external magnetic field applied along the *c*-axis. It is probably somehow related to the net ferromagnetic moment along the *c*-axis, present in GdInO_3 in the ordered phase (see the appendix for further discussion).

The temperature evolution of the resonance linewidth is shown in fig. 4.33(a). The linewidths for the magnetic field applied along the *ab*-plane and the magic angle behave very similar, albeit the resonance is broader for fields applied along the *ab*-plane (as was already evident from the angle-dependence of the linewidth). They are

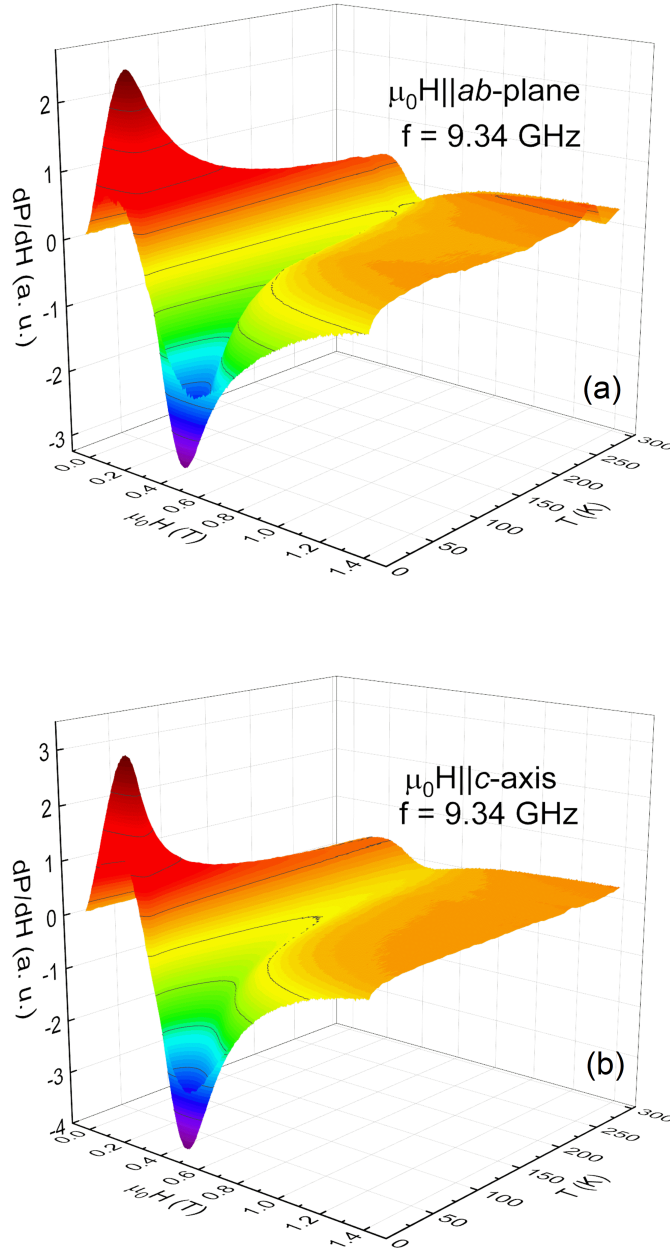


Figure 4.31: Temperature-dependence of X-band ESR spectra for external magnetic fields applied along the (a) ab -plane and (b) c -axis. Corresponding individual spectra can be found in the appendix (fig. 6.14).

roughly constant with temperature down to $T = 80$ K. Below 80 K both linewidths increase ever more drastically towards lowest temperatures. For external magnetic fields applied along the crystallographic c -axis of the sample, the qualitative temperature evolution of the resonance linewidth is different. It slightly decreases in width for the whole temperature regime under study down to $T = 20$ K, where the

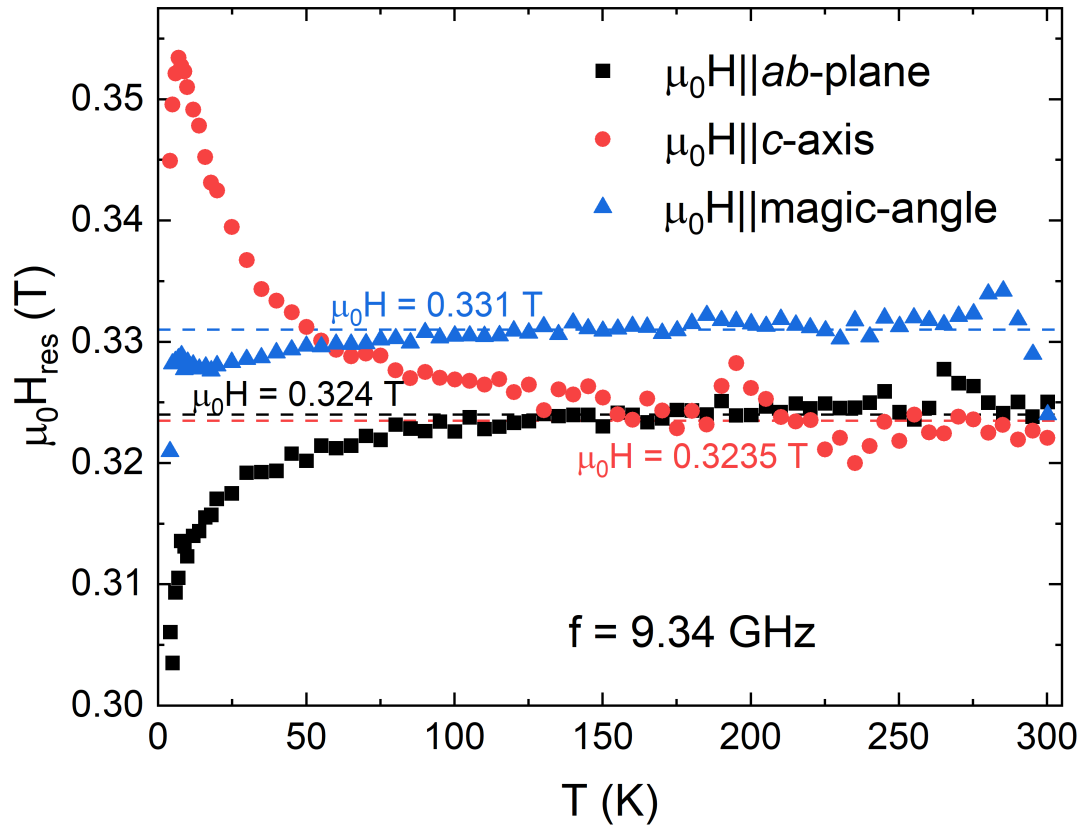


Figure 4.32: Temperature-dependence of the resonance positions extracted from X-band ESR spectra for external magnetic fields applied along the c -axis (red), ab -plane (black) and magic angle (blue).

linewidth exhibits a minimum. This temperature roughly coincides with the temperature where the angle-dependence of the linewidth shows a change in its qualitative behavior (fig. 4.28). Towards lower temperatures the linewidth increases again. Such a behavior is predicted for 2D Heisenberg systems [101]. However, as already discussed in the previous section, it is not clear if GdInO_3 exhibits typical 2D behavior, as the exchange interactions in-plane and out-of-plane are only two orders of magnitude different and the angle-dependence can be described in terms of a 3D model. If the minimum in the linewidth should not be due to the low dimensionality of the system, there must be another yet elusive contribution, increasing the linewidth towards higher temperatures. Down to $T \approx 14$ K, the linewidth for external fields applied along the c -axis is larger than for the other field directions. At 14 K there is a crossover and the linewidth for resonances with the external field along the c -axis becomes smaller than for the other directions. This crossover is also visible in fig. 4.34, where the ratio of the different linewidths is plotted. The crossover temperature also corresponds well to the observed change in the qualitative behavior of the angle-dependence of the linewidth at the same temperature (compare fig. 4.28 in the section 4.2.2).

Huber *et al.* have shown that the linewidth in exchange coupled systems can be expressed as:

$$\Delta H(T) = \frac{\chi_0(T)}{\chi(T)} \Delta H_\infty, \quad (4.18)$$

with $\chi_0(T) \propto T^{-1}$ being the free-spin (Curie) susceptibility and $\chi(T)$ the measured susceptibility [105]. ΔH_∞ denotes the constant linewidth at high temperatures. As will be shown later the ESR susceptibility perfectly matches the static susceptibility above T_N . Hence, it will be used for the following analysis instead of the static susceptibility, because it naturally covers the exact same temperature range as the linewidth. In the inset of fig. 4.33(a) curves given by eq. 4.18 are plotted as solid lines with the scaling factor c^i (i stands for the three magnetic field directions c -axis, ab -plane and magic-angle), which is used to scale the expression to the high temperature value of the linewidth. Experimental data and theory match well down to about $T = 140$ K for external magnetic fields applied within the plane or at the magic angle. For fields applied perpendicular to the plane theory and data deviate already at about $T = 170$ K. In fig. 4.35 the experimental linewidth is multiplied by T and χ_{ESR} . This should give a constant value in the temperature regime, where the Huber theory can explain the data. It shows that the observed linewidth can be explained by the Huber model but only in the temperature regime, where both the linewidth as well as the ratio of susceptibilities is roughly constant. Thus, the temperature evolution of the linewidth must be influenced by other contributions such as dipole-dipole interaction, which starts to dominate towards lower temperatures as

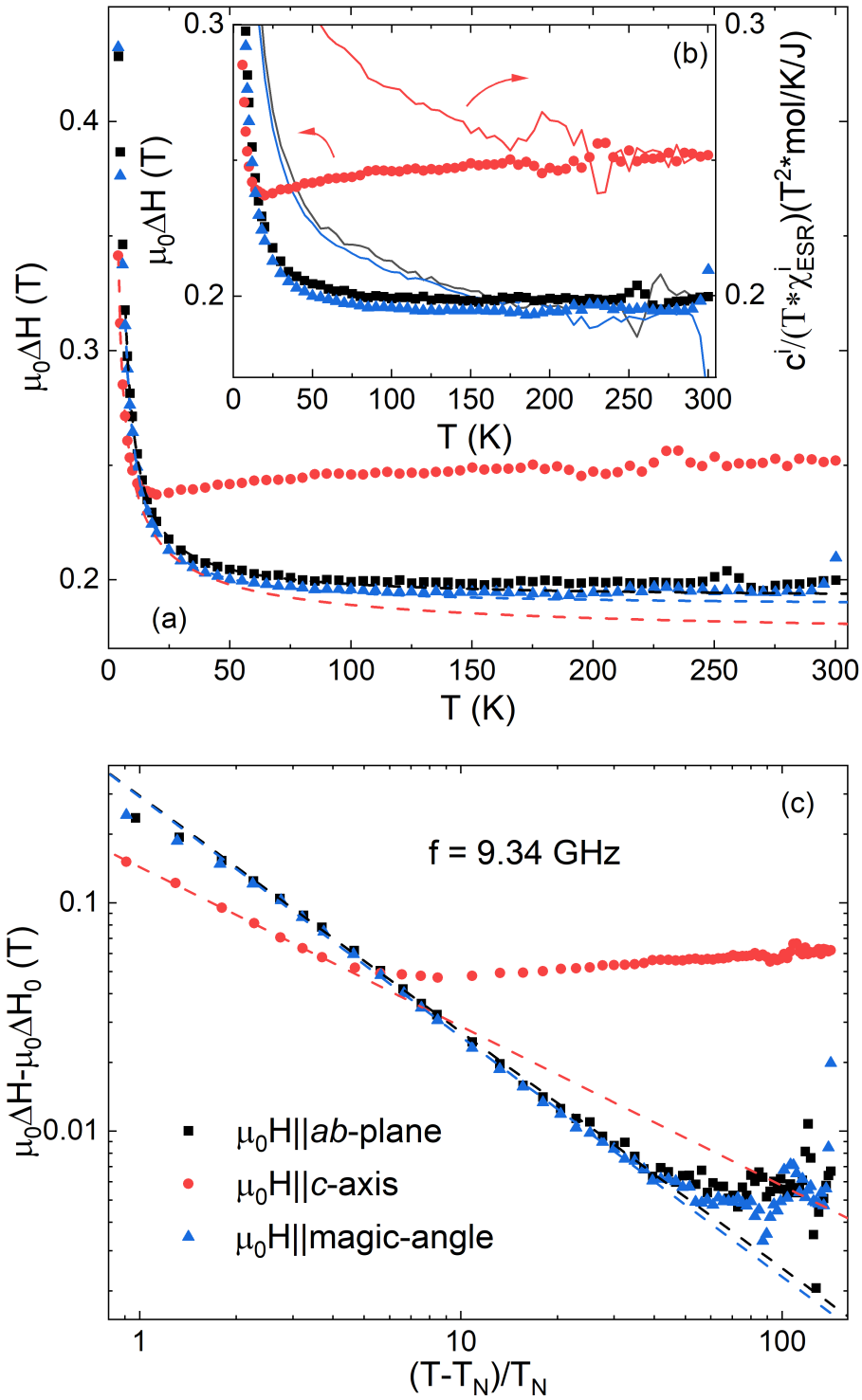


Figure 4.33: (a) Temperature-dependence of the FWHM linewidths from X-band ESR spectra for external magnetic fields applied along the c -axis (red), ab -plane (black) and magic angle (blue). In the inset solid lines are the Huber-model scaled to match the experimental linewidth at high temperatures (see text for details). Dashed lines are critical behavior fits to the linewidth (see text for details). (b) The FWHM linewidth minus the constant temperature-independent part vs. the reduced temperature with $T_N = 2.1$ K. Dashed lines are linear fits to the linear regime of the data.

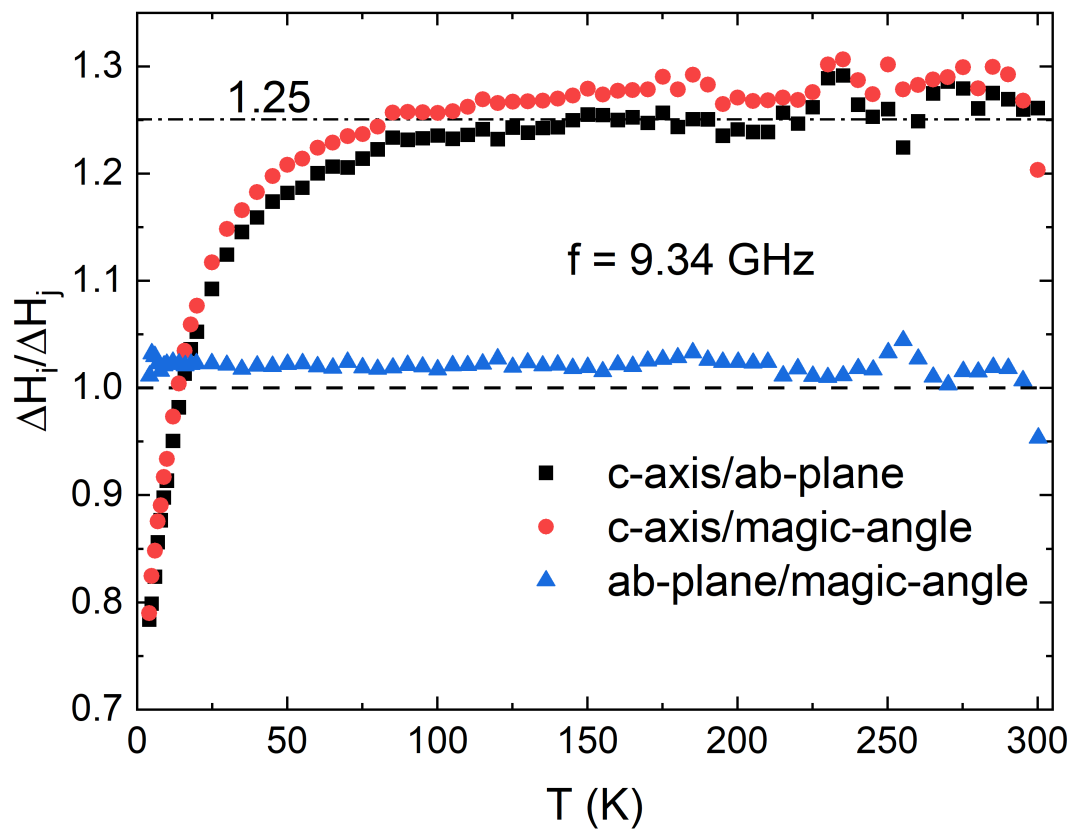


Figure 4.34: Temperature-dependence of the ratio of the FWHM linewidths from X-band ESR spectra. The dashed line marks unity and the dash-dotted line marks the constant high temperature ratio of $\Delta H^c / \Delta H^{ab}$.

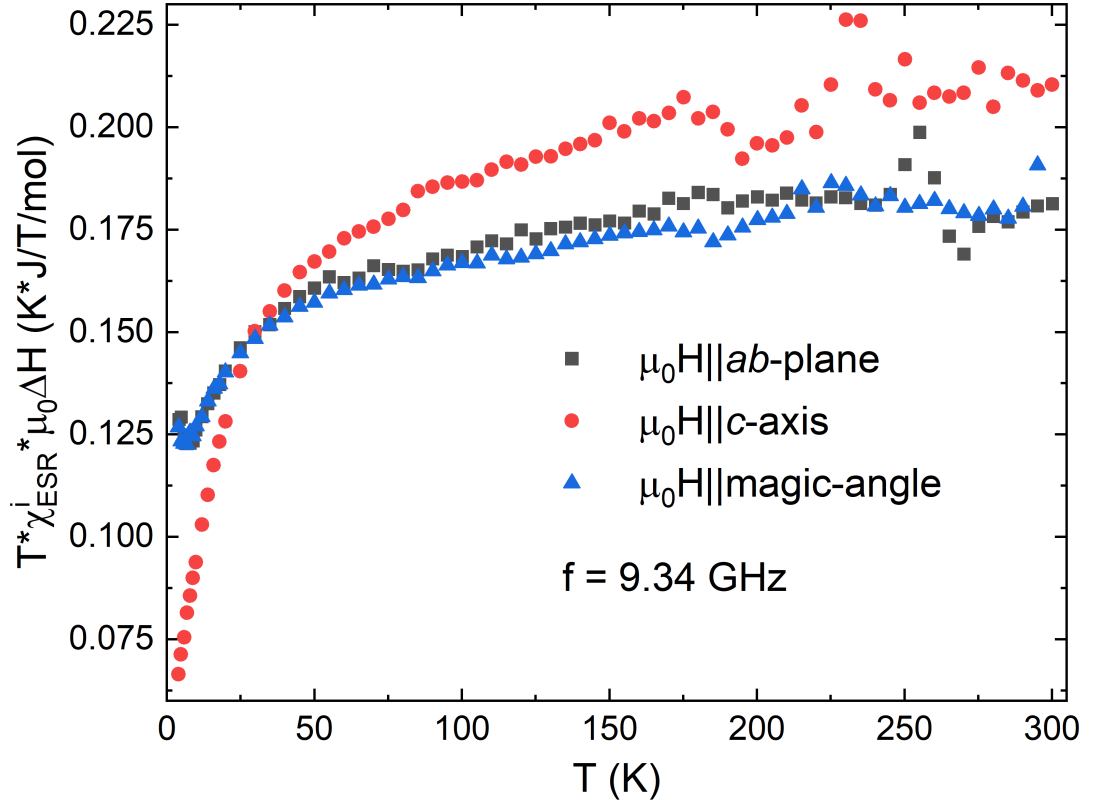


Figure 4.35: Temperature-dependence of the resonance FWHM linewidth multiplied by the temperature and the ESR susceptibility for external magnetic fields applied along the c -axis (red), ab -plane (black) and magic angle (blue).

argued from the angle-dependence of the data. The scaled data in fig. 4.35 also shows that the linebroadening towards lower temperatures can be fully explained by the increase in the susceptibility ratio $\frac{\chi_0(T)}{\chi(T)}$. The observed linewidth even increases less rapidly than predicted by eq. 4.18, meaning that other contributions could be slowing down this behavior towards lower temperatures. This also means that the increase in linewidth towards the Néel temperature is probably not due to critical broadening. Nevertheless, for comparison, a critical broadening analysis will be performed in the following.

First, a fit of equation eq. 4.6 to the data in the whole temperature range is performed to estimate ΔH_∞ (not shown). The fit routine yields $\Delta H_\infty^{ab} = 0.1931(7)$ T and $\Delta H_\infty^{magic} = 0.1897(8)$ T. For the linewidth with external magnetic fields applied perpendicular to the plane the minimum at $T = 20$ K and the subsequent increase in linewidth with increasing temperatures makes it difficult to extract the high temperature linewidth from the fit. Thus, a rough estimate of $\Delta H_\infty^c \approx 0.1900$ T is used. Note that these values differ from the experimental values, as the critical theory may not always recover the high temperature linewidth evolution [83]. Additional broad-

ening mechanism as e.g. already evident from the linewidth for the magnetic field along the c -axis can contribute to the high temperature value. This can typically happen when there are spin-phonon relaxation paths contributing to the linewidth, which would cause a linear increase in the linewidth [84, 85]. Linear increase however, is clearly not observed in GdInO_3 . The obtained high temperature linewidths are subtracted from the respective experimental data, which is plotted in a log-log-plot vs. the reduced temperature $(T - T_N)/T_N$ with $T_N = 2.1$ K from magnetisation data in [19] (fig. 4.33(b)). As expected a linear behavior can be seen in a large temperature regime when plotting the data in a log-log plot vs. the reduced temperature, except for the linewidth for magnetic fields applied along the c -axis, where the additional contribution to the linewidth towards higher temperatures causes a deviation from the low-temperature linear regime already at $T = 12$ K. The linewidth for the other two field directions deviates slightly from the linear behavior below $T = 6$ K and at high temperatures above about $T = 90$ K. The deviation at low temperatures towards the phase transition is often observed in low dimensional materials [83, 82, 4] and can be attributed to a crossover into the effective 3D regime in 2D materials [4]. A linear function was fitted in the temperature range of 4 K to 10 K for the c -axis data and in the range 7 K to 80 K for the other two data sets. Fitting a linear function to the linear regime in the log-log plot has the advantage that it is immediately visible in which temperature regime the fit should be valid. Finally, the critical fit was repeated in the plot with linear axes in the same temperature regime (fig. 4.33(a)) in order to see, if it still describes the data well. The obtained fit parameters are shown in table 4.3. Low exponents in the range of 0.1-1.2 are typical for 2D materials [4]

linear fit	c -axis	ab -plane	magic angle
p	0.698(9)	1.034(9)	1.051(7)
critical fit			
p	0.58(7)	1.00(2)	1.01(2)
ΔH_∞ (T)	0.1720(130)	0.1919(7)	0.1884(7)
C (T)	0.1610(130)	0.2870 (G)	0.2840(50)

Table 4.3: Fit parameters for the linear and critical fit according to eq. 4.6 to the FWHM linewidth data vs. temperature from X-band measurements at $f=9.34$ GHz.

but exponents of roughly unity may be an indication that the linebroadening with decreasing temperature is mainly caused by the change in susceptibility ratio $\frac{\chi_0(T)}{\chi(T)}$ as was already mentioned above. Table 4.4 shows the fit parameters obtained from fits to the HF-ESR linewidth data from measurements performed at varying temperatures (fig. 4.37, 4.39, 4.40 and 4.41). The corresponding plots are shown in the appendix (fig. 6.9 and 6.10). Note that the absolute value of the linewidth obtained from HF-ESR data is not very reliable as it is influenced by the setup, which does

not include a resonance cavity. Nevertheless, exponents in the range typical for 2D materials are also found from the HF-EPR data.

frequency	linear fit	<i>c</i> -axis	<i>ab</i> -plane	loose powder	fixed powder
~ 54 GHz	p	0.20(5)	0.42(6)	0.63(2)	0.51(3)
~ 110 GHz	p			0.29(2)	
~ 240 GHz	p			0.43(4)	
~ 260 GHz	p				0.25(2)
frequency	critical fit	<i>c</i> -axis	<i>ab</i> -plane	loose powder	fixed powder
~ 54 GHz	p	0.3(11)	0.66(10)	0.57(9)	0.55(7)
	ΔH_∞ (T)	0.2(5)	0.26(4)	0.21(3)	0.21(2)
~ 110 GHz	p			0.3(2)	
	ΔH_∞ (T)			0.0(2)	
~ 240 GHz	p			0.43(10)	
	ΔH_∞ (T)			0.04(6)	
~ 260 GHz	p				0.24(3)
	ΔH_∞ (T)				0(6)

Table 4.4: Fit parameters for the linear and critical fit according to eq. 4.6 to the FWHM linewidth vs. temperature of HF-ESR spectra.

Lastly, fig. 4.36 shows the temperature-dependence of the ESR susceptibility (the resonance intensity obtained by graphically integrating the resonance peak) in comparison to the static magnetic susceptibility for external magnetic fields of 0.5 T applied along the *c*-axis and *ab*-plane respectively. The excellent agreement shows, that the same spins are measured in both routines. Below T_N a spin gap opens as evidenced by the vanishing resonance in the low temperature measurements on GdInO₃ powder and the corresponding ESR susceptibility (fig. 6.8 in the appendix). HF-ESR susceptibilities are also shown in the appendix (fig. 6.11 and 6.12). There, a decrease in intensity below 4 K is observed for nearly all data sets up to a frequency of $f = 260$ GHz. The exact temperature where the decrease in intensity sets in varies between the data sets of different measuring frequency and the data in general has large variance. Hence, no definite conclusion as to the validity of the intensity decrease can be drawn from the HF-ESR data in this respect. Additionally, none of the EPR data sets exhibit a clear correlation maximum at temperatures higher than T_N , which would be typical for low dimensional materials.

In the HF-ESR setup, measurements were performed both on a single crystal as well as on polycrystalline powder of GdInO₃. For external magnetic fields applied along the *c*-axis and the *ab*-plane of the single crystal respectively as well as for measurements on a loose and fixed powder sample of GdInO₃ the temperature evolution of the HF-ESR spectra at roughly $f = 54$ GHz was investigated. For the loose powder

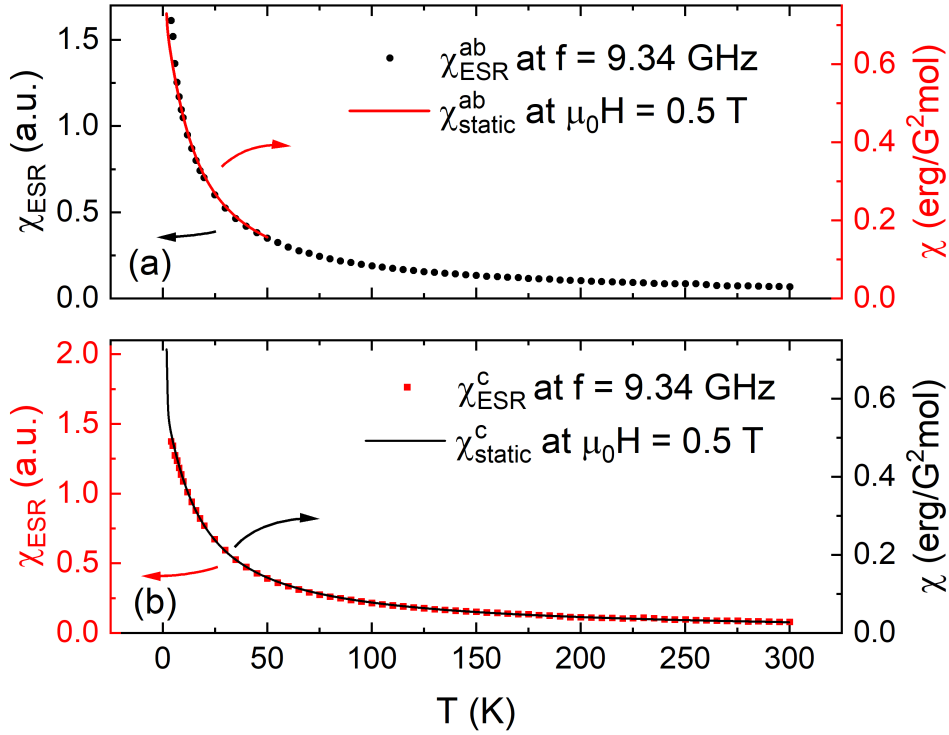


Figure 4.36: X-band ESR susceptibility and static magnetic susceptibility for external magnetic fields applied along the (a) *ab*-plane and (b) *c*-axis.

additional temperature evolutions were measured at $f = 110$ GHz and $f = 240$ GHz and for the fixed powder at $f = 260$ GHz. HF-ESR spectra at different temperatures and $f \approx 54$ GHz are shown in fig. 4.37 for the different sample setups. In all four cases one main resonance feature is visible, which shifts in field for varying temperatures. For external magnetic fields applied along the *c*-axis (fig. 4.37(a)) the resonance position shifts towards higher fields with temperature until $T = 6$ K. For even higher temperatures it shifts back towards lower fields until it stays at a constant field of about $\mu_0 H = 1.89$ T from $T = 60$ K upwards. Thus, intrinsic magnetic fields start to develop at about $T = 40$ K (compare also fig. 4.38), however they cause a shift in resonance field position opposite in direction to what is seen at the vicinity of $T_N = 2.1$ K below 4 K. In contrast the resonance position for fields applied along the *ab*-plane (fig. 4.37(b)) shifts towards lower field position from $T = 1.8$ K to $T = 2$ K and subsequently towards higher fields until $T = 40$ K. At even higher temperatures the resonance field stays at a constant field position of about 1.88 T. Thus, fluctuations set in at about $T = 30$ K causing a shift in opposite direction to the former case where fields were applied along the *c*-axis (compare also fig. 4.38). Similarly to before, the resonance field shifts in opposite direction below T_N as compared to above T_N , but opposite to the *c*-axis case. Such a shift in opposite direction is an indication for the development of anisotropy towards lower temperatures. This

anisotropy can not be due to the g -tensor anisotropy, since such an anisotropy would be rather temperature independent.

In the loose powder the grains should align with the *easy*-axis to the magnetic field yielding pseudo-single-crystalline spectra. Comparing the direction of the shift in resonance position of the loose powder sample of GdInO_3 with the shift of the single crystal should thus allow to conclude, which of the crystallographic directions is the magnetic *easy*-axis (or if the magnetic axes do not coincide with the crystallographic axes, which of the crystallographic axes lies closer to the magnetic *easy*-axis.) (fig. 4.37(c)). Below $T = 40$ K the resonance feature mainly shifts towards lower magnetic fields with decreasing temperature, while a slight shoulder develops at the same field position as the resonance feature had at high temperatures above 40 K. Hence, the *ab*-plane seems to be the *easy*-plane, which is corroborated by magnetisation data [19]. The resonance shoulder is most pronounced at $T = 3$ K. This could be a weak signal from a few grains, which might not be aligned with their *easy*-plane to the field and thus instead might have the magnetic field along their *c*-axis. Since the resonance feature for external magnetic fields applied along the crystallographic *c*-axis shifts back towards lower fields at the lowest temperatures, this can explain why the shoulder is most pronounced at $T = 3$ K. In the fixed powder sample of GdInO_3 the magnetic field is applied along all crystallographic axes at the same time. Thus, one should see a combination of the different behaviors observed on the single crystal. At a first glance, however, the evolution with temperature looks similar to the one observed on the loose powder sample of GdInO_3 . The resonance shifts towards higher field positions for temperatures above $T = 2$ K and reaches a constant position of roughly 1.9 T at $T = 30$ K. Again, a shoulder develops on the right side of the resonance feature for temperatures below 8 K. It is less pronounced than in the loose powder sample of GdInO_3 . This can be explained by the random alignment of the powder grains causing spectral weight to be distributed in a broad field range. The larger spectral weight on the low magnetic field side of the resonance feature also suggests *easy*-plane anisotropy, as two anisotropy axes would have larger coinciding g -values.

However, when comparing the resonance fields $\mu_0 H_{\text{res}}$ obtained from fits to the data, one can see that the fixed powder of GdInO_3 contains the combined information of the single crystal (fig. 4.38). For the single crystal of GdInO_3 the resonance field was obtained by fitting a single lorentzian to the spectra. For the loose powder two lorentzians were fitted for lower temperatures and for higher temperatures only one was necessary. The spectra of the fixed powder GdInO_3 sample were fitted by the EasySpin routine, which takes the angle distribution of the powder grains into account. At high temperatures both for the single crystal as well as the fixed powder only one resonance field is extracted from each data set. This suggests that

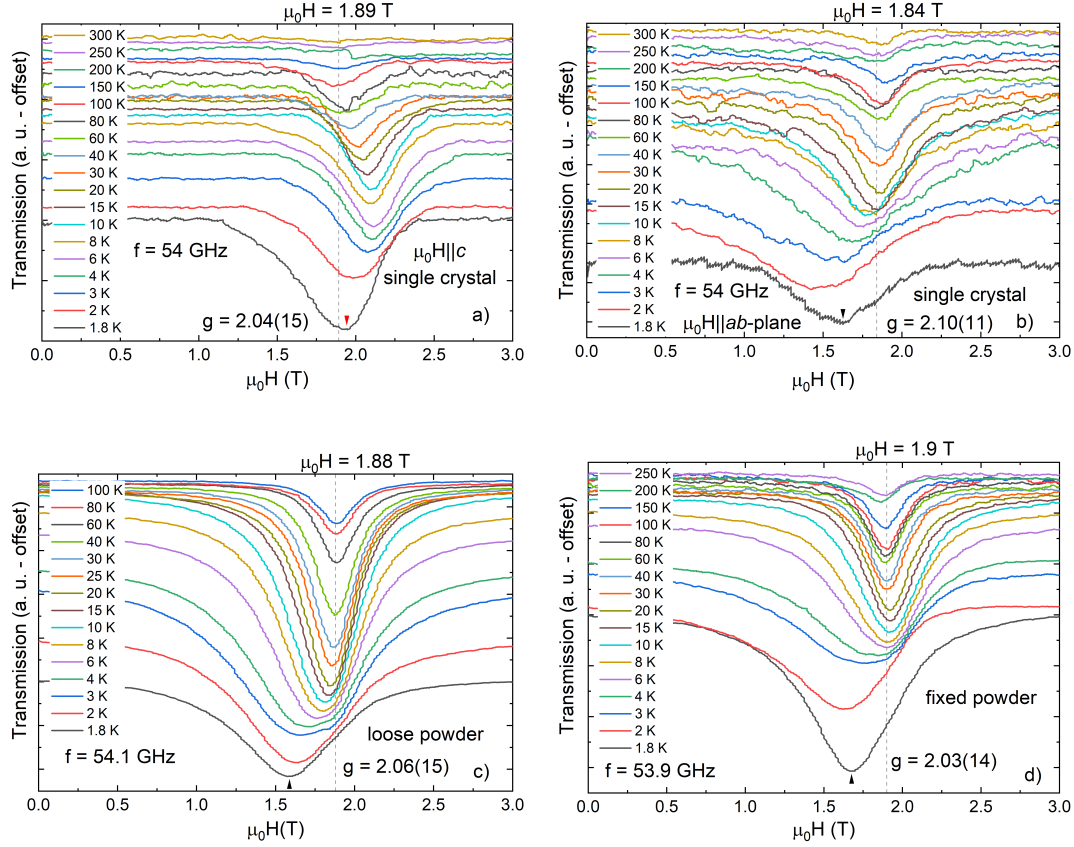


Figure 4.37: HF-ESR spectra measured at varying temperatures and ca. 54 GHz for a) the single crystal of GdInO_3 and $\mu_0 H \parallel c$ -axis, b) the single crystal of GdInO_3 and $\mu_0 H \parallel ab$ -plane, c) the loose powder GdInO_3 sample and d) the fixed powder GdInO_3 sample. Dashed vertical lines mark the resonance field at highest temperature and the value is given above the plot. The corresponding g -value is written on the bottom of the plot. Small arrows mark the resonance position in the ordered state. The colour matches the colour of the corresponding branch in the frequency-field-diagram (fig. 4.47).

there is no or only very little anisotropy between the c -axis and the ab -plane at high temperatures, as one would expect for Gd^{3+} ions with quenched orbital moment.

At 110 GHz the resonance observable on the loose powder sample of $GdInO_3$ clearly exhibits a shoulder on the high field site. With increasing temperature the main feature shifts to higher field values while the shoulder gets less pronounced (fig. 4.39). At $T = 20$ K the feature can be described with just one lorentzian and at $T > 60$ K it assumes a constant field position of $B = 3.86$ T. A very similar feature is observed in the 2D kagome lattice system $Mg_2Gd_3Sb_3O_{14}$ at a frequency of $f = 222$ GHz [111]. There the temperature-dependence of the anisotropy evolution is attributed to the onset of anisotropic spin-spin correlations, which are suspected to be caused by dipole-dipole interactions. A similar scenario for $GdInO_3$ is supported by results of the analysis of data obtained from measurements at different angles of the applied magnetic field in the previous section, where dipole-dipole interactions are shown to be dominant at low temperatures. Wellm *et al.* [111] rule out single-ion anisotropy or anisotropy due to crystal fields in their system, because they do not observe lorentzian lineshapes, indicative of exchange narrowing. Exchange narrowing is however necessary to reduce the individual resonances from fine splitting to one feature. Furthermore, they argue that the exchange coupling should be roughly $J \approx 12D$ for the exchange narrowing to be effective. In $GdInO_3$ where lorentzian lineshapes show that exchange narrowing is active, the exchange coupling $J \approx 0.5$ K would yield $D \approx 0.04$ K for the above approximation, resulting in $DS^2 \approx 11$ GHz, which would nicely correspond to a spin gap of 10-30 GHz, as it is suggested by the X-band and HF-ESR data. At the same time this value of D is much smaller than what was obtained above from the analysis of the angle-dependence of the resonance linewidth.

At 240.4 GHz the single resonance feature is even broader than at 110 GHz but overall shows similar behavior (fig. 4.40). The shoulder on the right disappears at 150 K and the constant resonance position at high temperatures is at 8.58 T.

The temperature evolution of the resonance feature at 260 GHz measured on the fixed powder sample is shown in fig. 4.41. The broad feature decreases in width with temperature. In this case the feature is more pronounced on the high field site, which is indicative of $GdInO_3$ having *easy*-axis anisotropy and at odds with the earlier observations from data measured at 54 GHz for increasing temperatures. The shoulder on the left seems to have disappeared at 150 K. The resonance fields shown in fig. 4.41(b) were obtained by an EasySpin-fit to the data. It did not match the feature very well below 6 K, so obtained resonance fields at these temperatures should be considered with caution. For higher temperatures, however, the fit was feasible and in difference to all the other temperature evolutions two different resonance fields

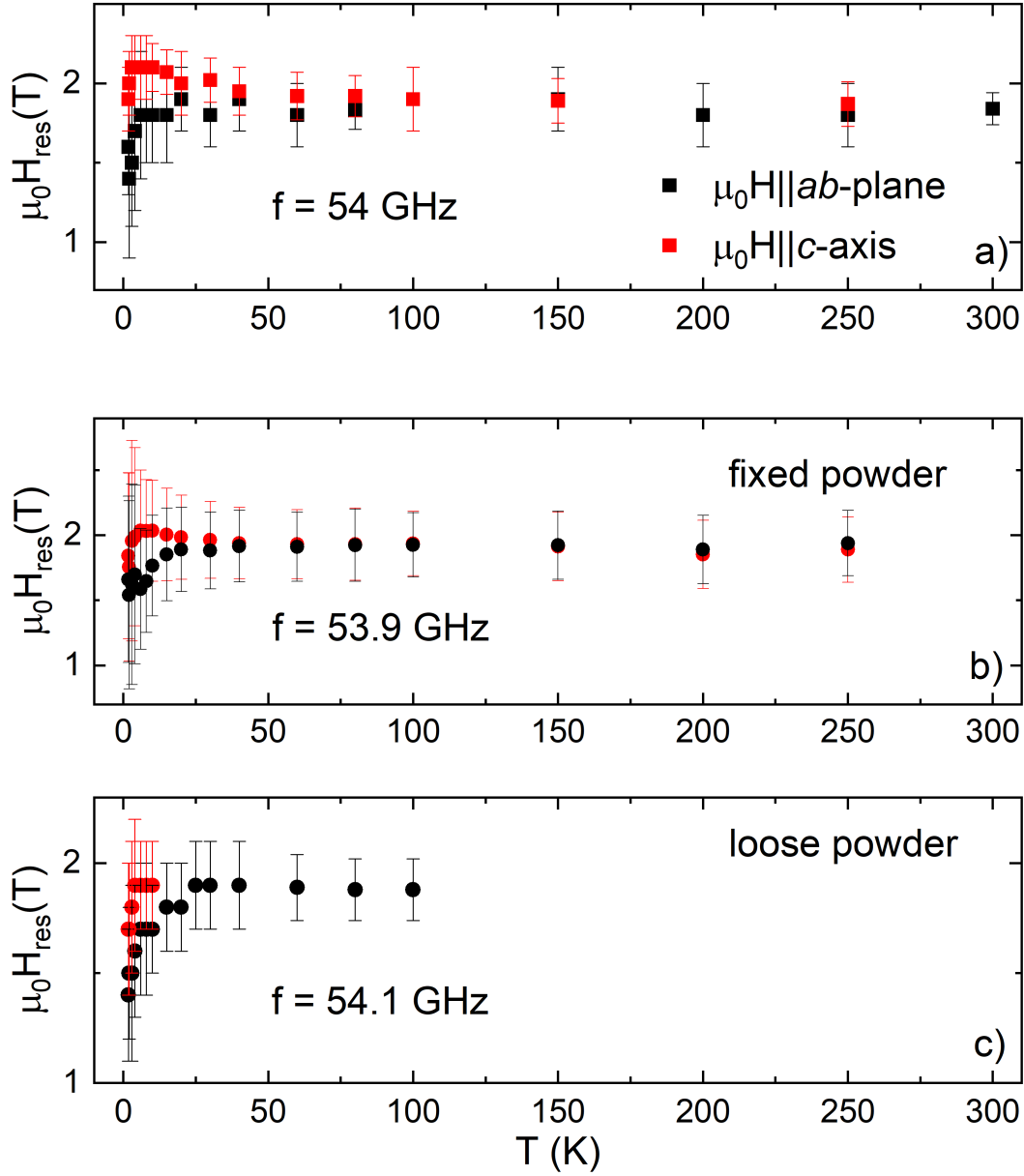


Figure 4.38: Resonance fields obtained from measurements performed at varying temperatures and at roughly 54 GHz. a) values obtained from HF-ESR spectra collected on the GdInO_3 single crystal with fields applied along the crystallographic c -direction and within the ab -plane. b) Resonance fields obtained from an EasySpin fit to the HF-ESR spectra of the fixed powder GdInO_3 sample. c) Resonance fields obtained from a fit of two or one lorentzian peak functions to the HF-ESR spectra collected from the loose powder GdInO_3 sample. In (b) and (c) different colours for the different resonance fields are chosen such that they correspond to the colours given above for the data from the single crystal.

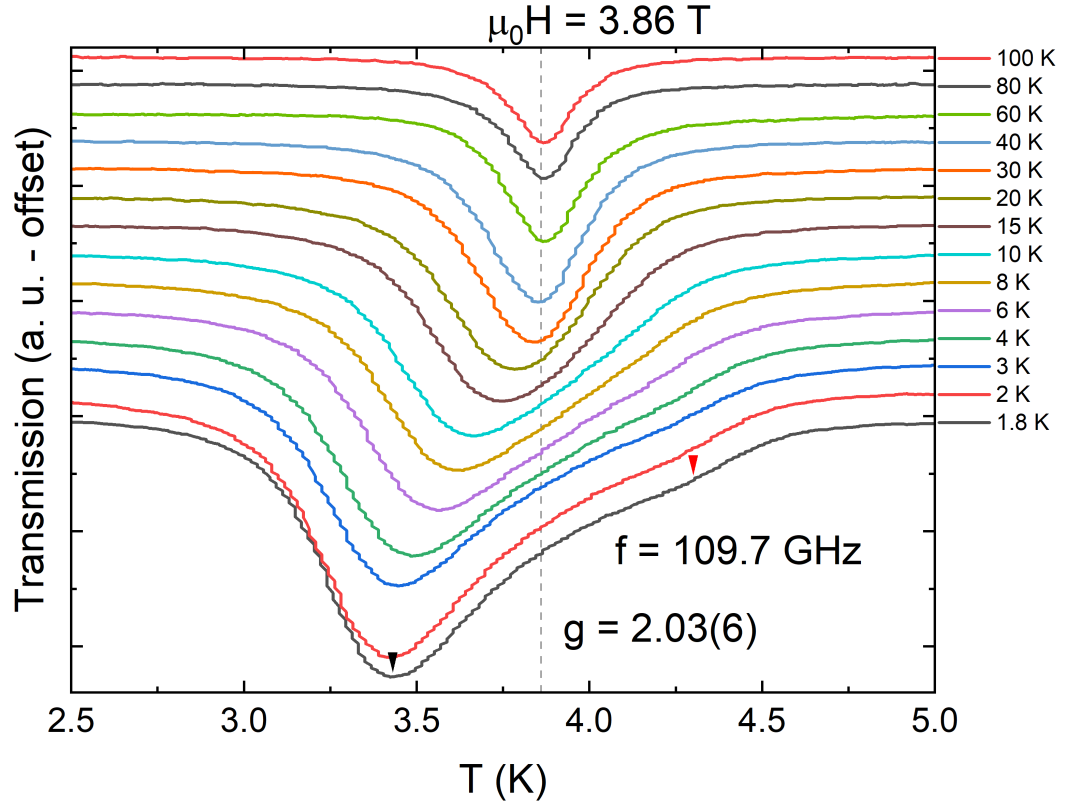


Figure 4.39: HF-ESR spectra measured at varying temperatures and at 110 GHz on the second loose powder sample of GdInO_3 containing less powder (see section on the experimental setup for details). The dashed vertical line marks the resonance field at highest temperature and the value is given above the plot. The corresponding g -value is written on the bottom of the plot. Small arrows mark the resonance position in the ordered state. The colour matches the colour of the corresponding branch in the frequency-field-diagram (fig. 4.47).

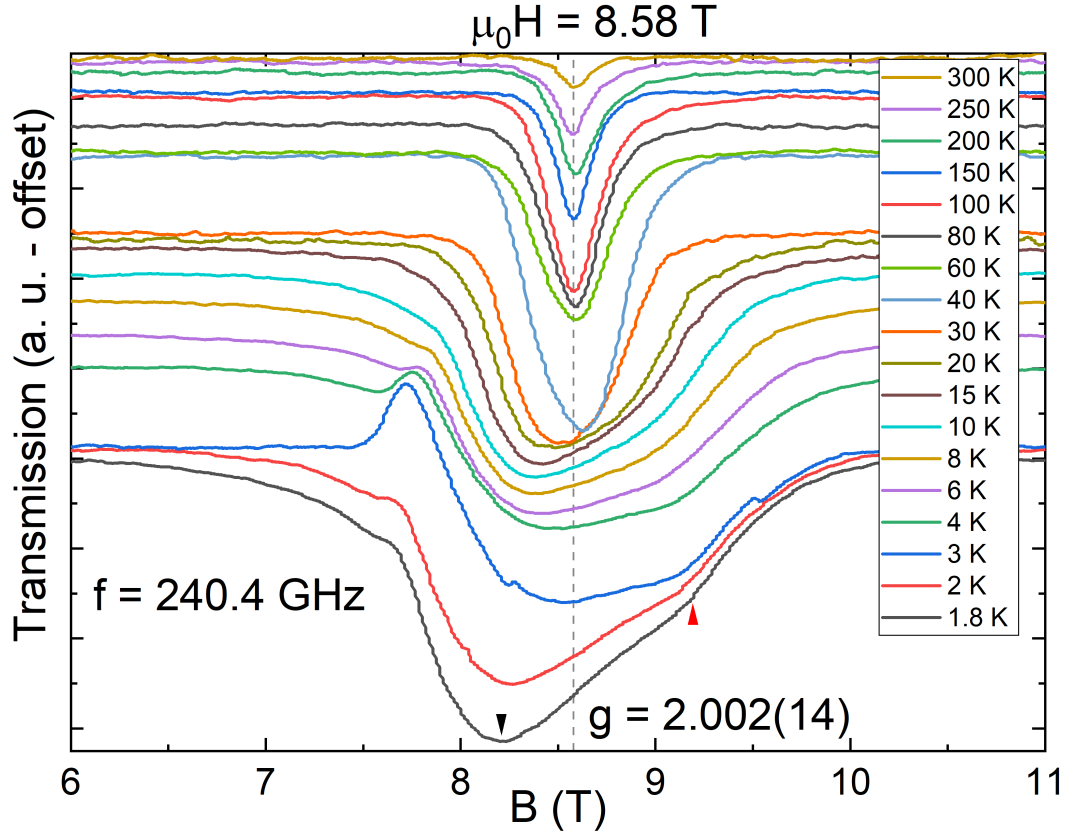


Figure 4.40: HF-ESR spectra measured at varying temperatures and at 240 GHz on the loose powder sample of GdInO_3 . The dashed vertical line marks the resonance field at highest temperature and the value is given above the plot. The corresponding g -value is written on the bottom of the plot. Small arrows mark the resonance position in the ordered state. The colour matches the colour of the corresponding branch in the frequency-field-diagram (fig. 4.47).

can be observed at high temperature here. This is maybe due to the higher frequency causing a higher splitting of the anisotropic feature. At 150 K the corresponding g -values are 1.98(4) and 1.94(3). Alternatively, since the splitting of the two observed high temperature resonance fields did not assume a constant value at $T = 150$ K (yet), it might also be attributed to short range correlations causing the anisotropy even at 150 K. This would correspond to $71 \cdot T_N$.

In table 4.5 the high temperature g -values of all aforementioned temperature evolutions for different setups and frequencies are summarized. Due to the large linewidth, their uncertainty is large and no cogent conclusion can be made with regard to the exact value of the g -factor or its anisotropy. The fact that at most frequencies, especially in the fixed powder, only one resonance feature is observed, however, strongly suggests very little to no g -factor anisotropy. This is corroborated by the similar saturation magnetisation fields for magnetic fields applied parallel and perpendicular to

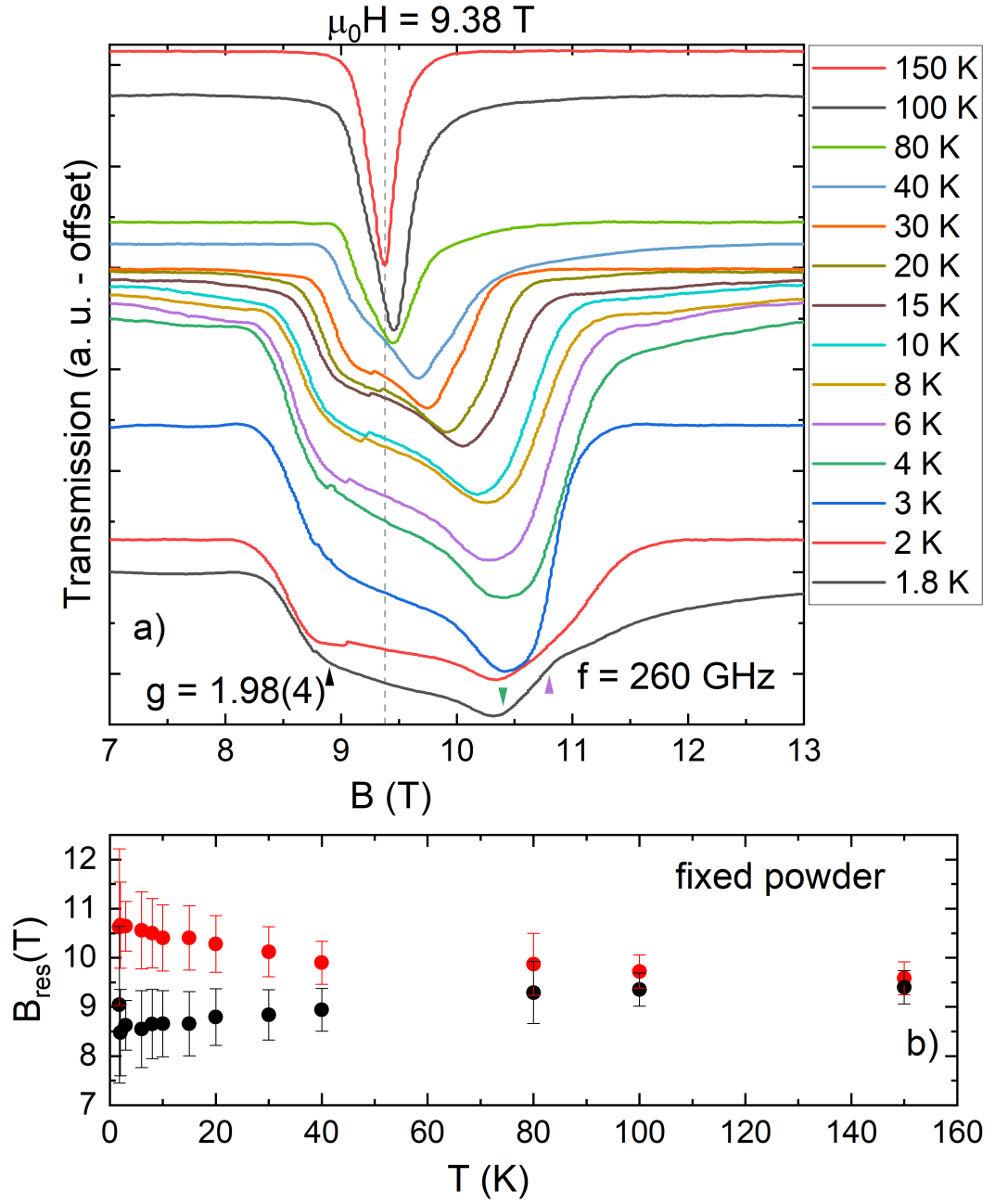


Figure 4.41: (a) HF-ESR spectra measured at varying temperatures and at 260 GHz on the fixed powder sample of GdInO₃. The dashed vertical line marks the resonance field at highest temperature and the value is given above the plot. The corresponding g -value is written on the bottom of the plot. Small arrows mark the resonance position in the ordered state. The colour matches the colour of the corresponding branch in the frequency-field-diagram (fig. 4.47). (b) Resonance positions of the above HF-ESR spectra extracted by means of an EasySpin fit. The colours of the data points correspond to the colours given in fig. 4.38.

the ab -plane of the single crystal [19].

g -values for	loose powder	fixed powder	$\mu_0 H c$ -axis	$\mu_0 H ab$ -plane
~ 54 GHz	2.06(15)	1.99(13) 2.04(14)	2.06(15)	2.10(11)
~ 110 GHz	2.03(6)			
~ 240 GHz	2.002(14)			
~ 260 GHz		1.94(3) 1.98(4)		

Table 4.5: High-temperature ($T \geq 100$ K) g -values for different sample setups of GdInO₃ and different applied microwave frequencies.

ESR-Data at Different Frequencies

In the HF-EPR setup measurements were first performed on the single crystal with the magnetic field applied along the crystallographic c -axis and ab -plane. Figure 4.42 shows the spectra obtained for the external magnetic field applied along the c -axis at different frequencies. At low frequencies one resonance feature is visible, which shifts towards higher magnetic fields with increasing frequency. It splits into two signals at 90.1 GHz and into three signals at 110 GHz. For higher frequencies more and more features appear, being so numerous and varying in intensity that it is impossible to trace their individual behavior through the increasing frequencies. At 496.9 GHz no resonance features are observable any longer as they lie outside the accessible field range.

Figure 4.43 shows the HF-ESR spectra at different frequencies for magnetic fields applied within the ab -plane of the crystal. Similarly to before, there is one feature visible for low frequencies while higher frequencies show numerous features similar to the former case, where the field was applied along the c -axis.

The resonances observed on the single crystal are summarized in a frequency-magnetic-field diagram (fig. 4.44). For lower frequencies up to 110 GHz the position of individual resonances is indicated. At higher frequencies it was not feasible to extract individual resonance positions from the spectra. Thus, in fig. 4.44 long horizontal bars indicate the field range in which resonances are observed. The origin of the numerous and irregular resonance features distributed in a large field range is unclear. As one will see later from measurements on a polycrystalline powder they do not seem to be intrinsic excitations. For crystals exhibiting parallel surfaces perpendicular to the direction of the applied field, long wavelength (with respect to the dimensions of the crystal) excitations can develop [112, 113, 114]. These walker modes appear in the vicinity of the spin excitation, their field range is determined by the strength of

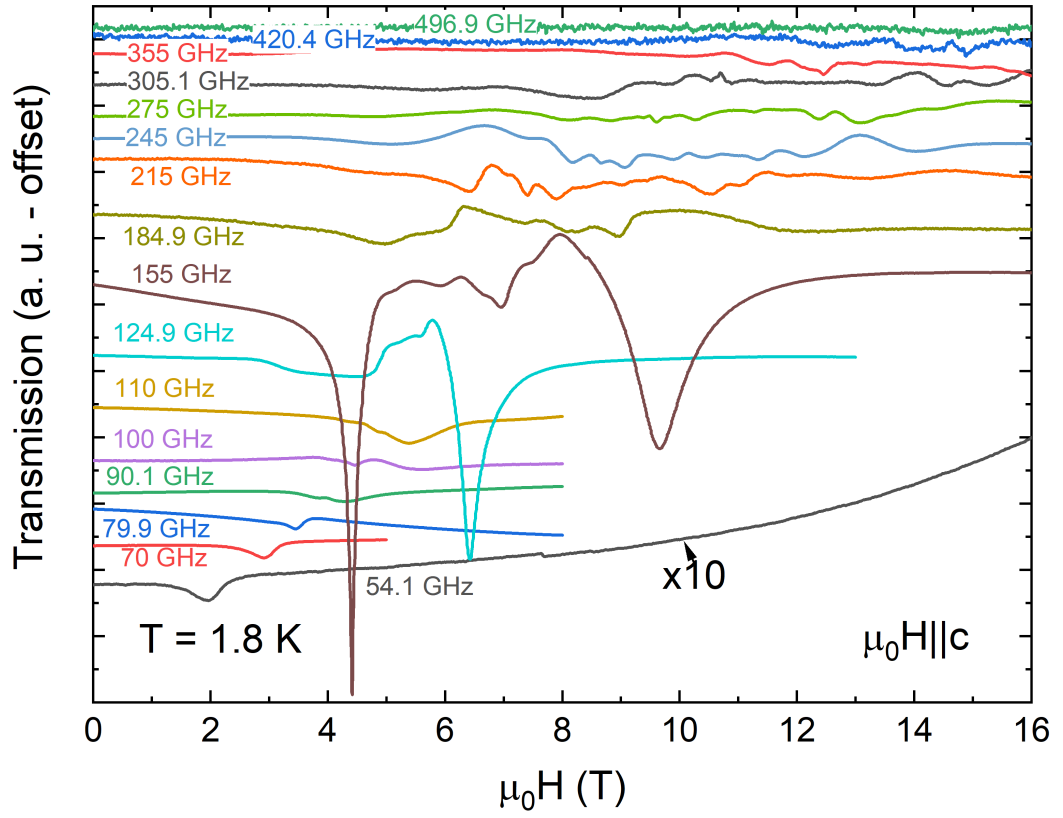


Figure 4.42: HF-ESR spectra obtained on the single crystal at $T = 1.8$ K and varying frequencies (54.1 GHz - 496.9 GHz) in fields between 0 T and 16 T applied along the crystallographic c -axis. The curves are vertically shifted and partially scaled for better visibility.

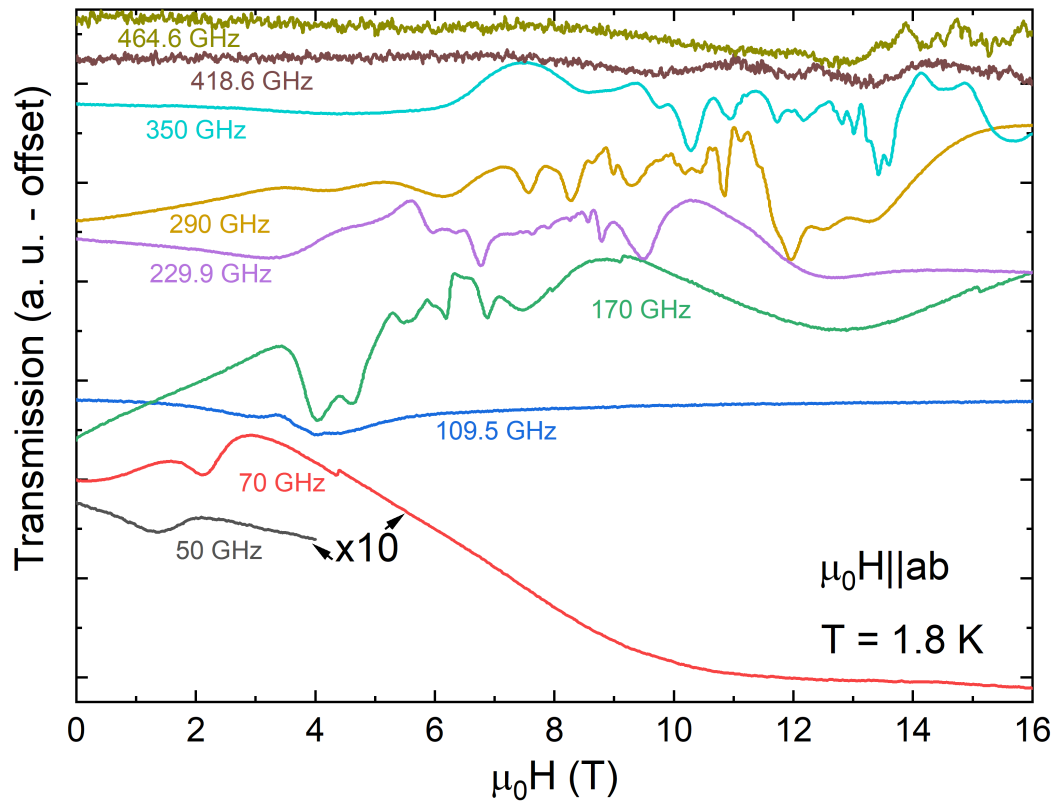


Figure 4.43: HF-ESR spectra obtained on the single crystal at $T = 1.8$ K and varying frequencies (50 GHz - 464.6 GHz) in fields between 0 T and 16 T applied perpendicular to the crystallographic ab -plane. The curves are vertically shifted and partially scaled for better visibility.

the exchange interaction and anisotropy of the system [114]. The resonances observed here do not match this behavior and most importantly also appear in a crystal where two apposing surfaces where cut in an acute angle (compare fig. 3.3). In a crystal with such a shape, walker modes should not develop [22]. Interestingly, similar numerous and varying features were observed in the kagome systems $\text{Nd}_3\text{Ga}_5\text{SiO}_{14}$ and $\text{Pr}_3\text{Ga}_5\text{SiO}_{14}$ as well as the triangular system $\text{Ba}_3\text{CoNb}_2\text{O}_9$ [115, 116, 117]. They were attributed to spin wave excitations in short range correlated spin clusters. Since the cluster size varies with applied magnetic field, the excitations can not be traced through frequency, as one would normally do for ESR signals. Due to their strong similarity, it is reasonable to assume, that such excitations in short range correlated spin clusters are also observed here in GdInO_3 . This could be due to the close proximity to the phase transition at $T_N = 2.1$ K, since measurements were done at $T = 1.8$ K. It is not immediately clear, why this effect is not observed in the polycrystalline samples but as discussed in the appendix, the polycrystalline sample seems to have impurity phases, which might hinder the formation of spin clusters.

In order to learn more about the resonance features at high frequencies in GdInO_3 , measurements were also performed on a polycrystalline powder of GdInO_3 . The spectra from a loose powder sample are shown in figure 4.45. At low frequencies there is one resonance peak, which develops a shoulder on the high field site at 99.6 GHz. With increasing frequency this shoulder gets more and more pronounced while moving away from the main feature towards higher fields. Such a broad resonance feature is reminiscent of what one would expect in a fixed powder, if the resonance fields of different modes lie close enough together, mimicing a paramagnetic fixed powder spectrum. At some frequencies there are large v-shaped features. Such features are indicative of an oversaturated signal. This can happen for very strong coupling between the microwaves and the sample. In such a case the system is driven into excitation in a broad energy range close to the main excitation, causing the high intensity feature. This feature masks the intrinsic resonance and is often misleading in its position. For this reason a second set of measurements was done on a smaller amount of loose powder, to avoid the strong coupling. The data is not shown but was still partially used to extract the resonance positions.

In figure 4.46 the HF-ESR spectra obtained on a fixed powder sample are shown. Fixing the powder has the advantage that all crystallographic axes can be probed at the same time. The single resonance visible at 54 GHz again develops into a broad feature at 100 GHz. This feature broadens and moves to higher fields with increasing intensity. At some frequencies the shoulder on the right seems to consist of two overlapping resonances. At 349.9 GHz this right most shoulder becomes significantly less pronounced and moves closer to the shoulder on the left. This left shoulder becomes more pronounced and splits into two features at the same frequency. For

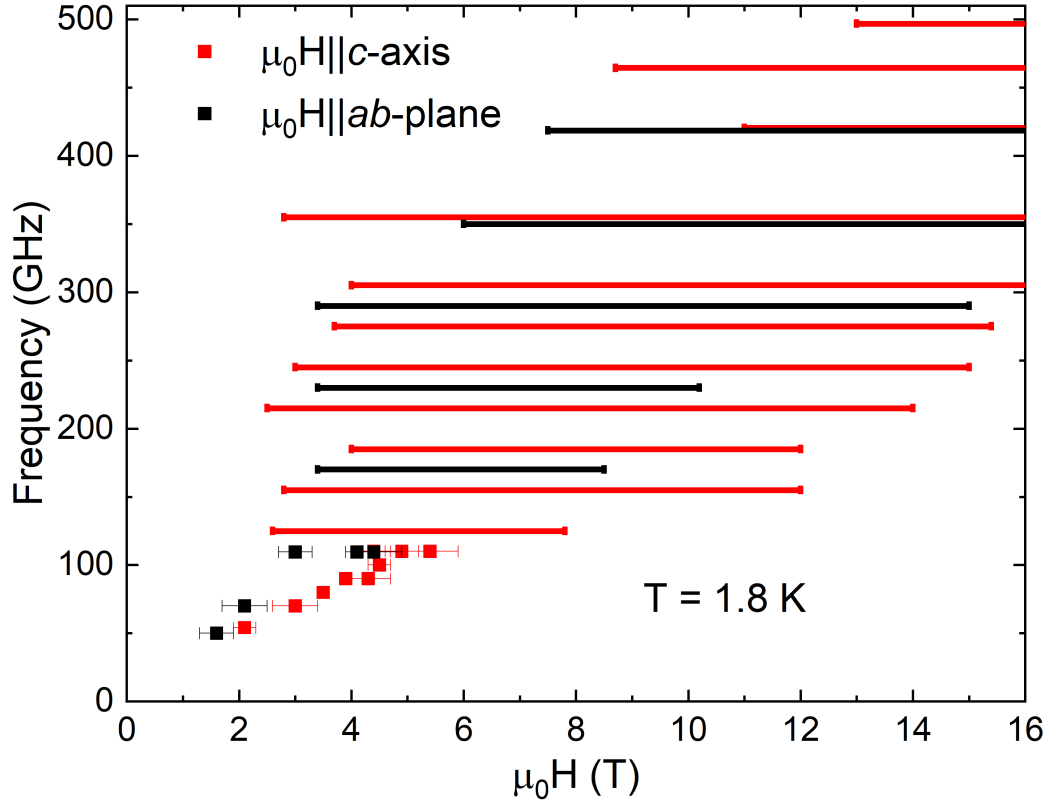


Figure 4.44: Frequency-field diagram showing the resonance positions in field of the single crystal of GdInO₃ for magnetic fields applied along the *c*-axis (red squares) and within the *ab*-plane (black squares). Long vertical bars indicate the range where unambiguous resonance features were observed in higher frequencies (see text for details).

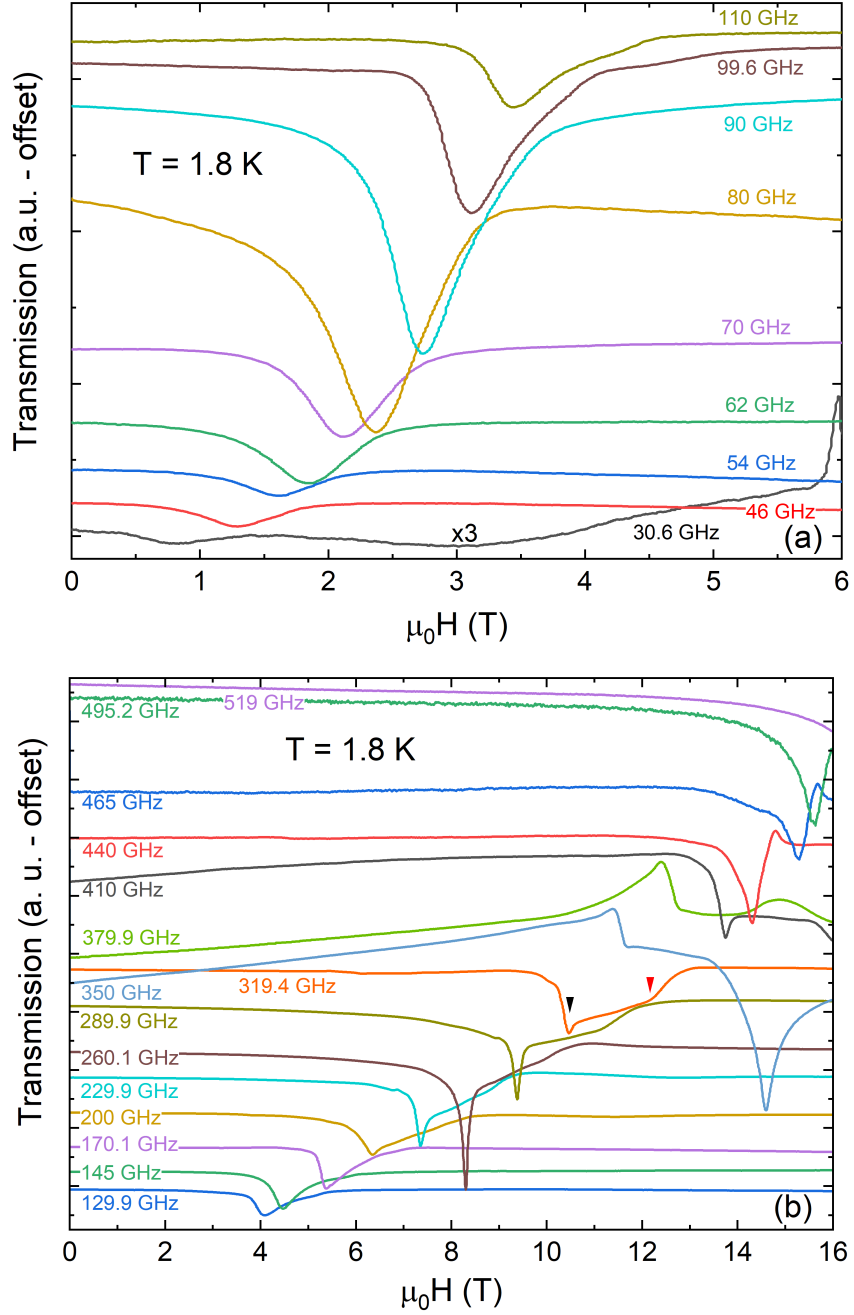


Figure 4.45: HF-ESR spectra obtained on a loose powder sample of GdInO₃ at $T = 1.8$ K and varying frequencies ((a) 30.6 GHz - 110 GHz and (b) 129.9 GHz - 519 GHz) in fields between 0 T and 16 T. Phase mixing was corrected and the curves are vertically shifted and partially scaled for better visibility. Small arrows mark the resonance position. The colour matches the colour of the corresponding branch in the frequency-field-diagram (fig. 4.47).

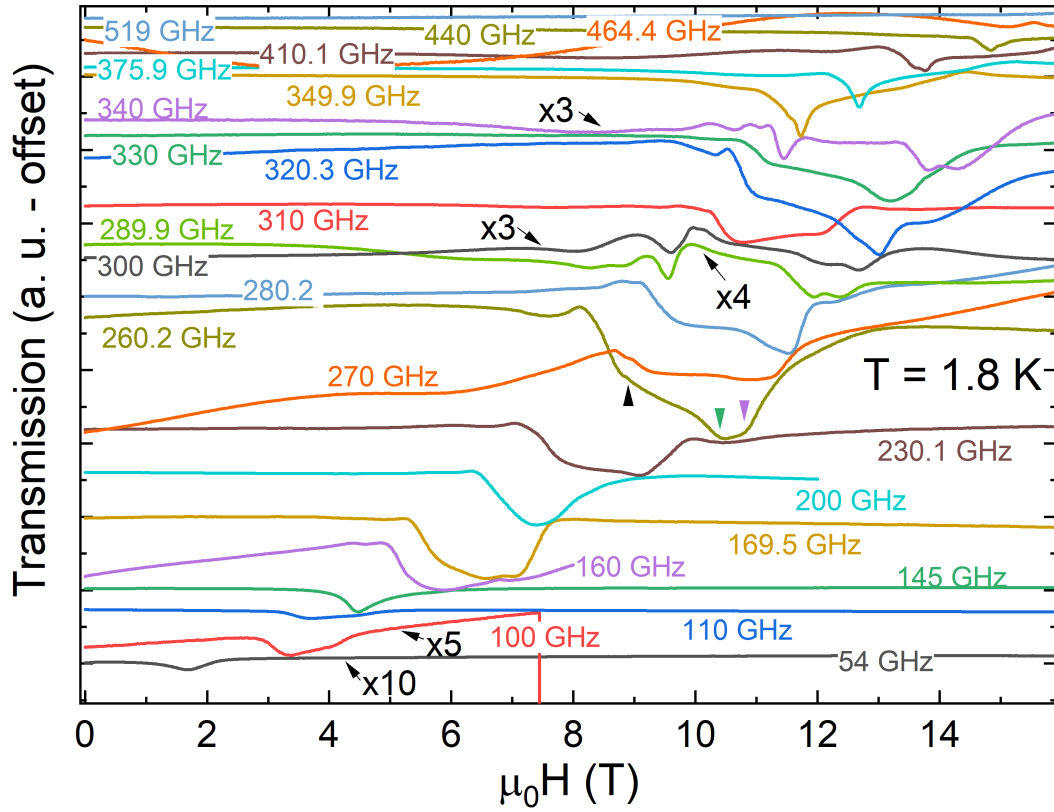


Figure 4.46: HF-ESR spectra obtained on a fixed powder sample of GdInO_3 at $T = 1.8$ K and varying frequencies (54 GHz - 519 GHz) in fields between 0 T and 16 T. Phase mixing was corrected and the curves are vertically shifted for better visibility. Small arrows mark the resonance position. The colour matches the colour of the corresponding branch in the frequency-field-diagram (fig. 4.47).

some frequencies small additional features are visible to the left or right of the main resonance.

The results of all four different measurement setups are collected in a frequency-field diagram (fig. 4.47). The resonance features in low frequencies for magnetic fields applied along the ab -plane of the single crystal lie on the same resonance branch (black) as the left-most resonances from both the loose powder and fixed powder sample of GdInO_3 . Furthermore the same holds true for the resonances of the single crystal for fields applied along the c -axis and the main right-most shoulders of the powder samples (red branch). In the frequency range of 250 GHz to 350 GHz the fixed powder shows a double resonance feature on the high field site which lies consistently at higher magnetic fields as compared to the feature observed in the loose powder. For all other frequencies their field position coincides. Although the shift is not significant its consistent behavior in a large frequency range suggest this double resonance to be independent of the single resonance on the high-field side

observed on the loose powder sample of GdInO_3 . At frequencies of 400 GHz and above, the double resonance is not visible anylonger, as it probably lies outside the accessible field range. At these higher frequencies the right shoulder of the resonance in the fixed powder sample of GdInO_3 was already described as less pronounced and shifted to smaller magnetic field strength. This feature coincides with what is visible in the loose powder sample of GdInO_3 and was probably masked by the more prominent double feature at lower frequencies. Smaller resonance features or those which could not be observed consistently throughout different frequencies are represented by smaller symbols in the diagram. Linear functions are fitted to the data points from the loose powder spectra as well as the ones of the double feature observable on the fixed powder sample of GdInO_3 . Their effective g -values are $g_{\text{eff}} = 2.11(2)$ (black) and $g_{\text{eff}} = 1.92(2)$ (red). The (phenomenological) zero field excitation gaps are $\Delta_{\text{black}} = 9(2)$ GHz and $\Delta_{\text{red}}^{\text{phen}} = -8(3)$ GHz (note that a negative intercept with the ordinate corresponds to an intercept of the abscissa at zero frequency, which means that this magnon branch probably shows mode softening), which roughly coincides with what was found at X-band frequencies (~ 9.34 GHz), where an excitation gap opened below T_N (see fig 6.7 in the appendix). The red linear fit describes the data still very well, when the zero field gap is set to zero. Because the fixed polycrystalline sample of GdInO_3 shows additional sharp resonances, which are attributed to impurity phases in the crystal (compare fig. 6.7 in the appendix), it is reasonable to assume, that these features should appear in the powder sample of GdInO_3 in high frequencies as well. The effective g -factor from the slope of the red linear fit (right shoulder in the loose powder resonances) matches the g -factor obtained for the additional resonance features of the powder measured in X-band frequencies. This paramagnetic-like resonance branch is thus likely to be due to the impurity phase(s) in the polycrystalline sample.

For the double feature (green and purple branch) the zero field gaps amount to $\Delta_{\text{green}} = 10(20)$ GHz and $\Delta_{\text{purple}} = 7(7)$ GHz. The slopes of the linear fit are very similar to each other with $g_{\text{eff}} = 1.69(14)$ (green) and $g_{\text{eff}} = 1.67(4)$ (purple). Dotted vertical lines mark the field positions where phase boundaries are expected from magnetisation data [19] both for fields applied along the c -axis (red) and along the ab -plane (black). None of the observed resonance branches seem to show any changes of their behavior at the field positions where a phase transition is expected. For external magnetic fields applied along the c -axis of the GdInO_3 single crystal an up-up-down (uud) spin arrangement is expected for fields between $\mu_0 H = 2.7$ T and $\mu_0 H = 4.12$ T, where a $1/3$ magnetisation plateau is observed [19]. This is at odds with other triangular *easy*-plane systems, where $1/3$ magnetisation plateaux appear for external magnetic fields applied along the planes [118, 119, 120, 121]. In these materials the resonance branches for external magnetic fields applied along

the c -axis can be described with a six-sublattice model in the field range below $B_{\text{uud}}^{\parallel c}$ [118, 119, 120, 121, 122, 123]. This model yields two resonance branches with the same zero field gap. One of the branches increases in frequency with increasing field, while the other decreases [118, 119, 120, 121, 122, 123]. Such a model could fit to the c -axis data, as the branch decreasing in field would lie below the accessible frequency range. However, in GdInO_3 the magnetisation plateau is observed for magnetic fields applied along the c -axis [19], such that the aforementioned model might not apply in the case of GdInO_3 . As already discussed *easy*-axis anisotropy is not supported by the ESR data, however Vasiliev *et al.* describe the *easy*-axis triangular sodium iron phosphite with an effective two sublattice ferrimagnetic model, which exhibits two linear magnon excitation modes [124]. The corresponding resonance branches behave similar to what is observed in GdInO_3 as they do not show any changes in behavior when the system enters the uud state. However, with increasing field both modes gradually merge, while the modes observed here diverge with increasing field. Without the knowledge of the exact spin-state(s) in GdInO_3 and some theoretical effort, the observed branches cannot be described or discussed exhaustively.

4.2.3 Conclusions

X-band-ESR as well as HF-ESR measurements were performed on single crystals and polycrystalline powder of the filled-honeycomb system GdInO_3 . Dependence of the X-band data on the angle of the applied magnetic field reveal strong dipole-dipole anisotropy as well as strong anisotropy due to crystal field effects. At temperatures below $T \approx 15$ K the dipole-dipole anisotropy contribution to the linewidth dominates. Below T_N a spin gap opens in the ordered state as evidenced by the vanishing resonance signal at X-band frequencies. Thus, a zero field excitation gap must lie between 10 GHz and 30 GHz, as HF-ESR data in the ordered phase show a resonance for 30 GHz. The linewidth vs. temperature for external magnetic fields applied along the c -axis shows additional broadening above $T \approx 20$ K, the origin of which is still elusive but could be attributed to a 2D character of GdInO_3 . There is no critical linewidth broadening towards T_N , as the increase in linewidth can already be explained by the increase in the susceptibility ratio. Furthermore, the ESR susceptibility most likely does not show a correlation maximum above the ordering temperature, as would be typical for low-dimensional materials. HF-ESR data suggest *easy*-plane anisotropy in agreement with magnetisation data. Short range correlations set in well above T_N possibly already at 150 K, which can be caused by low dimensionality, competing interactions or strong frustration. Altogether the ESR data does not seem to show typical 2D behavior for GdInO_3 .

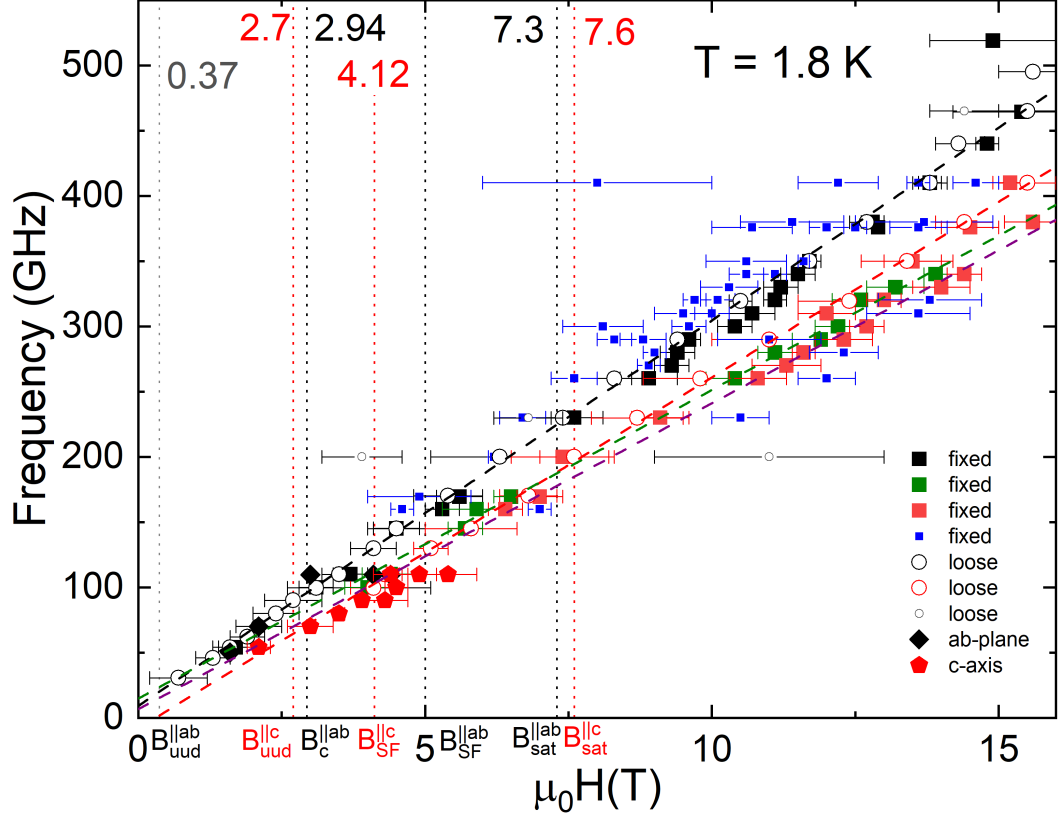


Figure 4.47: Frequency-field diagram showing the resonance positions in field of the GdInO_3 single crystal for magnetic fields applied along the c -axis (red pentagons) and within the ab -plane (black rhombus). Additionally, resonance positions obtained on the loose powder (open red and black circles) and the fixed powder sample (solid squares) of GdInO_3 are shown. Less pronounced resonance features are represented with smaller symbols. Dotted vertical lines indicate where magnetic phase transitions are expected for magnetic fields applied along the c -axis (red) and along the ab -plane (black). Dashed lines are linear fits to the main features of the loose powder sample (black and red) as well as to the double feature of the fixed powder sample (green and purple).

In the frequency-field diagram at least three linear, gapped excitation modes can be observed for GdInO_3 , none of which show any changes in behavior at the critical fields. The excitation gaps obtained from linear fits to the branches are in the order of 10 GHz, which matches the dipole-dipole anisotropy found from X-band ESR. One gapless mode is attributed to a paramagnetic resonance from impurity phases in the polycrystalline GdInO_3 sample. The observed modes can not be explained by the standard molecular field models usually used for triangular systems. Knowing the exact spin-structure is crucial for further analysis. Thus, neutron diffraction data is highly desirable for this compound.

5 Conclusions

In the presented thesis two frustrated and potentially low-dimensional antiferromagnets, $\text{PbCuSeO}_4(\text{OH})_2$ and GdInO_3 have been investigated by means of electron spin resonance spectroscopy. $\text{PbCuSeO}_4(\text{OH})_2$ is isostructural to the well-studied multi-ferroic linarite but exhibits a larger frustration parameter than its sister compound and axial instead of planar anisotropy. The ferroelectric GdInO_3 has the magnetically active gadolinium ions arranged on layers of a filled-honeycomb lattice, suggesting a quasi-two dimensional character and strong frustration.

In both compounds local magnetic fields develop well above the ordering temperature ($15 \cdot T_N$ for $\text{PbCuSeO}_4(\text{OH})_2$ and $71 \cdot T_N$ for GdInO_3), which can be a signature of low dimensionality, frustration or otherwise competing magnetic interactions. It is not possible to draw an immediate conclusion, which of the aforementioned mechanisms, if not all, is responsible for such an early onset of short range order correlations in the respective materials.

While low-dimensional behavior is suggested by the correlation maximum observed in the static and dynamic susceptibility of $\text{PbCuSeO}_4(\text{OH})_2$, GdInO_3 does not exhibit a clear sign of low-dimensionality in the magnetic properties, hence, low-dimensionality does not seem to play a significant role in this compound.

Linewidth analysis provides valuable insights to the type of relevant microscopic interactions in the investigated materials. In $\text{PbCuSeO}_4(\text{OH})_2$ either anisotropic or antisymmetric exchange seem to be the dominant contributions to the linewidth. In contrast GdInO_3 shows significant influence of crystal field effects at high temperatures, while dipole-dipole interactions seem to dominate for low temperatures above T_N . These differences in the underlying interactions causing anisotropy in each system can be explained by the fact that copper is a 3d ion, where spin-orbit coupling and thus single-ion anisotropy plays a major role. While, due to the half-filled 4f shell in the gadolinium ion and thus, quenched orbital moment, spin-orbit coupling is a secondary effect in the GdInO_3 . Hence, anisotropic exchange (both symmetric and antisymmetric) is suppressed and due to the smaller spatial extension of the 4f shells, exchange in general is less pronounced in such systems. This is evident by exchange interaction being two to three orders of magnitude larger in $\text{PbCuSeO}_4(\text{OH})_2$ than in GdInO_3 . Despite the suppressed spin-orbit coupling, crystal field splitting unexpectedly seems to play a significant role in GdInO_3 , which shows that admixture of

excited states should not be underestimated in materials with Gd ions as the magnetic centers. Additionally, due to the large spin of $S = 7/2$ in GdInO_3 compared to a (quantum) spin of $S = 1/2$ in $\text{PbCuSeO}_4(\text{OH})_2$, it makes sense that dipole-dipole interactions significantly influence the properties in the former compound, while they are negligible in the latter.

As expected for low-dimensional and frustrated systems, both compounds investigated in this study show a complex phase diagram, with afm order setting in at low temperatures ($T_N = 4.8$ K for $\text{PbCuSeO}_4(\text{OH})_2$ and $T_N = 2.1$ K for GdInO_3). In the frequency-field diagram, showing the field dependence of the resonance frequencies, several magnon resonance branches were observed in the ordered states. In neither of the materials the standard molecular field model magnon mode solutions describe the data. In such cases, where the theoretical description of the observed magnon modes is missing, only little quantitative information about, e.g., the anisotropy of the system can be gained from the frequency-field diagram. Qualitatively, hardly any information about the spin order can be derived either. In order to use the method of HF-ESR at its full potential, neutron diffraction experiments and theoretical analysis of the data should complement the respective study.

6 Appendix

6.1 Comparison of Fit Routines on $\text{PbCuSeO}_4(\text{OH})_2$ Data

Different fit routines for the temperature evolution of the resonance peaks at different frequencies are compared to extract resonance position and linewidth. To this end the fixed powder spectra measured at 315 GHz at different temperatures were fitted with an EasySpin simulation. Three different simulations are compared in fig. 6.1. All three allow for three independently varied g -values. In the first, the linewidth was kept at a fixed value of 200 mT. In the second the linewidth is allowed to vary and in the third anisotropic broadenings are simulated for three axes. In all cases lorentzian lineshapes were used. At 2 K all three simulations fit well to the data with the second simulation reproducing the data best, while at 13 K neither can reproduce the observed data. At high temperatures of 260 K all three simulations fit the data equally well. The general trend is that the simulations fit the data increasingly better for higher temperatures and the simulation with anisotropic linewidth is overall more successful. However, this could already be caused by the increased number of fit parameters and does not mean that there is indeed anisotropic linebroadening present in the spin-system. The temperature evolution of the linewidth extracted from the second and third simulation does not show any meaningful trend (data not shown) and generally the simulations are not good enough to give reliable information about the linewidth. Thus, the linewidth data extracted for the temperature evolution of the fixed powder resonance at 315 GHz is not used for any further analysis.

At 90.2 GHz the temperature evolution is more complex, as the additional resonance at low temperatures disappears for temperatures above the phase transition. The main feature, which prevails up to the highest measured temperatures (200 K), exhibits a slight shoulder on the left hand side, indicating the anisotropy present in the system. For this frequency five different fit approaches are compared: i) a fit of three respectively two Lorentz curves, ii) a single Lorentz curve, iii) a single Gauss curve, iv) an EasySpin simulation taking into account the random alignment of the powder grains with fixed linewidth (300 mT above 4 K, 200 mT below 5 K, the additional feature at 2 K was cut from the data) and v) an EasySpin simulation with varying

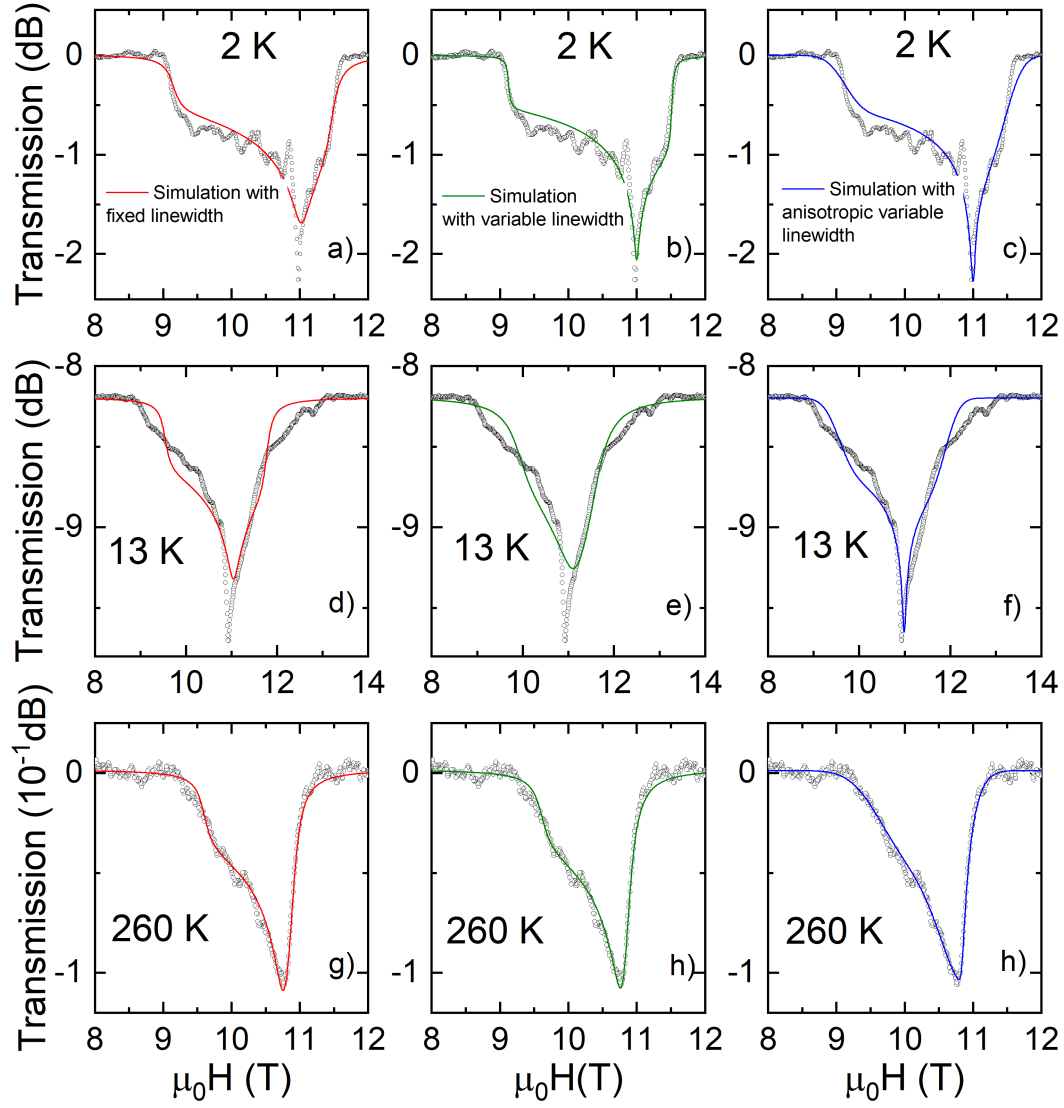


Figure 6.1: Comparison of different simulations fitted to the HF-ESR spectra measured at 315 GHz and different temperatures. See text for details.

linewidth. For both EasySpin simulations a lorentzian lineshape was assumed. Examples for selected temperatures are shown in figure 6.2. At high temperatures the single Lorentz and Gauß curve fit the data but the Gauss curve does not reproduce the data at lower temperatures. This shows, that exchange narrowing prevails up to very high temperatures, possibly all the way up to 200 K because the Lorentz curve still describes the data well at these temperatures. At the same time spin-diffusion becomes unlikely even at high temperatures because in that case neither gaussian nor lorentzian lineshape is expected [125]. However, it can not be ruled out either because for spin diffusion a lineshape between lorentzian and gaussian is expected. Since both curves fit the data well enough, some intermediate behavior should do so too. The single lorentzian fails to reproduce the shoulder in the main feature at 5 K and the more complex signal at 2 K. Both the EasySpin simulations fit the data reasonably well and there is no significant difference between the simulation with fixed linewidth and the one with varying linewidth. Especially at high temperatures, the sum of two Lorentz curves fits the data perfectly, while at 5 K and 2 K the fit has a more pronounced shoulder than the data. At 2 K, 3 K and 4 K three Lorentz curves were fitted instead of two to account for the additional resonance. In a fixed powder one would expect to see anisotropic behavior due to the random alignment of the powder grains. Thus, the EasySpin simulation, which takes this random alignment into account, should give the best fit results. However, especially for high temperatures, simply fitting two Lorentz curves seems to give the better results. Assuming some magnon mode contribution at such high temperatures, which could be described by a simple Lorentz curve, seems unreasonable. The difference in fit quality might instead be attributed to the number of available free fit parameters (6 for the two Lorentz curves, 3-4 for the EasySpin Simulation).

In the loose powder the signal at 60 GHz is so small that no meaningful analysis of the linewidth can be made. At 230 GHz the resonance feature does not show a behavior, which could be easily fitted by a simple peak function. The feature itself seems to be made up of two peaks. However, there is a rather broad regime of spectral weight between them similar to what one observes in a fixed powder. In an attempt to extract the linewidth from both peaks a sum of two Lorentz peaks is simulated/fitted to the data. At 2 K and 3 K both position and linewidth of the curves are fixed to 6.8 T & 7.9 T and 0.09 T & 0.4 T as well as 6.77 T & 8.0 T and 0.1 T & 0.3 T. For higher temperatures all fit parameters are allowed to vary. The fit gets better with increasing temperature.

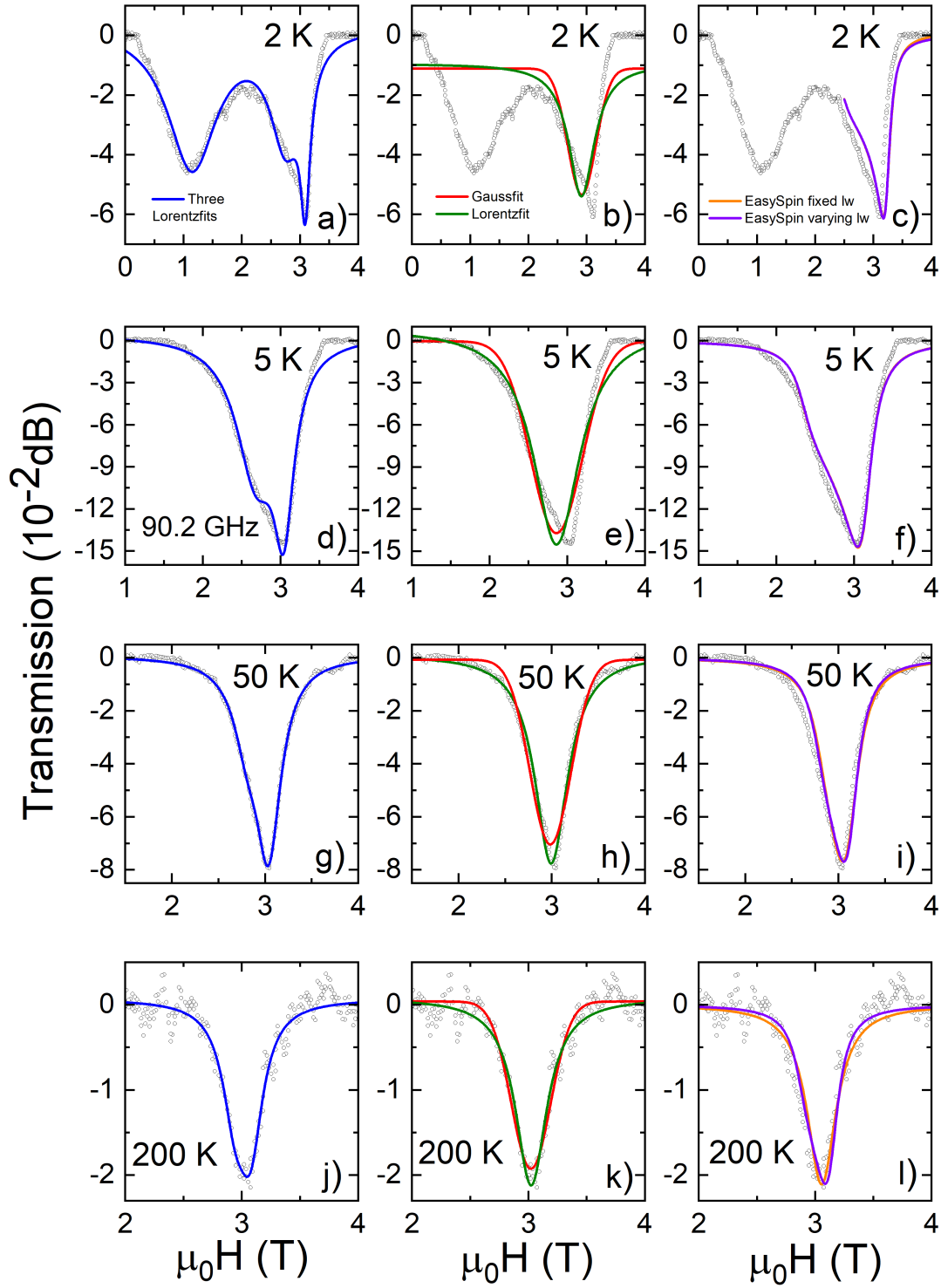


Figure 6.2: Comparison of different simulations fitted to the HF-ESR spectra measured at 90.2 GHz and different temperatures. See text for details.

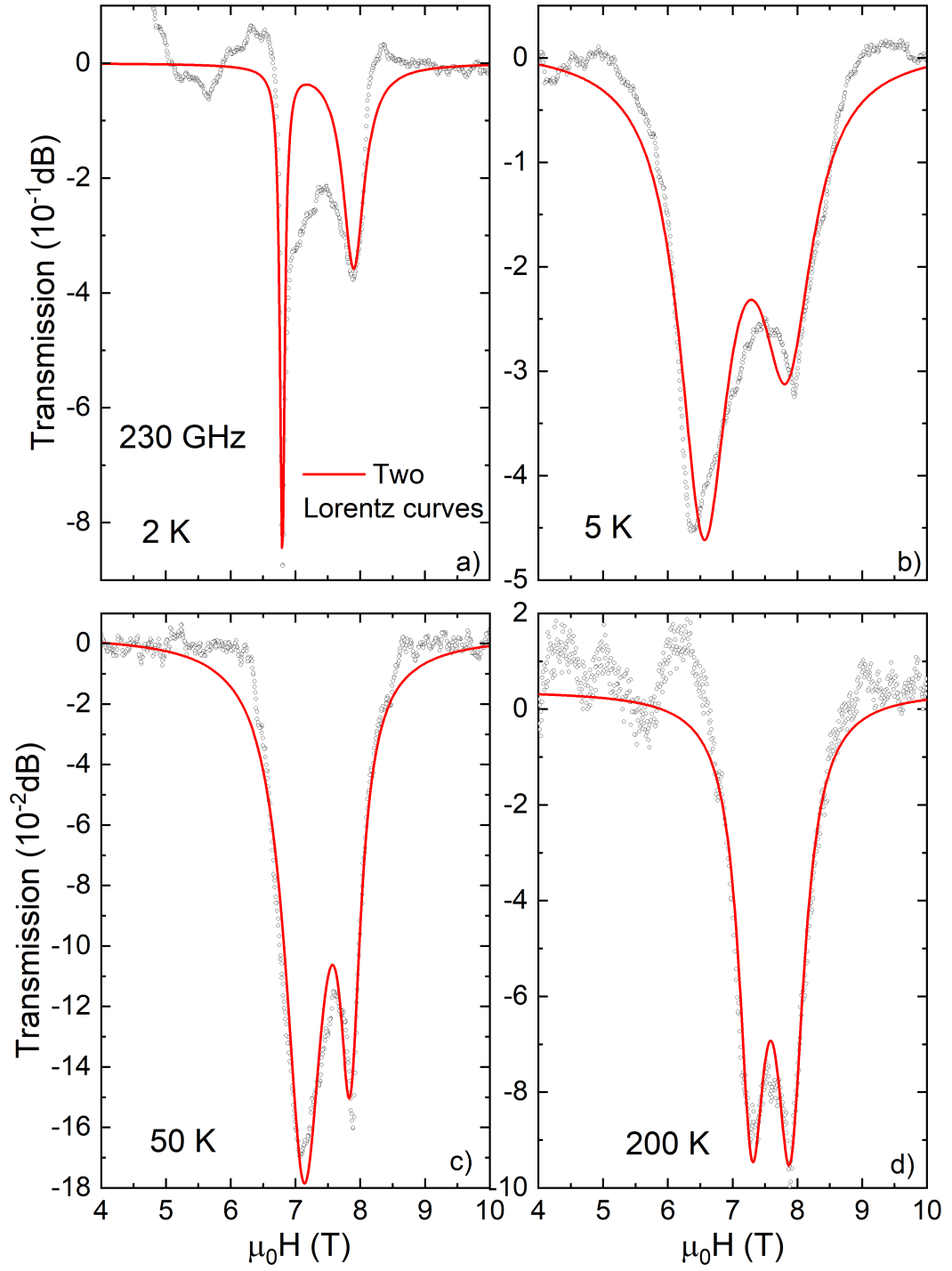


Figure 6.3: HF-ESR spectra measured at 230 GHz and different temperatures and a sum of two Lorentz curves fitted to them. See text for details.

6.2 ESR-Data of GdInO_3 at Different Temperatures

Fig. 6.4 shows the X-band ESR spectra of sample 1 of GdInO_3 at temperatures between 4.2 K and 1.7 K. Strong background fluctuations are visible in the temperature regime of the λ -point of liquid helium. The weak intensity and large linewidth of the resonance feature for external fields applied along the ab -plane render it nearly undetectable in the measurements (fig. 6.4(a)). For magnetic fields applied along the c -axis (fig. 6.4(b)) the linewidth of the resonance feature is smaller. The broad feature can be traced down to $T = 2.2$ K. For temperatures below T_N it is no longer visible. Instead, at very low external fields a steep decrease in the absorption power is visible (fig. 6.4(b)). This anomaly exhibits a hysteresis of about 0.0090 T (fig. 6.5), when ramping the field up and down. As can be seen from magnetisation data at $T = 1.8$ K (fig. 6.6) in the ordered phase, there is a net magnetic moment of about $m_{\text{eff}}^c = 0.08\mu_B/\text{f.u.}$ along the c -axis in GdInO_3 . Although the exact origin of the hysteretic anomaly in the absorption power is unknown, one is tempted to relate it to this net magnetic moment in c -direction in the ordered phase of GdInO_3 .

In order to get a stronger signal intensity, polycrystalline powder of GdInO_3 was measured in the X-band ESR at low temperatures as well. Fig. 6.7 shows that there are two additional dominant resonance features in the measurements on the GdInO_3 powder. Their intensity increases with decreasing temperature, while the resonance field seems to be constant. These additional features might be due to impurity phases in the crystallites, showing paramagnetic resonance. As in the single crystal, a broad resonance feature is visible as well, which disappears in the ordered phase, while the step like decrease at low magnetic fields shows up again. The ESR susceptibility of the whole resonance feature is obtained by doubly integrating the spectra. It is shown in fig. 6.8. There is a steplike decrease in ESR susceptibility at $T = 3.3$ K, which might be caused by part of the resonance signal lying outside the experimental range above this temperature. Below $T = 3.3$ K the susceptibility increases up to T_N and decreases with temperature below T_N . This shows that a spin gap opens in the ordered phase, as only the paramagnetic resonances of the impurity phase(s) contribute below T_N .

Fig. 6.9 and 6.10 show the temperature-dependence of the linewidth of the high-frequency resonance features of the single crystal as well as the powder sample of GdInO_3 . Fig. 6.9 shows only the linewidths from the features obtained at $f \approx 54$ GHz and 6.10 those for measurements done at about 110 GHz, 240 GHz and 260 GHz. The data in the linear plot was fitted by a critical fit in the temperature regime, where the log-log-plot (insets) shows linear behavior. The same data was fitted by a linear fit in the log-log-plot. For the loose powder sample of GdInO_3 measured at $f = 54$ GHz and $f = 110$ GHz, two features were extracted from the data by means

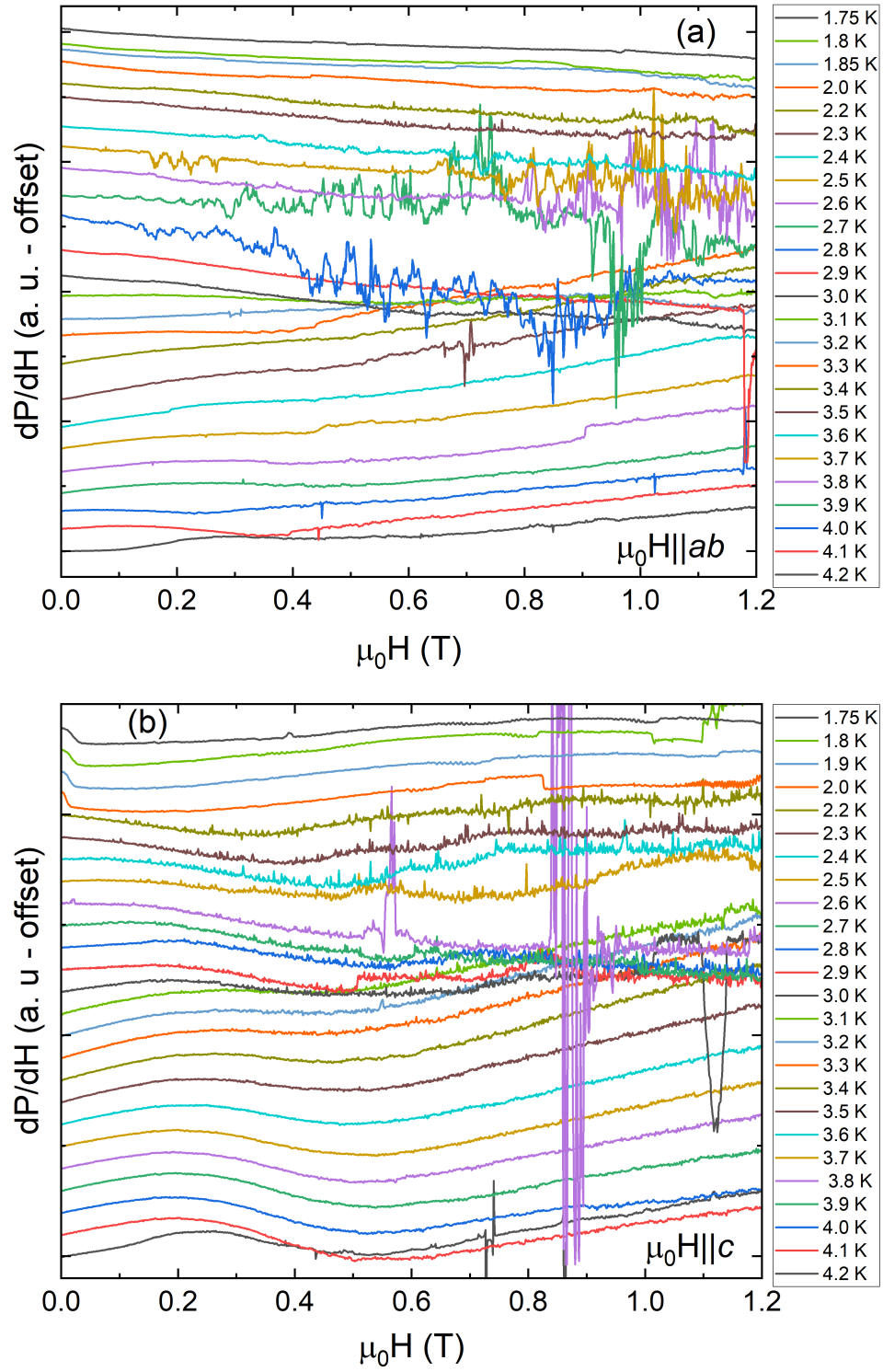


Figure 6.4: X-band ESR spectra measured at varying temperatures with (a) $\mu_0 H \parallel ab$ and (b) $\mu_0 H \parallel c$ on sample 1 of GdInO_3 . The noise between ~ 2.2 K and ~ 3.0 K is attributed to the λ point of the liquid helium in the dewer.

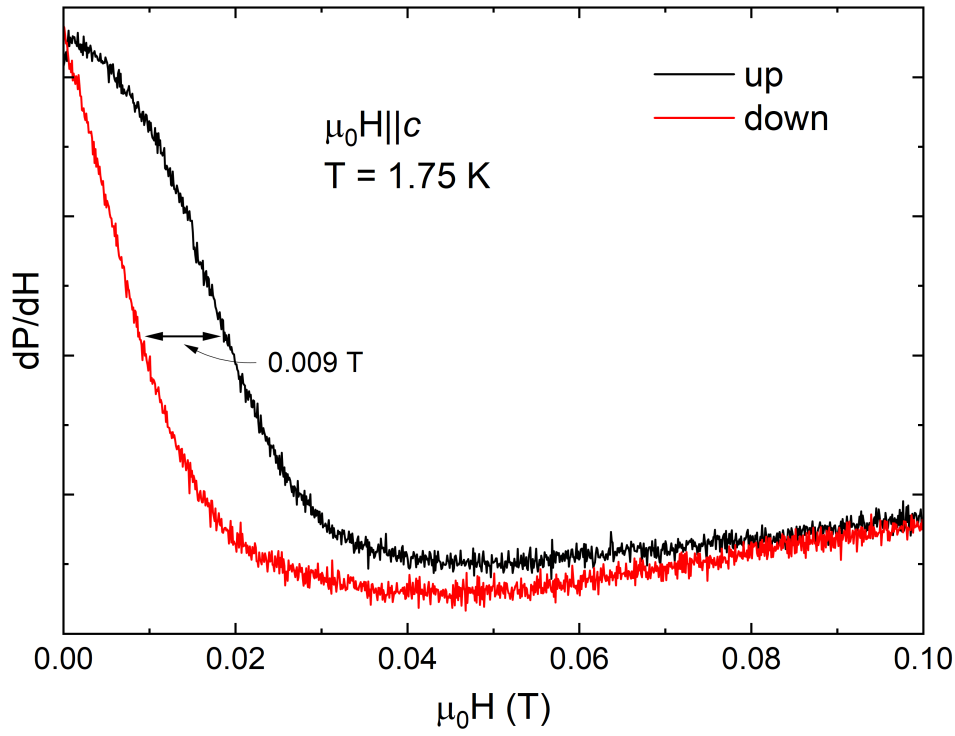


Figure 6.5: X-band ESR spectrum at $T = 1.75$ K measured with $\mu_0 H || c$ on sample 1 of GdInO_3 .

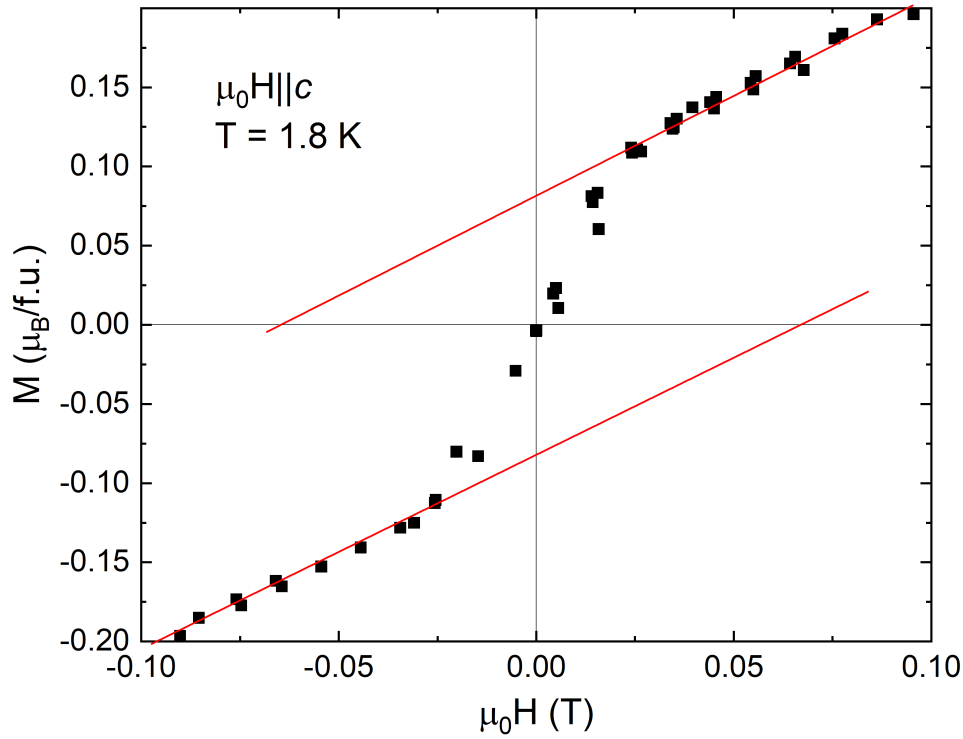


Figure 6.6: Isothermal magnetisation at $T = 1.75$ K measured with $\mu_0 H || c$ on sample 1 of GdInO_3 [19].

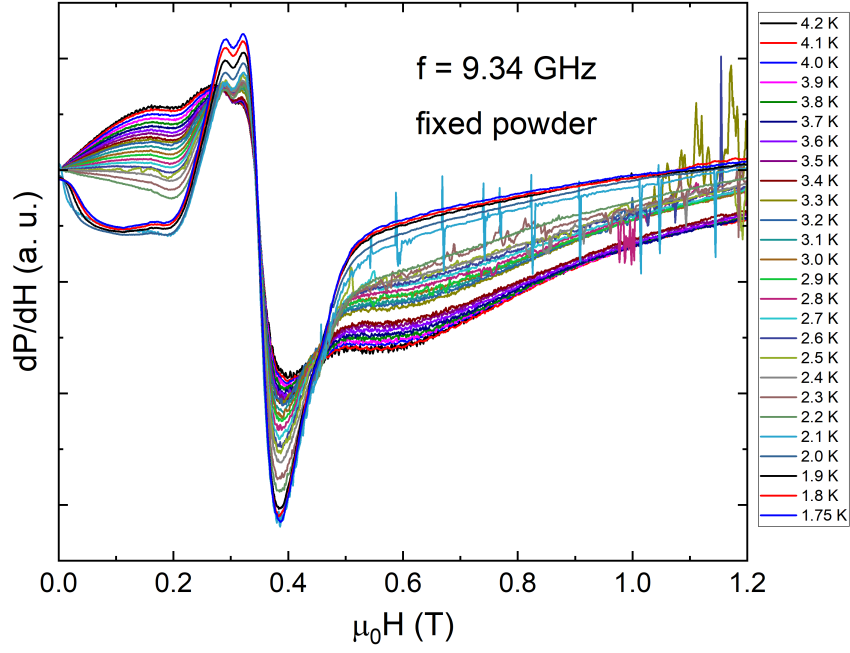


Figure 6.7: X-band ESR spectra measured on a polycrystalline powder sample of GdInO_3 at varying temperatures.

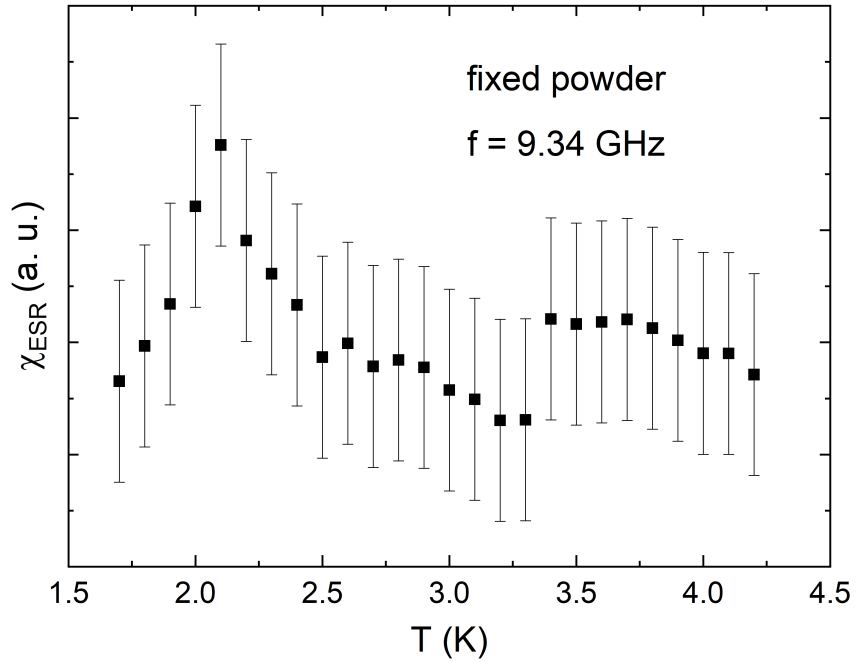


Figure 6.8: Temperature-dependence of the X-band ESR intensity (χ_{ESR}) obtained by doubly integrating the spectra measured on a polycrystalline powder sample of GdInO_3 .

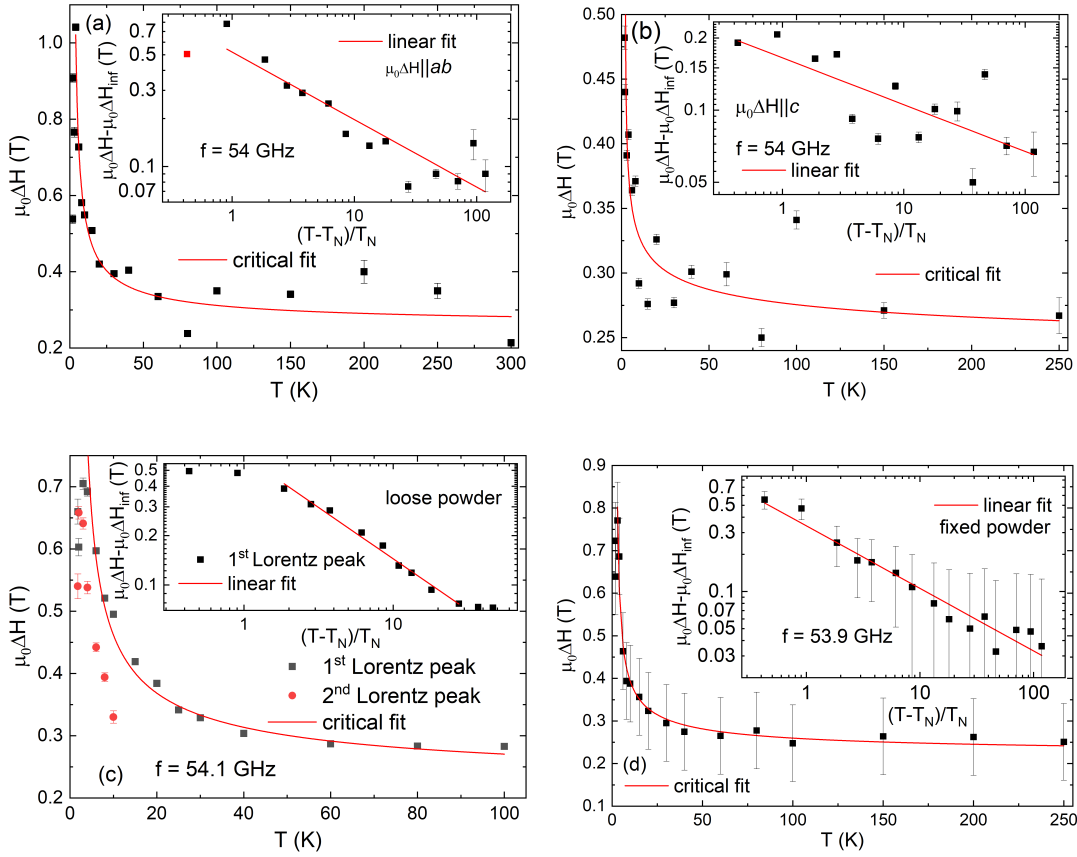


Figure 6.9: FWHM linewidth extracted from Lorentz fits to the single crystal and loose powder HF-ESR spectra and EasySpin fits to the HF-ESR spectra of the fixed powder sample of GdInO_3 measured at $f \approx 54$ GHz for (a) $\mu_0 H \parallel ab$, (b) $\mu_0 H \parallel c$ for the single crystal of GdInO_3 and on the (c) loose and (d) fixed powder sample of GdInO_3 . Solid lines are fits to the data.

of a double Lorentz fit. Only the linewidth of the first feature, which can be traced to the highest measured temperatures, was fitted. The fit parameters are collected in table 4.4 in the main chapter.

The temperature-dependence of the resonance feature intensity, which corresponds to the ESR susceptibility, is shown in fig. 6.11 and fig. 6.12. For the measurements on the single crystal with the external fields applied along the ab -plane and the c -axis the data is compared to the static susceptibility measured at $\mu_0 H = 2$ T. The ESR susceptibility of the loose powder sample of GdInO_3 (fig. 6.11(d) and fig. 6.12(a)) is compared to the static susceptibility of the single crystal for magnetic fields applied along the ab -plane, because the ab -plane is suspected to be the *easy*-plane, such that the loose powder grains are expected to align with their ab -plane to the external magnetic field. In order to be able to compare static susceptibility to the ESR susceptibility obtained from measurements on the fixed powder, a weighted average

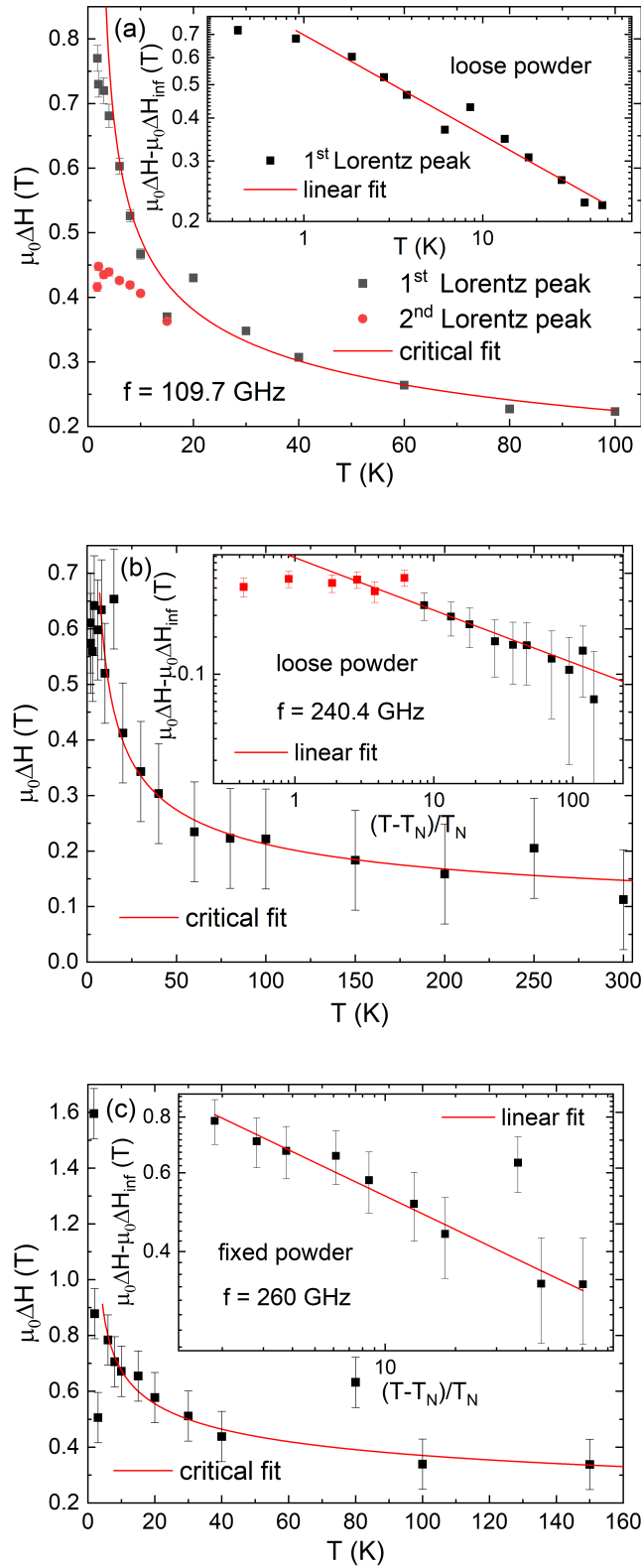


Figure 6.10: FWHM linewidth extracted from Lorentz fits to the single crystal and loose powder HF-ESR spectra and EasySpin fits to the HF-ESR spectra of the fixed powder sample of GdInO₃ measured at (a) $f \approx 110$ GHz, (b) $f \approx 240$ GHz on the loose and at (c) $f \approx 260$ GHz on the fixed powder sample of GdInO₃. Solid lines are fits to the data.

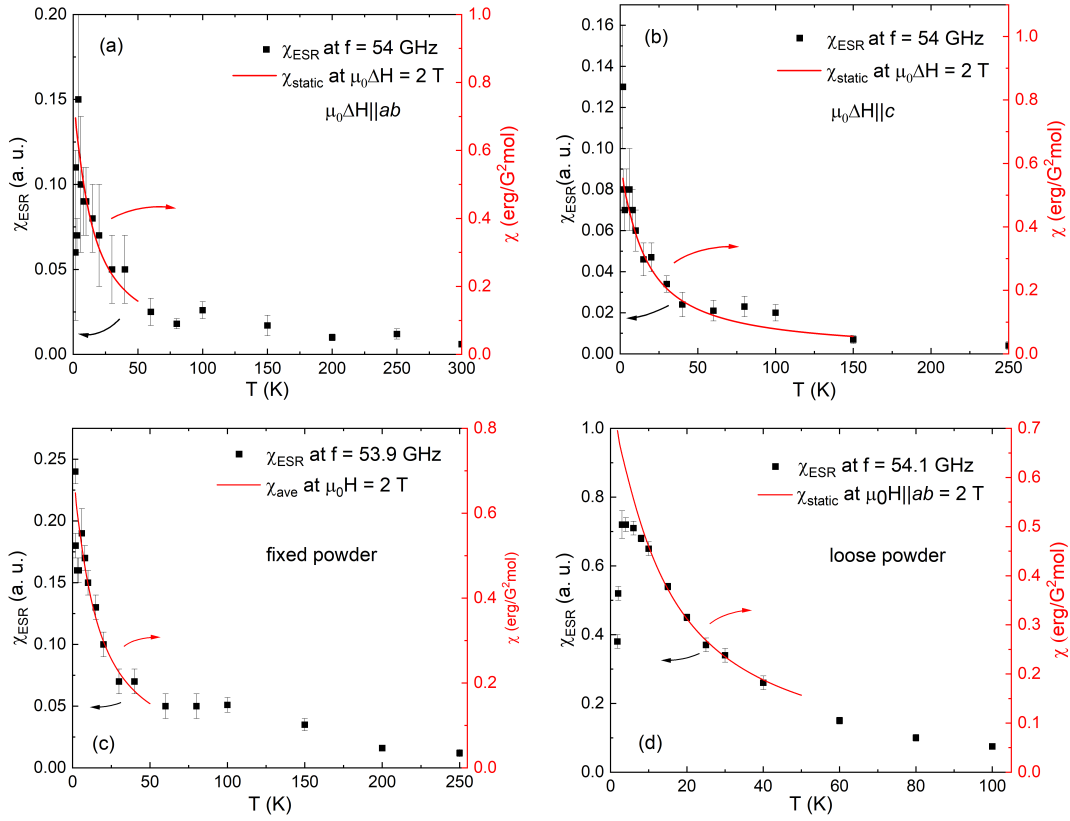


Figure 6.11: Resonance intensity (χ_{ESR}) extracted from Lorentz fits to the single crystal and loose powder HF-ESR spectra and from EasySpin fits to the HF-ESR spectra of the fixed powder sample of GdInO_3 measured at $f \approx 54$ GHz for (a) $\mu_0 H \parallel ab$, (b) $\mu_0 H \parallel c$ for the single crystal of GdInO_3 and on the (c) fixed and (d) loose powder sample of GdInO_3 . For the single crystal data χ_{ESR} is compared to χ_{static} at $\mu_0 H = 2$ T. In (c) the data from HF-ESR spectra is compared to the weighted average of χ_{static} of the single crystal for $\mu_0 H \parallel ab$ and $\mu_0 H \parallel c$. (d) χ_{ESR} extracted from the HF-ESR spectra measured on the loose powder sample of GdInO_3 is compared to χ_{static} of the single crystal with external magnetic field applied along the ab -plane (see text for details).

is calculated from the static susceptibilities of the single crystal for magnetic fields applied along the ab -plane and c -axis respectively: $\chi_{\text{ave}} = (2\chi_{ab} + \chi_c)/3$. There is excellent agreement between static and dynamic susceptibility in a large temperature range. However, at temperatures below 4 K most data sets show a drop in χ_{ESR} . Except for the data of the loose powder measured at 54 GHz, this drop does not seem very significant and often lies within the experimental error.

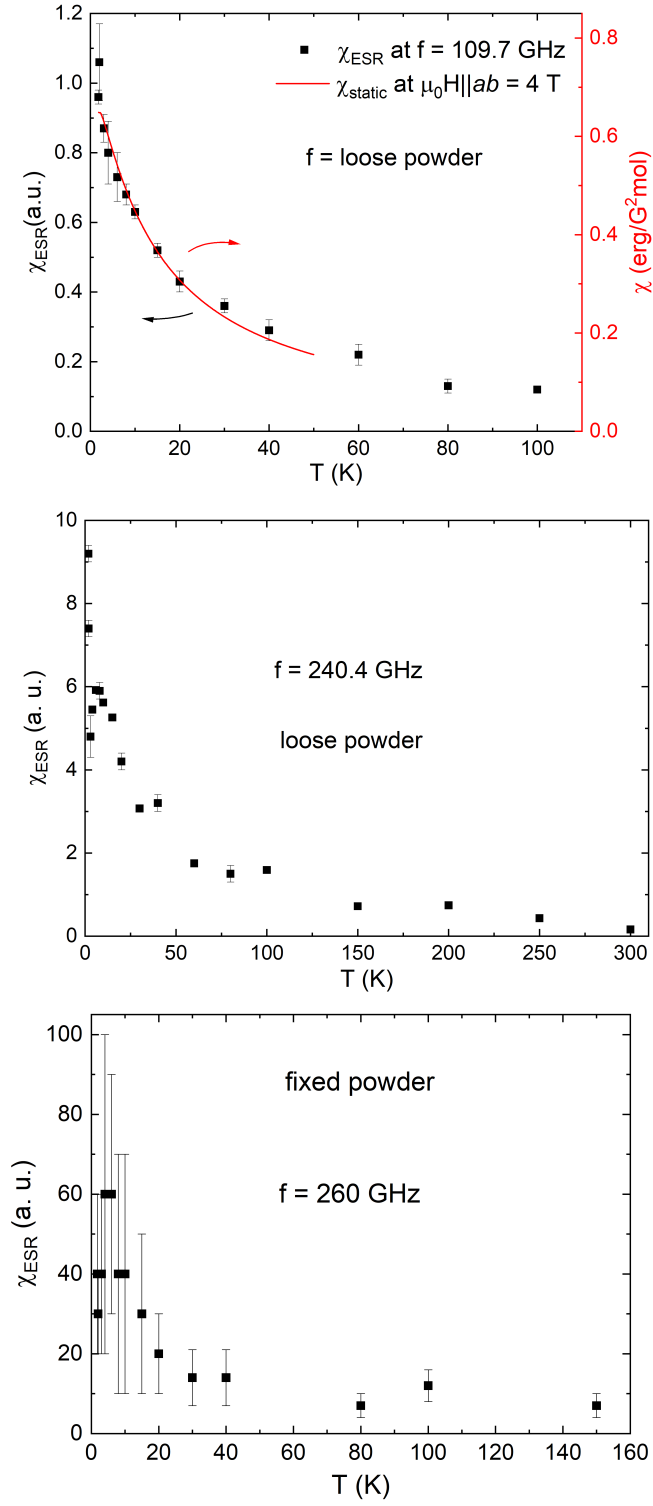


Figure 6.12: Resonance intensity (χ_{ESR}) extracted from Lorentz fits to the loose powder HF-ESR spectra and from EasySpin fits to the HF-ESR spectra of the fixed powder sample of GdInO_3 measured at (a) $f \approx 110$ GHz, (b) $f \approx 240$ GHz on the loose and at (c) $f \approx 260$ GHz on the fixed powder sample of GdInO_3 . In (a) the data is compared the the static susceptibility of the single crystal for external magnetic fields applied along the ab -plane.

6.3 Original Data to the 3D Plots

Figures 6.13 and 6.14 show the individual datasets corresponding to the 3D plots in the main section in fig. 4.26 and fig. 4.31.

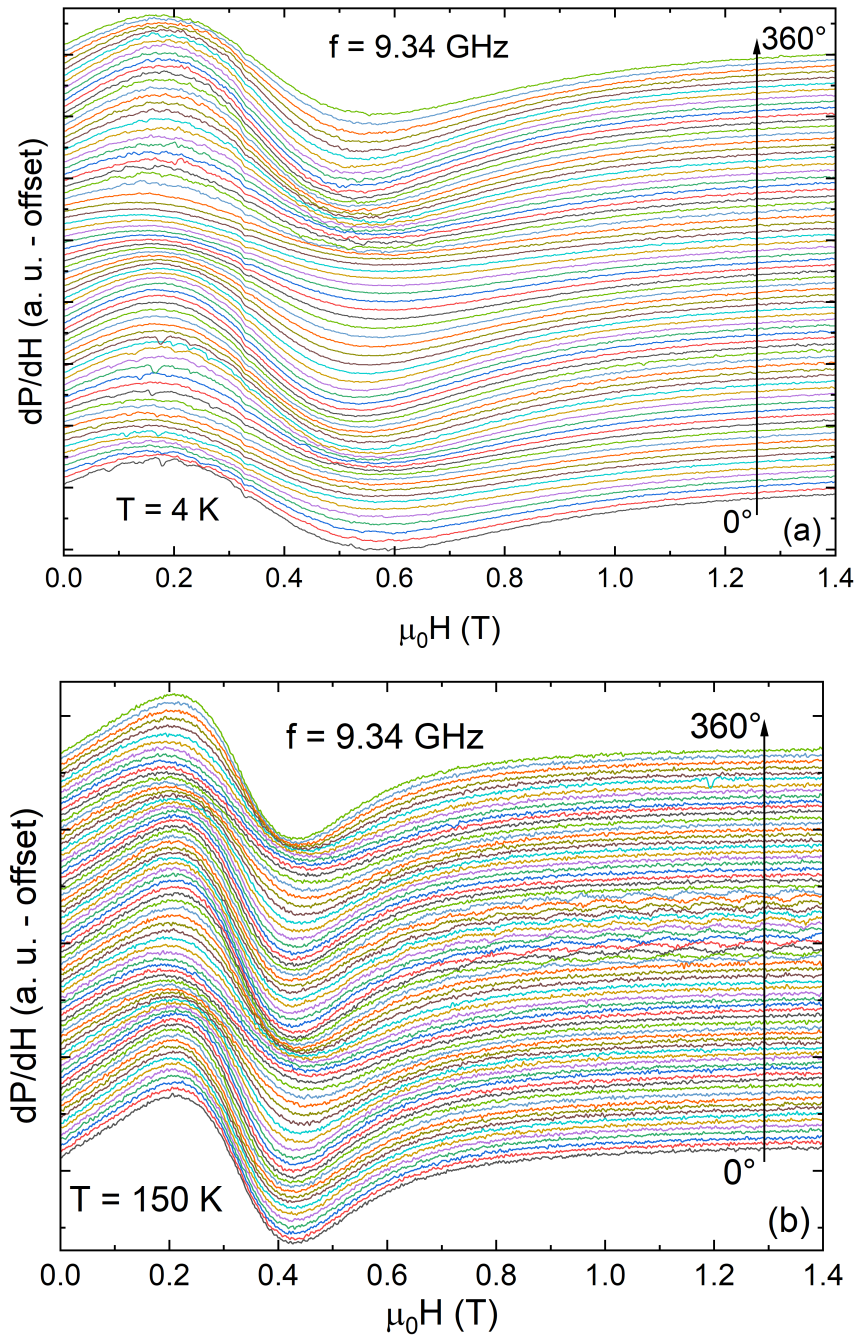


Figure 6.13: X-band ESR data for different angles of the applied magnetic field with respect to the crystallographic c -axis of GdInO₃ in 5 degree steps at temperatures of (a) 4 K and (b) 150 K. 35° correspond to $\mu_0 H || ab$ and 125° correspond to $\mu_0 H || c$.

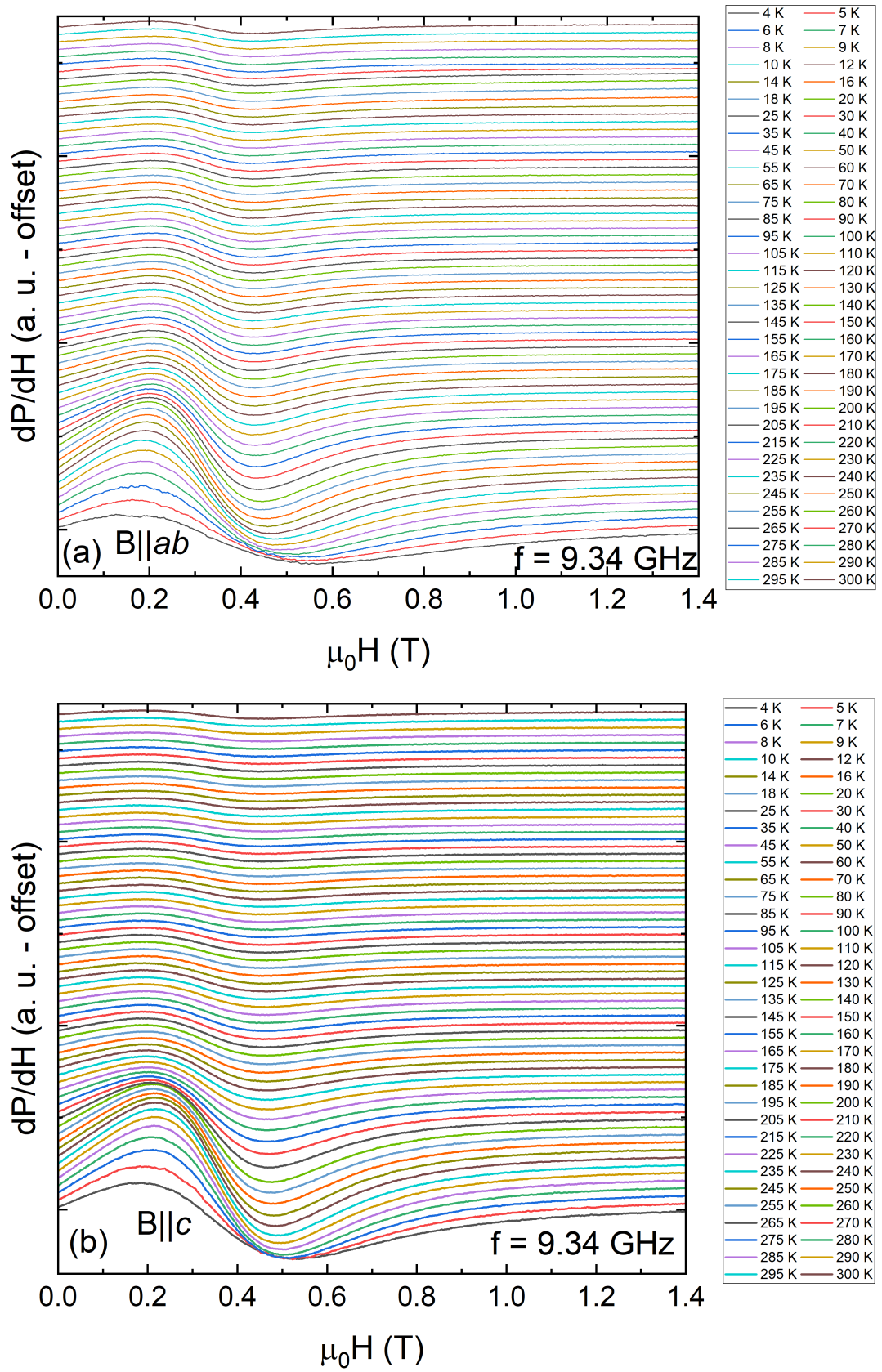


Figure 6.14: X-band ESR data different temperatures and the external field (a) $\mu_0 H \parallel ab$ and (b) $\mu_0 H \parallel c$.

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Erklärung

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

Heidelberg, den R. Ohlendorf,