High field electron magnetic resonance in complex correlated spin systems

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Abstract

Low dimensional (low-D) strongly correlated spin systems are an important topic in condensed matter physics. The dimension of the system and the spin value play a crucial role for the nature of ground states. The reduced dimension and the interplay between spin, orbital and charge degrees of freedom yield a variety of fascinating phenomena like superconductivity, quantum liquid and spin gap states, chiral phases, etc. Magnetic materials realizing these systems are quite often found in transition metal oxides such as cuprates and vanadates. In this thesis, we used the electron spin resonance spectroscopy (ESR) to investigate magnetic properties of low dimensional vanadium and copper oxides in which small quantum spins ($S = 1/2$) are arranged in 1D chains or 2D layers. In particular, we applied the technique of frequency tunable sub-Terahertz ESR in strong magnetic fields to gain insights into the complex and rich physics of these systems. The results of other techniques, in particular nuclear magnetic resonance and magnetization measurements, were largely involved in the discussion of the ESR data to obtain a comprehensive understanding of the magnetic properties of the studied materials.

The thesis covers five different low-D spin systems. They turned out to be experimental realizations of some of the most interesting theoretical models in the field of quantum magnetism. The thesis is divided into seven chapters. In the first chapter, the fundamentals of the 1D, quasi-1D and 2D spin systems are reviewed. The second chapter is devoted to the basics of the ESR technique and its applications in the field of low-D magnetism.

1D-systems: in the third chapter we present a systematic study of the properties of 1D zigzag chain $\text{In}_2\text{VO}_5$ compound. Our measurements reveal a crossover from the ferromagnetic and conducting regime at high temperatures to the insulating and predominantly antiferromagnetic behavior at low temperatures. This crossover eventually results in a frustrated glassy-like magnetic ground state without long-range order. In the fourth chapter we investigate the effect of Zn doping on the properties of quasi-1D spin-chain spin-ladder compound $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$. We found that Zn has a significant impact on the spin relaxation and conductivity. Our results emphasize the critical role of the hole redistribution between chains and ladders.

2D-systems: the fifth chapter highlights the low-D character of magnetism in the new 2D copper nitrate monohydrate $\text{Cu(NO}_3)_2\cdot\text{H}_2\text{O}$ compound. Various gapped resonance modes have been observed using high field ESR. These features are discussed by considering the ground state and magnetic excitations of random spin clusters which are realized in $\text{Cu(NO}_3)_2\cdot\text{H}_2\text{O}$. The sixth chapter reveals the nitrosonium nitratocuprate ($\text{NO})[\text{Cu(NO}_3)_3$] as a new 2D spin system, which according to our results provides the exact realization of the so called ‘confederate flag model’ (Nersesyan-Tsvelik model). The seventh chapter focuses on the magnetic properties of the $\text{InCu}_{2/3}\text{V}_{1/3}\text{O}_3$ compound, which is the realization of the 2D honeycomb model. Our results give evidence for Néel-like antiferromagnetic ground state that occurs in this material despite the low spin coordination number, the structural two dimensionality and in-plane structural disorder.

A summary and lists of the references for all chapters and publications can be found at the very end of the thesis.
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Preface

The field of strongly correlated spin systems in condensed matter physics is a fascinating story of mystery and surprise. In these systems, the interactions of the electrons strongly influence their physical properties and lead to many complex and exciting phenomena. Particularly in low dimensional spin systems, the interaction effects are usually very strong. In such systems, quantum fluctuations are more pronounced and the interaction of electrons with each other and with other degrees of freedoms gives rise to new phenomena that are very different from those familiar in the three dimensional systems. Hence, low dimensional spin systems are of special interest and subject to intensive research work.

The story dates back to 1925, only few years after the formulation of quantum mechanics, when Ernest Ising solved the known 'Ising model' in one dimensional (1D) spin system to provide a microscopic justification for Weiss’ molecular field theory [1]. In 1931 Hans Bethe published his paper describing the 'Bethe ansatz' method to find the exact quantum mechanical ground state of the antiferromagnetic Heisenberg model [3, 2]. At a meeting of the New York academy of science, 28 February 1942, Lars Onsager announced his solution of the two-dimensional (2D) Ising model in zero magnetic field and the details were published two years later [4]. This solution was the first exact solution of any kind to a system composed of more than two particles, hence it has been considered one of the greatest theoretical achievements of the past century. By the 60’s, theoreticians succeeded in calculating excitation energies, correlation functions and thermal properties for the quantum mechanical 1D Heisenberg model and (some of) its anisotropic generalizations and they connected between classical models in 2D and quantum mechanical models in 1D [5]. Therefore, theoreticians consider this field as playground for testing different methods and models.

At the beginning, experimentalists considered low dimensional spin systems as a theoretician’s toy. However in the 1970s, several families of magnetic compounds with linear chain structures were discovered and their properties recommended them as the realization of theoretical models developed a decade earlier [6]. During the last three decades the field of low-dimensional magnetism grew rapidly into one of the most active areas of contemporary condensed matter physics. There was an explosion of realization of such systems. CuCl$_2$.2NC$_5$H$_5$ is important as the first quantum chain which was investigated experimentally [7]. In 1992, CuGeO$_3$ (quasi-1D spin- 1/2 antiferromagnet) was discovered as the first inorganic spin-Peierls material [8]. In the mid eighties, the discovery of high temperature superconductors HTCS’s triggered an intensive research in the field of 2D cuprates. These HTCS’s exhibit 2D copper planes and the superconductivity is believed to be connected to the strong magnetic fluctuations which are possible in low dimensional materials [9, 10, 11].

An important characteristic of pure low dimensional magnets is the absence of long range order in models with a continuous symmetry at any finite temperature as stated
in the theorem of Mermin and Wagner [12], and sometimes even the absence of such ordering in the ground state [13]. These systems give unique possibility to study ground and excited states of quantum models, possible new phases of matter and the interplay of quantum fluctuations and thermal fluctuations. Hence, both theoretical and experimental research strongly interact and cooperate to provide better understanding to these systems.

Nonetheless, after many years of continuous study, the field of low dimensional spin systems still attracts an increasing interest. Several new unexplained problems and phenomena arise from the behavior of these systems and need farther researches and investigations.

The present thesis concentrates on studying the magnetic properties of low dimensional spin systems using the electron spin resonance spectroscopy. Other techniques, in particular NMR and SQUID, have appropriate contribution to the presented research work. The thesis covers five different low dimensional systems based on transition metal oxides ‘mainly Cu’. These systems turned to be the experimental realization of some of the most interesting theoretical models in the field of quantum magnetism. The thesis is divided into seven chapters.

- In the first chapter, the fundamentals of the low-dimensional spin systems are reviewed. The discussion is presented on general grounds and starts with the theoretical backgrounds. Later, we embark on our low-dimensional journey and move systematically from 1D to quasi-1D and reach finally 2D spin systems.

- The second chapter is devoted to the Electron spin resonance (ESR) technique. Through the chapter, the basics of the experimental techniques and a description of the used devices are presented. Then, a short survey on the applications of the ESR spectroscopy for studies of low dimensional magnetism is introduced.

- The third chapter is the actual beginning of my research work in this thesis. Here, we present a systematic study of the properties of 1D zigzag chain In$_2$VO$_5$ compound.

- The fourth chapter starts with an introduction to the quasi-1D spin-chain spin-ladder compound (known as the telephone number compound) Sr$_{14}$Cu$_{24}$O$_{41}$, followed by the investigation of the effect of Zn doping on the properties of this system.

- The fifth chapter highlights the low dimensional character of magnetism in the new 2D copper nitrate monohydrate Cu(NO$_3$)$_2$·H$_2$O compound.

- The sixth chapter reveals the nitrosonium nitratocuprate (NO)[Cu(NO$_3$)$_3$] as a new 2D spin system, which turned out to be the exact realization of the so called ’confederate flag model’ (Nersesyan-Tsvelik model).

- The seventh chapter focuses on the magnetic properties of the 2D InCu$_{2/3}$V$_{1/3}$O$_3$ compound, which is the realization of the spin-1/2 honeycomb model.

A summary and lists of the references for all chapters and publications can be found at the very end of this thesis.
1 Low dimensional spin systems

1.1 Theoretical principles

1.1.1 Pauli spin matrices and spinors

It has been experimentally found that an electron possesses an intrinsic magnetic moment, or spin. The existence of such a moment is a consequence of relativistic effects that are described by the Dirac wave equation. The quantum spin state of a spin-$\frac{1}{2}$ particle can be described by a complex-valued vector with two components, called a two-component spinor. When spinors are used to describe quantum states, quantum mechanical operators are represented by $2 \times 2$ complex Hermitian matrices. The Pauli spin matrices are [14]:

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$ (1.1)

It is convenient to think of these as a vector of matrices,

$$\sigma = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$$ (1.2)

and the spin angular momentum operator is defined as:

$$S^i = s \sigma_i$$ (1.3)

where $i = (x, y, z)$ and $s = \frac{1}{2}$ in units of $\hbar$, so that the angular momentum associated with an electron is actually $\hbar S$. It is only the $\hat{\sigma}_z$ which is diagonal with eigenvalues $m_s = \pm \frac{1}{2}$ and the corresponding eigenstates are $| \uparrow_z \rangle$ and $| \downarrow_z \rangle$ where

$$| \uparrow_z \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad | \downarrow_z \rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$ (1.4)

correspond to the spin pointing parallel and antiparallel to the $z$-axis, respectively. Hence

$$S^z | \uparrow_z \rangle = \frac{1}{2} | \uparrow_z \rangle, \quad S^z | \downarrow_z \rangle = -\frac{1}{2} | \downarrow_z \rangle$$ (1.5)
1.1. Theoretical principles

1. Low dimensional spin systems

The eigenstate of the spin pointing parallel and antiparallel to the \(x\)- and \(y\)-axis are:

\[
|\uparrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |\downarrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}
\]

\[
|\uparrow_y\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}, \quad |\downarrow_y\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}
\]

This two component representation of the spin wave functions is known as a spinor representation and the states are referred to as spinors. The spinors form the complete basis for the Hilbert space describing the spin-\(\frac{1}{2}\) particle. Thus, linear combinations of these two states can represent all possible states of the spin. Using Pauli matrices and spinors we get the following non-zero coupling amplitudes between spin states for spin operator components:

\[
\langle \downarrow | S^x | \uparrow \rangle = \langle \uparrow | S^x | \downarrow \rangle = 1/2 \\
\langle \downarrow | S^y | \uparrow \rangle = -\langle \uparrow | S^y | \downarrow \rangle = i/2 \\
\langle \downarrow | S^z | \uparrow \rangle = -\langle \uparrow | S^z | \downarrow \rangle = 1/2
\]

1.1.2 Exchange interactions

Exchange interaction is the most important interaction that allows the magnetic moments in a solid to communicate with each other and potentially to produce various ordering phenomena. From a classical perspective, one might expect two magnetic moments to interact via the classical dipolar force. The potential energy of configuration of two moments \(\mu_1\) and \(\mu_2\) separated by a distance \(r\) is [14]:

\[
E = \frac{\mu_0}{4\pi r^3} [\mu_1 \cdot \mu_2 - \frac{3}{r^2}(\mu_1 \cdot \hat{r})(\mu_2 \cdot \hat{r})]
\]

It is easy to estimate the order of magnitude of this interaction. For typical atomic moments of order 1 \(\mu_B\) separated by a distance \(r \sim 1 \text{ Å}\), such interaction amounts approximately to \(E < 1 \text{ K}\). Since many materials order at much higher temperatures, the magnetic dipolar interaction must be too weak to account for the ordering of most magnetic materials. However, it becomes important in the properties of those materials which order at milliKelvin temperature. Quantum-mechanical exchange is a much larger effect, and the dipolar interactions are therefore normally neglected in the discussions of magnetic interactions in solids. Exchange interactions are nothing more than electrostatic interactions, arising because two quantum mechanical spins can be in either a spin triplet (total \(S = 1\)), or singlet (total \(S = 0\)). Since these electrons are also charged, there will be a large energetic difference between the two spin configurations due to Coulomb interaction.

Assuming only two electrons with a total wave function composed of the product of single electron states \(\psi_a(r_i)\) and \(\psi_b(r_j)\), the wave function squared must be invariant for the exchange of both electrons. Since electrons are fermions, they must fulfill the Pauli exclusion principle which leads to an antisymmetric wave function. By considering the spin of the electrons two possibilities are given: a symmetric spatial part \(\psi\) in combination
with an antisymmetric spin part $\chi$ or antisymmetric spatial part in combination with a symmetric spin part. The first case represents a singlet state with total spin $S_{\text{total}} = 0$, and the second one represents a triplet state with $S_{\text{total}} = 1$ [15]. For these two cases, the total wave functions are given by:

$$
\Psi_S = \frac{1}{\sqrt{2}}(\psi_a(r_i)\psi_b(r_j) + \psi_a(r_j)\psi_b(r_i)) \cdot \chi_S
$$

(1.10)

$$
\Psi_T = \frac{1}{\sqrt{2}}(\psi_a(r_i)\psi_b(r_j) - \psi_a(r_j)\psi_b(r_i)) \cdot \chi_T
$$

(1.11)

taking into account normalized spin part of the singlet and triplet wave function

$$
S^2 = (S_i + S_j)^2 = S_i^2 + S_j^2 + 2S_i \cdot S_j
$$

(1.12)

Thus:

$$
S_1 + S_2 = \frac{1}{2}S_{\text{total}}(S_{\text{total}} + 1) - \frac{1}{2}S_i(S_i + 1) - \frac{1}{2}S_j(S_j + 1)
$$

(1.13)

for electrons $S_i = S_j = \frac{1}{2}$ and hence:

$$
S_i + S_j = \frac{1}{2}S_{\text{total}}(S_{\text{total}} + 1) - \frac{3}{4} = \begin{cases}
-\frac{3}{4} & \text{for } S_{\text{total}} = 0 \text{ (singlet)} \\
\frac{1}{4} & \text{for } S_{\text{total}} = 1 \text{ (triplet)}
\end{cases}
$$

(1.14)

The effective Hamiltonian in this case is:

$$
\mathcal{H} = \frac{1}{4}(E_s + 3E_T) - (E_s - E_T)S_1 \cdot S_2
$$

(1.15)

The exchange constant $J_{ij}$ can be defined as:

$$
J_{ij} = \frac{E_T - E_s}{2}
$$

(1.16)

The name 'exchange interaction' comes from the fact that operator $J_{ij}$ exchanges spins $i$ and $j$ providing the system with a possibility to lower the energy depending on the relative orientation of the spins of the two electrons. From Eq. (1.16), it is clear that in case of $J_{ij} < 0$ (ferromagnetic (FM) exchange) the spins favor parallel configuration and antiparallel configuration minimizes energy in case of $J_{ij} > 0$ (antiferromagnetic (AFM) exchange). The strength of the exchange interaction $J_{ij}$ falls down rapidly as the distance between interacting spins increases. For discussing the magnetic properties of materials it is sufficient to consider only the spin dependent term. Hence, the exchange interaction is of purely quantum mechanical nature and the form of this interaction was derived simultaneously by Heisenberg and Dirac in 1926. The most well known model of interacting spins is the Heisenberg model with the Hamiltonian:

$$
\mathcal{H} = \sum_{\langle ij \rangle} J_{ij} S_i \cdot S_j
$$

(1.17)

where the factor 2 is included in the double counting within the sum.
1.1. Theoretical principles

1. Low dimensional spin systems

1.1.3 Heisenberg Hamiltonian

Real magnetic solids are three dimensional (3D) but can be effectively considered as low dimensional systems if the exchange interactions have different strengths in different directions. The solid may be considered as a linear chain (1D) compound if the intrachain interactions are much stronger than the interchain ones. In planar magnetic systems (2D), the dominant exchange interactions are intraplanar. For many systems, the sites \( i \) and \( j \) in Eq. (1.17) are nearest neighbors (NN) on the lattice. If \( J_{ij} \)'s have the same magnitude \( J \) for all the NN interactions we will end with the isotropic Heisenberg model and the Hamiltonian then becomes:

\[
H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \tag{1.18}
\]

In the general case the \( J \) coupling is anisotropic and the fully anisotropic (NN) Heisenberg Hamiltonian in 1D is given by:

\[
H = \sum_{i=1}^{N} [J_x S_x^i \cdot S_x^{i+1} + J_y S_y^i \cdot S_y^{i+1} + J_z S_z^i \cdot S_z^{i+1}] \tag{1.19}
\]

The above Hamiltonian is symmetric for the three spin components \( S_x, S_y \) and \( S_z \). Generalizing Eq. (1.19) to arbitrary spin dimensions yields the \( n \)-component vectorspin model \( n \)-vector model [16]. For example \( n = 1 \) yields the Ising model, with one spin component \( S_z \). The spin dimensionality \( n \) must not be confused with the real space dimensionality \( D \) of the lattice. For example the square-lattice Ising model is characterized by \( n = 1 \) and \( D = 2 \) [17]. The spin-\( \frac{1}{2} \) Ising model is the simplest model of finite-temperature magnetism. Its advantage is the restriction to two spin states per site, \( | \uparrow \rangle \) and \( | \downarrow \rangle \), which are usually interpreted as the \( z \) components of the atomic moment. This greatly simplifies the calculation, although the main problem, namely the exponential dependence on the number \( N \) of spins, remains. Nevertheless, for NN interactions, the ferromagnetic Ising model has been solved in one dimension (Ising 1925)[1] and in two dimensions (Onsager 1944)[4].

Figure 1.1: Various models for a spin-\( \frac{1}{2} \) chain as a function of \( J_z/J_{xy} \). From Ref. [17].
As mentioned above, the models can be classified as \( n \)-vector models. According to the number \( n \) of spin components (spin dimensionality), we have:

\[
\begin{align*}
    n = 1 & \quad (\text{Ising model}) & J_{xx} = J_{yy} = 0, J_{zz} \neq 0 \\
    n = 2 & \quad (\text{XY model}) & J_{xx} \neq J_{yy} \neq 0, J_{zz} = 0 \\
    n = 3 & \quad (\text{Heisenberg model}) & J_{xx} = J_{yy} = J_{zz} = J
\end{align*}
\]

For example, Ising models \((n = 1)\) include Ising chains \((D = 1)\), thin films \((D = 2)\), and bulk magnets \((D = 3)\). The \( n \)-vector model has been useful in the understanding of phase transitions, revealing essential differences between magnets with continuous symmetry \((n \geq 2)\) and without continuous symmetry \((n = 1)\).

Let us keep the rotation symmetry in the \( xy \) plane and chose different exchanges in the \( xy \) plane and the \( z \) direction, hence \( J_x = J_y = J_{xy} \neq 0 \) and \( J_z \neq 0 \). This is known as the \( XXZ \) Model and the Hamiltonian is given by:

\[
\mathcal{H}_{XXZ} = \sum_{i=1}^{N} J_{xy}(S_i^x \cdot S_{i+1}^x + S_i^y \cdot S_{i+1}^y) + J_z S_i^z \cdot S_{i+1}^z \quad (1.20)
\]

This allows to represent the various domains as function of \( J_z \) as shown in Fig. (1.1). If \(|J_z| > |J_{xy}|\), the positive region is the Ising FM model and the negative one is the Ising AFM model. However, for \( J_z = \mp J_{xy} \) this is the case of the Heisenberg FM and AFM models respectively. In a special case and when \( J_z = 0 \), we will end with the pure \( XY \) Model.

### 1.2 One-dimensional spin systems

In contrast to magnetic systems with classical long-ranged ferro- or antiferromagnetic order, novel ground state properties arise due to the existence of strong quantum fluctuations in reduced dimensions. Therefore, the term quantum magnetism is commonly in use for this field of research. The Mermin and Wagner theorem stated [12]:

*An infinite \( D \) dimensional lattice of localized spins cannot have long-range order (LRO) at any finite temperature for \( D < 3 \) if the effective exchange interactions are isotropic and of finite range.*

In 1D spin systems, the quantum fluctuations are particularly strong and the AFM order is often suppressed even at zero temperature. However, it implies the possibility of complex excitations which are still far from being completely understood. A 1D array of spins is known as a spin chain. The individual spins can lie parallel or anti parallel to a particular direction (Ising spins), or may be free to point anywhere in a fixed plane (\( XY \) spins), or even free to point in any direction (Heisenberg spins). The spin chains are realized when the crystal structure allows the interaction of the spins in certain direction.
1.2. One-dimensional spin systems

Figure 1.2: Spin excitations on a 1D Heisenberg antiferromagnetic spin chain. a) to c) The generation of two spinons (dashed lines) and then the free propagation process. d) Dispersion relation for spinons in the 1D AFM Heisenberg chain.

to be much stronger than in the other two directions, hence this direction will be the chain direction.

In the Ising spin-$\frac{1}{2}$ chains, the excitations are associated with the creation of domain walls and which costs a finite amount of energy. Once the excitation is created it can move freely along the chain [14]. Whereas, in Heisenberg AFM half-integer ($S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ...$) spin chains, the ground state is given by a spin-singlet with total spin zero characterized by a 'spin liquid'. In the thermodynamic limit with 'periodic boundary conditions' the excitations are described as massless $S = \frac{1}{2}$ spinons. Such excitations can be created only in pairs because a total spin must be either integer or half-integer. Thus, in the Heisenberg chain the conventional magnons are deconfined into spin-$\frac{1}{2}$ spinons, giving rise to a two-spinon continuum. These excitations (spinons) are gapless and have the dispersion relation:

$$\hbar \omega = \pi |J \sin(qa)|$$

where $J$ is the AFM exchange coupling, $a$ is lattice constant and $q$ is the wave vector, both $a$ and $q$ measured along the chain direction. However the Heisenberg AFM integer ($S=1,2,3,....$) spin chains have a different behavior.

1.2.1 Haldane chains

Haldane conjectured that the 1D Heisenberg antiferromagnet chain with integer spin, in contrast to the case of half-integer spin, has a unique disordered ground state with unbroken rotational symmetry and with a finite excitation gap ($\Delta$) in the spectrum [18]. A one-dimensional chain of integer spins is therefore known as a Haldane chain and the gap in the excitation spectrum as Haldane gap. These phenomena are different from the usual source of gaps in magnets; namely, single ion anisotropy, which does not involve quantum correlation effects. The fundamental difference between half-integer and integer spin chains
is related to the difference between fermions and bosons under exchange, which has a dramatic effect on the nature of the excitations.

The physical understanding of these phenomena is based on the so called '(AKLT) model' which was introduced by Affleck, Kennedy, Lieb and Tasaki [19]. The ground state can be represented as bilinear-biquadratic Hamiltonian [20]:

$$H = J \sum_{i=1}^{N} (S_i \cdot S_{i+1}) + \beta (S_i \cdot S_{i+1})^2$$

Here, $S_i$ is the $S = 1$ spin operator, $\beta$ is a relative coupling constant in the chain, and the sign of $J$ determines the FM or AFM regimes. The ground state wavefunction of the Hamiltonian (1.22) was constructed by considering each original $S = 1$ spin as two $S = 1/2$ spins in a triplet state. Then the ground state is obtained by coupling into a singlet state all nearest-neighbor spins-$1/2$, thus forming a crystalline pattern of valence bonds. This state is called the valence-bond-solid state (VBS) [21]. The VBS state of the $S = 1$ AFM chain is characterized by the development of string correlations which reflect a hidden topological long-range order [22, 23].

The properties of the ground state are determined by an angle, $\theta$, such that $J = |a| \cos \theta$ and $J\beta = |a| \sin \theta$. A rich phase diagram can be obtained as shown in Fig. (1.3). In this diagram the Haldane phase should occur in the region $\theta \in [-\pi/4, \pi/4]$, with $\theta = 0$ being the Heisenberg point and $\theta = \arctan 1/3$ being the (AKLT) point [19], which is of particular importance because it can be described with an exact valence bond wave function [24]. The gap vanishes for $\theta = \pi/4$ which is critical points separating the Haldane phase from the trimerized AFM phase, this point is known as the Uimin-Lai-Sutherland (ULS) critical

Figure 1.3: Phase diagram of the bilinear-biquadratic $S=1$ chain. From Ref. [20].
point \([25, 26, 27]\). The Takhtajan-Babujian critical point (TP) is another critical point at \(\theta = -\frac{\pi}{4}\) \([28, 29]\), which displays a second order phase transition into a dimerized gapped phase, and with an exactly solvable model at \(\theta = -\frac{\pi}{2}\) \([30, 31]\).

### 1.2.2 Spin-Peierls transition

The half-integer AFM chains are gapless, unless magnetoelastic coupling opens up a gap. This happens at the spin-Peierls transition. In a simplified picture, above the transition temperature \(T_{sp}\), there is an uniform AFM next neighbor exchange in each chain; below \(T_{sp}\), the distances between neighboring spins are no longer uniform but alternate. Due to the magnetoelastic coupling this leads to an alternation of the exchange coupling and each pair of stronger-coupled spins is forming a spin singlet which is known as a dimer.

The dimerization leads to a gain of magnetic energy which overcompensates the loss of elastic energy arising from the alternating structural distortion along the spin chains. The dimerization increases gradually as the temperature decreases and reaches a maximum at zero temperature. Such chains possess an energy gap between the singlet ground state and the lowest lying band of triplet excited states. The magnitude of the the gap is related to the degree of dimerization and so the degree of lattice distortion \([14]\). The uniform chain has zero lattice distortion and hence zero dimerization so that we return back to the gapless spinon case. In this sense, the spin-Peierls transition is a 3D structural phase transition which is driven by the 1D magnetism. The name ‘spin-Peierls (SP) transition’ arises from the fact that this transition is the magnetic analogue of the ‘Peierls transition’, which is a metal insulator transition occurring in (quasi-) one-dimensional metals.

There are several characteristic features which hallmark the spin-Peierls transition experimentally. Below \(T_{sp}\), superstructure reflections can be observed due to the structural distortion leading to the doubling of the unit cell. Also, \(T_{sp}\) shows a very characteristic magnetic field dependence. In addition, there is a drop of the magnetic susceptibility below \(T_{sp}\) due to the formation of non-magnetic spin singlets. Thus the magnetic susceptibility \(\chi(T)\) shows a knee at \(T_{sp}\). The realization of the SP state is very rare especially in the inorganic compounds. The AFM chains often become three-dimensionally ordered at low temperature due to the interchain interaction.

The formation of a spin-Peierls ground state is possible when the spin-phonon coupling is strong enough to dominate the interchain spin-spin coupling which is realized only in a few materials. In 1993, CuGeO\(_3\) was recognized, on the basis of magnetic susceptibility measurements as the first inorganic compound showing a SP transition \([8]\). Later, TiOCl was discovered as the second inorganic SP compound \([32]\). The inorganic nature of these compounds has opened the door to new investigations on the nature of SP compounds.
1.2. One-dimensional spin systems

1.2.3 AFM alternating chains and frustration

In the general case, an AFM alternating-exchange Heisenberg chain is the one in which NN spins in the chain interact via a Heisenberg interaction, but with two AFM exchange constants \( J_2 \leq J_1 \), \( J_1, J_2 \geq 0 \) which alternate from bond to bond along the chain. The alternating chain is realized in nature in many materials that have two important but structurally inequivalent superexchange paths that are spatially linked, so that a series of spin-spin interactions of strength \( J_1 - J_2 - J_1 - J_2 \) results [Fig (1.4b)]. A perfect example of materials of this type is Cu(NO\(\text{3}\))\(\text{2} \cdot 2.5\text{H}_2\text{O}\) system [33, 34]. Alternating chains may also arise as a result of the spin-Peierls effect [see Sect. (1.2.2)]. The Hamiltonian of the alternating Heisenberg linear chain may be written as:

\[
\mathcal{H} = \sum_{i=1} J_1 S_i \cdot S_{i+1} + J_2 S_i \cdot S_{i+2} \tag{1.23}
\]

where \( J_1 \) and \( J_2 \) are NN and next nearest neighbor (NNN), respectively. Introducing an alternation parameter \( \alpha = J_2/J_1 \), the Hamiltonian can be written as:

\[
\mathcal{H} = J_1 \sum_{i=1} (S_i \cdot S_{i+1} + \alpha S_i \cdot S_{i+2}) \tag{1.24}
\]

The uniform gapless AFM Heisenberg chain is one limit of the alternating chain in which the two exchange constants are equal (\( \alpha = 1, J_1 = J_2 = J \)). At the other limit is the isolated dimer in which one of the exchange constants is zero (\( \alpha = 0 \)) and the energy gap equal to the intra-dimer coupling \( J_1 \). For \( \alpha > 0 \) exhibits the effects of frustration from these two competing interactions.
In frustrated systems, it is impossible to satisfy all the interactions in the system to find the ground state. In this case, no single unique ground state can be found but a variety of similar low energy states on which the unhappiness (non-minimization of the energy) is shared around as much as possible [14]. The origin of their complex can be illustrated by as few as three spins on the triangle as shown in Fig. (1.4c). Once two of these spins are antialigned to satisfy their AFM interaction the third spin can no longer point in a direction opposite to both other spins. Thus not all interactions can be minimized simultaneously. In other words, AFM interactions are incompatible with the triangular lattice symmetry, a situation known as geometrical frustration [35]. Considering a chain of spins as presented in Fig. (1.4d), both the NN interaction $J_1$ and NNN interaction $J_2$ are AFM. When $J_2 \ll J_1$, all NN bonds are satisfied but the NNN ones are not. However, when $J_2$ exceeds a critical value, both the NN and NNN bonds are not fully satisfied. These cases are equivalent to the zigzag chain shown in Fig. (1.4e), which is also known as a two leg zigzag ladder. All this chains can be described by the same Hamiltonian presented in Eq (1.23) and Eq (1.24).

In general, frustration suppresses AFM correlations and the tendency towards the Néel order. Classical systems, for example, often show a helical ordered state in their ground states in the presence of strong frustration. In quantum spin systems, the interplay of frustration and quantum fluctuations plays an important role which causes exotic phenomena, e.g., a spin-liquid state and a spontaneous symmetry breaking. The generic Hamiltonian for dimerized and frustrated spin chains reads:

$$\mathcal{H} = J \sum_{i=1}^{\text{site}} \left[1 + (-1)^i \delta \right] (S_i \cdot S_{i+1} + \alpha S_i \cdot S_{i+1})$$

where $\delta$ is the parameter of the dimerization. In the classical limit the system develops spiral order in the ground state for $\alpha > \frac{1}{4}$ whereas for $S = \frac{1}{2}$ the system undergoes a Berezinskii-Kosterlitz-Thouless (BKT) type quantum phase transition from spin liquid to dimerized phase at $\alpha = \alpha_c \approx 0.24$ [36, 37]. When $\alpha < \alpha_c$, the completion between the NNN and NN interactions does not change the character of the simple antiferromagnetic case $\alpha = 0$, whose ground state is described as spin liquid with massless spinon excitations.
When $\alpha > \alpha_c$, the frustration term is relevant and the ground state changes to the strong-coupling dimerized phase. This dimerized state is characterized by a singlet ground state with the doubled lattice constant and twofold degeneracy and an excitation gap to the first excited states, a band of triplets. With such explicit dimerization the ground state is unique and a gap opens up immediately, $E_g \propto \delta^{2/3}$ [38]. The ground state prefers to have singlets at the strong bonds and the lowest excitations are propagating one-triplet states [6]. The model with both NNN exchange and alternation is equivalent to a spin ladder and will be discussed in more detail in Sect. [1.3].

A new phase with a broken parity and characterized by the nonzero value of chirality would appear in an anisotropic (easy-plane) AFM $S = \frac{1}{2}$ chain with sufficiently strong frustrating NNN coupling [39]. The chiral phases were numerically found for $S = \frac{1}{2}$ [40][41] and the resulting phase diagram for $S = \frac{1}{2}$ is shown in Fig. (1.5).

### 1.3 Quasi 1D spin systems

Let us now turn to the 3D coupling of the 1D chains, which is of prime importance in order to compare with realistic compounds. However, this is a very complicated problem, because in addition to the chain Hamiltonian we should add an AFM coupling between the chains [17]

$$H_{\text{inter}} = J_\perp \sum_{\langle ij \rangle} S_{n,i} \cdot S_{n,j}$$

(1.26)

where $n$ is the site index and $i, j$ the chain index. $\langle ij \rangle$ denotes the NN in the 2D or 3D lattice of chains. An ordered state for the spin system is expected in the presence of the interchain coupling. However, the critical temperature at which the system orders has to be a function of the transverse couplings and has to go to zero when this coupling vanishes. If the interchain coupling is weak compared to the intrachain coupling, then the perturbation caused by the 3D coupling is negligible compared to the ‘bandwidth’ of the 1D system. The AFM order is the slowest decaying correlation function in the 1D, hence one expects the 3D coupling to stabilize this order. The important question now is how to move from the 1D world toward the 2D or 3D one and thus to consider a small number of coupled chains (tow, three, four, etc.) and to investigate how the physical properties evolve with the number of chains. This is known as spin ladders.

#### 1.3.1 The even-leg ladder

Spin ladders are quasi-1D spin systems which consist of two or more coupled spin chains and thus are ideally suited for study the crossover from 1D chain to the 2D AFM. Ladders of various types ($n = 2, 3$ legs) are shown in Fig. (1.6). The prototype of spin ladders has the geometry shown in Fig. (1.6a) and is defined by the Hamiltonian [42]

$$H = J_{\|} \sum_{i=1,2} \sum_n S_i(n) \cdot S_i(n+1) + J_\perp \sum_n S_1(n) \cdot S_2(n)$$

(1.27)
1.3. Quasi 1D spin systems

The NN isotropic couplings along the chains and the rung exchange interactions are of strength $J_\parallel$ and $J_\perp$ respectively. In order to discuss the different properties of the spin ladders we consider the system of Eq. (1.27) with varying $J_\perp/J_\parallel$ ratio.

- **The decoupling limit** $J_\perp/J_\parallel = 0$

  One obtains two decoupled AFM spin chains for which the excitation spectrum is known to be gapless.

- **The isotropic limit** $J_\perp/J_\parallel = 1$

  This the case of the ‘standard’ ladder which results for the equal AFM exchange $J_\parallel = J_\perp = J > 0$. Whereas the corresponding classical system has an ordered ground state of the Néel type the quantum system is a spin liquid with short range spin correlations and an energy gap [43, 44, 45].

- **The strong coupling limit** $J_\perp/J_\parallel = \pm$ and large

  In this limit, where the exchange coupling along the rung is much higher than the coupling along the chains. For $J_\perp/J_\parallel > 0$, the rung coupling is AFM and the two spins of the rung lock into a singlet state ‘dimer’ and the overall spin of this system is zero. The rung singlets interact weakly with each other and hence the ground state is the direct product of the spin singlets

  \[ |\Psi_s\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \]  

  In order to produce a spin excitation, a rung singlet must be promoted to a rung triplet and this cost an energy $\Delta_{\text{dimer}} = J_\perp$ [46] and thus the coupling $J_\parallel$ can not change this ground state. The local excitation can propagate along the ladder and its energy acquires a momentum dependence with a dispersion law

  \[ \omega(k) = J_\perp + J_\parallel \cos(k) \]
1.3. Quasi 1D spin systems

1. Low dimensional spin systems

Figure 1.7: Spin gap $\Delta_{\text{spin}}$ versus the ratio $J_\perp/J_\parallel$ for the two-leg ladder. From Ref. [46]

Such a spin liquid state is well described by a short range resonance valence band RVB state[47]. With increasing $J_\parallel$ the triplet excitations form a band with bandwidth $\approx J_\parallel$ and the gap decreases to become $\Delta \approx 0.4J_\perp$ in the weak coupling limit [48, 49]. The spin gap of the 2-leg ladder opens immediately upon turning on the rung coupling and the actual spin gap behavior as a function of the ratio of $J_\perp/J_\parallel$ is shown in Fig. (1.7). On the other hand, for $J_\perp/J_\parallel < 0$, the strong ferromagnetic interchain coupling leads to the formation of local spins $S = 1$ associated with each rung of the ladder, thus producing a conventional spin $S=1$ Heisenberg AFM with a nonzero Haldane gap in the excitation spectrum. In contrast to the previous case, the bandwidth of the triplet excitations and the spectral gap are of the same order of magnitude, $J_\parallel$.

For higher even $n$, the $S = \frac{1}{2}$ spin along the rung continue to form a singlet ground state and as the case of the 2-leg ladder, the creation of of $S = 1$ excitation requires a finite amount of energy. The energy gap should decrease as $n$ increase so that the gap less 2D square lattice limit is recovered but its magnitude will remain nonzero for any finite $n$ (even) [46, 50, 51].

1.3.2 The odd-leg ladder

An odd leg ladder behaves quite differently. For $n$ odd legs ladder it is impossible to make singlet state with odd numbers of spins on the a rung and a $S = \frac{1}{2}$ degree of freedom remains free. Each rung can thus be replaced by a $S = \frac{1}{2}$ and the odd legged ladder is thus equivalent to a single 1D Heisenberg chain. The interaction of the spins in the odd-leg ladders is more long range than that of spins in the even-leg ladders and the spin-spin correlation falls off not exponentially but power-law-like. Hence the magnetic susceptibility decays linearly at low temperature. Moreover, a large susceptibility is observed even at low temperatures.
1.3. Quasi 1D spin systems

1. Low dimensional spin systems

Figure 1.8: (a) Simplified representation of the ground state of a two-leg ladder. Pairs of spins along the same rung tend to form a spin singlet. (b) Doping the ladder with holes destroys the spin singlets. (c) The holes tend to share the same rung forming hole bound-states in order to minimize the energy damage. From Ref. [54].

1.3.3 Hole-doped spin ladder

A major reason for the strong research interest in ladders is that the doped ladder models are toy models of strongly correlated systems. The doped ladder is a simple model system in which the consequences of strong correlations can be studied with greater accuracy than in the case of structurally more complex SC cuprate systems. Dagotto showed via numerical calculations that upon doping the 2-leg ladder with holes the ground state becomes dominated by superconducting (SC) correlations [52]. This prediction was confirmed experimentally by Uehara in the hole-doped 2-leg compound Sr$_{0.4}$Ca$_{13.6}$Cu$_{24}$O$_{41}$ [53], which becomes a superconductor under high pressure (3 GPa) and has a transition temperature $T_c \sim 12$ K. The strongly correlated doped ladder is described by the $t$-$J$ Hamiltonian

$$H = \sum_{\langle i,j \rangle} (J_{ij} S_i \cdot S_j - \frac{1}{4} n_i n_j) - \sum_{\langle i,j \rangle, \sigma} (t_{ij} \hat{C}_{i,\sigma}^* (1 - n_{i,-\sigma})(1 - n_{j,\sigma}) \hat{C}_{j,\sigma} + \text{H.C.})$$

(1.30)

where $t$ is the hopping amplitude, $\hat{C}_{i,\sigma}^*$, $\hat{C}_{i,\sigma}$ are the hole creation and annihilation operators with spin $\sigma$ on the site $i$, $n_i, n_j$ are the occupation numbers of the $i$-th and $j$-th sites respectively. The $t$-$J$ model describes the motion of holes in the background of antiferromagnetically interacting spins. In the $t$-$J$ model the degrees of freedom at each site are either a $S = \frac{1}{2}$ spin that mimics the Cu$^{2+}$ ion with nine electrons in its $d$-shell or a ‘hole’ that represents a Cu$^{3+}$ state, usually assumed to be made out of a spin singlet combination of an oxygen hole and the $S = \frac{1}{2}$ Cu ion forming a so-called Zhang-Rice singlet. The correlations corresponding to the operator that creates or destroys hole pairs at nearest-neighbour sites and working at a small concentration of doped holes were very robust which is a reflection of a ground state dominated by strong superconducting tendencies.

The ground state of the 2-leg ladder predominantly consists of singlets along the rungs. Despite doping with holes, the spin gap of the 2-leg ladder remains but it changes discontinuously on doping. Introducing a hole break a singlet spin pair and a hole exists with a free $S = \frac{1}{2}$ and it no longer reduces its energy by singlet formation. In the case of two
holes on two separate rungs, each one breaks a rung singlet and the exchange interaction energy associated with two rungs is lost Fig (1.8b). In this case, the two free spins combine to give rise to an excited triplet state. However, if the two holes are located on the same rung, the number of damaged spin singlets are reduced from two to one and the exchange interaction energy of only one rung is lost Fig (1.8c). The two holes located on the same rung form bound pair of holes with $S = 0$ to reduce the cost of magnetic interaction. Hence the ground state is a singlet and consists of a bound pair of holes. Binding pairs of holes gives the lightly-doped ladder a bosonic character, which turn to be a necessary step on the way to superconductivity.

1.4 2D spin systems

In this section we move another step forward by considering a two dimensional spin system. Two-dimensional magnetic systems are favorite models to study the influence of quantum fluctuations on magnetic order. As illustrated by Mermin-Wagner theorem, in dimensions $D \leq 2$, thermal fluctuation prohibit the existence of long range magnetic order at non-zero temperature in an isotropic system. For the magnetic ordering in the ground state, the transition from one to two dimensions seems to be crucial. As mentioned before, one-dimensional Heisenberg quantum antiferromagnet does not possess Néel LRO even at zero temperature. On the other hand, it is now well-established that the Heisenberg antiferromagnet on the 2D square lattice exhibits semi-classical Néel LRO. In addition to frustration, the competition of non-equivalent NN bonds destroys the Néel ordering in the ground states of unfrustrated 2D HAFMs. Such competition is of pure quantum nature and leads to the formation of local singlets of two (or even four) coupled spins. Quantum phases without semi-classical Néel order are often described by quantum ‘disorder’ or ‘quantum spin liquid’. However, these quantum phases may exhibit quite different complex properties. We shall prefer the notation ‘quantum paramagnet’ to stress their common feature, namely the absence of magnetic order at $T = 0$ K [55].

In 2D spin systems we obtain a large number of different archimedean lattices with different coordination numbers $z$ and topologies (frustrated and nonfrustrated; equivalent nearest-neighbor (NN) bonds and non-equivalent NN bonds). The degree of geometric frustration and the coordination number are important quantities that strongly influence the magnetic properties. In this section we will focus on both of the square lattice and the Honeycomb model which are relevant to the work introduced in this thesis.

In two dimensional magnets, there are two kinds of simple bipartite lattices, a square lattice and a honeycomb lattice, if only nearest-neighbor AFM interactions are considered. A spin system on a bipartite lattice has a ground state with an AFM order in a large spin-magnitude limit. The question appears whether or not a disordered spin-gap phase appears with destroyed AFM order, when the spin magnitude becomes small so that quantum fluctuations are large. Quantum fluctuations are further enhanced by frustration among AFM interactions and by distortion as inhomogeneity in interactions. Hence a disordered state will interestingly appear with various strengths of frustration and distortion.
1.4. 2D spin systems

1.4.1 2D square lattice

The 2D square lattice of Heisenberg antiferromagnet (2D HAFM) is an array of magnetic moments placed in the corners of an infinite 2D grid. These magnetic moments interact only with the nearest NN through an isotropic Heisenberg magnetic exchange $J$ (Fig. 1.9a). In the ideal 2D case, the layer of the 2D spins is considered to be perfectly isolated or decoupled, and no interaction perpendicular to the planes $J_\perp$ (which represent the interaction from layer to layer in real systems) is included in the model. The Heisenberg Hamiltonian describing this system is:

$$H = J \sum_{i,j} S_i \cdot S_j$$ (1.31)

In this case, the ground state is LRO at only $T_N = 0$ K as stated by Mermin and Wagner theorem. The main reason for this are the strong quantum spin fluctuations which inhibit the formation of LRO at any nonzero temperature. However, the pure 2D magnetic lattice is quite difficult to realize because some weak interaction perpendicular to the magnetic layers $J_\perp$ is always present which transforms the system into a quasi two dimensional (Q2D) system. Hence, real systems show a LRO because of the three dimensional correlations and the anisotropy effects which stabilize the LRO.

1.4.2 Frustrated 2D square lattice

The role of the NNN interaction is drastic on the 2D square lattice. By triggering this interaction, which competes with the NN interaction, a frustration arises and we obtain a frustrated 2D HAFM. Figure (1.9b) shows square with NN and NNN competing interaction, which can be represented by $J_1 - J_2$ model Hamiltonian:

$$H = J_1 \sum_{\langle i,j \rangle} S_i \cdot S_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} S_i \cdot S_j$$ (1.32)

Figure 1.9: (a) The typical 2D square lattice with isotropic exchange interaction $J$. (b) Square lattice with NN and NNN competing interactions, which is represented by the $J_1 - J_2$ model.
1.4. 2D spin systems

1. Low dimensional spin systems

Figure 1.10: Schematic phase diagram for $J_1 - J_2$ model. From Ref. [57, 58].

where $\langle i, j \rangle$ and $\langle \langle i, j \rangle \rangle$ denote pairs of NN and NNN respectively. Although quite simple appearance, this spin model realizes several interesting phenomena which are relevant to a large class of 2D frustrated quantum magnets: classical degeneracy, order by disorder, destruction of some LRO by quantum fluctuations, etc [56]. The relative strengths between the NN interaction $J_1$ and NNN interaction $J_2$ expressed by the ration $\alpha = J_2 / J_1$. The properties of the square lattice and its ground state strongly depend on this ratio $\alpha$ [57]. The phase diagram of the $J_1 - J_2$ model depending on the ratio $\alpha$ for both $J_1$ and $J_2$ are AFM is shown in Fig. (1.10).

- $\alpha = \infty$ where $J_1 = 0$ and $J_2 > 0$ (AFM)

The system consists of two decoupled sublattices formed by NNN interaction which are rotated 45° with respect to the original NN square lattice. From the classical point of view, the spins produce a local field which vanishes at on each site of the other sublattice. Hence, the ground state is degenerated and these subsystems can be rotated independently. However, at the quantum level, short-wavelength fluctuations lift this degeneracy producing new correlations at long wavelengths and selecting the collinear ordered state, that is, when the spins along $x$ or $y$ axis are ferromagnetically aligned.

- When $J_2 \ll J_1$, $J_1$ and $J_2$ are AFM

The NNN interaction $J_2$ competes with $J_1$ and acts as a frustrating perturbation. In this case, the system is near to the Q2D HAFM and Néel ordering is expected. At critical $\alpha_{c1} = 0.34$, the ground state is characterized by Néel ordering with a columnar dimerization.
1.4. 2D spin systems

1. Low dimensional spin systems

Figure 1.11: Phase diagram for $J_1 - J_2$ model. Numbers represent the value of $\alpha = J_2/J_1$ at the phase boundaries [59].

- When $J_1 \ll J_2$, $J_1$ and $J_2$ are AFM

This is the opposite case of $J_2 \ll J_1$. Hence the roles are interchanged and the system is in a collinear ordered state.

- $0.38 < \alpha < 0.6$, $J_1$ and $J_2$ are AFM

Due to the strong frustration, the ground state is quantum disordered and dominated by the formation of short-range, dimer like, order with a finite gap. Within this region, two second order phase transitions can be found. At $\alpha_{c2} = 0.38$, the ground state is a simple columnar dimerized spin liquid. As $\alpha$ reaches $\alpha_{c3} = 0.5$, the ground state transform to a columnar dimerized spin liquid with plaquette type modulation. Above $\alpha_{c4} = 0.6$, the system favor the collinear ordered state as for $J_1 \ll J_2$.

Considering one of $J_1$ and $J_2$ interactions 'or both of them' to be of ferromagnetic nature obviously has an impact on the phase diagram. The general phase diagram of $J_1 - J_2$ model with mixed AFM and FM interactions was theoretically studied [59]. Despite of having only one adjustable parameter '\(\alpha\)', the phase diagram is of extreme rich. The properties of this model depend only on the relative and not the absolute value of the exchange interaction $J_2$ and $J_2$. Hence, it is possible to characterize it by an overall energy scale.

$$J_c = \sqrt{J_1^2 + J_2^2}$$  \hspace{1cm} (1.33)

and with frustration angle $\phi$ where

$$J_1 = J_c \cos(\phi) \quad J_2 = J_c \sin(\phi) \quad \tan(\phi) = J_2/J_1$$  \hspace{1cm} (1.34)
According to this transformation, the general phase diagram of \( J_1 - J_2 \) model can be constructed as shown in Fig. (1.11) \cite{59}. Now, the critical values of \( \alpha \) are replaced by a critical angles in the new phase diagram.

The phase diagram consists of three major ordered phase; the Néel antiferromagnetic (NAF), the collinear antiferromagnetic (CAF) and the ferromagnetic phases as illustrated in Fig. (1.11). In the phase transition between the NAF and CAF, a disordered region appears. The equivalent critical angle for previously discussed \( \alpha_{c1}, \alpha_{c2}, \alpha_{c3} \) and \( \alpha_{c4} \) are \( \phi_{c1} = 18.778^\circ, \phi_{c2} = 20.807^\circ, \phi_{c3} = 26.565^\circ \) and \( \phi_{c4} = 30.964^\circ \), respectively. For \( J_1 < 0 \) (ferromagnetic), another critical angle appears at \( \phi_{c5} = 153.435^\circ \) \( (\alpha_{c5} = 0.5) \) in the boundary line between CAF order region and FM part of the phase diagram. Finally, At \( \phi_{c6} = 270^\circ \), a transition from FM to NFM order occurs when \( J_1 > 0 \) (AFM) and \( J_2 < 0 \) (FM) at \( \alpha_{c2} = -\infty \).

### 1.4.3 Confederate flag model

In order to generalize the \( J_1 - J_2 \) model, we consider a spatially anisotropic 2D square lattice. By allowing the NN interactions to be of different strength \( J \) and \( J' \) in the two orthogonal spatial lattice dimensions, while keeping all NNN interactions across the diagonals to have the same strength \( J_2 \) as presented in Fig. (1.12). The resultant \( J - J' - J_2 \) model was named the ‘Confederate flag model’ by Nersesyan and Tsvelik \cite{60}. This model is equivalent to a Q1D AFM system consisting of antiferromagnetic spin chains with exchange constant \( J \) along the horizontal (chain) direction. These chains are interacting with their NN via weak AFM exchange interaction in the vertical \( J' \) and diagonal with respect to the chain \( J_2 \), directions. The Hamiltonian of this \( J - J' - J_2 \) model reads:

\[
\mathcal{H} = \sum_{m}^{M} \sum_{l}^{L} [JS_{l,m} \cdot S_{l+1,m} + J'S_{l,m} \cdot S_{l,m+1} + J_2(S_{l,m} \cdot S_{l,m+1} + S_{l,m} \cdot S_{l,m-1})] \quad \text{(1.35)}
\]
1.4.2D spin systems

1. Low dimensional spin systems

Figure 1.13: Honeycomb lattice as a two-dimensional dimerized lattice.

which may also be viewed as an array of \( M \) spins chains of length \( L \) if \( J' < J \). All exchange interactions are assumed positive (AFM) \([61]\). When \( J' = J \), it is the normal \( J - J_2 \) model. As in the \( J - J_2 \) model, \( J - J' - J_2 \) model has two types of classical ground state; Néel state at weak frustrations and a stripe or collinear Néel state at strong frustrations. The model is particularly interesting for a special ratio \( J'/J_2 = 2 \) where the ground state was first argued to be resonant valence bond (RVB) in the anisotropic limit \( J \gg J' \) \([60]\). This result has been questioned since then and the ground state is suggested to be a valence bond crystal (VBC) instead \([61, 62, 63]\).

1.4.4 Honeycomb lattice

Despite its simple structure, the honeycomb lattice provides non-trivial physical phenomena which can not be observed in the ordinary square lattice. The honeycomb lattice can be split into two identical sub-lattices. Frustrated models such as the triangular lattice case, do not have this property. Like the square lattice, this lattice is a bipartite system, which is not geometrically frustrated for antiferromagnetic NN interactions but it has the minimum co-ordination number possible of any regular two-dimensional lattice. The 1D chain, which has the smallest co-ordination number possible in any lattice, suffers from the greatest quantum fluctuations effects, which destroy the LRO and drive the system into liquid singlet ground state. The co-ordination number of the honeycomb lattice is \( z = 3 \), which is larger than \( z = 2 \) of the 1D chain, but smaller than \( z = 4 \) of the square lattice. Thus the quantum fluctuations in the honeycomb lattice are expected to be weaker than the 1D chain case, but stronger than those in the 2D square lattice case. Hence, the AFM order for the honeycomb lattice is more fragile \([64, 65]\). the simulation of a honeycomb structure is achieved by viewing the honeycomb lattice as a double dimerized model with Hamiltonian:

\[
\mathcal{H} = J_x \sum_{x,y,z} [1 + (-1)^{x+y+\delta}] S_{x,y,z} \cdot S_{x+1,y,z} + J_y \sum_{x,y,z} S_{x,y,z} \cdot S_{x,y+1,z} + J_z \sum_{x,y,z} S_{x,y,z} \cdot S_{x,y,z+1} \tag{1.36}
\]
and $\delta, J_x = \frac{1}{2}$ and $J_y = J$. This Hamiltonian has different dimerizations in $x$-direction for $y$ even and $y$ odd, where $J$ is the exchange coupling of the Honeycomb system as shown in Fig (1.13)[66]. The coupling in $z$-direction between the layer is $J_z$. As expected for 2D system, the honeycomb lattice has no magnetic ordering at any finite temperature. Switching on the interlayer coupling $J_z$ and anisotropies and its impact on the ground state of this system still under investigation. Recently, the honeycomb lattice was realized in InCu$_{2/3}$V$_{1/3}$O$_3$ [67, 68] and Na$_3$T$_2$SbO$_6$ [69] compounds.
Chapter 2

Electron spin resonance

2.1 Introduction

Electron spin resonance (ESR), known also as electron paramagnetic resonance (EPR), is the main technique used in the present thesis to investigate the properties of the low dimensional spin systems. Therefore, this chapter is devoted to the ESR fundamentals, experimental set up and spectrometers. Later on, we shortly discuss some of the interesting features of low dimensional systems which can be explored using an ESR experiment.

2.2 Electron spin resonance

Since the discovery of ESR, by E. Zaviosky in 1944, it became a powerful and widely applied spectroscopic tool used in physics, chemistry, biology, medicine, and materials science. Therefore, nowadays, ESR is a well established technique and a fundamental introduction to it can be found in many textbooks, for example, Slichter 1963 [70], Abragam and Bleaney 1970 [71], Poole 1983 [72], Pilbrow 1990 [73], Möbius and Savitsky 2008 [74], and Brustolon and Giamello 2009 [75].

An electron has a magnetic moment and a spin quantum number $S = \frac{1}{2}$. Applying an external homogeneous magnetic field along the $z$-axis, $H = H_z e_z$, a free electron spin quantizes with respect to the field direction and can accept two discrete values; $m_s = -\frac{1}{2}$ for spins align parallel to the magnetic field and $m_s = +\frac{1}{2}$ for the spins align antiparallel to the magnetic field. The energy of this two alignment is the Zeeman energy

$$E(m_s) = g\mu_B S \cdot H = g m_s \mu_B H_z$$

(2.1)

where the proportionality factor $g$ is the gyromagnetic factor (g-factor). The difference between these two spin projections increases with increasing the applied magnetic field as illustrated by the Zeeman effect shown in Fig. (2.1). The parallel alignment is favorable for the spins since it corresponds to the lower energy state. The energy difference between $m_s = -\frac{1}{2}$ and $m_s = +\frac{1}{2}$ is given by

$$\Delta E = g\mu_B \Delta m_s H_z$$

(2.2)
2.2. Electron spin resonance

Figure 2.1: Zeeman effect for a $S = \frac{1}{2}$ system. The splitting of the energy level by applying an external magnetic field $H$. At the resonance condition, microwave with energy $h\nu = g\mu_B H_{res}$ induces a spin flip.

A magnetic dipole transition between the levels is possible by absorption or emission of the electromagnetic quantum ($h\nu$) with an energy equal to the energy difference between these levels. In this case the resonance condition is

$$\Delta E = h\nu = g m_s \mu_B H_{res} \quad \text{Resonance condition}$$

In the ESR spectroscopy, a linearly polarized electromagnetic radiation in the microwave region is applied in the direction where its magnetic component is perpendicular to the applied magnetic field to initiate a spin flip from one energy level to another. For a $S = \frac{1}{2}$ system, it is obvious that the only possible transition is from $m_s = -\frac{1}{2}$ to $m_s = +\frac{1}{2}$ which is associated with the absorption of the microwave quanta. However, a photon releases in the inverse transition; from $m_s = +\frac{1}{2}$ to $m_s = -\frac{1}{2}$. As mentioned before, the parallel alignment is favorable, hence the population of the $m_s = -\frac{1}{2}$ level is higher and so the net effect of the spin transition processes is always absorption. At a finite temperature and in thermodynamic equilibrium, the parallel alignment is favorable, hence the population of the $m_s = -\frac{1}{2}$ level is higher and so the net effect of the spin transition processes is always absorption. This statement is true also for more than two energy levels and the thermal population is described by Boltzmann statistic

$$\frac{n_{s+1}}{n_s} = \exp[-\frac{E(1/2) - E(-1/2)}{k_B T}] = \exp(-\frac{\Delta E}{k_B T}) = \exp(-\frac{h\nu}{k_B T})$$

where $n_{s+1}$ and $n_s$ is the population of the states and $k_B$ is the Boltzmann constant. For systems with higher spin values the emerging possibilities for transitions between the various spin states are restricted by the quantum mechanical selection rules:

$$\Delta L = 0, \quad \Delta S = 0, \quad |\Delta m_s| = 1 \quad \text{selection rules}$$
2.3 The resonance phenomena

According to the resonance condition in Eq. (2.1), a sharp peak is expected in the spectrum at the resonance field \((H_{\text{res}})\). However, due to the involvement of different spin relaxation processes, the measured ESR lines have always a finite width. The width of the ESR line is determined mainly by the inhomogeneous broadening, the spin-lattice relaxation and the spin-spin relaxation. The lower limit for the ESR linewidth \(\Delta H\) basically originates from the finite lifetime of the occupied spin state which is associated with the Heisenberg’s uncertainty, as stated in the Heisenberg’s relation \(\tau \Delta E \geq h\), hence, \(\Delta H \geq \gamma \frac{\tau}{2}\).

Focusing on an individual magnetic moment and following it through different interactions and relaxation processes to describe the microscopic origin of the ESR signal is a very complicated task. Therefore, theoretical treatments of such effects on the resonance commonly utilize a phenomenological approach. The sum of the magnetic moments of the spin participating in the resonance phenomena is the magnetization density (magnetization, \(M\)). Bloch equations of motion describe the time evolution of \(M\) and introduce phenomenological terms for the lifetime of the longitudinal and transversal spin polarization.

\[
\frac{dM}{dt} = \gamma M \times H - (M - \chi_0) \left( \frac{1}{T_1} e_\parallel + \frac{1}{T_2} (e_{\perp 1} + e_{\perp 2}) \right) \tag{2.6}
\]

where \(\chi_0\) is the temperature independent susceptibility and \(M_0 = \chi_0 H\). \(e_\parallel\), \(e_{\perp 1}\) and \(e_{\perp 2}\) are the unit vectors parallel and perpendicular to the direction of the magnetic field \(H\).

The spin-lattice relaxation (longitudinal relaxation) time \(T_1\) relates to the characteristic lifetime of the electronic state and is determined by the exchange in energy via thermal vibrations of the lattice. In contrast to the spin-lattice relaxation, the spin-spin relaxation (transversal relaxation) \(T_2\) is concerned with the mutual spin flips caused by dipolar and exchange interactions between the assembly of spins making up the sample. The purely spin lattice broadened line has a lorentzian shape, however, the line dominant by spin-spin broadening tends to be more Gaussian-like. [73]

In real ESR measurements the sweep rate of the applied magnetic field is so slow that the magnetization maintains a constant magnetization in the coordinate system rotating with the time varying field. Hence, the derivative of the magnetization in the reference system goes to zero and the solution of Eq. (2.5) is

\[
M_{\pm} = \frac{\gamma H_1 M_\parallel}{\gamma H_z + \omega \mp i/T_2} e^{\pm i \omega t} \tag{2.7}
\]

\(H_1\) is the amplitude of the magnetic field component in \(e_{\perp 1}\) and \(e_{\perp 2}\), \(H_z\) is the magnetic field along the \(z\)-axis and \(\omega\) is Precession frequency. In experiment, only one component of the transverse magnetization is measured. Using the complex susceptibility \(\chi = \chi' + \chi''\) to express the magnetization we obtain

\[
\frac{\chi'}{\chi_0} = \frac{\omega L (\omega L - \omega)}{\Delta \omega^2 + (\omega L - \omega)^2 + \gamma^2 H_1^2 T_1 \Delta \omega} \tag{2.8}
\]

\[
\frac{\chi''}{\chi_0} = \frac{\omega L \Delta \omega}{\Delta \omega^2 + (\omega L - \omega)^2 + \gamma^2 H_1^2 T_1 \Delta \omega} \tag{2.9}
\]
where $\omega_L = \gamma H_z$ is the Lamor frequency and $\Delta \omega = \frac{1}{T_2}$. The real part of the frequency produce a change in the resonant cavity, while the imaginary part produces energy absorption and thereby lower the quality factor. The power absorbed by the system proportional to imaginary part of the susceptibility $\chi''$ where

$$P \propto \omega_{mw} \chi'' H_1^2$$

(2.10)

From the technical point of view, it is more simple to sweep the magnetic field and keep the frequency constant. Hence, we observe the magnetic resonance at a certain field $H_{res}$ and the lineshape of the absorbed power as a function of the applied field $H$ is a Lorentzian which can be described as

$$P(H) \propto \frac{\Delta H}{(H - H_{res})^2 - (\Delta H)^2}$$

(2.11)

### 2.4 ESR Experiment

As illustrated by Eq. (2.3), the resonance field is proportional to microwave frequency. Therefore, application of higher magnetic fields and microwave frequencies results in spectacular improvements of spectral and time resolution [74]. This why different frequency bands are used in ESR spectrometers. Some of the typical frequency bands in ESR spectroscopy and the equivalent resonance field for $g = g_e = 2$ are summarized in Table (2.1).

<table>
<thead>
<tr>
<th>Wave Band</th>
<th>Frequency (GHz)</th>
<th>Resonance field $H_{res}$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>3</td>
<td>0.11</td>
</tr>
<tr>
<td>X</td>
<td>9.5</td>
<td>0.34</td>
</tr>
<tr>
<td>K</td>
<td>24</td>
<td>0.86</td>
</tr>
<tr>
<td>Q</td>
<td>35</td>
<td>1.25</td>
</tr>
<tr>
<td>W</td>
<td>95</td>
<td>3.4</td>
</tr>
<tr>
<td>D</td>
<td>140</td>
<td>5</td>
</tr>
<tr>
<td>J</td>
<td>285</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Table 2.1: Frequency bands in ESR and the equivalent resonance field of $g = g_e = 2$

In conventional ESR spectrometers, Gunn-diodes or klystrons generate a continuous wave radiation field at a single frequency. They commonly utilize rectangular single-mode waveguides for the propagation of the radiation and the cavity perturbation technique paired with a lock-in method to get a sufficiently sensitive detection scheme. Versions of spectrometers working with $\nu = 9.5$, 34, and 94 GHz (X, Q, and W-band, respectively) are commercially available. Most commonly used are devices operating in the X-band. While these facilities operate at a fixed frequency, the frequency of the broad band spectrometers denoted with, e.g., Millimeter wave Vector Network Analyzer (MVNA) are tunable within orders of magnitude (8 GHz up to $\sim$ 1 THz). [76]

In this thesis, X-band and high field / high frequency (HF-) ESR measurements are presented. These measurements were performed in the ESR labs at the Institute for Solid State Research (IFF) (part of the Leibniz Institute for Solid State and Materials Research Dresden IFW).
2.4. ESR Experiment

2.4.1 X-band spectrometer

The X-band ESR measurements have been performed with a conventional Bruker EMX spectrometer. Figure (2.2) shows a simplified block diagram including most important subunits of the spectrometer.

The microwave source is a Gunn-diode which is easily tuned electrically and characterized by high stability power up to 200 mW maximum power. The spectrometer has a rectangular cavity which lies between the poles of an electromagnet. The microwave cavity has to satisfy two contradictory goals: it has to maximize the interaction of the sample with the magnetic component of the microwave field while simultaneously minimizing dielectric losses due to the sample. The microwaves transmitted to and from the cavity through rectangular waveguides. The cavity is coupled to the waveguide using an impedance transformer implemented as a movable short at the end of the waveguide. An electromagnet is used to create the magnetic field needed for 9.5 GHz ESR (about 0.34 T at \( g = 2 \)) and is specified for static fields up to 1 T. The samples are inserted into the cavity vertically from the top. The sample capillaries are limited to an outer diameter of 0.55 cm. For all X-band experiments in this work, quartz capillaries with an outer diameter of 0.55 cm and an inner diameter of 0.45 cm were used. An Oxford ESR 900 continuous helium flow cryostat is utilized to reach low temperatures (from 300 down to 3.4 K). The advantage of this cryostat is that it has satisfactory temperature stability (\( \Delta T \approx \pm 0.1 \) K). The temperature sensor was fixed very close to the sample, therefore a good accuracy of temperature measurements is achieved. More details can be found in the Bruker user manual.[77]

The magnetic field generated by the electromagnet is oriented horizontally. Since the probe head allows to rotate samples about the vertical axis, a goniometer was used to measure ESR spectra as a function of the sample orientation with respect to the magnetic field.
2.4. ESR Experiment

2.4.2 High field ESR spectrometer

Since its discovery, ESR has typically been performed at frequencies lower than 40 GHz (specially at X-band frequency). Such low frequency commercial ESR spectrometers are perfectly suited for many applications in biology, chemistry and physics when narrow ESR lines are expected in limited field ranges. Indeed, they are often insufficient in solid state physics where large linewidths and considerable zero-field splittings occur. The recent developments in microwave sources, detectors, and magnet technology allowed to overcome this limitation of low frequency experiments. HF-ESR measurements have many advantages: increased g-tensor resolution, better resolution of the zero-field-splitting tensor, investigating systems where the fast spin dynamics depend on the strength of the static magnetic field, etc. As the ESR frequency increases, however, conventional microwave propagation techniques become exceedingly lossy, and the usual components for constructing a microwave bridge are unavailable above 150 GHz. [78]

The high field / high frequency ESR measurements were carried out using a home made HF-ESR spectrometer on the basis of the Millimeterwave Vector Network Analyzer (MVNA) from AB Millimetre, Paris. The MVNA is a fully tunable high frequency designed
2.4. ESR Experiment

ESR Experiment

for operation between 8 and 1000 GHz which employs purely solid-state electronics. A phase-sensitive detection of the mm/sub-mm waves is achieved by phase-locked source and detector signals which allows for vector measurements. Schematic diagram of the MVNA, the magnet system and sample probe of the HF-ESR spectrometer is presented in Fig. (2.3). A tunable fundamental wave of \( F_1 = 8 \pm 18 \) GHz is generated by yttrium iron garnet (YIG) oscillators (source \( S_1 \)) and passes through a Schottky diode multiplier (harmonic generator \( HG \)) which is optimized to produce the desired harmonic \( N \) HF signal \( F = N \times F_1 \). Detection is then achieved by mixing the signal \( F \) with the signal from a second source \( S_2 \), at a second Schottky diode (harmonic mixer \( HM \)) [79]. In order to optimize the microwave power over this wide frequency range, so called ESA extensions (\( ESA_0, ESA_1 \) and \( ESA_2 \)), which basically consist of tunable Gunn oscillators (\( \sim 70 - 110 \) GHz), other millimeter wave components and assemblies are used. The MVNA allows simultaneous measurements of both the amplitude and the phase of transmitted signal.

The MVNA is used in combination with a 15-17 T superconducting magneto-cryostat (from Oxford Co. Ltd.) [80] installed in the \( ^4 \)He space. The maximum magnetic field is 15 T at 4.2 K, and 17 T at 2.2 K using the lambda plate. The magnetic field generated by the magnet is oriented vertically. Such setup allows ESR spectrometer with an effective frequency range of 20-475 GHz. The lower limitation of the range is actually determined by the experimental hardware (available transitions and waveguides, bore hole of the coil) while the upper one is due to the resonance condition (at \( \nu = 475 \) GHz; \( H_{res} \sim 16.96 \) T for \( g = 2 \)).

The sample probe head is designed to fit into the variable temperature insert (VTI) of the utilized magneto-cryostat in order to apply magnetic fields up to 17 T and temperatures between 2-300 K. It consists of two long waveguides for propagating mm waves from the harmonic generator, into the magnet cryostat (incidence waveguide), and back to the harmonic mixer (transmission waveguide). At the bottom, the waveguide is soldered to a prism shaped sample holder made from copper which includes also a Cernox sensor and a heating coil for temperature stabilization. The outer tube is filled with a low pressure heat exchange gas (helium gas) to achieve better thermal energy exchange during the experiment.

More details of the HF-ESR spectrometer can be found on two earlier PhD theses out of the ESR group in the IFW by C. Golze [76] and U. Schaufuß [81].

2.4.3 ESR spectrum

ESR provides an experimental route to study the dimensionality of the spin system, electron localization and the interaction of the spin with the lattice and other spins. Such information is obtained by analyzing the ESR signal.

A typical ESR signal obtained from the X-band experiment is presented in Fig. (2.4a). In the X-band device, we record the first derivative of the absorbed microwave power \( (dP/dH) \) as function of the applied magnetic field. Whereas, in the HF-ESR, we record
Figure 2.4: a) Example of the ESR signal observed in the X-band spectrometer: the first derivative of the absorbed microwave power \(dP/dH\) as a function of the applied magnetic field. This data is for \(\text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41}\) and \(x=0.25\) [presented in Ch. 4 of this thesis]. The solid red line represents the lorentzian fitting. b) The absorption line calculated through the integration of \(dP/dH\). The ESR parameters are illustrated: resonance field (\(H_{\text{res}}\)), peak to peak linewidth (\(\Delta H_{\text{pp}}\)) and integrated intensity \(I_{\text{ESR}}\). The half width at half maximum of the absorption line \(\Delta H = \sqrt{3}\Delta H_{\text{pp}}/2\).

directly the absorbed lines. By integrating \(dP/dH\), the absorbed lines can be calculated as presented in Fig. (2.4b). Four important parameters can be obtained from such signal as illustrated in Fig. (2.4).

- The lineshape

The ESR lineshape contains useful information about the nature of the exchange interaction in the studied systems. For example, an isotropic exchange interaction reduces the linewidth (the phenomenon is therefore known as ‘exchange narrowing’) and a symmetric Lorentzian lineshape is expected. For metallic or higher conducting samples, the skin effect resulting from the screening of the incident microwave field by the conduction electrons yields asymmetric lineshape, which is known as a dysonian line. [82, 83] Throughout the present thesis, and since we are studying systems with significant role of exchange interaction, a Lorentzian lineshape was observed for all the measured samples. In Figure (2.4a), the Lorentzian fit of the ESR signal obtained for \(\text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41}, x=0.25\) (presented in Ch. 4 of this thesis) is illustrated by the solid red line.

- The \(g\)-factor

ESR experiment is the only direct method to measure the \(g\)-factor, which is straightforwardly related to the resonance field \(H_{\text{res}}\) and excitation frequency \(\nu\) used in the experiment by

\[
g = \frac{h\nu}{\mu_B H_{\text{res}}} \quad \text{\(g\)-factor} \tag{2.12}
\]
This equation is generally true for \( S = 1/2 \), as long as the g-factor is isotropic. If not, the investigated system is magnetically anisotropic, implying an angular dependence of \( g \) with respect to the field direction. Accordingly, \( g \) is now represented by a \( 3 \times 3 \) interaction matrix. For this reason, \( g \)-factor is used to probe the local environment surrounding the unpaired spins. Usually the measured \( g \)-factor differs for the free electron one \( g_e = 2.002319 \). This can result from the spin orbital coupling or the development of an internal field which shifts \( H_{\text{res}} \) of the ESR lines.

- The linewidth

A number of phenomena may contribute to the width of the ESR line. The most trivial is the lack of homogeneity of the applied static magnetic field \( H \) [70]. However, in our experiment, a rather high homogeneity is achieved and the effect on the width of the resonance line is reduced. The homogeneity also depends on the sample size. The typical size of the measured samples is \( 0.4 \times 0.5 \times 0.5 \) cm. Since the width of resonance lines is substantially greater than the magnet inhomogeneity, it is possible to study the line shape in details without instrumental restrictions. Another contribution to the ESR linewidth is rising from the limited lifetime of the Zeeman states, which effectively cause a line broadening by order of \( \hbar / T_1 \).

The width of the ESR signal provides vital information about the spin interactions with its surroundings, neighboring spins and the lattice. In the X-band experiment, the peak to peak distance (\( \Delta H_{\text{pp}} \)) of \( dP/dH \) is used to define the linewidth as shown in Fig. (2.4a). For an absorption line, the half width at half maximum (\( \Delta H \)) definition is used to express the linewidth. The relation between these two definitions for a Lorentzian lineshape is \( \Delta H = \sqrt{3} \Delta H_{\text{pp}}/2 \).

- The integrated intensity \( I_{\text{ESR}} \)

The intensity of the ESR line is the area under the absorption signal. Through the integration of the measured signal, (in the case of X-band measurements, the signal is integrated twice), \( I_{\text{ESR}} \) is obtained. As ESR measures the imaginary part of the dynamic susceptibility, the integral of a particular resonance is a measure of the absolute number of resonating spins and hence, \( I_{\text{ESR}} \) is proportional to the spin susceptibility, \( \chi_{\text{spin}} \). The magnetization techniques measure the total susceptibility \( \chi \) of the sample. ESR, which measures the local spin susceptibility, however, can distinguish between the contribution from impurities and from the localized spins. If most of the spins contributing to the bulk static susceptibility also participate in the magnetic resonance, we observe an agreement between \( I_{\text{ESR}} \) and \( \chi \).

In order to figure out how the ESR parameters reflect the different physical properties realized in the measured samples, we need to understand the spin Hamiltonian that describes the resonance spins within these systems.
2.5 Spin Hamiltonian

So far uncoupled spins have been considered, only interacting with the magnetic field. If the spins are coupled by interactions, the physics becomes much more complicated. The spin Hamiltonian of a system with an electron spin $S$ interacting with the external magnetic field and magnetic moments from other electron spins can be described as:

$$H = H_e + H_{CF} + H_Z + H_{LS}$$  \tag{2.13}

where $H_e$ is the electron Hamiltonian discussed in chapter (1), $H_{CF}$ is due to the crystal field splitting, $H_Z$ describes the electron Zeeman interaction and $H_{LS}$ represents the spin orbital coupling (LS).

The interaction between the electron spin and the externally applied magnetic field $H$ is described by the electron Zeeman term. The Zeeman energy for a free electron is described earlier in Eq. (2.2). In solids, the applied magnetic field also interacts with the orbital angular momentum $L$ and the Zeeman Hamiltonian is:

$$H_Z = \mu_B (L + g_e S) \cdot H$$  \tag{2.14}

Due to the spin-orbital coupling, the $g$-factor should be replaced by the Landé $g$ factor

$$g_L = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)}$$  \tag{2.15}

In this case, the total spin of an incomplete shell $S$ is coupled to its total orbital momentum $L$ and the spin orbital term is given by:

$$H_{LS} = \lambda L \cdot S$$  \tag{2.16}

where $\lambda$ is the coupling strength, which is positive for less than half filled shells and negative otherwise.

Now, we consider the crystal field effects by considering a central 3$d$ transition metal ion which is surrounded by a regular array of coordinated atoms or ligands. Accordingly, the ligands are assumed to be sources of the negative charge which perturb the energy levels of this ion. Therefore, the size and nature of the of crystal field effects depend crucially on the symmetry of the local environment.

A standard example, the Cu$^{2+}$ ion has the configuration 3$d^9$. Since 3$d^{10}$ would be a completely filled shell, it is justified to consider Cu$^{2+}$ as having one $d$-hole with $S = 1/2$. Without the effect of the spin orbital coupling, Cu$^{2+}$ would have a spin-only magnetic moment corresponding to $S = 1/2$. However, the spin orbital coupling has two important effects. First, it acts to restore some orbital angular momentum. Second, by tying the spin to the orbital motion which is influenced by the crystal fields, it provides a mechanism whereby the spin 'feels' the orientation of the crystal axis. This is how the phenomenon of magnetic anisotropy arises [84]. By placing the Cu$^{2+}$ cation in the center of the negatively
Figure 2.5: The effect of the crystal field on the d-state energies. Left panel: for the free 3d-ion: d-orbital states are fully degenerate in energy. Whereas, in an octahedral coordination the energy degeneracy is partially lifted. If the symmetry of an octahedron is lowered from cubic to tetragonal, further splitting of the d-orbital states is obtained. Right panel: the crystal field effect acts in the opposite way in tetrahedral environment.

charged sphere, the d orbitals will be all degenerated. The d orbitals fall into two classes, the t_{2g} orbitals, d_{xy}, d_{yz} and d_{zx}, which point between the ligands in x, y and z axes and the e_{g} orbitals which point along these axes directly towards the ligands (d_{3z^2-r^2}: points along the z-axis and d_{x^2-y^2}: points along both the x-axis and the y-axes).

In the octahedral symmetry, the Cu^{2+} positively charged ion will be surrounded by six negatively charged ions as shown in the left panel of Fig (2.5). The six ligands form an octahedron and the symmetry is exactly cubic. The total electronic energy of all the d orbitals will not change but the orbitals will no longer be degenerate [14]. In this case, the t_{2g} orbitals, d_{xy}, d_{yz} and d_{zx}, are equivalent and will have lower energy since they are not exactly pointing to the surrounding ions and therefore, placing an electron will not be faced with strong repulsion. Whereas, e_{g} orbitals (d_{3z^2-r^2} and d_{x^2-y^2}), are pointing directly to the surrounding ions and hence, they have higher energies. Thus, the crystal field splits the 3d levels as shown in Fig (2.5). By lowering the symmetry from cubic to tetragonal through elongating the apex and in-plane oxygen bonds, the crystal field causes further splitting of the 3d levels. The e_{g} level splits into the a_{1t} and the b_{1t}-level, while t_{2g} into the, still, twofold degenerate e_{t} and the b_{2t}-level.

If the local environment is not octahedrally symmetric, the crystal field may even work in the opposite sense. In the tetrahedral symmetry, the orbitals which point along the axes now maximally avoid the charge density associated with the atoms situated on four of the
2.5. Spin Hamiltonian

2. Electron spin resonance

Figure 2.6: Example of the anisotropy of the $g$-factor following the axial symmetry Eq. (2.18). These measurements are for Sr$_{14}$Cu$_{24-2x}$Zn$_x$O$_{41}$ and $x=0.75$ [presented in Ch. 4 of this thesis].

corners of the cube which describe a tetrahedron. Therefore, in this case, the $e_g$ are lower in energy as show in right panel of Fig. (2.5).

By switching on the magnetic field $H$, the Zeeman energies are

$$E = \pm \frac{\mu_B H}{2} \sqrt{g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta} \quad (2.17)$$

where the anisotropy of the $g$-factor is represented by

$$g = \sqrt{g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta} \quad (2.18)$$

g-factor axial symmetry

the angle $\theta$ is the angle between the magnetic field and the tetragonal fourfold axis. This is also valid for axial, hexagonal, and trigonal symmetry. For Cu$^{2+}$, the isotropic $g$-factor should be replaced by an anisotropic quantity [84]

$$g_\parallel = 2 - \frac{8 \lambda}{\Delta_0} \quad (2.19)$$

$$g_\perp = 2 - \frac{2 \lambda}{\Delta_1} \quad (2.20)$$

where $\lambda$ is the spin orbital coupling and the energies $\Delta_{0,1}$ represent the splittings between the $e_t - b_{2t}$ and $b_{2t} - b_{1t}$ levels, respectively. In this case, the magnetic moment is still mainly a spin moment, (the deviation from the $g$-factor of 2 is small), and the restortion of the orbital magnetic moment is a weak effect. A more elegant way to present these results is by introducing the $g$ tensor

$$g = \begin{pmatrix} g_\perp & 0 & 0 \\ 0 & g_\perp & 0 \\ 0 & 0 & g_\parallel \end{pmatrix} \quad (2.21)$$
By introducing the tensor $D$ which represents the single ion anisotropy and relates to the anisotropic $g$-factor, the crystal field term in the Hamiltonian Eq (2.11) can be written as

$$H_{CF} = S \cdot D \cdot S$$

(2.22)

In this case, the total Hamiltonian takes the form

$$H = H_e + S \cdot D \cdot S + \mu_B (L + g_e S) \cdot H + \lambda L \cdot S$$

(2.23)

ESR is the only experimental technique which can directly measure the value of the $g$-factor. Therefore, within the next chapters and when we investigate the anisotropy of the Cu$^{2+}$ ions in the studied systems, we will often use the axial symmetry expression [Eq (2.16)] to describe this anisotropy.

### 2.6 ESR in low dimensional spin systems

Since its discovery, ESR was widely recognized as a very powerful and useful tool to study the magnetic properties from a microscopic point of view. A lot of ESR studies have been devoted to various low dimensional spin systems, in order to elucidate the magnetic interactions, magnetic ground states, collective excitations of interacting spin systems, critical behaviors near the phase transitions, and so on.

#### 2.6.1 The Kubo-Tomita theory of linewidth

The theoretical approaches to electron spin resonance were developed mainly during the 1950’s-1960’s. As early as the second half of 1940’s, an extensive study was made on the magnetic resonance phenomenon. The outcome was clearly pointing to the observed spectra as a probe to the mechanism of interaction between the resonating magnetic moments and their surroundings. The shift, splitting and broadening of the resonance line were believed to spot the crystalline fields, the hyperfine interaction and the dynamical behavior of the interacting degrees of freedom.

The idea of exchange narrowing was first suggested by Gorter and Van Vleck in 1947 [85], and more detailed description of the narrowing process was revealed by Anderson and Weiss later in 1954 [86, 87]. In the same time, 1948, the role of the dipolar interaction was formulated by Van Vleck [88]. In 1954, thanks to the pioneer work of Kubo and Tomita [89], the first general theory of the magnetic resonance absorption was developed. Kubo and Tomita theory (KT) describes an exchange coupled magnetic system by a Hamiltonian that consists of two terms

$$H = H_0 + H'$$

(2.24)

where the main term $H_0$ is the unperturbed Hamiltonian and gives rise to sharp resonance lines. This Hamiltonian is nothing but the sum of the isotropic Heisenberg exchange $H_e$ and Zeeman interactions $H_Z$

$$H_0 = H_e + H_Z = \sum_{ij} J_{ij} S_i \cdot S_j + \mu_B \sum_i g_i \cdot S_i \cdot H$$

(2.25)
In this case, the resonance lines have an identical shape to ESR in noninteracting spins in spite of an arbitrary strong exchange interaction. On the other hand, the intensity of these resonance lines are generally affected by the exchange Hamiltonian $H_0$. For example, in a spin gap system at zero temperature, the ESR intensity of line ($I_{ESR}$) goes to zero if the applied field is smaller than the gap.

However the second term, $\mathcal{H}'$, is a fluctuating time dependent perturbation which causes the shift and the broadening of the main line and the appearance of satellite lines. This term contains the dipole-dipole (DD), anisotropic exchange (AE) and Dzyaloshinsky-Moriya (DM) interactions. [90]

$$\mathcal{H}' = \mathcal{H}_{DD} + \mathcal{H}_{AE} + \mathcal{H}_{DM}$$  \hspace{1cm} (2.26)

where

$$\mathcal{H}_{DD} = g^2 \mu_B^2 \sum_{i \neq j} \frac{1}{r_{ij}^3} \left[ S_i \cdot S_j - \frac{3(S_i \cdot r_{ij})(S_j \cdot r_{ij})}{r_{ij}^2} \right]$$  \hspace{1cm} (2.27)

$$\mathcal{H}_{AE} = \sum_{i \neq j} S_i \cdot A_{ij} \cdot S_j$$  \hspace{1cm} (2.28)

$$\mathcal{H}_{DM} = \sum_{i \neq j} d_{ij} \cdot S_i \times S_j$$  \hspace{1cm} (2.29)

### 2.6.2 Angular dependence of the linewidth

The ESR absorption line at a frequency $\omega$ can be calculated as a Fourier transform [91]

$$I(\omega - \omega_0) = \int_{-\infty}^{\infty} \Phi(t) e^{i(\omega-\omega_0)t} dt$$  \hspace{1cm} (2.30)

of the relaxation function $\Phi(t)$ which is related to the autocorrelation function $\Psi(\tau)$ of the fluctuating local magnetic field, where $\tau$ is the fluctuation time

$$\Phi(t) = \exp \left[ \int_0^t (t - \tau) \Psi(\tau) d\tau \right]$$  \hspace{1cm} (2.31)

The correlation function can be calculated from the perturbation Hamiltonian $\mathcal{H}'$ and the magnetization associated with the total spin of the system $M_{\pm} = g\mu_B S_{\pm}$

$$\Psi(\tau) = \frac{1}{\hbar^2} \frac{\langle [\mathcal{H}'(\tau), M_{+}][M_{-}, \mathcal{H}'(\tau)] \rangle}{\langle M_{+} M_{+} \rangle}$$  \hspace{1cm} (2.32)

where $[ \cdot ]$ is the commutator and the brackets $\langle \cdot \rangle$ indicate the thermal average. The linewidth of the Lorentzian-shaped ESR line ($\Delta H$) can be expressed as

$$\Delta H \approx \frac{\hbar}{g\mu_B} \Psi(0) \tau_c$$  \hspace{1cm} (2.33)

with a characteristic time $\tau_c \approx \hbar/|J|$, and the function $\Psi(0)$ corresponds to the second moment $M_2(J/kT)$. This gives us the second moment representation of the $\Delta H$

$$\Delta H \approx \frac{\hbar^2}{g\mu_B |J|} M_2$$  \hspace{1cm} (2.34)
2.6. ESR in low dimensional spin systems

The time dependence of the correlation function of the system can be divided into three regions as shown in Fig. (2.7). The diffusion regime is preceded by a fast Gaussian dissipation of the correlation function [92]

\[ \Psi_T(t) = M_2 \exp(-\omega_e^2 t^2/2) \]  

(2.35)

where \( \omega_e^2 \sim J/\hbar \) is the exchange frequency. At \( \tau_1 \) a transition occurs from the rapid dissipation directly to the diffusion regime,

\[ \Psi_{\text{dif}}(t) \sim \tau^{-D/2} \]  

(2.36)

with \( D \) represents the dimensionality of the magnetic system. At long times a cutoff of the diffusion process occurs:

\[ \Psi_j(t) = \Psi_{\text{dif}}(\tau - \tau_2) \exp(\tau_2/\tau_2) \]  

(2.37)

where \( \tau_2 \) is the cutoff time determined by the interplane exchange or the intralayer dipole-dipole interaction. Thus the time interval \( \tau_1 - \tau_2 \) is the region of the diffusion regime. Therefore, the total resonance linewidth consists of the short-time and diffusion contributions to the correlation function \( \Psi(\tau) \).

Now, we consider a 1D system that consists of chains along the \( c \)-axis. For DD, AE, and DM interactions, the respective second moments at high temperature limit (\( J/kT = 0 \)) \( M_2^{DD}(0) \), \( M_2^{AE}(0) \) and \( M_2^{DM}(0) \) are given as follows [93]:

\[ M_2^{DD}(0) = g^4 \mu_B^4 \frac{3S(S+1)}{2\hbar^2} \sum_{i>j} \frac{(1 + \cos^2 \theta_{ij})}{r^6} \]  

(2.38)

\[ M_2^{AE}(0) = \frac{1}{4} A^2 (1 + \cos^2 \theta) \]  

(2.39)
2.6. ESR in low dimensional spin systems

Electron spin resonance

Figure 2.8: Representative of the 1D anisotropy of the linewidth $\Delta H_{pp}$ fitted by Eq. (2.41). This data is obtained for the 1D chain of the Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ and $x = 0.5$ [presented in Ch. 5 of this thesis].

$$M_{2DM}^D(0) = \begin{cases} \frac{-1}{8}d_{ij}^2(2 + \sin^2 \theta) & \text{for } d_{ij} \perp c \\ \frac{1}{2}d_{ij}^2(1 + \cos^2 \theta) & \text{for } d_{ij} \parallel c \end{cases}$$  \hspace{1cm} (2.40)

where $\theta$ is the angle between the applied magnetic field and the $c$-axis. Accordingly, the anisotropy of the linewidth in the 1D case follows the $(1 + \cos^2 \theta)$ term. This is why the angular dependence of linewidth of the 1D systems studied in the present thesis [Figure (2.8) is shown as an example] will be fitted using the expression:

$$\Delta H_{pp} = A(1 + \cos^2 \theta) + B$$ \hspace{1cm} (1D linewidth anisotropy) (2.41)

In 2D systems, Richards and Salamon [94] pointed out that, in contrast to the 1D case, the short time-correlation and the diffusion part contribute to $\Delta H$ with different angular dependencies. Spin correlations are restricted in the direction perpendicular to layers and as a result of a very slow decay of the $\Psi(\tau)$ the contribution from spin diffusion becomes apparent and for a given wave vector $q$ the spin correlation can be described as [91]

$$\langle S_q(t)S_q(0) \rangle = S(S+1)e^{-D_se^2t}$$ \hspace{1cm} (2.42)

where $D_s$ is the spin diffusion coefficient defined in $\partial \Psi/dt = D_s\nabla^2 \Psi$. For the direction perpendicular to the layers, the line shape deviates from Lorentzian shape and the linewidth is the largest. The linewidth is strongly depending on the angle $\theta$ between magnetic field and the normal to the layer. Such behavior is characteristic for 2D systems and the peak-to-peak line width has a spin-diffusive type form

$$\Delta H_{pp} \propto A \cdot (3 \cos^2 \theta - 1)^2$$ \hspace{1cm} (2.43)

Figure 2.9: Representative of the 2D anisotropy of the linewidth $\Delta H_{pp}$ fitted by Eq. (2.44). This data is obtained for Cu(NO$_3$)$_2$·H$_2$O [presented in Ch. 5 of this thesis].
where the zero contribution is at the 'magic angle' $\theta = 54.7^\circ$ when $\cos^2 \theta = 1/3$. Taking into account the background dipolar contribution in exchange narrowing regime, the total line width can be parameterized as:

$$\Delta H_{pp} = A \cdot (3 \cos^2 \theta - 1)^2 + Q \cos^2 \theta + B$$

2D linewidth anisotropy (2.44)

where $Q$ and $B$ contain the dipolar linewidth $M_2/\omega_e$ ($\omega_e$ is isotropic exchange frequency) and a contribution related to the spin correlation functions. In Eq. (2.42) it is assumed that the dipolar contribution has tensorial-type angular axial dependence with the principal axis along the normal to the layer. Figure (2.9) illustrates the anisotropy in the 2D compound Cu(NO$_3$)$_2$$\cdot$H$_2$O [discussed in Ch. 5 of this thesis] which follows Eq. (2.42).

### 2.6.3 T-dependence of the ESR parameters

As mentioned above, the angular dependence of the g-factor spots the symmetry around the magnetic ion. Whereas, the angular dependence of the linewidth gives useful information about the dimensionality and exchange interactions within the studied system. The development of the ESR parameters with temperature can reveal many interesting features in the investigated low dimensional spin systems.

The temperature dependence of the ESR spectra can be studied from a different point of view. The most direct change is that of the intensity of the resonance $I_{ESR}$, due to the proportionality of the absorption intensity to the temperature dependent static magnetic susceptibility. The absolute measurements of $I_{ESR}$ as function of the temperature are possible with high accuracy in the case of the X-band technique, where we have a tunable microwave power and a cavity designed to work in the X-band frequency. In the HF-ESR measurements, and due to technical reasons (absence of the cavity, longer waveguides, etc.), the absolute determination of $I_{ESR}$ is rather difficult.

The temperature dependence of $I_{ESR}$ can be treated in the same way as the static susceptibility $\chi$. For example, the well known Curie-Weiss law

$$\chi = \frac{C}{T - \Theta_W}$$

(2.45)

can be used to fit $I_{ESR}$. According to the sign of the Curie temperature $\Theta_W$, the nature of the dominant interaction (positive for FM and negative for AFM) is determined. The value of $\Theta_W$ is helpful to estimate the energy scale of the interactions within the studied system.

One of the important signatures of the low dimensionality of the system is that the T-dependence of the susceptibility $\chi(T)$ usually exhibits a hump. In this case, the maximum of $\chi(T)$ (maximum of the hump) is qualitatively a measure of the energy scale of the exchange interaction $J$. Also, the susceptibility can give information about the possible existence of an energy gap. In the ungapped low dimensional systems, $\chi(T)$ has a finite value at zero temperature. This is not the case for the gaped systems. For example, in
2.6. ESR in low dimensional spin systems

The alternating spin chain discussed in Section (1.5), Johnston et al. [95] calculated $\chi(T)$ for different $\alpha = J_2/J_1$ as shown in Fig. (2.10a). In the dimerized case ($\alpha \neq 1$), $\chi$ goes to zero at $T = 0$ K, which is in agreement with the gapped ground state. Whereas, for the uniform Heisenberg AFM chain $\alpha = 1$, $\chi(T)$ is finite at $T = 0$ K, which corresponds to the ungapped ground state.

An experimental example, the 1D spin chain in VOHPO$_4 \cdot \frac{1}{2}$H$_2$O, which is shown to be an alternating chain compound, exhibits an energy gap due to the formation of a spin dimer ground state as indicated by $\chi(T)$ in Fig. (2.10b) [96]. The normalized $I_{ESR}$ [Fig. (2.10c)] shows a very good agreement with $\chi(T)$. These results match very well with the theoretical calculation of the dimer model and alternating spin chain model as illustrated by the fitting in Fig. (2.10).

$H_{res}$, and accordingly the effective $g$-factor, is very sensitive to the environment surrounding the resonance spins. Lattice expansion and structural phase transitions produce variations in the local internal fields ‘seen’ by the spins, then including changes with temperature in the overall position of ESR response of the system. For example, in the spin-Peierls system CuGeO$_3$ [97], $H_{res}$ is almost constant above the spin-Peierls transition temperature.
T_{sp}. Whereas, for T < T_{sp} it shifts gradually. This shift can be understood on the basis of the change of crystalline field due to the local distortion caused by the SP transition. [98]

The dipolar field, produced by the dipole-dipole interactions, induce a shift in the $g$-factor. The effective magnetic field acting on the spins is given by the applied external field $H$ and an internal magnetic field $H_{int}$ due to spin interactions:

$$H_{eff} = H + H_{int}$$ (2.46)

The $H_{int}$ term is important in the low temperature range where a preferred spin orientation exists due to dipolar interactions with the other spins and vanishes in high temperatures where the spins are randomly oriented. In this case, the temperature dependence of the $g$-factor can be described by $1/T$-dependence:

$$g_i = g_i(0) + \frac{C_i}{T}$$ (2.47)

where, $i$ represents the different crystallographic directions and $g_i(0)$ is the component of $g_0$ tensor for the isolated spins in $i$-direction. The proportionality factor $C_i$ is a direct measure of the internal dipolar magnetic field. Such behavior was observed for different low dimensional systems [99, 100, 101, 102].

- Critical behavior of the ESR parameters

Another interesting point, the low spin lattice dimensionality gives rise to specific dynamic properties, namely the critical behavior at the magnetic phase transition. The development of spin correlation over the short range or long range ordering region produces an effective field, and therefore causes a shift of $H_{res}$. Such resonance is understood as a result of the violation of Larmor frequency by perturbation terms. The slowing down of the spin fluctuations near to the ordered configuration causes an anomalous behavior of the spin-spin relaxation which is associated with a rapid increase of the ESR linewidth. This critical behavior depends on the dimensionality of the spin lattice. [103] In the short-range magnetic order region, where the line broadening is due to the space variation of the spin correlations, the critical behavior of $\Delta H(T)$ can be expressed as:

$$\Delta H(T) = \Delta H(\infty) + A((T - T_N/T_N)^{-p}$$ (2.48)

where $p = (35 - 2\eta)/\nu$ and $p = (3 - 2\eta)/\nu$ for 1D and 2D systems, respectively. $\nu$ is the critical exponent for the inverse correlation length and $\eta$ is the critical exponent related to the static correlations. [104, 105]

- Oshikawa and Affleck Theory

In the $S = 1/2$ AF chain perturbed by an alternating $g$ tensor and/or the Dzyaloshinskii-Moriya interaction, the application of a uniform external field $H$ induces an effective transverse staggered field $h \propto H$, which leads to the opening of an energy gap $\Delta \propto H^{2/3}$ in contrast to the pure Heisenberg case. [106, 107, 108] Oshikawa and Affleck proposed a
new theory for low-temperature ESR in half-integer spin AFM chains [109, 110]. They showed that the staggered DM interaction produces divergent behaviors of the linewidth proportional to $\Delta H \propto (H/T)^2$ [see Fig. (2.11)] and the shift of the resonance frequency proportional to $\Delta H_{\text{res}} \propto (H/T)^3$ at low temperatures. They applied this theory to the 1D chains of Cu-benzoate, where they found a very good agreement of the experimental findings. [111]
2.7  Further measurement techniques

Throughout this work, further techniques were used to investigate the different physical properties of the studied systems. In particular, NMR and magnetization measurements were carried out in parallel with our ESR measurements. In this section, some remarks concerning the NMR, magnetization and specific heat measurements are given.

2.7.1  Nuclear magnetic resonance NMR

Nuclear magnetic resonance (NMR) is a very versatile and highly sophisticated spectroscopic technique which has been applied to growing number of diverse applications in science, technology and medicine. The nuclear magnetic moment is much smaller than that of the electron one, so the precession frequency is much lower. For typical laboratory magnetic fields, the electromagnetic radiation used in NMR experiments is in the radio frequency range. NMR measurements provide information at the atomic scale about electronic and magnetic properties of materials by inducing and observing transitions among nuclear spin levels.

In this thesis, the NMR measurements were carried out by E. Vavilova using a Tecmag pulse solid-state NMR spectrometer [112] in a magnetic field up to 9.2 T ‘produced by a superconducting magnet from Magnex Scientific’ [113] and in a temperature range 1.5 - 300 K.

2.7.2  SQUID magnetometer

SQUID (Superconducting Quantum Interference Device) is a very sensitive instrument for magnetic characterization of materials as a function of magnetic field and temperature. The system is designed to measure the magnetic moment of a sample, from which the magnetization and magnetic susceptibility can be obtained. Nowadays, this instrument is widely used worldwide in research laboratories.

In this work, susceptibility and magnetization measurements were carried out using two Quantum Design instruments, MPMS and VSM SQUID, they allow measuring the magnetic moment of the sample at applied field up to 5 and 7 tesla, respectively, in the temperature range 1.8 K and 300 K.

2.7.3  Specific heat

The specific heat measurements were carried out in a PPMS of the company Quantum Design. This equipment allows measurements in the temperature range between 350 K and 1.9 K. Additionally, magnetic fields up to 9 T can be used.
Chapter 3

1D zigzag chain $\text{In}_2\text{VO}_5$

3.1 Introduction

There has been considerable interest in vanadium oxides over several decades due to their diverse structural chemistry and unconventional physical properties. In particular, metal-insulator transitions occur in several binary vanadium oxides as prominent examples [114]. While studies of spin-ladder and spin-chain compounds were mostly concentrated on cuprate compounds such as KCuBr$_3$ and TiCuCl$_3$, [115] Sr$_2$CuO$_4$ and SrCuO$_2$, [116] or LaCuO$_{2.5}$, [117] quasi-low-dimensional vanadium systems such as VO$_2$P$_2$O$_7$ (Ref. [118]) or A$_x$V$_2$O$_5$ A=alkaline or alkaline-earth metal [119, 120] have experienced recent attention due to their variety of interesting quantum spin phenomena. [120, 121, 46] Spin ladders [122] consist of two or more parallel chains, often referred to as "legs" with an intrachain exchange interaction parameter $J$. Interchain interactions along the "rungs" are then represented by the parameter $J'$. In most cases with an even number of legs, the smallest magnetic entity is then given by a rectangle or exclusively by the rungs which are equivalent to dimers. These systems are representatives for a spin gap.

$\text{In}_2\text{VO}_5$ is the experimental realization of a one-dimensional two-leg spin-$\frac{1}{2}$ ladder with "sheared" legs, the so called zigzag chain, where the onset of antiferromagnetic AFM exchange along and between the legs can be attributed to the magnetic properties of a triangle as the smallest magnetic entity, whereby frustration phenomena might occur. Although $\text{In}_2\text{VO}_5$ has been first synthesized long ago, [123] its electronic and magnetic properties have not been explored so far.

In this chapter, the crystal structure, magnetization, resistivity, nuclear magnetic resonance (NMR) measurements of $\text{In}_2\text{VO}_5$ are introduced. Later, we present a detailed investigation of the magnetic properties of this compound by means of X-band and high field / high frequency electron spin resonance. Interestingly, these measurements reveal an interplay between structural, charge, and spin degrees of freedom in $\text{In}_2\text{VO}_5$. The results of this work have been published in Ref. [124] and Ref. [125].
3.2 Experiment

Single crystal and powder samples for the present study were prepared as described by Senegas et al. \cite{123} In$_2$O$_3$ (Chempur, 99.9 \%) and VO$_2$ (Chempur, 99.5\%) were dried before grounding. The reaction mixture of typically 1.3 g was then encapsulated under a vacuum in a silica ampoule. The sealed ampoule was heated directly to 1323 K. After three days, the furnace cooled down to room temperature at a rate of 5 K/h. Small black single crystals of In$_2$VO$_5$ were obtained and he crystals were of needle shape and typically $0.1 \times 0.1 \times 0.3$ mm$^3$ in size. Single crystal x-ray diffraction was performed at 293 and 100 K on an IPDS II diffractometer (Stoe&Cie). For powder x-ray diffraction (Cu K) radiation, a Siemens D5000 diffractometer equipped with a self-assembled helium cryostat for low temperature measurements was used. Lattice constants were derived from a LeBail fitting routine using the program FULLPROF. \cite{126}

Magnetization measurements were carried out on a physical property measurement system vibrating sample magnetometer (Quantum Design). The electrical resistivity (standard four-point method) was measured on a pressed and then at 1073 K (12 h) sintered powder pellet. The purity of the sample after sintering was checked again by powder x-ray diffraction. Absorption spectroscopy was performed on standard polyethylene (far infrared) and KBr (midinfrared) pellets at room temperature using a Bruker IFS-66v/s spectrometer. KBr diluted powder pellets were measured on a Cary 05E (Varian) spectrometer in the near infrared-visible-UV range at temperatures from 293 to 20 K.

ESR measurements were carried out at a frequency of $\nu = 9.5$ GHz with a standard X-band Bruker EMX spectrometer (Section 2.4.1) and also in a frequency range of 140-360 GHz with the high-field ESR spectrometer (Section 2.4.2). $^{51}$V NMR data were recorded on a Tecmag pulse solid-state NMR spectrometer in a magnetic field of 9.2 T in a temperature range 4.2-200 K. The NMR spectra were acquired by a point-by-point magnetic field sweeping. The transversal and the longitudinal relaxation times $T_2$ and $T_1$ have been measured at the frequency of the maximum intensity of the spectrum. $T_2$ has been determined from the Hahn spin echo decay. A method of stimulated echo has been used to measure $T_1$.

3.3 Crystal structure

In 1975, Senegas et al. \cite{123} reported the synthesis and crystal structure of In$_2$VO$_5$ at room temperature. We have redetermined the crystal structure at 293 and 100 K and the previous structure solution is confirmed by our data. Furthermore, no structural phase transition has been observed from single crystal data down to 100 K. Therefore, the structure description will be limited to the important structural features for understanding the physical properties and for more detailed discussion of the interatomic distances and angles we refer to Ref. \cite{123}. Figure 3.1 gives a perspective view of the crystal structure of In$_2$VO$_5$. A three-dimensional network of [InO$_6$] octahedral units is present. This constitutes $\frac{3}{\infty}$[In$_4$O$_{10}$] slabs of edge sharing entities which are connected via corner oxygens.
3.3. Crystal structure

3. 1D zigzag chain In$_2$VO$_5$

Figure 3.1: Perspective view of the crystal structure of In$_2$VO$_5$ with [InO$_6$] and [VO$_5^-$] polyhedra illustrated in gray and red, respectively, O1 (white), O2-O4 (blue), and O5 (cyan). Below, the structural feature of a zigzag chain type, $\frac{1}{\infty}[\{O_3V(O5)\}_{3/3}]_2$, is depicted. The larger V-O5 distances are represented by dotted lines.

O1 with identical slabs, giving rise to a $\frac{3}{\infty}[\text{In}_4\text{O}_8]$ framework. It should be noted that the coordination sphere of O1 consists only of four In atoms in a tetrahedral fashion with three In belonging to a common and one to an independent slab. Thereby, a nonmagnetic anionic framework with one-dimensional cavities along [010] is formed. The magnetic cations (V$^{4+}$, 3d$^1$, S = $\frac{1}{2}$) are connected to the network via oxygens O2, O3, and O4. Two O5 complement the coordination sphere of each V, which can be described as a distorted trigonal bipyramid. These entities are linked exclusively via O5 to zigzag chains $\frac{1}{\infty}[\{O_3V(O5)\}_{2/2}]$, in [010]. The second coordination sphere increases the coordination number of V from 5 to 6 and the (sheared) ladder-type structural feature is accomplished: $\frac{1}{\infty}[\{O_3V(O5)\}_{3/3}]_2$. The prominent structural difference between 100 and 293 K is the decreasing distance of V-O5 connecting two legs by 1.5 pm, marked by dotted lines in Fig. (3.1).

From the x-ray powder data, the lattice parameters were extracted and the evolution of the cell axes and the cell volume is shown in Fig. (3.2). The cell volume decreases roughly linearly with temperature down to 120 K and remains constant within standard deviations at temperatures below. The overall decrease in cell volume from 290 to 120 K is $\sim$ 0.25%. We found no indication of a structural transition down to 20 K from powder x-ray diffraction data, but rather a continuous change from an isotropic decrease of the lattice constants to an anisotropic behavior at $\sim$ 150 K. Below 200 K, the decrease of the a and b parameters levels off and turns into a slight increase by further lowering the temperature from $T^* \sim$ 120 to 20 K. This is in contrast to the behavior of the c parameter,
3.4 Magnetization measurements

Figure 3.2: Temperature dependence of lattice parameters and cell volume of In$_2$VO$_5$ as determined from x-ray powder diffraction (lines are a guide for the principal changes). The anisotropic temperature dependence sets in below $\sim 150$ K. For $T < T^* \sim 120$ K, a slight increase of the a and b axes occurs, which decreases almost linearly down to 50 K. It should be noted that the absolute values of the lattice parameters do not alter with temperature by more than 0.2 relative to 290 K. As will be shown below, the important consequence of the anisotropic temperature dependence of the lattice parameters for the magnetism of In$_2$VO$_5$ is that below a certain temperature $T^*$, the V-V distance along [010] begins to increase slightly or stays almost constant, whereas it decreases for two adjacent chains.

3.4 Magnetization measurements

The static susceptibility $\chi(T)$ of In$_2$VO$_5$ was measured on a powder sample in external fields of 1 T in field cooled FC and zero field cooled ZFC modes and at 14 T in a ZFC mode. The results are shown in Fig. (3.3). The inverse susceptibility $\chi^{-1}(T)$ exhibits a broad kink around a characteristic temperature $T^* \sim 120$ K which separates two linear regimes with different slopes of $\chi^{-1}(T)$. The fit of the experimental data above $T^*$ to the Curie-Weiss law

$$\chi = \frac{C}{T - \Theta_W}$$

(3.1)

yields the Curie constant $C=0.385$ emu K/mol and a positive Weiss temperature $\Theta_W \sim +15$ K that indicates FM interactions between the V spins. A similar fit at $T < T^*$ yields $C = 0.615$ emu K/mol and a negative $\Theta_W \sim -50$ K, implying the net AFM exchange between the V spins. The value of $C$ at $T > T^*$ corresponds approximately to the Curie constant of uncorrelated paramagnetic $S = \frac{1}{2}$ moments with the g factor $g = 2$. An appreciable increase of $C$ for $T < T^*$ indicates the significance of the magnetic correlations in the low temperature regime which will be discussed below. The FC and ZFC measurements of $\chi(T)$ in a field of 1 T reveal no differences over the whole temperature range. The ZFC
3.4. Magnetization measurements

Figure 3.3: Inverse susceptibility $\chi^{-1}(T)$ of In$_2$VO$_5$ at 1 T with linear fits according to the Curie-Weiss law for dominant FM (red) and AFM (blue, dashed) interaction above and below $T^*$, respectively. The inset shows the static susceptibility $\chi(T)$ for 1 T (black) and 14 T (red).

Curves for the two fields 1 and 14 T are also similar within the experimental error except the low temperature range $T < 15$ K where the susceptibility measured at 14 T is smaller as compared to the 1 T data see inset of Fig. (3.3).

Measurements of the field dependence of the magnetization $M(H)$ at several selected temperatures are shown in Fig. (3.4). $M(H)$ curves reveal no hysteresis and are linear in the accessible field range $H \leq 14$ T except at the lowest temperature of 1.9 K. The Brillouin function of noninteracting moments ($S = \frac{1}{2}$, $g = 2$) is shown for comparison. One notices that compared to the Brillouin function, the experimental $M(H)$ curves exhibit larger slopes for $T \geq 120$ K, whereas the slopes are strongly reduced at low temperatures and no tendency to the saturation even at the highest applied field can be seen. This evidences, similarly to the $\chi(T)$ data, a crossover from the FM to the AFM type of interactions between the vanadium spins with decreasing temperature. A nonlinear initial increase of $M(H)$ curve in small fields at 1.9 K [see inset of Fig. (3.4)] suggests the occurrence of $\sim 2\%$ of impurity spins which are saturated in a field of a few tesla at low $T$’s. That would explain the smaller low-$T$ values of $\chi(T)$ measured at $H = 14$ T.

We note that although our static magnetic data reveal appreciable magnetic correlations, no evidence for the occurrence of long-range magnetic order in In$_2$VO$_5$ can be found in the studied temperature range. This is supported by our measurements of the specific heat between 2 and 200 K data, which give no indications for a transition to a magnetically ordered state.
3.5 Electric resistivity and spectroscopic characterization

The electrical resistivity $\rho$ of a pressed and sintered powder pellet of In$_2$VO$_5$ in the temperature range of 100-540 K is shown in Fig. (3.5). In the high temperature regime, $\rho$ does not change significantly as indicated by $\rho(290K) = 3.30\Omega$ cm and $\rho(500K) = 2.66\Omega$ cm, whereas below $\sim 150$ K, the resistivity increases dramatically. Except at temperatures close to $T^* \sim 120$ K, the resistivity follows the Arrhenius law which yields a linear dependence of the logarithmic plot of the conductivity $\sigma = \rho^{-1}$ versus $T^{-1}$ with the slope given by the activation energy $E_g \sim 150$ meV [Fig. (3.5), inset]. By approaching $T^*$, the conductivity drops down, indicating the transition from semiconducting to insulating behavior. Notably, one can relate this transition to the crossover in the $T$ dependence of the magnetic susceptibility occurring around $T^*$ [Fig. (3.3)]. We recall that at this temperature also, the crystallographic $a$ and $b$ axes begin to increase slightly Fig. (3.2), whereas the anisotropic lattice contraction sets in below $T^* \sim 150$ K.

Standard optical characterization of In$_2$VO$_5$ reveals in the infrared region the expected vibration modes phonons below 800 cm$^{-1} \approx 100$ meV spectra (not shown here). Above 1000 cm$^{-1}$, transmittance is significantly reduced, reaching a constant value at $\sim 1100$ cm$^{-1} \approx 135$ meV, which corresponds approximately to the optical band gap and is in agreement with the band gap $E_g$ obtained from the resistivity measurements.

As suggested by the resistivity data, insulating behavior is present below $T^* \sim 120$ K. Therefore, we studied the temperature dependence of In$_2$VO$_5$ in the near infrared-visible part of the electromagnetic spectrum 4000-20000 cm$^{-1}$. No changes in the absorbance were detected and no indication of electronic $d - d$ transitions according to a localized [VO$_6$] chromophore was observed. This again corroborates the picture of a semiconductor with a band gap thermal or optical activation energy at lower energies than the studied spectral range, e.g., $< 0.5$ eV.
3.6 NMR measurements

To elucidate the interplay between structure, conductivity, and magnetism in In$_2$VO$_5$ suggested by the experimental data in the previous sections, we have studied the magnetic resonance of the nuclear and electronic spins at the vanadium site. NMR and ESR probe on a local scale the electron spin dynamics and spin correlations.

3.6 NMR measurements

$^{51}$V NMR in In$_2$VO$_5$ has been studied at a frequency of 103 MHz in a temperature range 4.2-200 K. Typical spectra are shown in the inset of Fig. (3.6). The $^{51}$V nucleus has a spin $I = \frac{7}{2}$ and possesses a nuclear quadrupole moment. Owing to the interaction of the quadrupole moment with the gradient of the electrical crystal field, the $^{51}$V NMR spectrum may generally acquire a structure consisting of the main central line and six satellites. However, in the case of In$_2$VO$_5$, the satellites are unresolved in the powder spectrum and its shape can be described by a single Gaussian line profile indicated by solid and dashed lines in the inset of Fig. (3.6). The NMR line shape, the resonance field, and the linewidth are almost unchanged in the studied temperature range. Only by approaching the lowest temperature of 4.2 K can a small broadening of the signal and a shift of its position to lower fields be observed. However, both the nuclear transversal spin-spin and the longitudinal spin-lattice relaxation rates, $1/T_2$ and $1/T_1$, show a temperature dependence as shown in the main panel of Fig. (3.6). There is a sharp enhancement of both relaxation rates peaked at 20 K followed by their slowing down at higher temperatures. The $1/T_2$ rate levels off at $\sim$ 70 K and exhibits a small hump at about 150 K, which only slightly exceeds the experimental error. $1/T_1$ continues to decay smoothly up to $\sim$ 100 K, where it reaches a constant value of 16 s$^{-1}$. 

![51V-NMR](image-url)
Generally, the nuclear relaxation can be caused by electric quadrupole and magnetic interactions. The strong enhancement of the nuclear relaxation processes near 20 K can be straightforwardly related to the critical slowing down of magnetic fluctuations in the electronic subsystem. The electron spins of vanadium, fluctuating with some characteristic frequency \( \omega_{sf} \), exert an effective field at the vanadium nuclear spin owing to the on-site hyperfine coupling. The transverse component of this field \( h_{eff} \) contributes to the longitudinal nuclear spin relaxation as

\[
T_1^{-1} = \frac{\gamma_N^2 h_{eff}^2}{\omega_{sf}(1 + \frac{\omega^2}{\omega_{sf}^2})}
\]

where, \( \gamma_N \) is the nuclear gyromagnetic ratio and \( \omega_L \) is the nuclear Larmor precession frequency. [127] The relaxation is maximum when the fluctuations of the electron spins slow down to the NMR frequency, \( \omega_{sf} = \omega_L \). The rate \( 1/T_1 \) reduces in the case of both fast \( \omega_{sf} > \omega_L \) and slow fluctuating \( \omega_{sf} < \omega_L \) or static electron spins. The peak in the \( T \) dependence of \( 1/T_1 \) thus clearly indicates a transition to a magnetically ordered or very slowly fluctuating phase in \( \text{In}_2\text{VO}_5 \) at \( T_{SRO} \sim 20 \) K. A similar spin fluctuating relaxation mechanism may give a contribution \( 1/T_2^{sf} \) to the total transversal nuclear spin relaxation rate \( 1/T_2 = 1/T_2^{sf} + (1/T_2)^{sf} \) in addition to the contribution \( 1/T_2^{sf} \) arising from nuclear spin-spin couplings, e.g., magnetic dipolar or indirect interactions. [127] The fact that the peak in the dependence of \( 1/T_2 \) versus \( T \) occurs at the same temperature \( T_{SRO} \) as for the \( 1/T_1 \) rate corroborates its assignment to the onset of a (quasi-) static magnetic order.

However, below \( T_{SRO} \), we do not observe a significant broadening and/or splitting and shift of the NMR line indicative of the development of the staggered magnetization in the long-range AFM ordered state. The occurrence of the peak in the nuclear relaxation rates is associated with only a small broadening and shift of the NMR line at \( T < T_{SRO} \). It is therefore plausible that only a short-range (glassylike) magnetic order (SRO) is realized in \( \text{In}_2\text{VO}_5 \) below \( T_{SRO} \), which can be detected by local magnetic resonance techniques [see also Section (3.7)] but not by the bulk thermodynamic measurements discussed before (Section 3.4).

The longitudinal relaxation rate \( 1/T_1 \) of the vanadium nuclei arising due to the hyperfine coupling with the electron spins is proportional to the imaginary part of the momentum \( q \) and frequency \( \omega \) dependent electron dynamic susceptibility \( \chi''(\omega, q) \), at small energies as \( 1/T_1 \propto T \chi''(\omega, q) \). [128] The independence of \( 1/T_1 \) on temperature at \( T > T^* \) implies then a Curie-like dependence of \( \chi'' \) consistent with the behavior of the susceptibility in the static limit [see Fig. (3.3)]. Therefore, in spite of a significant reduction of the resistivity and evidence for the delocalization of the \( d \) electrons above \( T^* \) from the ESR measurements [see Section (3.7)], \( \text{In}_2\text{VO}_5 \) has not yet reached the limit of a band metal for which a \( T \)-independent susceptibility and a linear in temperature Korringa-like relaxation \( 1/T_1 \sim T \) are expected. [129]

Interestingly, the longitudinal relaxation rate \( 1/T_1 \), which probes the dynamic spin susceptibility of the electronic system on the NMR time scale and can also be sensitive to
3.7 Electron spin resonance measurements

3.1D zigzag chain In$_2$VO$_5$

Figure 3.7: The field derivative of the ESR signal at X-band frequency of 9.5 GHz at different temperatures. The small sharp signal is due to small amounts of 'isolated' paramagnetic impurities.

charge fluctuations via the quadrupole relaxation channel, remains appreciably $T$ dependent even far above $T_{SRO}$. Thus, it is tempting to associate the onset of this $T$ dependence with a crossover from band to localized AFM interacting $d$ states that is identified in the ESR measurements [see Section (3.7)] at the same characteristic temperature $T^* \sim 120$ K. Moreover, one can speculate that a small hump in the $T$ dependence of the nuclear spin-spin relaxation rate $1/T_2$ is related to the change of the lattice contraction from the isotropic to anisotropic regime at $\sim 150$ K. Because these structural changes affect the nearest-neighbor distances and bond angles between V sites, this could alter the nuclear dipole-dipole interactions contributing to $1/T_2^*$.

3.7 Electron spin resonance measurements

No ESR response from the powder sample of In$_2$VO$_5$ can be detected at room temperature regardless of the frequency of the measurement. However, a well-defined ESR signal, which can be associated with the resonance of bulk V$^{4+}$ ($3d^1, S = 1/2$) ions, emerges below $\sim 130$ K. At $\nu = 9.5$ GHz (X band), ESR is measured by a lock-in phase-sensitive detection with a sample placed in the resonance cavity. With this technique, the detected signal is a field derivative of the microwave absorption $dP/dH$. For $20$ K $< T < 120$ K, the shape of the signal from In$_2$VO$_5$ can be described by a single-derivative Lorentzian line profile as shown in Fig. (3.7). The line is very broad at high temperatures. However, the width of the signal $\Delta H_{pp}$ rapidly decreases with decreasing the temperature down to 40 K and then starts to increase again as illustrated in Fig. (3.8b). The position of the resonance $H_{res}$
3.7. Electron spin resonance measurements

3. 1D zigzag chain $In_2VO_3$

Figure 3.9: The typical ESR signals measured at $T = 30$ K for different microwave frequencies. Two resonance lines (denoted weak and main) are indicated within the fitted signals.

Figure 3.10: The frequency-resonance field diagram of the two resonance lines for different temperatures.

Shifts to lower fields in the same temperature range [Fig. (3.8a)]. Remarkably, the ESR signal vanishes upon approaching a temperature of $\sim 20$ K.

In the high frequency regime (140-360 GHz), the transmission of the microwave radiation through the sample has been measured as a function of magnetic field without a resonance cavity. The typical ESR signals at $T = 30$ K for different microwave frequencies are shown Fig. (3.9). Unlike the X-band measurements, the fit of the absorption lines requires two Lorentzians: a strong main resonance line and a weak satellite on the left shoulder as indicated by the blue and green lines. The frequency versus magnetic field relation of these two resonance modes is shown in Fig. 9. The $\nu(H)$ dependence of the main signal is linear. Its extrapolation to low fields intersects the origin and matches very well with the measurement at $\nu = 9.5$ GHz. In contrast to the main line, the $\nu(H)$ branch of the weak satellite has an appreciable frequency offset $f_0 \sim 100$ GHz corresponding to an energy gap for this resonance excitation.

From the slope of the main linear $H$ branch, the $g$ factor $g = 1.95$ can be calculated, in perfect agreement with the results of the angular overlap model (AOM) calculations ($g_{av} = 1.94$ and the principal $g$ values of 1.92, 1.94, and 1.96, see next section). Note that at all measured frequencies, no deviation from the Lorentzian shape has been observed,
3.7. Electron spin resonance measurements

3. 1D zigzag chain \( \text{In}_2\text{VO}_5 \)

Figure 3.11: Evolution of the ESR spectrum with temperature at \( \nu = 270 \) GHz. Dashed and dotted Lorentzian line profiles depict the decomposition of the spectrum below 15 K into the paramagnetic and AFM modes, respectively.

indicating that the anisotropy of the \( g \) factor which should yield the spread of the resonance fields in the polycrystalline samples is smaller than the width of the resonance. With the linewidth of the order of 1 T, the estimated anisotropy of the \( g \) factor is smaller than a few percent, which corroborates the AOM calculation.

The evolution of the ESR spectrum with temperature at \( \nu = 270 \) GHz is shown in Fig. (3.11). Note that at this frequency, the weak satellite merges with the main line [Fig. (3.9)]. Therefore, the signal can be described by a single Lorentzian absorption profile in a wide temperature range. The \( T \) dependence of \( H_{\text{res}} \) and \( \Delta H \) obtained from the Lorentzian fit is shown in Fig. (3.12). \( H_{\text{res}} \) is temperature independent, whereas \( \Delta H \) continuously increases with lowering the temperature. Below 20 K, the signal not only broadens but also acquires an asymmetrical shape, indicating the development of an additional resonance mode. Fitting the line profile for \( T \leq 15 \) K with two Lorentzians [Fig. (3.11)] yields the \( T \) dependence of the linewidth and the resonance field for the additional mode which is plotted in Fig. (3.12). One can observe the shift and narrowing of this mode, whereas the main absorption line continues to broaden with \( H_{\text{res}} \approx \text{const} \).

The development of the additional mode corresponds nicely with the occurrence of the SRO state in \( \text{In}_2\text{VO}_5 \) at \( T_{\text{SRO}} \sim 20 \) K suggested by the NMR data. It can be related to an AFM-like collective magnetic excitation in the SRO regions which sharpens and shifts away from the paramagnetic line. The coexistence of this mode with the paramagnetic signal
implies the presence of nonordered regions at \( T < T_{SRO} \), which would be consistent with a continuous spinglass freezing scenario. Such an extremely broad ESR response below \( T_{SRO} \) can only be observed at high excitation frequencies and not in a 'low' frequency X-band measurement.

Rapid disappearance of the ESR signal from the localized \( d \) states of \( V^{4+} \) by heating the sample over a characteristic temperature \( T^* \sim 120 \) K is unusual. In particular, it coincides with a significant increase of the conductivity of \( \text{In}_2\text{VO}_5 \) around this temperature. Therefore, one can speculate that \( T^* \) is a characteristic temperature for delocalization of the \( d \) electrons which at \( T > T^* \) begin to contribute to the conductivity. That would naturally explain the vanishing of the ESR signal. Even if delocalization occurs on a scale of some lattice constants, it would yield the momentum scattering of electrons which, owing to the significant spin-orbit coupling, should result in extremely short spin relaxation times.

The occurrence of the weak satellite mode with an excitation energy gap \( f_0 \sim 100 \) GHz is not expected if one considers the resonance of an \( S = 1/2 \) system, like isolated \( V^{4+} \) ions or ions coupled in a chain. Here, one requires a correlated spin cluster with a total spin \( S_t \geq 1 \). Feasible AFM correlations of \( V^{4+} \) spins on a triangular pattern along the vanadium chain will be discussed in next Section. By considering, for simplicity, an isolated AFM triangle of spins \( \frac{1}{2} \), one can qualitatively explain the ESR observations as shown in Fig (3.13). Speculatively, the weak satellite may correspond to a resonance transition between the \( |S_t = \frac{1}{2}; S_z = \pm \frac{1}{2} \rangle \) ground state of the triangle and its high energy \( |S_t = \frac{3}{2}; S_z = \pm \frac{1}{2}, \pm \frac{3}{2} \rangle \) state. In ESR, the total spin \( S_t \) is a conserved quantity. Therefore, a transition between different spin multiplets is forbidden. However, in the presence of anisotropic magnetic interactions, such as, e.g., the Dzyaloshinskii-Moriya interaction, different spin states can be mixed and the resonance between them may become visible. [130] In this scenario, the excitation gap \( f_0 \sim 100 \) GHz is a measure of the energy separation between the \( S_t = \frac{1}{2} \) and \( S_t = \frac{3}{2} \) states of the triangle.
3.8 Discussion

In order to grasp the different aspects of the rich physics of In$_2$VO$_5$ emerging from the structure, magnetization, and spectroscopy measurements, it is useful to start with the properties of the orbital states of the V$^{4+}$ ($3d^1$) ion. The degeneracy of the ground state $t_{2g}$ orbitals, where a single $d$ electron resides, will be lifted mainly by the $\pi$-antibonding interactions with the O$^{2-}$ ligands for the [VO$_6$] metal-ligand complex. A convenient method based on ligand field theory is an analysis within the AOM. [131, 132, 133] The AOM calculations include the interatomic distances and angles derived from the single crystal structure determination, and therefore, distortions from an octahedral ligand field can be accounted for. Since the interaction between V$^{4+}$ and O$^{2-}$ depends on the interatomic distances, it is quite reasonable to assume a first and a second coordination sphere, [VO$_5^{+1}$], comprising five nearest-neighbor oxygens (O2, O3, O4, and two O5) on the first one and the sixth neighbor O5 on the second sphere, respectively [see Fig. (3.14) and Section (3.2)]. Then, the orbital splitting for all ligands within an orthogonal coordination frame will correspond to sketch A in Fig. (3.14) with the degenerate $d_{xz}$ and $d_{yz}$ orbitals being lowest in energy. Inclusion of the observed deviation from linearity along [011] for the two nearest O5 ligands parametrized by the angle $\alpha$ [Fig. (3.14)] will lift this degeneracy [Fig. (3.13), sketch B]. The relative energy difference of the $d_{xy}$ to the lower $d_{xz}$ orbital is then entirely dependent on the different amount of the $\pi$-antibonding interaction for the first and second coordination spheres. Since for the $d_{xz}$ orbital this interaction, based upon distances, will be much smaller than the former one, the ground state will be associated with the $d_{xz}$ orbital in any case for the local structure.

To check these results, the relative energy separation $\Delta E$ between the $d_{xz}$ and $d_{xy}$ as a function of $\pi$-antibonding interaction and the corresponding average molecular $g$ value including spin-orbit coupling were calculated. From these calculations, one can estimate that $\Delta E$ should be at least $\sim 0.25$ eV to account for $g \sim 1.95$ as observed in

![Diagram](image-url)
the ESR experiment. The complete calculation, including all distances and angle dependences of the ligands, will shift the relative energy of the $d_{yz}$ orbital highest to $\sim 0.5$ eV. The ground state $E(xz)$ configures the occupied $d$ orbitals in a $\delta$-stacking fashion along the $b$ axis which practically do not overlap. On the other hand, the two excited states $E(xy, yz)$ are oriented in a $\pi$ arrangement in this direction, which might lead to an effective overlap involving O5 orbitals whereby a significant covalency is anticipated. In this scenario, one would expect a considerable degree of delocalization along the $b$ direction for the electrons promoted into these overlapping molecular orbitals. One may speculate about a narrow band formation that is depicted in sketch C in Fig. (3.14), which would favor a ferromagnetic polarization of the $d$ electrons. Strong indications for the relevance of this scenario in the high temperature regime above $T^*$ are given by significant conductivity, ferromagnetic sign of the net exchange derived from the $\chi(T)$ measurements, and the absence of the ESR response which is suggestive of the itinerant character of the $d$ states.

Lowering the temperature yields a crossover to the anisotropic thermal contraction which sets in at $\sim 150$ K. Below $T^* \sim 120$ K, the $b$ lattice parameter even starts to increase slightly. The shrinking of the $c$ lattice parameter implies a decrease of the distance between the vanadium and the O5 ligand in the neighboring chain as shown in Fig. (3.15), thus increasing the overlap of the $xz$ orbitals with the $p$ orbitals of that ligand. Considering the orientation of the $xz$ orbitals and the interchain bond angle V-O5-V of 106°, one would expect an increase of the AFM superexchange between the vanadium chains. Concomitantly, owing to the increasing $b$ lattice parameter, the width of the hybridized band in the chain direction [Fig. (3.14), sketch C] should decrease and become thermally depopulated. One could speak therefore of a temperature and structurally driven crossover from the itinerantlike FM correlated linear chain along [010] with the effective exchange $J$ (FM) to the zigzag chain of localized spins with the AFM nearest-neighbor interaction $J'$ (AFM) [Fig. (3.15)]. Indeed, the band structure calculations reveal significant V-O hybridization and yield a stable FM solution for the room temperature crystal structure of In$_2$VO$_5$. [134]

In agreement with our results, a thermodynamical study of In$_2$VO$_5$ in Ref. [135] also suggests the presence of magnetic disorder and frustration and formation of the spin-glass state in this material. This is contrasted by a conjecture of a formation of the global spin-singlet state in In$_2$VO$_5$ published recently in Ref. [136]. Obviously the complexity of In$_2$VO$_5$ requires further experimental studies of this material.
3.9 Conclusion

In summary, we have studied the structure, magnetization, electrical resistivity and nuclear- and electron spin resonance (NMR and ESR) of this compound. The data reveal a remarkable interplay between lattice, spin and orbital degrees of freedom.

At high temperatures In$_2$VO$_5$ is semiconducting and exhibits ferromagnetic correlations in the spin sector. This is contrasted with the insulating behavior and predominantly antiferromagnetic (AFM) exchange between the localized V$^{4+}$ spins below a characteristic temperature $T^* \sim 120$ K. ESR and NMR measurements reveal a short-range quasi-static magnetic order at $T_{SRO} \sim 20$ K but surprisingly no long-range ordered magnetic ground state can be observed. We attribute such an unusual crossover in the electronic and magnetic properties at $T^*$ to the anisotropic thermal contraction of the lattice which yields magnetic frustration: Below $T^*$ the $c$-axis continues to shrink whereas the $b$-axis begins to expand. The related changes in the overlap of the orbitals yield the localization of 3$d$-electrons which AFM interact on a frustrated triangular pattern.

Transitions between different spin configurations give rise to an additional gapped ESR mode which is not expected in a spin-1/2 chain without frustration. The ESR gap $f_0 \sim 100$ GHz evidences the energy separation $\Delta \sim 5$ K between the ground state $S_t = 1/2$ configuration of a frustrated spin triangle and its excited $S_t = 3/2$ state.

Our measurements on In$_2$VO$_5$ give experimental evidence for the interplay of structural and electronic changes that induce a transition from a semiconducting behavior with ferromagnetic correlations at high temperatures to the insulating regime with predominantly antiferromagnetic interactions between vanadium localized moments at low temperatures. This eventually results in a frustrated glassylike magnetic ground state without long-range order. Our results bring additional insights into the rich physics of complex vanadium oxides and call for theoretical modeling of the band structure and magnetic interactions in In$_2$VO$_5$. 
Chapter 4

The quasi-1D cuprates

4.1 Introduction

Low-dimensional quantum spin systems with spins and charges arranged in chains and ladders are under intensive study experimentally as well as theoretically [46]. Various interesting magnetic and electronic properties are inherent to these systems because of their unique arrangement of spins and charges. In particular, theoreticians predicted that doped even-leg ladder compounds can produce superconductivity relevant to that in the underdoped high-$T_c$ cuprates [50],[137] (see Sec. (1.3)). In an undoped even-leg ladder spin singlets located on rungs produce a ground state which is usually described as a gapped spin-liquid. Doping with holes, the added holes tend to share the same rung on the ladder in order to minimize the energy paid to break the spin singlets. In this case, the formation of hole pairs is expected to lead to superconductivity with $d$-wave symmetry [52]. Upon doping, the spin gap remains constant or slightly decreases in size, but it is still finite when superconductivity sets in. A competing charge density wave (CDW) phase may arise due to the quasi-one dimensional nature of ladders and disturb the superconducting phase. Thus, such ladder systems provide a challenging possibility to study spin and charge dynamics and their interplay in a spin-gapped environment with clear significance for the phase diagram of high-temperature superconducting cuprates [138].

For the understanding of high-$T_c$ superconductivity in the cuprates physicists are studying materials with related crystallographic structures showing similar electronic properties. Among those materials, the spin-chain spin-ladder compound Sr$_{14}$Cu$_{24}$O$_{41}$ is a good candidate. A detailed review on the quasi-one dimensional (q1D) cuprates (La,Y,Sr,Ca)$_{14}$Cu$_{24}$O$_{41}$ can be found in Ref. [138]. They belong to a rich class of strongly correlated materials of transition metal oxides. These compounds exhibit some of the most excited phenomena in condensed matter physics. The discovery of superconductivity in the Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ (SCCO) for $x = 13.5$ compound under pressure triggered this broad interest [53], in particular since this system is the first superconducting copper oxide material with a non-square-lattice.
4.2 Structure of SCO

The Sr$_{14}$Cu$_{24}$O$_{41}$ compound possesses a complex layered structure as shown in Fig (4.1). It contains two different substructures: stacks of Cu$_2$O$_3$ two-leg ladders and stacks of CuO$_2$ chains, separated by sheets of Sr atoms. The CuO$_2$ chains consist of edge-sharing CuO$_4$ plaquetts. However, the two-leg ladders Cu$_2$O$_3$ layers are arranged from of two zig-zag chains composed of edge-sharing CuO$_4$ squares and neighboring ladders are offset by $c_L/2$. Thus the so-formed ladders consist of both corner and edge-sharing squares.

The layers in both subcells are stacked along the $b$-axis, whereas the chains and the two-legged ladders are aligned incommensurably along the $c$-axis which leads to additional modulations of the crystallographic positions. Both of these two sublattices have orthorhombic symmetry, where the lattice parameters are: $a=11.469$ Å, $b=13.368$ Å, along the $c$-direction the unit cell for the ladders is $c_L=3.931$ Å, and for the chains $c_C=2.749$ Å. Hence, the lattice constants of the two subsystems are roughly related as $7 \cdot c$ (ladder) and $10 \cdot c$ (chain) [139]. The chains and ladders are extremely sensitive to variations in external parameters, such as temperature, doping and pressure. Such sensitivity originates from the essential influence of correlations on this material, which leads to the interplay between spin and charge degrees of freedom in the two subsystems. The average Cu valence in Sr$_{14}$Cu$_{24}$O$_{41}$ amounts to 2.25 yielding an intrinsically doped compound with holes. These holes are strongly localized and mainly located in the chains. [140]
4.3 Magnetic structure of SCO

In the Cu$_2$O$_3$ two-leg ladders the Cu ions are coupled via 180° strong AFM Cu-O-Cu superexchange along the the rungs and the legs. On the other hand, neighboring ladders can be considered as magnetically decoupled because they are connected by 90° Cu-O-Cu bonds, which gives rise to a weak ferromagnetic and frustrated interladder by exchange interaction. Whereas, in the CuO$_2$ chains, the nearest neighbor (NN) Cu spins are coupled by a nearly 90° weak FM superexchange along the c axis. Whereas, the next nearest neighbor (NNN) Cu spins are coupled by AFM interaction.

The chain and the ladder subsystems exhibit a spin singlet ground state. Hence, the presence of a spin gap is obvious for both subsystems. The ladders possess a large gap due to singlet pair formation on the rungs. This gap amounts to 380 K [142, 143, 144] and it is almost independent of finite numbers of holes. In contrast, the chain subsystems have a smaller gap amounting to 130 K which strongly depends on the number of holes in the chains. The holes in the chains are believed to be localized at the oxygen sites, where they couple with copper spins, producing a nonmagnetic state which is usually referred to as the Zhang-Rice (ZR) singlet. This influences strongly the magnetism of the spin chain resulting in a dimerized ground state. Two Cu$^{2+}$ ions that are separated by a Cu$^{3+}$ on a ZR singlet couple antiferromagnetically (AFM) [145]. If they are surrounded by two localized holes at both sides, they form almost independent dimers as shown in Fig (4.2).

The dimerized nonmagnetic state in the chain subsystem is experimentally well established and is recognizable as a dramatic decrease in the magnetic susceptibility below 80 K as shown in Fig (4.3). The magnetic susceptibility is a bulk observable which should not be able to distinguish between the subsystems. However, the Cu$^{2+}$ spins in the ladder are virtually inert below 300 K due to the large spin gap. Therefore, magnetic susceptibility...
4.4. Hole distribution and physical properties

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measurements below 300 K is mainly dominated by Cu spins in the chain subsystem. The temperature dependence of the magnetic susceptibility $\chi(T)$ can be very well fitted with

$$\chi = \frac{N_A g^2 \mu_B^2 H}{24k_B} \left( \frac{2N_d}{T[3 + \exp(-J_d/k_BT)]} + \frac{N_s}{4T} \right)$$

(4.1)

which contains two terms: $\chi_{\text{dimer}}(T)$ is due to weakly interacting AFM dimers and $\chi_{\text{Curie}}(T)$ is the Curie contribution. $N_d$ is the number of dimers per formula unit and $J_d$ is the intradimer exchange, $J_d/k_B = 134$ K. The Curie contribution is a genuine property of the CuO$_2$ chain subsystem. In this case, the hole-doped chains are not regular sequences of weakly interacting spin dimers, but instead they host a small percentage of almost quasifree spins and/or spin trimers [145]. On the other hand, above 150 K the susceptibility behavior gradually deviates from the AFM dimer behavior. This deviation is due to the increased ladder contribution to the susceptibility.

4.4 Hole distribution and physical properties

Sr$_{14}$Cu$_{24}$O$_{41}$ system is intrinsically hole doped due to stoichiometric reasons. As mentioned before, the average Cu valence in Sr$_{14}$Cu$_{24}$O$_{41}$ is 2.25 instead of 2, which leads to 6 holes per formula unit (f.u.). However, the distribution of the holes among chains and ladders is one of the fundamental questions in this system. Moreover, the redistribution of these holes upon doping SCO with 'Ca and La' is one of most important factors which control the physical properties (in particular superconductivity) in these systems. Indeed, experimentally and since its discovery, the precise determination of hole distribution in SCO and its redistribution upon doping is still under debate, since different experimental techniques have provided contradictory results.

In Sr$_{14}$Cu$_{24}$O$_{41}$, most of the 6 holes are generally believed to reside essentially in the chain, where they are localized (5 holes for every 10 Cu’s in the chain and 1 hole for every 14 Cu’s in the ladder). From the chemical formula its easy to calculate the average valence
of Cu and the number of holes per formula unit. For \( \text{La}_{x}\text{Ca}_{14-x}\text{Cu}_{24}\text{O}_{41} \) and \( x = 6 \), the Cu valence is 2 and thus this system is no longer doped with holes. Now the important question is: what is happening with the gradual substitution of Ca and La instead of Sr? Indeed, the total number of holes is known. However, where are these holes and how can they affect the physical properties is the main target of this section.

First, we introduce the effect of Ca doping in SCO. A substitution of \( \text{Sr}^{2+} \) by the isovalent \( \text{Ca}^{2+} \) leaves the hole number constant and equal to 6 for any Ca content, but due to the increasing chemical pressure, holes tend to be transferred from the chains into the ladders. Tafra et al. [147] summarized the debate over the redistribution of the holes between the chain and ladder subsystems in \( \text{Sr}_{14-x}\text{Ca}_{x}\text{Cu}_{24}\text{O}_{41} \) \((0 \leq x \leq 12)\) as shown in the inset of Fig. (4.4). For the parent compound SCO, Hall coefficient, near-edge X-ray-absorption fine structure (NEXAFS), optical conductivity and NMR measurements suggest one hole or less per f.u. in the ladder subsystems [147, 148, 140, 149]. Rusydi et al. [150] performed a semiempirical analysis X-ray absorption spectroscopy (XAS). The interpretation of the data lead to 2.8 holes in the ladders and 3.2 in the chains, which obviously contradict with other techniques. While for Ca doped samples, all these techniques suggest a hole transfer from the chains to the ladder by increasing Ca content due to the increased chemical pressure. However, they again disagree on how strong is this redistribution of the holes.

The effect of Ca doping is more pronounced in the physical properties of the system. The hole transfer from the chains to the ladders destabilizes the charge ordered ground state which is present for \( x = 0 \). Among all, the effect of Ca doping on the transport properties is what attracts the attention to this system. As the Ca content increases, a drop in the resistivity can be observed and a cross-over from semiconductor-like to a metallic-like behavior takes place for higher \( x \). Superconductivity was found for high Ca content \((x \geq 11)\) at higher pressures for the stoichiometry \( \text{Sr}_{2.5}\text{Ca}_{11.5}\text{Cu}_{24}\text{O}_{41} \) under a 6 GPa pressure and \( \text{Sr}_{0.4}\text{Ca}_{13.6}\text{Cu}_{24}\text{O}_{41} \) under a 4.5 GPa [53]. The electronic phase diagram
In the magnetic susceptibility measurements, increasing the Ca content significantly affects the properties at low temperatures. Due to the large gap in the ladders, $\chi(T)$ below 200 K is still dominant by Cu spins in the chains. The signature of the dimer gap, a broad maximum of $\chi(T)$ around 75 K, which is very pronounced in the undoped compound, becomes much weaker upon Ca doping. The susceptibility for $T \geq 25$ K increases upon doping for $x \leq 8$ and is nearly independent of the Ca content for larger $x$. Whereas the Curie contribution increases significantly with increasing the Ca content [151].

On the basis of the same argument used to interpret static susceptibility data, the dominant contribution to the ESR signal below $T \leq 300$ K can be attributed to the Cu$^{2+}$ spin-$1/2$ in the chains. The most significant result is that the Cu$^{2+}$ spin relaxation is strongly influenced by the hole dynamics in the chains, resulting in a strong temperature dependence of the ESR linewidth $\Delta H_{pp}$ above a crossover temperature $T^*$ as shown in Fig. (4.5). [152] In Sr$_{14}$Cu$_{24}$O$_{41}$, $\Delta H_{pp}$ is almost constant between 30 K and 180 K, while it increases rapidly above $T \geq 200$K. Kataev et al. suggested that below $T^* \approx 200$ K the temperature-independent linewidth is due to the hole localization in the chains. Whereas,
4.5. Why Zn doping in SCO?

The idea of the present chapter is to generate nonmagnetic defects in the SCO and investigate the impact on the magnetic and transport properties. This was achieved by substituting small amount of nonmagnetic Zn\(^{2+}\) for Cu\(^{2+}\) with \(S = 1/2\). Similar to the Ca doping, Zn doping has no effect on the total number of holes. Therefore, for Sr\(_{14}\)Cu\(_{24-x}\)Zn\(_{x}\)O\(_{41}\) \((x = 0, 0.125, 0.25, 0.5, 0.75)\) the number of holes \(n_h = 6\) remains constant. However, replacing magnetic Cu\(^{2+}\) by nonmagnetic Zn\(^{2+}\) may lead to a dramatic changes on the chains or/and ladders subsystems depending on where the Zn goes. The sensitivity of the ESR to local magnetic correlations open a window to the deep study of such changes. For comparison, we studied also La\(_5\)Ca\(_9\)Cu\(_{24-x}\)Zn\(_{x}\)O\(_{41}\), \(x = 0.576\) sample, where the number of holes is reduced to one hole per f.u. located in the chain subsystem. In this case, the role of \(n\) can be examined.

4.6 Experimental

Single crystals of Zn doped q1D cuprates Sr\(_{14}\)Cu\(_{24-x}\)Zn\(_{x}\)O\(_{41}\) \((x = 0, 0.125, 0.25, 0.5, 0.75)\) and La\(_5\)Ca\(_9\)Cu\(_{23.424}\)Zn\(_{0.576}\)O\(_{41}\) were synthesized by the traveling solvent floating zone method [139, 156]. The details of the crystal growth can be found in ref. [157]. The measurements were performed on pieces with a typical length between 2 and 6 mm and of about 1-3 mm for the other two directions.
4.7. Anisotropy of the ESR parameters

First, we studied the angular dependence of the ESR response at \( T = 50 \) K. Then, the temperature dependence of ESR parameters, the integrated intensity \( I_{ESR} \), resonance field \( H_{res} \) (\( g \)-factor) and peak to peak linewidth \( \Delta H_{pp} \), are presented. We compared \( I_{ESR} \) to static susceptibility (\( \chi(T) \)) and \( \Delta H_{pp} \) to electrical conductivity data. Finally, the obtained results are discussed.

4.7 Anisotropy of the ESR parameters

In principle, the ESR signal may originate from both chain and ladder subsystems. However, due to the large spin gap of the ladders, the main contribution to the ESR signal below \( T \leq 300 \) K is expected to be due to the Cu\( ^{2+} \) ions in the chains. In the entire temperature range of the measurements and for all the measured samples, the ESR response is characterized by a single Lorentzian line associated with Cu\( ^{2+} \) (\( S = 1/2 \)) spins. The ESR signals of Sr\(_{14} \)Cu\(_{24-x} \)Zn\(_x \)O\(_{41} \) with \( x = 0.25 \) at \( T = 50 \) K and for \( H \parallel b \) (normal to the planes of chains and ladders) and \( H \parallel c \) (parallel to both chains and ladders) are shown in Fig. (4.7). This figure is representative example for all ESR spectra, Lorentzian fitting and the anisotropy of the linewidth and resonance field of the Sr\(_{14} \)Cu\(_{24-x} \)Zn\(_x \)O\(_{41} \) (\( x = 0, 0.125, 0.25, 0.5, 0.75 \)) systems. As illustrated in Fig. (4.7), both the position of the resonance and the width of the signal depend on the direction of the applied magnetic field (\( H \)) with respect to chain/ladder direction. The resonance field \( H_{res} \) is maximum for a \( H \parallel c \), whereas it reaches a minimum for \( H \parallel b \). For the peak to peak linewidth \( \Delta H_{pp} \), the opposite situation is achieved, minimum linewidth for \( H \parallel c \) (\( \Delta H_{pp}[c] \)) and maximum for \( H \parallel b \) (\( \Delta H_{pp}[b] \)).
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Figure 4.8: Angular dependence of the \( g \)-factor of \( \text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41} \) for different Zn content at \( T = 50 \) K. \( \theta = 0 \) corresponds to \( H \parallel c \), whereas \( \theta = 90 \) represents \( H \parallel b \). Solid lines denote the fitting according to Eq. (4.3).

- Anisotropy of the \( g \)-factor

The \( g \)-factor can be related to the measured resonance field as

\[
g = \frac{\hbar \nu}{\mu_B H_{\text{res}}} \quad (4.2)
\]

Figure (4.8) shows the angular dependence of the \( g \)-factor of \( \text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41} \) for different Zn content at \( T = 50 \) K. These angular dependences follow the usual axial symmetry equation

\[
g = \sqrt{g_c^2 \cos^2 \theta + g_b^2 \sin^2 \theta} \quad (4.3)
\]

The \( g \)-factor is minimum in the direction parallel to Cu planes 'c-direction with \( g_c \)', whereas it reaches a maximum perpendicular to it 'b-direction with \( g_b \)'. The development of \( g_b \) and \( g_c \) as a function of the increasing Zn concentration is shown in Fig. (4.9a), while in the inset the correspondent difference between the two \( g \)-factors \( \Delta g = g_b - g_c \) is presented. First, both \( g_b \) and \( g_c \) increase by the initial doping with Zn. Further doping tends to decrease the \( g \)-factors. For \( x = 0 \), \( \Delta g = 0.187 \) which is about 9.12% of \( g_c \) value. Increasing the Zn concentration to \( x = 0.125 \), \( \Delta g \) clearly increases where it amounts to \( \approx 0.23 \) (11.44%). However it remains almost constant for further increasing of \( x \).

Increasing the Zn concentration to \( x = 0.125 \), \( \Delta g \) clearly increases where it amounts to \( \approx 0.23 \) (11.44%). However it remains almost constant for further increasing of \( x \).

According to crystal field theory, the \( g \)-factor of \( \text{Cu}^{2+} \) ions in a \( (3d^9) \) configuration and a crystal field of a tetragonal symmetry can be calculated by

\[
g_b = 2 - \frac{8\lambda}{\Delta_{xy}}, \quad g_c = 2 - \frac{2\lambda}{\Delta_{yz,zz}} \quad (4.4)
\]
4.7. Anisotropy of the ESR parameters

The quasi-1D cuprates

where \( \lambda \) is the spin-orbit coupling constant for Cu\(^{2+}\), \( \Delta_{xy} \), \( \Delta_{yz,zx} \) are the energy differences between the ground state level \( d_{x^2-y^2} \) and the \( d_{xy} \) and \( d_{yz,zx} \) levels, respectively. Assuming \( \lambda = -100 \) meV for a free copper ion, the values of \( \Delta_{xy} \) and \( \Delta_{yz,zx} \) (eV) can be calculated as shown in Fig (4.9b inset). However, this naive estimate of the crystal-field levels should be taken with some reservation, since Eq. (4.4) is based on first-order perturbation theory and assumes a purely ionic bonding character. It neither accounts for a possible anisotropy of spin-orbit coupling in a low-symmetry coordination nor for a possible reduction of its magnitude due to covalency effects [152].

From the structural point of view, Cu ions in the chains do not have an apical oxygen and the chain layers are sandwiched between positively charged Sr layers, which may shift in particular the \( d_{yz} \) and \( d_{zx} \) levels to high energies. The change of energy difference between \( \Delta_{yz,zx} \) and \( \Delta_{xy} \) upon Zn doping is illustrated in Fig (4.9b). The increase of the energy difference between \( d_{yz}, d_{zx} \) levels and \( d_{xy} \) level by increasing the Zn content may originate from the change of Sr layer position or more interestingly, from the redistribution of the holes in the ladders by the gradual Zn doping.

- **Anisotropy of the linewidth**

The anisotropy of the peak to peak linewidth \( \Delta H_{pp} \) for different Zn concentration at \( T = 50 \) K is shown in the left panel of Fig (4.10). This anisotropy can be well fitted as

\[
\Delta H_{pp} = A(1 + \cos^2 \theta) + B \tag{4.5}
\]
4.7. Anisotropy of the ESR parameters

The quasi-1D cuprates

which is typical to 1D systems as discussed in Sec. (2.6.2). The development of the fitting parameter $A$ and $B$ upon Zn doping is illustrated in the right panel of Fig. (4.10).

Introducing Zn clearly affect the $\Delta H_{pp}$ for both $b$ and $c$ directions ($\Delta H_{pp}[b]$ and $\Delta H_{pp}[c]$, respectively). In the beginning, for $x = 0.125$, $\Delta H_{pp}$ decreases for both directions as illustrated in Fig (4.11 inset). Whereas, $\Delta H_{pp}[b]$ and $\Delta H_{pp}[c]$ increase for higher $x$. Remarkably, the effect of the Zn doping on $\Delta H_{pp}$ is anisotropic. The influence of the Zn doping on the width of the ESR signal is more pronounced in the $b$-direction than in $c$-direction. The broadening of $\Delta H_{pp}[b]$ is faster than that of $\Delta H_{pp}[c]$, which can be clarified by considering the change in linewidth,$\Delta H_{pp}[b]-\Delta H_{pp}[c]$, as presented in Fig (4.11). In the case of $x=0$, $\text{change in linewidth}= \approx 12.7$ (18.33% of $\Delta H_{pp}[c]$), whereas, it significantly rises to $\approx 60.95$ (38.69% of $\Delta H_{pp}[c]$) for $x = 0.75$. This increase can be fitted as (denoted by the red line in Fig.(4.11a))

$$\Delta H_{pp}[b] - \Delta H_{pp}[c] = 13.44 + 62.53x$$ (4.6)

Now, if we consider this increase as a percentage of $\Delta H_{pp}[c]$, as shown in Fig. (4.11b), an enhancement of the anisotropy of the linewidth is observed for any small Zn doping ($x = 0.125$), whereas it continuously increases linearly for higher $x$ as illustrated in the inset of Fig. (4.11b).

The anisotropy of $\Delta H_{pp}$ along with anisotropy of the g-factor indicate how sensitive is this system to Zn doping. Our observations suggest that increasing the Zn content yields a structural distortion which affects the crystal field and accordingly increases the splitting.
of the $d$ orbitals. In the same context, the change in the crystal field also influences the anisotropic spin-spin interaction which is reflected on the anisotropy of the ESR linewidth.

The anisotropy of $g$-factor and $\Delta H_{pp}$ for La$_{5.424}$Ca$_{9.576}$Cu$_{23.424}$O$_{41}$ is shown Fig. (4.12). The $g$-factor anisotropy still follows the axial symmetry expression (Eq. (4.3)). Whereas, $\Delta H_{pp}$ is fitted by the typical 1D (or 3D) formula (Eq. (4.5)). It is clear that the $g$-factor and $\Delta H_{pp}$ anisotropy is more pronounced than the case of the Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$. This behavior is similar to the behavior observed in La$_{5}$Ca$_{9}$Cu$_{24}$O$_{41}$ sample [158], which implies a weak effect of Zn doping on La$_{5}$Ca$_{9}$Cu$_{24}$O$_{41}$.

Since the determination of the ESR parameters is more accurate for narrow lines, the temperature dependence of the ESR signal was measured for a magnetic field parallel to the $c$-axis. The obtained results are presented in the following sections.
4.8 ESR intensity and static susceptibility

The integrated intensity of the ESR signal \( I_{\text{ESR}} \) is determined by the susceptibility of the spins participating in the resonance. In Fig. (4.13), the temperature dependence of the ESR intensities are normalized to the temperature dependence of the static susceptibilities for exactly the same samples and for a magnetic field along the \( c \)-axis. The \( \chi_{\text{static}}(T) \) was measured at 1 T. The absolute scale refers to the \( x = 0 \) data and other curves \('x = 0.125, 0.250.5 \text{ and } 0.75'\) are shifted by \([0.02, 0.04, 0.06 \text{ and } 0.09 (10^{-3})]\), respectively. As illustrated in this figure, a very good agreement between the \( I_{\text{ESR}} \) and the static susceptibility was achieved, which suggests that most of the spins contributing to the bulk static susceptibility also participate in the magnetic resonance.

As mentioned in Sec. (4.3), the broad maximum of susceptibility around 80 K of the pure SCO is a signature of the dimerized spin chain. Whereas, the upturn at low temperatures is due to quasifree spins. Increasing Zn content \( x \), the position of the minimum of \( \chi_{\text{static}}(T) \) (and \( I_{\text{ESR}} \)) is almost unchanged. Also, the \( 1/T \)-like upturn at lower temperatures is observed and even increases with the gradual Zn doping which indicates the increase of the number of quasifree spins.

The broad maximum is conceived for different \( x \), whereas its position shifts slightly to lower temperatures by increasing the Zn content. Hence, the obtained data for \( x = 0.125, 0.250.5 \text{ and } 0.75 \) can be fitted using the same Eq. (4.1) (used for pure SCO). In this case, the independent spin-dimer model with a spin gap between the nonmagnetic singlet ground state and the excited spin triplet state is assumed to be valid. Figure (4.14) shows
4.8. ESR intensity and static susceptibility

Figure 4.14: The magnitude of the intradimer exchange $J/k_B$ obtained from Eq. (4.1) as a function of Zn doping.

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Figure 4.15: The $T$-dependence of the ESR intensity normalized to the static susceptibility of La$_5$Ca$_9$Cu$_{23,424}$Zn$_{0,576}$O$_{41}$.

the intradimer exchange (the spin gap $J/k_B$) obtained from the fitting as a function of the Zn content $x$. It is clear that $J/k_B$ is decreasing systematically by increasing $x$. According to this scenario, Zn doping weakens the intradimer exchange and creates more quasifree spins in the chains, indeed, the dimerized state survives. However, these results should be taken with reservation, since for low Ca doping on SCO similar results were obtained [152, 151]. For Ca doped samples, the temperature dependence of $\chi_{\text{static}}(T)$ was fitted using Eq. (4.1), supposing the independent spin-dimer model to be realized. Surprisingly, the analysis of the field dependence (up to 15 T) of the magnetization at low temperatures gave an evidence for a finite susceptibility which is due neither to free spins nor to dimers. This accordingly suggests a much smaller gap 'if there is a gap' than the dimer one [151].

The temperature dependencies of the ESR intensity (for $H \parallel c$) and the static susceptibility (for $H \parallel b$ and $c$) of La$_5$Ca$_9$Cu$_{23,424}$Zn$_{0,576}$O$_{41}$ are shown in Fig. (4.15). $I_{\text{ESR}}$ is similar to $\chi_{\text{static}}$ at high temperatures. However, the deviation at low temperatures, mainly below 30 K, is related to the AFM ordering state. In this region, the ESR signal becomes very broad, which prevent the detection of the whole signal.

The behavior of $I_{\text{ESR}}$ of La$_5$Ca$_9$Cu$_{23,424}$Zn$_{0,576}$O$_{41}$ is similar to that observed for the pure La$_5$Ca$_9$Cu$_{24}O_{41}$ and qualitatively different from that of the Sr$_{14}$Cu$_{24-x}$Zn$_xO_{41}$. The independent spin-dimer model, which is used to describe Sr$_{14}$Cu$_{24-x}$Zn$_xO_{41}$, is not valid in the case of La$_5$Ca$_9$Cu$_{23,424}$Zn$_{0,576}$O$_{41}$. Moreover, the upturn of $I_{\text{ESR}}$ disappeared in La$_5$Ca$_9$Cu$_{23,424}$Zn$_{0,576}$O$_{41}$, this reflect a weaker contribution of the quasifree spins (if it exists) in this case. The dimerization process critically depends on the number holes in the chains subunit. Therefore, by reducing the number of holes to 1 hole per formula unit, the dimerization process can not take place anymore, which allows the establishment of the magnetic ordering.
4.9 Resonance field and g-factor

The temperature dependencies of the resonance fields $H_{\text{res}}$ and the correspondent $g$-factor of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ samples are shown in Fig. (4.16) and its inset. Below 25 K, the resonance field shifts slightly towards lower value for all measured samples. Whereas, above this temperature, the resonance field is temperature independent. The increase of $H_{\text{res}}$ for $x = 0.75$ above $T = 160$ K is due to the systematic error which originates from the rapid broadening and weakening of the ESR lines.

Translating these resonance fields into $g$-factors leads to a temperature independent value of $g = 2.04 - 2.05$ for different Zn concentration. The small change in the $g$-factor and $H_{\text{res}}$ below 25 K is related to the switching of the signal 'source' from the dimer spins to quasifree spins which are dominant at low temperatures. In the crossover region, no significant distortion of the shape of the ESR spectrum is observed. Observing the same behavior of $g$-factor (even the small change at 25 K) at all Zn concentrations is consistent with the dimerization scenario discussed in the previous section. This is not the case for Ca doped samples, where a decrease in the $g$-factor is observed below 25 K suggesting the development of magnetic ordering [152].

The temperature dependencies of $H_{\text{res}}$ and $g$-factor of La$_5$Ca$_9$Cu$_{23.424}$Zn$_{0.576}$O$_{41}$ are presented in Fig. (4.17) and its inset. Unlike the Zn doped samples, the pronounced decrease of the $g$-factor at low temperatures is the signature of approaching AFM phase transition. This is again in agreement with the measurements done in the La$_5$Ca$_9$Cu$_{24}$O$_{41}$ sample.
4.10 ESR linewidth and transport properties

- ESR linewidth

The temperature dependence of the ESR linewidth of Sr$_{14}$Cu$_{24}$-xZn$_x$O$_{41}$ (0 ≤ x ≤ 0.75) is shown in Fig. (4.18). Below 30 K, the Curie-contribution dominates the susceptibility for all Zn contents. Therefore, the anomalies of Δ$H_{pp}$ near to 25 K can be attributed to the crossover between dimerized spins ($T > 30$ K) and quasifree spins ($T < 30$ K). We approximate Δ$H_{pp}(T)$ phenomenologically as

$$\Delta H_{pp}(T) = \Delta H_0 + \Delta H_1(T) + \Delta H_2(T)$$

(4.7)

where

$$\Delta H_1(T) = B(T - T_1) \quad \rightarrow \quad 50 \text{ K} < T < T^*$$

(4.8)

$$\Delta H_2(T) = A(T - T^*) \quad \rightarrow \quad T > T^*$$

(4.9)

In this case, $T_1$ is the temperature where thermally activated holes begin to broaden the ESR signal and $T^*$ is the characteristic temperature of the crossover between the two distinctly different regimes, as defined by the shaded box in Fig. (4.17). For $x = 0$, Δ$H_{pp}$ is almost temperature independent below $T = 90$ K, this region is characterized by Δ$H_0$. Above 90 K, Δ$H_{pp}$ slightly increases until reaching 220 K where it finally increases rapidly and approximately linearly by increasing the temperature. These two regions, 90 K ≤ $T ≤ 220$ K and 220 K ≤ $T ≤ 300$ K, are characterized by Δ$H_1(T)$ and Δ$H_2(T)$, respectively.
The temperature independent contribution $\Delta H_0$ is determined mainly by the isotropic exchange narrowing effect, both magnetic and structural inhomogeneities, and anisotropic spin-spin interactions like, e.g., dipole-dipole interactions and anisotropic exchange [152]. This constant $\Delta H_0$ is related to the localization of the charge carries on the chains. Whereas, the other two terms, $\Delta H_1(T)$ and $\Delta H_2(T)$, are associated with the charge dynamics in the chains. As mentioned before, the spins in a dimer are coupled via a localized ZR singlet. Hence, the fluctuation of the holes around its equilibrium site by increasing the temperature will destabilize dimers and reduce its lifetime, this accordingly shortens its spin relaxation time, which reflects on the broadening of the ESR linewidth. This broadening is represented by $\Delta H_1(T)$. However, the strong increase of the linewidth above 220 K obviously indicates a characteristic energy scale for the appearance of a new degree of freedom and can be related to the melting of the charge ordering in the chains, which is accompanied by rapid increase of hole mobility. Therefore, $\Delta H_2(T)$ reflects the thermally activated hole mobility when $T > T^*$. 

Increasing the Zn concentration dramatically affects the temperature dependence of the ESR linewidth. For $x = 0.125$, the linewidth at $T < 90$ K is slightly narrower than for $x = 0$. However, increasing the temperature inverses this situation. For higher Zn content, $\Delta H_{pp}$ increases by increasing Zn content. Unlike Ca doping (Ca$_2$Sr$_{12}$Cu$_{24}$O$_{41}$ presented in Fig. (4.18) as an example), the charge ordering temperature $T^*$ seems to be unaffected upon Zn doping. On the other hand, below $T^*$, the effect of Zn doping is very interesting. As temperature exceeds the constant $\Delta H_0$ region, $\Delta H_{pp}$ increases linearly by increasing the temperature, in which the slope of the linewidth increases significantly depending on the Zn content $x$. Furthermore, the $\Delta H_0$ region becomes shorter upon Zn doping. At low temperatures (below 25 K), $\Delta H_{pp}$ broadens gradually with decreasing the temperature in the case of Ca doped samples, this is related to the onset of magnetic ordering. However for all Zn doped samples, below 30 K, $\Delta H_{pp}$ behaves in exactly the same way as in Sr$_{14}$Cu$_{24}$O$_{41}$, which is another evidence on the survival of the dimerization upon Zn doping.

The $T$-dependencies of $\Delta H_{pp}$ of La$_5$Ca$_9$Cu$_{23,424}$Zn$_{0.576}$O$_{41}$ and La$_5$Ca$_9$Cu$_{24}$O$_{41}$ are shown in Fig. (4.19). These compounds have only one hole per formula unit that resides in the chain subunit. Since the decrease of the number of holes completely destroys the charge ordering process, the temperature dependence of the linewidth greatly differs from that of SCO and Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$. For La$_5$Ca$_9$Cu$_{24}$O$_{41}$, at low temperatures, the increase of the $\Delta H_{pp}$ is characterized by the critical broadening $\Delta H_{\text{crit}}(T)$ near to the long range magnetic ordering temperature. Whereas at high temperatures and within the paramagnetic regime, very broad signals, almost temperature independent, are still observed. The reduction of the number of holes causes the dominance of the NN exchange which increases the anisotropic contribution to the linewidth. Accordingly, the linewidth dramatically increases [155]. Zn doping on the La$_5$Ca$_9$Cu$_{24}$O$_{41}$ has almost no effect on the behavior of the linewidth temperature dependence, which straightforwardly points to a critical role of the number of holes on the features observed in the Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$.
4.10. ESR linewidth and transport properties

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Back to the Sr$_{14}$Cu$_{24-\text{x}}$Zn$_x$O$_{41}$ system, we used Eq. (4.8) and Eq. (4.9) to fit the temperature dependence of the linewidth and the slopes of the linear behavior below and above $T^*$ were determined. These slopes, $A$ and $B$, along with $\Delta H_0$ are presented in Fig. (4.20). In the beginning $\Delta H_0$ decreases for $x = 0.125$, and then it increases almost linearly for further Zn doping. The slope of $\Delta H_1(T)$, $B$, increases significantly with increasing Zn content $x$. Whereas, the slope of $\Delta H_2(T)$, $A$, is almost constant for all $x$ values.

These results can be better resolved by subtracting the Sr$_{14}$Cu$_{24}$O$_{41}$ linewidth temperature dependence $\Delta H_{pp}[x = 0]$ from $\Delta H_{pp}[x]$ as shown in Fig (4.21). At low temperature, $T < 30$ K where quasi-free spins are dominant, $\Delta H_{pp}$ tends to behave in the very same way for all $x$ values. However, when $40$ K $\leq T \leq 220$ K, Zn doping adds a pronounced linear contribution to the linewidth, which increases gradually with increasing $x$. This reflects the increase of the hole mobility in the chains. Indeed, the charge ordering still conceived within the same temperature range $T^*$, since a significant change of the slope below and above $T^*$ is observed for all $x$ content. The $\Delta H_2(T)$ behavior, above $T^*$, is poorly depending on Zn doping. This leaves us with a clear message; Zn doping mainly increase the instability of the charge ordered state in the chains below the melting of the charge ordering temperature.

Figure 4.20: $\Delta H_0$, $A$ (slope of $\Delta H_2$ Eq. (4.9)), $B$ (slope of $\Delta H_1$ Eq. (4.8)) as function of the Zn concentration on Sr$_{14}$Cu$_{24-\text{x}}$Zn$_x$O$_{41}$ ($x$).

Figure 4.21: Subtracting the $\Delta H_{pp}[x = 0]$ from $\Delta H_{pp}[x]$ for different Zn concentration.
Figure 4.22: $T$-dependence of the conductivity along the $c$-axis of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ [Measured by H. ElHaes]. This is compared to the $T$-dependence of Sr$_{12}$Ca$_2$Cu$_{24}$O$_{41}$ and Sr$_9$Ca$_3$Cu$_{24}$O$_{41}$ samples imported from Ref. [159]. Inset: $T$-dependence of the resistivity of the Zn doped samples.

- The transport properties

Now it is very interesting to investigate the effect of the hole mobility suggested by the temperature dependence of ESR linewidth ($\Delta H_{pp}(T)$) on the transport properties. The temperature dependencies of the conductivity along the $c$-axis ($\sigma_c(T)$) of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$, Sr$_{12}$Ca$_2$Cu$_{24}$O$_{41}$ and Sr$_9$Ca$_3$Cu$_{24}$O$_{41}$ samples are presented in Fig (4.22) [measured by H. ElHaes]. It is easy to observe the similarity between the $\sigma_c(T)$ and $\Delta H_{pp}(T)$. $\sigma_c(T)$ increases with increasing the Zn doping. By comparing the increase of the conductivity of the Ca doped samples [159] and the Zn doped one, surprisingly, Zn doping has much stronger impact. The resistivity plot (inset of Fig. (4.22)) gives more information on the low temperature regime. It is clear that the resistivity decreases with increasing the Zn content, especially at low temperatures. This is remarkably consistent with the increase the instability of the charge ordered state in the chains below the charge ordering temperature suggested by $\Delta H_{pp}(T)$.

Figure (4.23) shows the temperature dependence of resistivity along the $a$-axis. Although the resistivity decreases by increasing the Zn content, this decrease is weaker compared to the decrease observed along the $c$-axis. The maximum of the derivative $dln\rho_a(T)/d(1/T)$ (inset of Fig. (4.23)) spots the charge ordering temperature at $T^* = 220$ K for $x=0$ along the $a$-axis. Increasing the Zn content, $T^*$ is almost temperature independent. For $x = 0.5$ and 0.75, the peak of $dln\rho_a(T)/d(1/T)$ is broad and $T^*$ can not be accurately identified.

Figure (4.24a) shows $\sigma_a$ as function of $x$ at different temperatures. At low temperatures (86 K and 100 K), the conductivity grows almost $10^3$ times upon Zn doping. Whereas,
increasing the temperature significantly decreases the influence of Zn doping.

The effect of the Zn doping on the conductivity along the $a$-axis is weaker than that along the $c$-axis (as presented in Fig. (4.24b)). The ratio $\sigma_c/\sigma_a$ as function of Zn concentration $x$ is presented in Fig. (4.24c). This ratio illustrates the development of the anisotropy of the conductivity between $a$ and $c$ directions upon Zn doping. As shown the anisotropy increases gradually by increasing the Zn content. Moreover, for the initial doping of Zn ($x=0.125$), a sudden increase in the anisotropy appears at low temperature. In the Ca doped samples, the conductivity shows anisotropic behavior between $a$ and $c$ directions. However, this anisotropy is decreasing gradually by applying an external pressure. This implies that the system moves gradually towards two-dimensional charge transport by increasing the pressure, and this where the superconductivity occurs [160].

4.11 Discussion

As shown in the previous sections, Zn doping clearly affects ESR, static susceptibility and transport measurements. On one hand, both ESR and static susceptibility are attributed to Cu$^{2+}$ spins in the chain subunit. On the other hand, conductivity measurements are governed by the ladders. Accordingly, a key question is: where does Zn go? The thermal conductivity ($\kappa$) measurements may provide helpful information regarding this question. Figure (4.25) shows the temperature dependence of $\kappa$ of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ at different Zn concentrations [161]. In Ref. [161], it has been suggested that Zn replaces equally Cu in chains and ladders. For SCO, the low temperature peak ($\sim 20$ K) is observed at all
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crystallographic directions and arises due to the usual phonon heat conductivity $\kappa_{ph}$. The peak at higher temperature is only observed along the $c$-axis and is the signature of strictly one dimensional magnetic heat conduction along the ladders in this material. Upon Zn-doping, $\kappa_c$ is progressively suppressed and exhibits less pronounced peaks. The magnetic peak simultaneously broadens and apparently shifts towards higher temperature since the peak structure evolves into a monotonic increase at high temperature. A possible scenario to explain these results is that Zn$^{2+}$ ions create nonmagnetic sites in a Cu$^{2+}$ $S = 1/2$ ladder and hence the magnetic excitations scatter on these sites [161].

The temperature dependencies of the thermal conductivities of Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$, La$_5$Ca$_9$Cu$_{24}$O$_{41}$ and La$_5$Ca$_9$Cu$_{23.424}$Zn$_{0.576}$O$_{41}$ are shown in Fig. (4.26). the number of holes is reduced to 1 hole per f.u. for La$_5$Ca$_9$Cu$_{24}$O$_{41}$ and La$_5$Ca$_9$Cu$_{23.424}$Zn$_{0.576}$O$_{41}$. In La$_5$Ca$_9$Cu$_{24}$O$_{41}$, the ladder subunit which is no longer doped by holes characterized by enhancement of the magnetic heat conductivity $\kappa_{mag}$ [162]. However, doping with Zn clearly suppress this magnetic contribution. Indeed, $\kappa_{ph}$ decreases for all samples with respect to the SCO. These results eventually suggest that the Zn mainly goes to the ladder subunit. However, we can not exclude that some fraction of the doped Zn substitutes Cu in the chains.

Now, the next question would be, how Zn doping in the ladders affects ESR and static susceptibility measurements? Furthermore, why nonmagnetic defects act in the favor of the conductivity?
As mentioned in the introduction, the ladder subunit exhibits a gap of about 380 K. This gap is the origin of the argument that Cu spins in the ladder are inert below 300 K and consequently the ESR and static susceptibility measurements are attributed to the Cu spins in the chains at this temperature range.

\[ \text{SrCu}_2\text{O}_3 \] is a typical two leg spin-ladder system with spin gap \( \Delta \sim 400 \text{ K} \). In this spin gapped system, even a small amount of disorder by the introduction of nonmagnetic Zn impurities at the Cu sites yields dramatic consequences. [163, 164, 165] Instead of the creation of free localized spin-1/2’s, Zn doping induces a staggered polarization along the leg of the ladder and causes an extended spin correlation, which yields long rang AFM ordering at \( T_N \). For \( \text{Sr(Cu}_{1-y}\text{Zn}_y)\text{O}_3 \), \( T_N \) depends on the Zn doping and ranges from 3 to 8 K for \( 0.01 \leq y \leq 0.08 \). [166, 167, 168]

In our measurements on \( \text{Sr}_{14}\text{Cu}_{23.5}\text{Zn}_{0.5}\text{O}_{41} \), we do not observe any of the signs of long range ordering. Normally, short range and long range magnetic ordering causes the shift of the ESR signal and the increase of its width as the temperature is lowered towards the ordering temperature. Since it is a 3D ordering, this behavior would be observed wether our ESR signal is attributed to the Cu\textsuperscript{2+} spins in the chain or in the ladder subunit. As indicated in our measurements, especially at low temperature where \( T_N \) is expected, the similarities between the behavior of the ESR parameters (\( I_{ESR} \) (compared to \( \chi_{static} \)), \( g \)-factor and \( \Delta H_{pp} \)) in Zn doped samples and \( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \) suggest that we are dealing with the same Cu\textsuperscript{2+} spins in the chains. Hence, we can conclude that Zn doping has a weak effect on the spin gap on ladders.
A very essential property of this system is the interplay between chain and ladder subunits. In particular, the distribution and redistribution of holes between the chains and ladders critically influence the physical properties. The dimerized chain is very sensitive even to small Ca doping. However, the similarities between the behavior of the ESR parameters in the Zn doped samples and Sr$_{14}$Cu$_{24}$O$_{41}$ below 30 K strongly suggest that we are dealing with the same quasifree spins. Whereas, both ESR intensity and $\chi_{\text{static}}$ shows the signature of the dimerization process. We argue that Zn which is mainly in the ladders has a weaker influence than the Ca doping on the spin dimers in the chains. Nevertheless, due to the interplay between chains and ladders, Zn doping still destabilizes the dimerized state, which is reflected in the gradual decrease of the intradimer coupling ($J$) shown in Fig. (4.14).

The survival of the dimerized ground state would logically suggests that the number of holes at low temperatures in the chains is independent (or weakly dependent) on Zn concentration. The temperature dependence of ESR linewidth for different $x$ can nicely fit in this scenario. First, not only does $\Delta H_{pp}(T)$ indicate the existence of the charge ordering but also suggests that $T^*$ is weakly depending on $x$. Secondly, the main impact of the Zn doping is reflected in a stronger temperature dependence of $\Delta H_{pp}(T)$ below $T^*$ upon the gradual increase of Zn content. This temperature dependence can be understood by considering weaker intradimer coupling [see Fig. (4.14)], which accordingly allows stronger fluctuations of the holes bound in the ZR sites. By the gradual decrease of $J$ upon Zn doping, the localization of the holes gets weaker, which yields as a higher value of $\Delta H_0$ as well as a shorter temperature independent region. Moreover, when temperature exceeds this region, the holes gain more mobility and cause further broadening in the ESR signal. This can explain the linear contribution shown in Fig. (4.21). When $T > T^*$, we observe the melting of the charge ordering as a pronounced change of $\Delta H_{pp}(T)$.

The building block of these arguments is that a significant fraction of Zn goes to the ladders. The anisotropy of the ESR parameters can give a hint on how Zn in the ladders can affect the chain subsystem. We suggested in section (4.7) that the increase of the $\Delta H_{pp}$ anisotropy upon Zn doping could originate from structure distortion which affects the crystal field field. This distortion increases the the splitting of the $d$ orbitals [Fig. (4.9)] and influences the spin relaxation. The number of holes in the ladder $n_L$ is under debate, however these holes can be found in three different Oxygen sites, O($r$), O($l$)$_a$ and O($l$)$_c$ as shown in Fig. (4.27). The ladders are separated by Sr sheets from the chains. Indeed, due to the interplay between the ladder and chain subsystem, it is possible to the holes in the ladder to affect the the chain subsystem. Depending on the distribution of these holes in the ladders, the effects differ. For example, according to Rusydi et al. [150], Ca doping leads to the transfer of the holes from the chains to the ladders. However, they suggested that O($l$)$_c$ sites receive more holes than both O($r$) and O($l$)$_a$ upon Ca doping. Although, Ca doping also leads to the increase of the conductivity, which may suggest that, not only $n_L$ affects the transport properties of the ladders but also the distribution of these holes within the different O sites. According to this scenario, holes on O($l$)$_c$ sites may open a ‘good’ channel to the conductivity. The conductivity enhanced upon Zn doping. In the
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same time, the charge ordering in the chains is still conceived, which indicates that the number of holes transfer from the chains to the ladders, if this transfer exists, in the Zn case is small below $T^*$. Therefore, we argue that Zn doping has a weak impact on the $n_L$, but it leads to a change in the orbital occupation of holes in the ladder. This process consequently influences the Cu sites in the chains, where it increases the anisotropy of both the $g$-factor and $\Delta H_{pp}$ of the ESR measurements. From this point of view, the effect when the magnetic field is applied parallel to the $b$-axis (where the ladders and chains are separated by the Sr sheets) is increasing upon Zn doping [Fig. (4.11)].
4.12 Conclusion

In this chapter, ESR, static susceptibility and transport measurements of the quasi-1D cuprates $\text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41}$ and $\text{La}_5\text{Ca}_9\text{Cu}_{23.424}\text{Zn}_{0.576}\text{O}_{41}$ have been presented and discussed. The results reveal very intersecting features of these systems. ESR and the transport results suggest an unusual increase of the hole mobility in $\text{Sr}_{14}\text{Cu}_{24-x}\text{Zn}_x\text{O}_{41}$ upon Zn doping. Surprisingly, nonmagnetic Zn, which is supposed to act as a defect, causes a strong enhancement in the electrical conductivity. In the same context, ESR measurements show a remarkable influence of the hole dynamics on the Cu-spin relaxation for all Zn contents and give an independent evidence for the increase of hole mobility. Both $\sigma(T)$ and $\Delta H_{pp}(T)$ reveal a charge ordering temperature $T^*$, which is almost independent on the amount of the Zn doping. The hump in the static susceptibility and the ESR intensity may reflect the survival of the dimerized ground state upon Zn doping. These results were discussed in the frame of the interplay between the chains and ladders subsystems realized in these quasi-1D systems. We stress on the role of distribution of the holes, not only between the chains and ladders but also within the different O sites in the ladders, on the physical properties of these compounds.
Chapter 5

Copper Nitrate Monohydrate

5.1 Introduction

Transition metal oxides based low-dimensional quantum spin systems attract significant attention because they exhibit a variety of unusual phenomena of fundamental interest. For example, frustrated spin systems, alternating spin chains and 2D spin systems with mixed antiferromagnetic AFM and ferromagnetic FM interaction present numerous quantum phenomena dealing with both the ground state and finite temperature properties. An external magnetic field alters the physics of such systems and induces a number of additional features.

Among these systems, the investigation of copper nitrate trihydrate Cu(NO$_3$)$_2$·2.5H$_2$O has played an important role in the development of low-dimensional magnetism. In this compound, Cu$^{2+}$ ions with spin $S = 1/2$ are situated in a square ligand coordination and form alternating isolated $S = 1/2$ chains whose ground state is a spin singlet [169, 170, 171]. Application of an external magnetic filed destroys this singlet state [172]. A good agreement between experimental data and theoretical calculations [173, 174] has been achieved for Cu(NO$_3$)$_2$·2.5H$_2$O and the basic conceptions of the behavior of the low dimensional magnetic systems have been developed.

In addition to the stable phase of copper nitrate trihydrate Cu(NO$_3$)$_2$·2.5H$_2$O, the same components form copper nitrate monohydrate Cu(NO$_3$)$_2$·H$_2$O [175], which is very unstable in air. O. S. Volkova et al [176] determined the magnetic phase diagram of Cu(NO$_3$)$_2$·H$_2$O by preforming the specific heat and magnetization measurements.

In this chapter, we present a single-crystal electron spin resonance (ESR) and nuclear magnetic resonance (NMR) measurements of the new low dimensional copper nitrate monohydrate Cu(NO$_3$)$_2$·H$_2$O. Our results suggest a two dimensional character of magnetic interactions in Cu(NO$_3$)$_2$·H$_2$O. The high field ESR and NMR measurements indicate the formation of random spin clusters at low temperatures. We discuss the obtained data by considering the possible exchange paths between inequivalent Cu-sites in this compound.
5.2 Structure of Cu(NO\(_3\))\(_2\)·H\(_2\)O

Copper nitrate monohydrate Cu(NO\(_3\))\(_2\)·H\(_2\)O single crystals were synthesized by interaction of CuO with anhydrous HNO\(_3\) [175]. The compound is crystalized in transparent blue thin plates which are very unstable in air and it was completely transformed to the Cu(NO\(_3\))\(_2\)·2.5H\(_2\)O when exposed to air for 5-10 hr. It has a monoclinic lattice with \(a = 6.377(1)\) Å, \(b = 8.548(1)\) Å, \(c = 9.769(1)\) Å, \(\beta = 100.41(1)^\circ\), \(Z = 4\), and space group P2\(_1\)/c. The [CuO\(_4\)] plaquettes are connected by bridging NO\(_3\) groups into a zigzag chains along the \(b\)-axis which are linked into layers by the longer Cu-O bonds as shown in Fig. (5.1).

5.3 Magnetic properties of Cu(NO\(_3\))\(_2\)·H\(_2\)O

The magnetic phase diagram of copper nitrate monohydrate Cu(NO\(_3\))\(_2\)·H\(_2\)O was determined by measuring the magnetization. [176] The temperature dependence of the magnetic susceptibility \(\chi(T)\) for a magnetic field \(H = 1\) T applied in the \(bc\) plane is shown in Fig. (5.2). The magnetic susceptibility \(\chi\) in a wide temperature range is described by the sum of the temperature-independent term \(\chi_0 = 3 \times 10^5\) emu/mol and the Curie-Weiss term

\[
\chi_{CW} = \frac{N_A\mu^2_{eff}}{k_B(T - \Theta_W)}
\]  

with a positive Weiss temperature \(\Theta_W = 6.5\) K, indicating a dominant ferromagnetic interaction in this system. However, \(\chi^{-1}(T)\) significantly deviates from the linear law at low temperatures, indicating the manifestation of the AFM exchange interaction. [176]
5.3. Magnetic properties of Cu(NO$_3$)$_2$·H$_2$O

At lower magnetic fields, $\chi(T)$ exhibits a peak at the Néel temperature $T_N$ as shown in the inset of Fig (5.2). For $H \leq 0.1$ T, $\chi(T)$ reaches a maximum at $T_N = 3.6$ K. An additional anomaly is seen at the temperature $T_R = 2.7$ K, which is likely attributed to the spin-reorientation transition. This anomaly is almost completely suppressed by a weak magnetic field of about $H = 5 \times 10^{-2}$ T. [176]

The magnetic field dependences of the magnetization $M$ for the magnetic field $H$ orientation in the $bc$ plane are shown in the inset of Fig (5.3). These dependences have different saturation levels at somewhat different values of the external magnetic field. The features of the magnetic response to the external magnetic field are most pronounced in the magnetic field dependences of the magnetization derivative $dM/dH$ at low temperatures shown in Fig. (5.3). The $dM/dH(H)$ dependences exhibit anomalies both in weak magnetic fields $H_{C1} \sim 0.05$ T and in strong magnetic fields $H_{C2} \sim 1$ T. [176]

In contrast to the $\chi_{bc}$, the magnetic susceptibility measured in the magnetic field directed along the $a$ axis $\chi_a$ varies only slightly with temperature. This behavior implies that the magnetic moments of the Cu$^{2+}$ ions lie in the $bc$ plane. The presence of the additional anomaly in the magnetic susceptibility at $T_R = 2.7$ K is only observed in $\chi_{bc}(T)$ and can be interpreted as the manifestation of the spin reorientation in the $bc$ plane. The magnetocrystalline anisotropy in the $bc$ plane is assumingly very small, because the peak at $T_R$ is suppressed by a weak magnetic field.

The phase diagram of Cu(NO$_3$)$_2$·H$_2$O determined from the dependences of the magnetization on temperature and magnetic field is shown in Fig. (5.4). In Ref. [176], it was
5.4 Specific heat measurements of \( \text{Cu(NO}_3\text{)}_2\cdot\text{H}_2\text{O} \)

In Ref. [176], the authors measured the specific heat at zero field. Figure (5.5) shows the temperature dependence of the specific heat \( C \) of \( \text{Cu(NO}_3\text{)}_2\cdot\text{H}_2\text{O} \). This dependence has a \( \lambda \) peak at \( T_N = 3.6 \) K and exhibits an excess contribution from the Schottky anomaly to the low-temperature specific heat. By measuring different samples, the relative contributions to the specific heat from these two features vary, so that a decrease in the \( \lambda \) peak is accompanied by an increase in the Schottky anomaly. The latter contribution is likely attributed to the specific heat of copper nitrate trihydrate formed on the surface of a sample in the process of its assembling. [176]

At low temperatures, the specific heat \( C \) can be described as the sum of two terms

\[
C_1 = k_1 T^3, \quad \text{and} \quad C_2 = k_2 \left( \frac{\Delta}{T} \right)^2 \cdot e^{-\frac{T}{T_0}} \tag{5.2}
\]

\( C_1 \) describes the sum of the phonon and magnon contributions to the specific heat of \( \text{Cu(NO}_3\text{)}_2\cdot\text{H}_2\text{O} \) and \( C_2 \) is the contribution to the specific heat from the Schottky anomaly likely attributed to the impurity phase \( \text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O} \) [176].
5.4. Specific heat measurements of Cu(NO$_3$)$_2$·H$_2$O

In Fig. (5.5), the solid line represents the impurity contribution to the specific heat by the $C_2(T)$ when $\Delta' = 3.8$ K. This contribution is compared to the impurity phase Cu(NO$_3$)$_2$·H$_2$O specific heat measured in ref. [170] with $\Delta'' = 4.6$ K, which is normalized to its expected content in the Cu(NO$_3$)$_2$·H$_2$O and illustrated by the red open circles in Fig. (5.5). In Ref. [176], the authors attributed the difference between $\Delta'$ and $\Delta''$ to the fact that the Schottky anomaly in Cu(NO$_3$)$_2$·H$_2$O is observed near the phase transition, where the $C_1(T)$ dependence is noticeably different from the cubic dependence.

It is important to note the absence of any special features in the specific heat at the spin reorientation temperature $T_R$, which again implies the weakness of this magnetic transition.

Measuring the temperature dependence of the specific heat at magnetic fields higher than 1 T clearly suggests the absence of the LRO. By applying $H = 3$ T, the $\lambda$ peak at $T_N$ is completely suppressed as shown in Fig. (5.5) [measured by N. Leps]. Such behavior is predicted from the magnetic phase diagram in Fig. (5.4). However, an unexpected broad anomaly appears at $T \approx 7$ K. The absence of such feature at $H = 0$ T would logically indicates a field induced nature of this anomaly. A similar observation of such anomaly was recognized as a signature of a field induced gap in the 1D chain compound Cu benzoate [177], the 1D heavy fermion Yb$_4$As$_3$ [178] and 1D [PM-Cu(NO$_3$)$_2$·(H$_2$O)$_2$]$_n$. [179] In the case of a field induced gap, a significant shift of the anomaly by applying higher magnetic field is expected.
5.5 ESR measurements at $\nu = 9.5$ GHz

The ESR measurements was carried out on a Cu(NO$_3$)$_2$·H$_2$O crystal in a sealed glass ampoule. ESR measurements were preformed using the standard X-band Bruker EMX spectrometer (Section 2.4.1) and also with the high-field/high frequency ESR spectrometer (Section 2.4.2). First, we discuss the ESR measurements of Cu(NO$_3$)$_2$·H$_2$O crystal at X-band frequency $\nu = 9.5$ GHz. The angular dependence of the ESR signals was studied at two temperatures, $T = 295$ K and 50 K, where we analyzed the anisotropy of the ESR parameters. Then, we investigated the temperature dependence of the ESR signal at different magnetic field orientations.

5.5.1 The angular dependence of the ESR signal at $\nu = 9.5$ GHz

The ESR spectrum of Cu(NO$_3$)$_2$·H$_2$O crystal at $\nu = 9.5$ GHz consists of a single resonance line which can be fitted very well by a Lorentzian line profile. The ESR spectra of Cu(NO$_3$)$_2$·H$_2$O are anisotropic. Both the position of the resonance field $H_{\text{res}}$ and the width $\Delta H_{pp}$ of the ESR signal depend on the orientation of the applied magnetic field with respect to the crystallographic axis. Figure (5.6) shows selected ESR spectra at room temperature, field derivative of the absorption, $dP(H)/dH$, recorded when the magnetic field $H$ is applied parallel to $a$- and $c$-axis. The solid red line is the Lorentzian fit of the ESR signal.

From the dependence of $H_{\text{res}}$ on the orientation of the magnetic field we calculated the angular dependence of the $g$-factor. The anisotropy of the $g$-factor within the $ac$-plane at $T = 295$ K and $T = 50$ K is presented in Fig. (5.7), where $\theta$ is the angle between the $a$-axis and the direction of the magnetic field $H$. For both $T = 295$ K and $T = 50$ K, $g$-factor is maximum when the magnetic field $H$ is parallel to the $a$-axis, where $g_a = 2.27$. On the other side, the $g$-factor reaches its minimum when the magnetic field $H$ is applied parallel

Figure 5.6: Representative ESR spectra of Cu(NO$_3$)$_2$·H$_2$O for two orientations of the applied magnetic field, $H \parallel a$ and $H \parallel c$ at room temperature. Solid lines: lorentzian fitting.
5.5. ESR measurements at $\nu = 9.5$ GHz

Figure 5.7: The anisotropy of $g$-factor of Cu(NO$_3$)$_2$·H$_2$O. (a) $T = 295$ K, (b) $T = 50$ K. Solid lines: fitting based on Eq. (5.3)

Figure 5.8: The anisotropy of the ESR linewidth $\Delta H_{pp}$. (a) $T = 295$ K, (b) $T = 50$ K. Solid lines: fitting based on Eq. (5.4).

to the $c$-axis and $g_c = 2.10$. The angular dependence of the $g$-factor can be well described by [94]:

$$g(\theta) = A + B(3 \cos^2 \theta - 1)$$

(5.3)

This form of the angular anisotropy of the $g$-factor has been explained by the non cubic-distribution of the dipole-dipole interaction in the 2D lattice. [180]

The angular dependences of the peak to peak linewidth $\Delta H_{pp}$ at $T = 295$ K and $T = 50$ K within the $ac$-plane are presented in Fig (5.8). The linewidth shows a behavior different from that of the $g$-factor. At $T = 295$ K, the linewidth has a minimum of $\Delta H_{pp} = 35$ Oe at $\theta = 0^\circ$, ($H \parallel a$) and goes through a maximum of $\Delta H_{pp} = 42$ Oe at around $\theta = 50^\circ$ as shown in Fig (5.8a). At $T = 50$ K, the linewidth reaches a minimum of $\Delta H_{pp} = 21$ Oe at $\theta = 0^\circ$, ($H \parallel a$) and has a maximum of $\Delta H_{pp} = 24.5$ Oe at around $\theta = 50^\circ$ as presented in Fig (5.8b). This observed angular dependence is a characteristic behavior of 2D spin systems [94] if the whole linewidth angular dependence is shifted by $50^\circ$. In this case, the variation of $\Delta H(\theta)$ follows the expression

$$\Delta H_{pp}(\theta) = A + B[3 \cos^2(\theta - 50) - 1]^2 + C \cos^2(\theta - 50)$$

(5.4)

where $A$, $B$, and $C$ are temperature dependent, experimentally determined parameters. At $T = 295$ K, we achieved the best agreement with experiment when $A = 36.6$ Oe, $B = 1.32$
5.5. ESR measurements at $\nu = 9.5$ GHz

Copper Nitrate Monohydrate

Figure 5.9: Detail of Cu(NO$_3$)$_2$·H$_2$O structure, two inequivalent Cu$^{2+} (S = \frac{1}{2})$ sites coupled via intrachain coupling $J_b$. On the left side, the conditions of exchange splitting of ESR signal are shown.

Figure 5.10: Angular dependence of the $g_{eff}$-factor of Cu(NO$_3$)$_2$·H$_2$O at room temperature. Dashed blue and green lines are the simulated angular dependence of A and B sites respectively.

Oe and $C = -5.61$ Oe. Whereas, at $T = 50$ K, the quality of the fitting is lower as shown in Fig (5.8b), which reflects the onset of a deviation from the 2D behavior at low temperatures. We had the best fitting of the experimental results when, $A = 22.2$ Oe, $B = 0.92$ Oe and $C = -1.37$ Oe. It is very important to notice that $\theta$ has a different meaning in Eq (5.4), here it is the angle between the axis perpendicular to the 2D plane and the applied external field.

To discuss the anisotropy of the ESR parameters in Cu(NO$_3$)$_2$·H$_2$O it is essential to return to the crystallographic structure. From structural point of view, [CuO$_4$] plaquettes form a zigzag chain along the $b$-axis. Within this chain, two magnetic inequivalent Cu$^{2+} (S = \frac{1}{2})$ sites are coupled via the intrachain exchange interaction $J_b$, which is realized through NO$_3$ group as shown in Fig. (5.9). At low magnetic fields, the Zeeman energy is smaller than $J_b$ and two resonance peaks are exchanged narrowed into one absorption line. In strong enough magnetic fields, the splitting of ESR signal is observed when the Zeeman energy difference between these two sites exceeds this $J_b$ and the two lines are separated under the following condition:

$$\sqrt{2}J_b \leq \Delta g \mu_B H$$

(5.5)

where $\Delta g$ is the difference of the $g$-factor of the two Cu$^{2+}$ sites. In this case, the magnetic field $H$ has different angles with $g$-tensor of each Cu-site and the observed $g$-factor in our measurements is averaged $g$-factor $g_{av}$, which is attributed to the existence of the exchange coupling between the (A) and (B) Cu$^{2+}$ sites.

$$g_{av} = \frac{1}{2}(g_A + g_B)$$

(5.6)

where $g_A$ and $g_B$ are $g$-factor of the two inequivalent Cu$^{2+}$ (A) and (B), respectively. It
is possible to calculate $g_A$ and $g_B$ by simulating the angular dependence of $g_{av}$ as shown in Fig. (5.10). For each Cu site the $g$-factor differs from 2.02 to 2.34, which is typical for the Cu$^{2+}$ ions in a $d_{x^2−y^2}$ ground state in a crystal field of an axial symmetry. According to the crystal field theory, the $g$-factor of Cu$^{2+}$ ions in a $(3d^9)$ configuration and a crystal field of a tetragonal symmetry can be calculated by

$$g_a = 2 - \frac{8\lambda}{\Delta_{xy}}, \quad g_c = 2 - \frac{2\lambda}{\Delta_{yz,zz}}$$

where $\lambda$ is the spin-orbit coupling constant for Cu$^{2+}$, $\Delta_{xy}, \Delta_{yz,zz}$ are the energy differences between the ground state level $d_{x^2−y^2}$ and the $\Delta_{xy}$ and $\Delta_{yz,zz}$ levels, respectively. For $\lambda = -100$ meV for a free copper ion, $g_a = 2.26$ and $g_c = 2.1$, we estimated $\Delta_{xy} = 2$ eV and $\Delta_{yz,zz} = 3$ eV.

The angular dependence of the linewidth crucially probes the spin dynamics of the low dimensional spin system. The linewidth is a sum of contributions from the short-time behavior ($\Delta H_s$) and the diffusive region ($\Delta H_d$)[181],[182]. The total linewidth is:

$$\Delta H_{pp}(\theta, T) = \Delta H_d(\theta, T) + \Delta H_s(\theta, T)$$

The parameters $A$ and $C$ in Eq. (5.3) relate to the short-time region of the total spin torque (TST) correlation function. The $\Delta H(\theta) \propto (3 \cos^2 \theta - 1)^2$ anisotropy is characteristic of 2D systems and arises from the long-time diffusional decay of the spin correlation function.

As shown in Fig (5.1), in addition to the intrachain exchange $J_b$, these chains are coupled with interchain coupling $J'$ which is realized via Cu-O-Cu exchange paths and the exchange angle is $107^\circ$, which corresponds to a weak AFM exchange. In this case, both the intrachain exchange $J_b$ and interchain exchange $J'$ act together to create a 2D Cu-network. The fact that $\Delta H_{pp}$ angular dependence is shifted by $50^\circ$ from the $a$-axis, suggests that the direction perpendicular to the plane, where this 2D Cu-network is realized, lies in the $ac$-plane and has a $50^\circ$ angle with the $a$-axis.

Both the dipole-dipole interaction and the anisotropic exchange interaction contribute to the form $(3 \cos^2 \theta - 1)^2$ of $\Delta H_{pp}$ angular dependence. This spin diffusion contribution of the angular dependence is relatively temperature independent at high temperature and the position of the minimum linewidth depends on the ratio $C/B$. The deviation of $\Delta H_{pp}$ angular dependence from the 2D behavior at $T = 50$ K is due to the development of short range spin order (SRO) below 70 K. This growth leads to effective interplaner exchange which gives rise to a spin correlations. Because of this quasi 3D character of the spin correlation, the linewidth deviate from its typical 2D behavior observed at high temperatures.
5.5. ESR measurements at $\nu = 9.5$ GHz

The temperature dependence of the ESR signal was measured at three different magnetic field orientations, $H \parallel a$, $H \parallel c$ and for $H \parallel$ to the direction of the maximum linewidth ($d_{\Delta H_{\text{max}}}$). The ESR spectrum is formed by a single, symmetrical, Lorentzian shape line. ESR spectra at selected temperatures are presented in Fig. (5.11) and the solid red lines represent the Lorentzian fit.

- The ESR intensity $I_{\text{ESR}}$

The total integral ESR intensity $I_{\text{ESR}}$, defined as the area under the ESR absorption curve, is proportional to the spin susceptibility. Figure (5.12) shows the $T$-dependence of $I_{\text{ESR}}$ in the $c$-axis normalized to the high temperature intensity ($T = 200$ K) and compared with that of the static susceptibility $\chi_{\text{stat}}$ in the $c$-direction for $H = 0.1$ T and $H = 4$ T.

The ESR intensity ($I_{\text{ESR}}$), shows the same behavior as $\chi_{\text{stat}}$, where it increases with decreasing temperature and reaches a maximum at $T = 3.6$ K. However, the low temperature $I_{\text{ESR}}$ is smaller than the low temperature static susceptibility at $H = 0.1$ T and higher than the low temperature static susceptibility at $H = 4$ T. This behavior is due to the saturation of magnetization at higher magnetic fields. Similar to $\chi_{\text{stat}}^{-1}(T)$, the temperature
5.5. ESR measurements at $\nu = 9.5$ GHz

Figure 5.13: $T$-dependence of the ESR intensity for $H \parallel a, c$-axis and $H \parallel d_{\Delta H_{\text{max}}}$

Figure 5.14: $T$-dependence of the resonance field of the ESR signal.

dependence of $I_{\text{ESR}}^{-1}$ at low temperatures clearly deviates from the linear behavior [Fig. (5.12b)], indicating the development of the AFM correlations at low temperatures.

The ESR intensity shows the same behavior when the magnetic field is applied parallel to the $a$-axis. Applying the magnetic field parallel to $d_{\Delta H_{\text{max}}}$ shows a different behavior at low temperatures, where $I_{\text{ESR}}$ reaches a maximum at $T \approx 5$ K and this maximum is much lower than the maximum intensity when $H$ is applied parallel to $c$ and $a$-axis. This may suggest that the AFM correlations in $d_{\Delta H_{\text{max}}}$ direction are stronger than that in $c, a$-direction.

- The $g$-factor

The temperature dependences of the resonance field ($H_{\text{res}}$) for $H \parallel a, c$ and $H \parallel d_{\Delta H_{\text{max}}}$ are shown in Fig. (5.14) and its inset. For $H \parallel a$, $H_{\text{res}}$ increases with decreasing temperature until it reaches an almost constant value for $20 \, K \leq T \leq 100 \, K$. Below $T = 10 \, K$, $H_{\text{res}}$ decreases rapidly with decreasing temperature. For $H \parallel c$, $H_{\text{res}}$ increases with decreasing temperature down to $T = 20 \, K$, where this increase speeds up with further decrease of temperature. On the other hand, for $H \parallel d_{\Delta H_{\text{max}}}$, the resonance field is almost constant for $70 \, K \leq T \leq 295 \, K$. Whereas, it significantly decreases below $70 \, K$ and reaches a maximum at $T = 4.6 \, K$ and then slightly decrease.

Figure (5.15a,b) shows the temperature dependence of the $g$-factor for three different magnetic field orientations. The change in the $g$-factor ($\Delta g$) as a function of temperature is presented in Fig (5.15c). It is clear that $\Delta g$ for $d_{\Delta H_{\text{max}}}$ is almost 4 times larger than $\Delta g$ for $a$ and $c$-axis. Furthermore, the decrease of the $g$-factor for $d_{\Delta H_{\text{max}}}$ direction becomes significant below $T = 70 \, K$ and continues down to $T = 5 \, K$. This shift is observed at temperatures far above $T_N$, which is a characteristic behavior of low dimensional spin systems. [183] In general, $H_{\text{res}}$ is very sensitive to the development of SRO and an internal field. Anisotropic ESR shifts is due to a combined effect of AFM correlations and the dipole-dipole interaction among short range ordered spins in the chains, and the shift is related to the magnetic susceptibility. [183, 184]
The linewidth $\Delta H_{pp}$

The $T$-dependence of the linewidth $\Delta H_{pp}$ for $H \parallel a, c$ and $d_{\Delta H_{\text{max}}}$ is shown in Fig. (5.16a). Lowering the temperature from 295 to 60 K decreases gradually $\Delta H_{pp}$ for all directions. However, for $H \parallel d_{\Delta H_{\text{max}}}$, $\Delta H_{pp}$ broadens rapidly below 60 K and reaches a maximum of 87 Oe at $T \approx 5.2$ K and then slightly decreases. This rapid increase of $\Delta H_{pp}$ for $H \parallel a$ and $c$ is shifted toward lower temperatures, where it starts at $T \approx 25$ K.

The rapid increase of $\Delta H_{pp}$ below $T_{\text{SRO}} \approx 70$ K coincides with the shift of the $g$-factor at the same temperature for $H \parallel d_{\Delta H_{\text{max}}}$. The drastic broadening of the ESR line below 60 K can be attributed to the slowing down of the spin fluctuations due to the development of the interplane spin correlations. This behavior is typical for low-dimensional spin systems, where an essential broadening of the ESR line can occur in a rather broad temperature range of about $1.5 T_N \leq T \leq 10 T_N$ [185]. The minimum of $\Delta H_{pp}$ usually reflects the beginning of the SRO in the lower temperature region. The common expression describes the critical broadening of the ESR signal due to the development of the LRO is [186]

$$\Delta H = \Delta H(\infty)[1 + \epsilon^{-p}]$$

(5.9)

where $\epsilon = (T - T_N)/T_N$. $p$ is the critical exponent, which reflects the anisotropy and the dimensionality of the system. For the X-band experiment, $H_{\text{res}} \approx 0.3$ T and from the phase diagram [see Fig. (5.4)], we obtain $T_N = 3.55$ K at this field. Using Eq. (5.10), we fit our experimental data in the interval $5 \text{ K} \leq T \leq 75$ K and obtain the best agreement when $p = 1.49$ as shown in Fig. (5.16c). This value of $p$ is in agreement with the observed values for a 2D Heisenberg AFM with interlayer 3D correlations [186]. Above 70 K, the
temperature dependence of $\Delta H_{pp}$ can be phenomenologically described as

$$\Delta H_{pp} = \Delta H_{pp}(0) + A \cdot T^2$$

(5.10)

where $\Delta H_{pp}(0) = 25$ Oe and $A = 1.9 \times 10^{-4}$ Oe/T$^2$.

Another interesting feature is the ratio $\beta$ between $\Delta H_{pp}(T)$ for $H \parallel a$ and $c$-axis and $\Delta H_{pp}(T)$ for $H \parallel d_{\Delta H_{max}}$. $\beta = \Delta H_{pp}(a,c)/\Delta H_{pp}(d_{\Delta H_{max}})$ decreases gradually below 60 K and shows a minimum around $T = 6.5$ K and then increases again [Fig. (5.16b)]. The temperature that shows the minimum linewidth should be the same for all field directions in the case of 1D AFM. However, for 2D systems the anisotropy plays a strong role. The initial decrease of $\Delta H_{pp}$ with decreasing temperature has to be associated with the loss of weight of the $q \rightarrow 0$ diffusive modes and to an increase in the spectral weight at $(\pi/a,0)$ [or $(0,\pi/a)$], which finally gives rise, in view of the slowing down of the critical fluctuations, to a peak near to $T_N$ [94]. Such transfer of spectral weight from $q \leftrightarrow 0$ to the critical wave vector causes also a modification in the angular dependence of $\Delta H$, where $\Delta H_{a,c}/\Delta H_{d\Delta H_{max}}$ is almost constant at high temperature and then this ratio decreases as the temperature lowered below $T_{SRO} = 70$ K.
5.6 High field measurements

High field ESR measurements of a sealed single crystal of Cu(NO₃)₂·H₂O were performed in a frequency range from 45 GHz up to 330 GHz, in magnetic fields up to 15 T and at temperatures between 2.5 and 280 K. The applied magnetic field \( H \) was in the direction parallel to the \( b \)-axis (the direction of the chains). NMR data were collected on a Tecmag pulse solid-state NMR spectrometer with a 9.2 T superconducting magnet from Magnex Scientific in a temperature range 4.2 - 100 K. NMR results were measured by E. Vavilova.

5.6.1 ESR measurements at \( \nu = 83 \) GHz

The ESR spectra of a Cu(NO₃)₂·H₂O crystal at \( \nu = 83 \) GHz for \( H//b \) are shown in Fig. (5.17). Above \( T_{SRO} \sim 70 \) K, the ESR signal consists of a single lorentzian absorption line \( L_1 \) which is associated with the resonance of Cu²⁺ (\( S = 1/2 \)) ions. Whereas, for \( T < T_{SRO} \), the spectra exhibit two absorption lines \( L_1 \) and \( L_2 \), by decreasing temperature, \( L_2 \) became more pronounced and gained considerable intensity in comparison to the main line \( L_1 \). Below 20 K a third ESR line \( L_3 \) emerged at low magnetic fields with \( H_{res} \) corresponds to an effective \( g \)-factor \( g_{eff} = 4.1 \). This line is attributed to a transition between the \( S_z = 1 \) and \( S_z = -1 \) states, which opens questions about the possible formation of ferromagnetic

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Figure 5.17: Temperature dependence of ESR absorption spectra of Cu(NO₃)₂·H₂O at 83 GHz for \( H//b \).

Figure 5.18: a) Temperature dependences of the \( g \)-factor and \( H_{res} \). b) Temperature dependences of the ESR linewidth \( \Delta H_1 \) and \( \Delta H_2 \). Solid line: the critical broadening of \( \Delta H_1 \).
5.6. High field measurements

(Copper Nitrate Monohydrate) dimers at low temperatures. More details on \( L_3 \) will be presented later in the frequency dependence measurements.

The temperature dependences of the g-factor and resonance field \( H_{\text{res}} \) are presented in Fig. (5.18a). For \( L_1 \), the resonance field \( H_{\text{res}1} \) is almost constant for \( T \geq T^{\text{SRO}} \). Below \( T^* \), \( H_{\text{res}1} \) shifts towards higher fields, whereas for \( L_2 \), \( H_{\text{res}2} \) shifts towards lower fields. The smooth splitting of the resonance line into two components below 70 K indicates the existence of two inequivalent centers of the Cu\(^{2+} \) ions in the system. The values of the effective g-factor for these centers at \( T = 4 \) K are \( g_1 = 2.15 \) and \( g_2 = 2.27 \). As shown in Fig. (5.18), in the case of \( L_1 \), the g-factor decreases with decreasing the temperature below 60 K. On the other hand, for \( L_2 \) the g-factor increases with decreasing the temperature below 60 K.

The width of the two ESR lines, \( \Delta H_1 \) and \( \Delta H_2 \), increases as the temperature is lowered below \( T^* \) as shown in Fig. (5.18b). The increase of \( \Delta H_{\text{ESR}2} \) is stronger than of \( \Delta H_{\text{ESR}1} \). It is important to notice that at \( H_{\text{res}} \approx 2.7 \) T, our measurements reveal no signatures of LRO down to 2.5 K as expected for \( H \geq 1 \) T from the phase diagram in Fig. (5.4). Hence we suggest that the increase of \( \Delta H_{1,2} \) is due to the development of the SRO, which may show even a stronger critical behavior [186]. By considering a very low \( T_N \), we calculated the critical broadening of \( \Delta H_1 \) using Eq. (5.9) and obtained the critical exponent \( p = 1.288 \), which is still in agreement with the observed values for 2D Heisenberg AFM with interplaner 3D correlations.

As mentioned before, in the X-band measurements, ESR signals of two inequivalent Cu\(^{2+} \) sites are exchange narrowed into a single line. In this case, the difference in the Zeeman energies for the two Cu sites due to a difference of g-factors \( \Delta g = g_2 - g_1 \) is obviously smaller than the energy of the isotropic exchange \( \Delta g \mu_B H_{\text{res}} \ll J_b \) and \( H_{\text{res}} \approx 3.2 \) T. The signs of the beginning of the SRO are clearly present when the magnetic field is applied parallel to \( d \Delta H_{\text{max}} \); the resonance field shifts toward lower values below \( T_{\text{SRO}} = 70 \) K, and the linewidth broadens significantly in the same range of temperature.

On other the hand, at \( \nu = 83 \) GHz, the magnetic field is applied parallel to \( b \)-axis which is the direction of the chains. The resonance field is about \( H = 2.7 \) T and as we lower the temperature below 70 K, a second ESR line \( L_2 \) emerge. The intrachain interaction \( J_b \) should be temperature independent and hence the absence of \( L_2 \) at high temperature indicates that the Zeeman energy at \( H = 2.7 \) T is still smaller than the intrachain coupling \( J_b \). However, by approaching the SRO region below \( T_{\text{SRO}} \), the development of the quasi static correlations and the increasing role of the magnetic anisotropies suppresses the exchange narrowing effect and allows the observation of both resonances.
5.6. High field measurements

Copper Nitrate Monohydrate

Figure 5.19: a) \(^1\)H-NMR spectra Cu(NO\(_3\))\(_2\)-H\(_2\)O at different temperatures for \(\nu = 28.244\) MHz. b) Temperature dependence of \(^1\)H-NMR resonance field. c) Temperature dependence of the \(^1\)H-NMR linewidth. Solid line: calculated critical broadening of \(\Delta H_{NMR}\). [measured by E. Vavilova]

5.6.2 NMR measurements

NMR signal from the hydrogen nuclei have been investigated. The \(T\)-dependence of the \(^1\)H-NMR spectra at \(\nu = 28.244\) MHz is shown in Fig. (5.17a) [measured by E. Vavilova]. At high temperatures the spectra consist of a single line. Whereas, decreasing the temperature to 20 K, the signal splits into two components and the second line becomes more pronounced for further decrease of temperature. Finally at \(T = 2\) K, the NMR response clearly consists of many lines.

The splitting of the NMR signal for \(T \leq 20\) K suggests that the proton sites probe two different local fields. The observation of many NMR lines at \(T = 2\) K indicates a magnetically ordered ground state at this temperature, which is in agreement with the suggested phase diagram [see Fig. (5.4) [176]].

The temperature dependencies of the width of the main \(^1\)H-NMR signal, \(\Delta H_{NMR}\), and the resonance field \(H_P\) are shown in Fig. (5.19b and c). \(H_P\) is almost constant above \(T = 20\) K. However, decreasing the temperature below \(T = 20\) K shifts gradually \(H_P\) to higher fields as shown in Fig. (5.19b). The shift of the position of the NMR line, which is a measure of the local magnetization at the proton sites, is consistent with the increase of ESR resonance field \(H_{res1}\), that can be related to the onset of
5.6. High field measurements

Copper Nitrate Monohydrate

the short range AFM ordering.

Similarly to the ESR linewidth $\Delta H_{1,2}$, the $T$-dependence of $\Delta H_{NMR}$ becomes pronounced by lowering the temperature below $T \sim 40$ K as shown in Fig. (5.19b). The significant increase of both ESR and NMR linewidths in the same temperature range can be straightforwardly related to the development of AFM SRO. Approaching the AFM LRO at the Néel temperature $T_N$, the line broadening is proportional to $[(T - T_N)/T_N]^{-p}$ as indicated in Eq. (5.9). From the phase diagram suggested in Fig. (5.4) [176], $T_N = 3.25$ K at $H = 0.6$ T. With this value of $T_N$, the fit of the $T$-dependence of the $\Delta H_{NMR}$ yields the value of $p = 0.73$, which is in a good agreement with the theoretically expected value for a two-dimensional Heisenberg antiferromagnet [186].

The dependence of the $^1$H-NMR spectrum on temperature at $\nu = 170.28$ MHz is presented in Fig. (5.20) [measured by E. Vavilova]. The resonance field in this frequency range is $H_0 = 4$ T and the presence of LRO is not expected at such field. For $T \geq 80$ K, the spectrum has a single peak and position of this peak is temperature independent. The spectrum, however, begins to split into four peaks below 80 K. The positions of these peaks are diverging by decreasing the temperature. The temperature at which the spectrum begins to split is in agreement with the $T_{SRO} \sim 70$ K suggested by the ESR measurements. The temperature evolution of the $^1$H-NMR signal at $\nu = 170.28$ MHz is different from that at $\nu = 28.244$ MHz, where the splitting was observed for $T \leq 20$ K. This behavior will be discussed latter by considering random spin clusters below $T_{SRO} \sim 70$ K.

Since NMR, as well as ESR, is a local probe, the shift of the peaks and the emerge of new ones would logically suggest changes in the local environments of the protons. Below $T_{SRO} \sim 70$ K, the emergence of new peaks reveals inequivalent proton sites. Whereas, the shift of these peaks by decreasing the temperature indicates that local fields acting on these proton sites are growing gradually at low temperatures. Such behavior may suggest the formation of spin-clusters at $T_{SRO} \sim 70$ K.
5.6. Frequency dependence measurements

In the previous sections, the ESR and NMR temperature dependencies reveal three important features:

- A gradual shift of the ESR signal below 70 K associated with a rapid broadening of the signal width ($\nu_{ESR} = 9.5$ GHz and $H_{ESR} \approx 0.3$ T)

- Shift, broadening and splitting of the $^1$H-NMR signal ($\nu_{NMR} = 28.224$ MHz and $H_{NMR} \approx 0.6$ T) at low temperatures.

- A smooth splitting of the ESR ($\nu_{ESR} = 83$ GHz and $H_{ESR} \approx 2.7$ T) and $^1$H-NMR ($\nu_{NMR} = 170.28$ MHz and $H_{NMR} \approx 4$ T) signals below 70 K.

These features were attributed to the development of the quasi static correlations and the increasing role of the magnetic anisotropies below $T_{SRO}$. Both ESR and NMR measurements at low fields ($H_{ESR,NMR} \leq 1$ T) are consistent with the magnetic phase diagram suggested in Ref. [176] [see Fig. (5.4)], where LRO is found in Cu(NO$_3$)$_2\cdot$H$_2$O.

At higher magnetic fields $H \leq 1$ T, ESR and NMR measurements illustrate a more complicated situation. No LRO was observed at high fields, as suggested by the phase diagram. However, the emergence of new lines in ESR and NMR patterns opens questions about the possible clusterization at low temperatures. Hence, it is important to study the frequency dependence of the ESR signal and to investigate the effect of higher magnetic fields on this compound.

The frequency dependence of the ESR signal of Cu(NO$_3$)$_2\cdot$H$_2$O for $H \parallel b - axis$ was measured at four different temperatures in a wide range of frequencies from 45 GHz to 390 GHz. In the high temperature regime, the frequency dependence was studied at $T = 150$ and 185 K. Whereas, in the low temperature regime, we studied the frequency dependence at $T = 4$ and 20 K.

5.6.4 Frequency dependence in the high temperature regime

The typical ESR spectra at various frequencies of Cu(NO$_3$)$_2\cdot$H$_2$O obtained at 150 K for $H \parallel b$ is shown in left panel of Fig. (5.21). As in the temperature dependence at 83 GHz for $T \geq 70$ K, only a single ESR line was observed up to 390 GHz. This line can be fitted with a lorentzian line profile.

The obtained results of the frequency dependence of the ESR parameters are summarized in Fig. (5.21 right panel). The resonance field of the ESR line shows a linear increase with increasing the frequency as shown in Fig. (5.21b). The obtained frequency dependence can be fitted by:

$$\nu(H) = \Delta + g \frac{\mu_B}{h} H_{res}$$

(5.11)

where $\Delta$ is an energy gap and the proportionality factor directly relates the $g$-factor. The observed line has no energy gap ($\Delta = 0$) and the $g$-factor amounts to $g = 2.17$. 

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100
Figure 5.21: Left panel: Frequency dependence of the ESR signal of Cu(NO$_3$)$_2$·H$_2$O at 150 K for $H \parallel b$. Solid red lines: lorentzian fitting. Right panel: Frequency dependence of the ESR parameters at $T = 150$ and 185 K. a) Frequency-field diagram at 20 K. Solid lines: fit according to Eq. (5.13). b) Linewidth as function of the magnetic field. Solid line illustrates $H^{\sqrt{2}}$ dependence of the linewidth, Eq. (5.12).

Figure (5.21a) shows the field dependence of the signal width $\Delta H$. $\Delta H$ increases gradually with increasing $H_{\text{res}}$ and can be described by:

$$\Delta H = A \cdot H^{\sqrt{2}}$$

(5.12)

The points measured at 185 K are in complete agreement with that of 150 K.

The increase of the linewidth as a function of the applied magnetic field may indicate a possible existence of a field induced gap in this system, which would be in agreement with specific heat data at 3 T [Fig. (5.5)]. A similar behavior was observed at high field ESR measurements on [PM-Cu(NO$_3$)$_2$·(H$_2$O)$_2$]$_n$ system [187].

In the high temperature regime, increasing the frequency up to 390 GHz with a resonance field $H_{\text{res}} = 13$ T has no effect on the number of observed ESR lines. This emphasizes that the Zeeman energy up to $H = 13$ T is still smaller than the intrachain coupling $J_b$. From Eq. (5.5), it is possible to estimate the lower limit of the intrachain coupling $J_b$, using $\Delta g = 0.32$ and $H = 13$ T, we obtain $J_b > 2$ K.
5.6.5 Frequency dependence in the low temperature regime

- Frequency dependence at $T = 20$ K

The typical transmission ESR spectra of Cu(NO$_3$)$_2$·H$_2$O for various frequencies at 20 K are presented in Fig. (5.22). The inset indicates the positions of the resonance fields of the observed peaks. The frequency dependence pattern at 20 K is completely different from that at high temperatures. By increasing the frequency, and consequently the required magnetic field for the resonance condition, we observe a gradual increase of the number of the detected lines.

The intensity of the new emerging lines is weak comparing to the main two ESR lines $L_1$ and $L_2$ discussed before in the temperature dependence at $\nu = 83$ GHz [see Section (5.6.1)]. In Fig. (5.23), we focus on the frequency dependence of the two main lines $L_1$ and $L_2$. The $g$-factors of $L_1$ and $L_2$ are $g_1 = 2.22$ and $g_2 = 2.17$, respectively, and the two lines have no energy gap. The field dependence of $L_1$ and $L_2$ linewidths is shown in Fig. (5.23a). Again, $\Delta H_{1,2}$ are proportional to $H^{\sqrt{2}}$ and can be fitted by Eq. (5.12).
The frequency-field diagram of the additional lines is presented in Fig. (5.24). Surprisingly, these lines show an antiferromagnetic resonance (AFMR) like behavior. The observed effective $g$-factors $g_{eff}$ and the estimated energy gaps are summarized in table (5.1):

<table>
<thead>
<tr>
<th>ESR line</th>
<th>Frequency, $\nu = \sqrt{\Delta^2 + (g_{eff} \mu_B H_{res})^2}$</th>
<th>$g_{eff}$</th>
<th>energy gap (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>4.1</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>$\sqrt{(g_{eff} \mu_B H_{res})^2 - \Delta^2}$</td>
<td>4.1 135</td>
<td></td>
</tr>
<tr>
<td>$L_3$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>$\Delta - g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>104</td>
</tr>
<tr>
<td>$L_4$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>65</td>
</tr>
<tr>
<td>$L_5$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>0</td>
</tr>
<tr>
<td>$L^*$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>310</td>
</tr>
</tbody>
</table>

Table 5.1: ESR lines observed in the frequency-field diagram at 20 K. $g_{eff}$ is the effective $g$-factor, and $\Delta$ is estimated energy gap.

$S_1$ is a set of three lines, each having the $g_{eff} = 4.1$. The central line has no gap, however the other two lines exhibit an energy gap of $\Delta_3 = 135$ GHz. As mentioned in Section (5.6.1), these lines are the signature of the forbidden transition between the $S_z = 1$ and $S_z = -1$ states of a ferromagnetic dimer. The observation of $g_{eff} = 4.1$ transition is
5.6. High field measurements

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Figure 5.25: Left panel: Frequency dependence of the ESR signal of Cu(NO$_3$)$_2$·H$_2$O at 4 K for $H//b$. Inset: ESR signal at $T=4$K and $\nu=270$ GHz and the arrows indicate the position of the peaks. Right panel: a) $\nu-H$ diagram at 20 K. Solid lines: fitting according to Eq. (5.11). b) $\Delta H$ as function of the magnetic field. Solid lines are the fitting according to Eq. (5.12).

obviously not possible in $S=1/2$ systems and straightforwardly suggests the formation of 'objects' with higher spin values at low temperatures. One possibility, by coupling two spins ferromagnetically we obtain a FM dimer with $S=1$, which allow the observation of $S_3$ transition. Such situation can be realized by cutting the ferromagnetic chains into fragments of FM dimers. In this case, the intradimer coupling is the FM $J_b$ interaction, whereas the interdimer coupling is the AFM $J'$ interaction. Thus, we constructed clusters of FM dimers which interact AFM with each others [see Fig. (5.27) and the discussion for more details].

The $L_3$ mode consists of two "mirror" absorption lines of $g_{eff}=2.06$ and shows a zero field transition at $\nu=108$ GHz which is the value of its gap $\Delta_3=108$ GHz. The intensity of the absorption line above 108 GHz is stronger than the intensity of line below 108 GHz. The $L_4$ mode is an absorption line of $g_{eff}=2.06$ which exhibits an energy gap of $\Delta_4=65$ GHz. $L_5$ is a gapless transition characterized by $g_{eff}=2.06$. Finally, $L^*$ consists of a two mirror absorption lines of $g_{eff}=2.06$ and has an energy gap $\Delta_5=310$ GHz.

- Frequency dependence at $T=4$ K

The typical transmission spectra of Cu(NO$_3$)$_2$·H$_2$O for different frequencies at 4 K and $H//b$ are shown in the left panel of Fig. (5.25). Similar to the situation at 20 K measurements, many lines continue to appear by increasing the frequency and the number of these lines at 4 K is higher than that at 20 K. The intensity of the observed lines is stronger at 4 K.
Concerning $L_1$ and $L_2$ lines, they are gapless as shown in the frequency-field diagram in Fig. (5.25b), whereas, the slope of the resonance field as function of the frequency reveals the divergence of the two lines and $g_1 = 2.29$ and $g_2 = 2.16$. This values of $g$ are consistent with the temperature dependence data at 83 GHz. In this case, the field dependencies of the width of the two lines show a similar behavior to $\Delta H$ at 20, 150 and 185 K and $\Delta H_{1,2}$ can be fitted by Eq. (5.12) [Fig (5.25a)]. Furthermore, we observe a peak in the field dependence of $\Delta H_2$ at 2.7 T.

The frequency-field diagram of the additional lines at 4 K is presented in Fig. (5.27). Since the intensity of the lines is stronger than at 20 K, we obtain a better resolution of these lines at 4 K. In general, it is possible to recognize 16 lines and the characteristic features of these lines are summarized in table (5.2):
<table>
<thead>
<tr>
<th>ESR line</th>
<th>Frequency, $\nu = \sqrt{\Delta^2 + (g_{eff} \mu_B H_{res})^2} - \Delta^2$</th>
<th>$g_{eff}$</th>
<th>energy gap $\Delta$ (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>4.1</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>4.1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>4.1</td>
<td>120</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>1.92</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>1.92</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>1.92</td>
<td>73</td>
</tr>
<tr>
<td>$S_3$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.35</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.35</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.35</td>
<td>73</td>
</tr>
<tr>
<td>$L_3$</td>
<td>$\Delta - g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>108</td>
</tr>
<tr>
<td>$L_4$</td>
<td>$\Delta - g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>108</td>
</tr>
<tr>
<td>$L_5$</td>
<td>$\Delta - g_{eff} \mu_B H_{res}$</td>
<td>2.06</td>
<td>0</td>
</tr>
<tr>
<td>$L_6$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.35</td>
<td>73</td>
</tr>
<tr>
<td>$L_7$</td>
<td>$\Delta + g_{eff} \mu_B H_{res}$</td>
<td>2.35</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 5.2: ESR lines observed in the frequency-field diagram at 4 K.

In addition to the lines observed at 20 K, we identify $S_2$, $S_3$, $L_6$ and $L_7$. $S_2$ is a set of three lines with $g_{eff} = 1.92$, the center line is gapless and the remaining two lines have an energy gap $\Delta = 73$ GHz. $S_2$ is another set of three lines with $g_{eff} = 2.35$. Again, the center line is gapless, whereas, the remaining two lines have the same energy gap observed for $S_2$, $\Delta = 73$ GHz. $S_2$ and $S_3$ exhibit the behavior of AFMR. The values of the $g$-factor of $S_2$ and $S_3$ are similar to the values expected in the direction parallel and perpendicular to the CuO$_4$ planes. $L_6$ and $L_7$ have a similar $g_{eff} = 2.35$, however, they exhibit different energy gaps $\Delta_6 = 73$ GHz and $\Delta_7 = 25$ GHz.
5.7 Discussion

According to the phase diagram of Cu(NO$_3$)$_2$·H$_2$O, the establishment of the long range AFM order is only expected below $T_N \approx 3.6$ K for magnetic fields up to $H = 1$ T. Therefore, the signatures of the LRO order can be detected in the NMR and ESR measurements at low fields. Indeed, in the X-band measurements, we observe the shift of ESR resonance field and rapid broadening of the signal width. Whereas, in the NMR results, the LRO is confirmed by the splitting of the $^1$H-NMR below $T_N$. However, the NMR signal at $H = 0.66$ T starts to split at $T = 20$ K, which is 6 times larger than the ordering temperature at this magnetic field. Furthermore, the critical behavior of the ESR parameters ($H_{res}$ and $\Delta H_{pp}$) starts at $T_{SRO} \approx 70$ K, which is almost 20 times larger than $T_N$. Such behavior may suggest a more complicated nature of the transition from the PM to the AFM phase.

If we move to higher magnetic fields ($H \geq 1$ T), the fundamental difference is the absence of LRO, which is confirmed in the high field specific heat, ESR and NMR measurements. However, the specific heat at $H = 3$ T exhibits a broad maximum at 7 K, which may suggest a field induced gap in this system. This observation finds a support from ESR results, where the width of the signal increases by increasing the magnetic field which indicates a possible existence of a field induced gap in this system. In the same time, our NMR and ESR measurements at high fields suggest the formation of spin clusters below $T_{SRO} \approx 70$ K. At this temperature both the ESR and NMR signals, (at 2.7 T and 4 T respectively), start to split into multiple lines.

The ESR can probe the establishment of AFM order, since AFM and PM resonance signals can be easily resolved. Above 1 T, it is expected to observe a PM signal in the whole temperature range. This PM resonance was, indeed, detected at high temperatures [see Fig. (5.21)]. However, decreasing the temperature to 20 K is accompanied by the emergence of many resonance lines in the frequency-field diagram [see Fig. Fig. (5.24)] with an AFMR like behavior. Finally, $\nu - H$ diagram at 4 K [see Fig. (5.26)] gives a straightforward picture of a system with many AFMR lines.
5.7. Discussion

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Figure 5.28: Calculated frequency-field diagram for a small AFM cluster of 8 spins (Imported from Ref. [188]). The magnetic field is supposed to act parallel to the easy axis of the antiferromagnet. The angular frequency $\omega$ and the field $H_0$ are normalized to the exchange interaction $J$.

The formation of spin clusters can be attributed to a random distribution of impurities and defects (for example, due to dehydration, the water content is reduced). These impurities cut the chains at random positions and hence locally destroy the PM state and lead to areas of correlated spins (spin clusters) as shown in Fig. (5.27). For a system with mixed FM and AFM couplings, the spin correlations within the clusters could be of FM or AFM nature.

Due to the random distribution of these impurities, volumes of these clusters are different. In the large AFM clusters, critical fluctuations give rise to the increase of ESR and NMR linewidths. For low fields $H \leq 1$ T, at the Néel point these clusters percolate through the macroscopic distance and hence the LRO is realized. For $H \geq 1$ T, the ground state is not a Néel ordered state, however, for the large AFM clusters it is possible to observe AFMR lines. The ESR frequency-field diagram of a small antiferromagnetic cluster containing 8 spins was calculated in Ref. [188]. As shown in Fig. (5.28), applying a magnetic field yields a complex frequency-field diagram consisting of large number of overlapping and crossing transition lines. It is easy to observe the similarity between Fig. (5.28) and $\nu - H$ diagram obtained from our ESR experiment at low temperatures [see Fig. (5.24) and Fig. (5.26)]. We can speculate that the differences in the size and the orientation of these clusters are the reason for the various values of energy gaps $\Delta$ and $g$-factors.

Furthermore, in clusters with FM spin correlations, the realization of FM dimers is possible. This would directly explain the observation of transitions lines with $g_{\text{eff}} = 4.1$ as discussed before. Of course for such random situation, some clusters may have higher spin values and some would continue to act as PM and give rise to narrow paramagnetic gapless lines.
5.8 Conclusion

Cu(NO$_3$)$_2$·H$_2$O is a new low dimensional spin system based on transition metal nitrates. ESR, NMR and specific heat have been measured to gain insights into the magnetic properties of this system. The anisotropy of the ESR measureables reveals a two dimensional nature of the Cu$^{2+} (S = 1/2)$ layers in this material. The temperature dependence of the ESR response for different field directions indicates a substantial magnetic anisotropy and occurrence of different exchange paths in the Cu layers.

ESR studies reveal a broad \((T, H)\)-parameter range above the AFM ordering phase boundary \(T_N(H)\) where pronounced quasi-static magnetic correlations dominate the magnetic resonance response. This observation suggests that the low dimensionality, the occurrence of inequivalent spin sites and the competing exchange interactions effectively destabilize the magnetic long range ordering in the studied system. Both HF-ESR and specific heat results indicate a possible field induced gap in Cu(NO$_3$)$_2$·H$_2$O. Various gapped resonance modes have been observed using high field ESR. These observations were discussed by considering the ground state and magnetic excitations of random spin clusters which are realized in Cu(NO$_3$)$_2$·H$_2$O.
Chapter 6

Two dimensional (NO)[Cu(NO$_3$)$_3$]

6.1 Introduction

Low dimensional quantum magnets have a very rich physics due to their reduced dimension and competing interactions which often push the transition to ordered states to very low temperatures or even preclude the onset of long range order at all. Geometric frustration is one of the effects which is believed to lead to possible non-classical states. As mentioned in chapter 1, a non-classical ground state does exist in a pure one-dimensional quantum antiferromagnet which is disordered and carries low-energy spinon excitations with fractional quantum numbers. A fundamental question is whether such non classical states can survive in higher dimensions and whether they could realize the long-sought resonant valence bond (RVB) state [189]. The concept of RVB state is of utmost importance in modern condensed matter physics, not only for frustrated magnetism in general but also in the context of high - temperature superconductivity of layered cupric compounds [190].

As discussed before in section (1.4.2), an interesting model is the frustrated $S = 1/2$ square lattice $J_1 - J_2$ and its extensions to further neighbor interactions. Depending on the ratio between the nearest - neighbor antiferromagnetic exchange $J_1$ and the second - neighbor coupling $J_2$ this model has a Néel ground state at weak frustration, and a stripe or collinear Néel state at strong frustration. There is a narrow region between the two phases, in the range $0.4 < J_2/J_1 < 0.6$ where there is now a consensus for the absence of magnetic order. Instead, a spin-liquid or a valence bond crystal state may be realized.

The search for experimental realizations of such a model has been pursued intensively in copper and vanadium oxides (see [191] for a recent review) but the narrow region of parameters where non-classical states may appear is clearly a challenge for chemistry. An alternative is offered by a different $J_1 - J_2$ model recently introduced by Nersesyan and Tsvelik (and named the "confederate flag" model) [60] which was discussed in section (1.4.3). It differs from the $J_1 - J_2$ model by the spatial anisotropy of the nearest neighbor couplings ($J, J'$) along the horizontal and vertical directions and the same $J_2$ along the diagonals. The model is particularly interesting for the special ratio $J'/J_2 = 2$ where the
ground state was first argued to be RVB in the anisotropic limit, \( J \gg J' = 2J_2 \) [60]. This result has been questioned since then and the ground state could be a VBC instead [61, 192, ? 193]. In any case, the special condition \( J'/J_2 = 2 \) forces the effective staggered field to vanish and makes the mean-field theory of coupled chains [194] (which would predict long-range Néel order at zero temperature) inapplicable.

Although it seems that the \( J'/J_2 = 2 \) condition requires again some fine-tuning of the couplings, we present in this chapter our measurements on the new nitrosonium nitratocuprates compound (NO)[Cu(NO\(_3\)]\(_3\)], which turn out to be the exact realization of this condition.

### 6.2 Experiment

The single crystals of nitrosonium nitratocuprates (NO)[Cu(NO\(_3\)]\(_3\)] were obtained by means of wet chemistry according to procedure described in Ref. [195]. The phase composition of the crystalline samples was determined by powder X-ray diffraction. The measurement was carried out on a DRON 3M diffractometer using a CuK\(_\alpha\) radiation in the \( 2\theta \) range of 5 - 60° [195]. The single-phase nature of the obtained samples was confirmed by similarity of the experimental X-ray diffraction patterns and theoretical ones calculated from single crystal X-ray diffraction data [195]. The bluish single crystals of (NO)[Cu(NO\(_3\)]\(_3\)] with dimensions \((3 - 6) \times (1.5 - 2.5) \times (0.5 - 1) \) mm\(^3\) in the form of elongated thickened plates are not stable in air and could be safely investigated in sealed glass ampoules only.

ESR measurements were carried out with a standard X-band Bruker EMX spectrometer (Section. 2.4.1). The magnetization measurements were preformed with a superconducting quantum interference device (SQUID) magnetometer from Quantum Design [measured by O. S. Volkova]. Besides, the specific heat was measured at low temperatures by PPMS "Quantum design" taking special measures against oxidation of the sample [measured by O. S. Volkova].

### 6.3 Crystal structure

The crystal structure of nitrosonium nitratocuprates (NO)[Cu(NO\(_3\)]\(_3\)] is represented by weakly coupled layers whose structure is shown in Fig. (6.1). Assumingly, the strongest interaction \( J \) between Cu\(^{2+} \) \((S = 1/2)\) ions is provided via NO\(_3\)\(^-\) groups forming therefore infinite horizontal chains along the \( b \)-axis. These chains are coupled via NO\(_3\)\(^-\) and NO\(^+\) groups in \( bc \) plane in such a manner that vertical exchange interaction along the \( c \)-axis, \( J' \), is exactly twice the exchange interaction along the diagonal, \( J_2 \): there are two symmetric superexchanges paths contributing to \( J' \) whereas there is only one (and equivalent by symmetry) contributing to \( J_2 \).

The interplane coupling along the \( a \) - axis is assumed to be weak and unfrustrated. Two equivalent exchange interaction routes along this axis pass via NO\(_3\) group but through apical oxygen at a Cu - O distance 2.539 Å. This is to be compared to single exchange...
6.4 Magnetization and specific heat measurements

The temperature dependence of the magnetic susceptibility $\chi$ of (NO)$_3$Cu(NO$_3$)$_3$ taken in a magnetic field 0.1 T oriented in the $bc$ plane is shown in Fig. (6.2). By decreasing the temperature, $\chi$ first increases, passes through a broad maximum, and then rapidly increases again, showing a pronounced Curie-like behavior. The latter feature is significantly suppressed by a magnetic field of 5 T.

The field dependence of the magnetization ($M$) at 2 K is illustrated in inset of Fig. (6.2). The $M$ vs. $H$ dependence is superlinear and could be represented by a sum of linear contribution presumably from the (NO)$_3$Cu(NO$_3$)$_3$ matrix and nonlinear contribution originating from impurities and/or defects whose concentration is estimated to be $5 \times 10^{-3}$ mol$^{-1}$. The origin of these defects is not clear since the method of preparation excludes the presence in the structure of any other cations except Cu$^{2+}$ and (NO)$^+$ and any other anions except (NO$_3$)$^-$ while high optical quality of the available crystals is apparent. The broad maximum in $\chi(T)$ can be seen as a signature of the low dimensionality of (NO)$_3$Cu(NO$_3$)$_3$ magnetic subsystem.

Figure 6.1: The crystal structure of (NO)$_3$Cu(NO$_3$)$_3$. Green spheres are the Cu$^{2+}$ ions. The dumbbells are the (NO)$^+$ groups. The (NO$_3$)$^-$ groups are tilted and flat triangles. Note, $J' = 2J_2$. Right upper part: The schematic representation of anisotropic confederate flag model.
6.4. Magnetization and specific heat measurements

Two dimensional (NO)[Cu(NO$_3$)$_3$]

Figure 6.2: Temperature dependence of magnetic susceptibility $\chi$ of (NO)[Cu(NO$_3$)$_3$]. The inset shows the field dependence of magnetization. Measured by O. S. Volkova.

Figure 6.3: Temperature dependence of reduced specific heat of (NO)[Cu(NO$_3$)$_3$]. Measured by O. S. Volkova.

No indication for the presence of a spin-gap was obtained in specific heat measurements of (NO)[Cu(NO$_3$)$_3$]. The $C/T$ vs. $T^2$ dependence, shown in Fig. (6.3), reveals large linear term $\gamma T$ superimposed on cubic term $\beta T^3$. While the latter contribution most probably can be attributed to phonons, the spin excitations within chains can be responsible for the former contribution.

Moreover, at low temperatures, $T < 25$ K, the increase of the specific heat by decreasing the temperature is slightly suppressed by external magnetic field. The low temperature upturn could signify the proximity to quantum critical point or phase transition into three-dimensional long-range ordered state which should be verified by study at even lower temperatures.
6.5 ESR measurements

In order to study the intrinsic spin susceptibility and to obtain insights into the spin dynam-ics, we have performed ESR measurements on a single crystalline sample of (NO)[Cu(NO3)3] at the X-band frequency (9.51 GHz) and within the temperature range from 3.4 to 300 K. The dependence of the ESR signal on the orientation of the external magnetic field was studied. Then, we follow the evolution of the ESR parameters with temperature in two orientations of the external magnetic field: The in-plane orientation parallel to the CuO4 plaquettes, and the out-of-plane orientation, perpendicular to the CuO4 plaquettes, $\parallel$ and $\perp$, respectively.

6.5.1 The anisotropy of the ESR signal

The ESR signal of (NO)[Cu(NO3)3] consists of a single resonance line associated with Cu$^{2+}$ ($S=1/2$) ions which can be well fitted by a Lorentzian line profile. In addition, we observe impurity signals with a resonance fields corresponds to $g \sim 2$ and $g \sim 4$. These impurities, which is also observed in the magnetic susceptibility measurements, may originate from free-like Cu spins and/or a small percent of 'foreign' phase which has $S = 1$ spin.

At room temperature, the main signal is anisotropic and rotating the sample with respect to the magnetic field change both the position of the resonance field and width of the signal. The typical ESR spectra at room temperature in the parallel and perpendicular field directions are shown in Fig (6.4). At $T = 80$ K, the signal is narrower which allow better resolution and well separation of the main line from the impurity signals. The g-factor can be calculated from the resonance field as

$$g = \frac{h\nu}{\mu_B H_{res}} \quad (6.1)$$
The anisotropy of the $g$-factor at 295 K and 80 K is presented in Fig. (6.5). The $g$-factor anisotropy is temperature independent, where it has a maximum of $g_\perp = 2.36$ when the field ordination is perpendicular to the CuO$_4$ plaquette. Whereas, it reaches a minimum of $g_\parallel = 2.06$ in the field orientation parallel to the CuO$_4$ plaquette. The obtained $g$-factor values are typical for a Cu$^{2+}$ ion in a planar square ligand coordination [73]. Such angular dependence can be described by:

$$g = \sqrt{g_\parallel^2 \sin^2 \theta + g_\perp^2 \cos^2 \theta}$$  (6.2)

The angular dependence of the ESR linewidth is shown in Fig. (6.6), where $\Delta H_{pp}$ differ from 196 Oe to 240 Oe for $\parallel$ and $\perp$ field orientation, respectively. The angular dependence of $\Delta H$ can be fitted by:

$$\Delta H_{pp} = A(1 + \cos^2 \theta) + B$$  (6.3)

which is usual for 1D spin systems. Since the intrachain interaction $J$ is much higher than the interchain interactions $J'$ and $J_2$, the anisotropy of $\Delta H_{pp}$ follows the typical behavior for 1D chains. Lowering the temperature to 80 K, where the signal is narrower and better resolved, the quality of the fitting of the angular dependence of both the $g$-factor and $\Delta H$ is better. At 80 K, the linewidth changes from 83 Oe to 98 Oe for $\parallel$ and $\perp$ field orientation, respectively.
6.5. ESR measurements

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6.5.2 $T$-dependence of the ESR signal

The typical ESR spectra at selected temperatures for a magnetic field applied parallel to CuO$_4$ plaquettes are shown in left panel of Fig (6.7). The solid red lines represent the Lorentzian fit. It is clear that position of the ESR signal (the resonance field $H_{res}$) is temperature independent. Whereas, increasing the temperature significantly influence both the intensity and the width of the signal.

- $T$-dependence of the $g$-factor

The temperature independent resonance field is translated into a constant $g$-factor as presented in Fig. (6.7). Remarkably, such temperature independent $g$-factors suggest that there are no indications for the development of local internal fields due to the onset of (quasi) static short- or long-range order in the entire temperature range of the study. This strongly supports our conjecture of the low dimensionality of the spin-1/2 Heisenberg lattice in (NO)Cu(NO$_3$)$_3$ where magnetic order is not expected at a finite temperature.

- $T$-dependence of the ESR intensity $I_{ESR}$

Generally, the integrated intensity of the ESR signal $I_{ESR}$ is directly proportional to the static susceptibility of the spins participating in the resonance [71]. Its analysis enables therefore an insight into the intrinsic magnetic susceptibility $\chi_{spin}$ of the spin lattice in (NO)Cu(NO$_3$)$_3$. The temperature dependence of the $I_{ESR}$ normalized to its value at 295
6. ESR measurements

Two dimensional \((\text{NO})[\text{Cu(NO}_3)_3]\)

6.5. ESR measurements

K is shown in Fig. (6.8 inset) for the parallel and perpendicular magnetic field orientations. For both field directions these curves are very similar and, if compared to the static magnetic measurements, show even more pronounced low dimensional behavior.

In a wide temperature range, the magnetic susceptibility is represented by three terms [Fig. (6.8)]: i) temperature independent term \(\chi_0\), ii) impurity (or defect) Curie - Weiss term \(\chi_{\text{imp}}\), iii) main contribution of Bonner - Fisher type \(\chi_{\text{main}} = \chi_{\text{ESR}}\):

\[
\chi_{\text{static}} = \chi_0 + \frac{C}{T - \Theta} + A \times \frac{\chi_{\text{ESR}}}{\chi_{\text{main}}}
\]  

(6.4)

where \(A\) is a scaling factor for the ESR intensity.

- **T-dependence of the linewidth \(\Delta H_{pp}\)**

Another important information can be obtained from the analysis of the linewidth \(\Delta H_{pp}\) which, in particular in spin-1/2 systems, is mainly determined by the relaxation rate of the spin fluctuations perpendicular to the applied field. The \(\Delta H_{pp}\) for both orientations of the external field shows a remarkably strong temperature dependence as illustrated in Fig. (6.9). In particular, below \(\sim 100\) K the linewidth decreases by almost an order of magnitude which at first glance might be interpreted as a strong depletion of the spin fluctuation density due to the opening of the spin gap.

In fact, in this temperature regime the \(\Delta H_{pp}(T)\) dependence can be phenomenologically reasonably well described by an exponential function

\[
\Delta H_{pp}(T) = A e^{\frac{-T}{\Delta}}
\]  

(6.5)

with an energy gap \(\Delta_\parallel \approx \Delta_\perp \sim 77\) K. However, the finite ESR intensity, i.e. the finite intrinsic spin susceptibility, observed down to the lowest temperature as well as the specific heat data contradict the spin gap scenario.
6.5. ESR measurements

Two dimensional (NO)[Cu(NO$_3$)$_3$]_3

![Figure 6.9: Temperature dependence of the ESR linewidth $\Delta H_{pp}$ for a magnetic field parallel and perpendicular to the plane of CuO4 plaquettes (symbols). Dash line is the scaled product $\chi_{spin}(T) \cdot T$.](image)

Alternatively, it is known that in a 2D antiferromagnet at temperatures far above the magnetic ordering temperature $T_N$ the linewidth is determined mainly by the long-wave $q \approx 0$ fluctuation modes whose strength decreases with lowering the temperature as $\chi_{spin}T$ (see, e.g., [94]). If a competing contribution due ‘short-wave’ spin fluctuations at the staggered wave vector $q = \pi$ remains small, e.g., if the spin system is still in the regime $T >> T_N$, one could indeed expect even for a gapless situation a progressive strong narrowing of the ESR signal due to the reduction of both the $\chi_{spin}$ and the temperature. The product of the normalized ESR intensity, i.e. the $\chi_{spin}$ and the temperature is shown in Fig. (6.9). The $\chi_{spin}T$ curve is scaled to match most closely the $\Delta H_{pp}(T)$ curves. Indeed, one observes a reasonably good qualitative agreement between the $\chi_{spin}T$ and the $\Delta H_{pp}(T)$ dependence. One notices that a substantial anisotropy of the linewidth at high temperatures strongly decreases at low temperatures [Fig. (6.6) and Fig. (6.9)] whereas the anisotropy of the $g$-factor stays constant [Fig. (6.5) and Fig. (6.7)]. Such a reduction of the linewidth anisotropy is expected if the strength of $q \approx 0$ modes decreases [94].

There is also a surprising similarity between the temperature behavior of the ESR linewidth for (NO)[Cu(NO$_3$)$_3$] and that for some 1D spin-1/2 systems like, e.g., KCuF$_3$ [90, 196], a spin-Peierls compound CuGeO$_3$ [97], and a quarter-filled spin ladder NaV$_2$O$_5$ [197]. In all of them a similarly strong temperature dependence of $\Delta H_{pp}(T)$ concomitant with a strong temperature variation of the anisotropy of the linewidth is ascribed to the Dzyaloshinsky-Moriya (DM) interaction, which is allowed by the crystal symmetry in those systems. It remains an open issue if the DM mechanism could be active in (NO)[Cu(NO$_3$)$_3$] and what implications on the static and dynamic magnetic properties should it have if up-scaled from a 1D to a 2D situation.
In order to extract some information on the magnetic couplings, the spin susceptibility was calculated by exact diagonalization of the Nersesyan-Tsvelik model (varying $\alpha = J'/J$). These calculations were done by P. Sindzinger and O. Cépas. They have used clusters of up to 24 spins with different geometries (a square of $4 \times 4$ spins, a ladder of $8 \times 2$ spins, and a stripe of $6 \times 4$ spins with periodic boundary conditions). Because of finite-size effects, the susceptibility is exact only for $T \geq 2T_{\text{max}}$, where $T_{\text{max}}$ is the temperature of the broad maximum of the susceptibility $\chi_{\text{max}}$ [see Fig. (6.10), solid and dashed lines for $\alpha = 0$, for instance]. It is therefore difficult to access to the low-temperature regime where the susceptibility decreases. Nonetheless, it appears that the product $\chi_{\text{max}} T_{\text{max}}$ is less sensitive to the size and is especially useful since we know the exact Bonner-Fisher result for decoupled chains ($\alpha = 0$), given by \[ \chi_{\text{max}} T_{\text{max}} = 0.0941 \frac{N A g^2 \mu_B^2}{k_B} \] (6.6)

When $\alpha = 0$, the product is a pure function of $\alpha$ and is shown in Fig. (6.10 left panel). We see that $\chi_{\text{max}} T_{\text{max}}$ is approximately linear in $\alpha$ and the slope is found to be weakly
size-dependent, where it is \(-0.0558\) (for the \(8 \times 2\)), \(-0.0614\) (for the \(4 \times 4\)) and \(-0.0607\) (for the \(6 \times 4\)). We note that the result at \(\alpha = 0\) almost coincides with Bonner-Fisher for the \(8 \times 2\) cluster (this is the shape with the longer chains). Combining these results, we have

\[
\frac{\chi_{\text{max}} T_{\text{max}}}{N_A g^2 g_B/k_B} = 0.0941 - 0.06 \cdot \alpha
\]  

By considering \(g^2\) from the ESR measurements, and averaging it for the powder sample, \(g^2_{\text{av}} = (1/3) g^2_{\perp} + (2/3) g^2_{\parallel} = 4.68\). We now comparing these calculations with the experiments, using the conversion to standard units gives

\[
\chi_{\text{max}} T_{\text{max}} = 0.165 - 0.105 \cdot \alpha \quad \text{Calculation} \tag{6.8}
\]

Given that, experimentally,

\[
\chi_{\text{max}} T_{\text{max}} = 0.163 \pm 0.007 \text{ emu.K/mol Experiment} \tag{6.9}
\]

we can conclude that \(-0.05 < \alpha < 0.09\). The system is therefore in the weak coupling regime: given the error bar, the interchain couplings could be either ferromagnetic or antiferromagnetic but we can exclude a strong coupling regime. \(J\) can then be estimated from the position of the maximum of the susceptibility for infinite decoupled chains, \(T_{\text{max}} = 0.6408 J\), giving \(J = 170\) K. [95]

It is of course difficult to assess the nature of the ground state of \((\text{NO})[\text{Cu(NO}_3)_3]\) in the view of the present experimental results. Nersesyan and Tsvelik have argued that, for small interchain couplings, the ground state remains disordered and realizes a chiral \(\pi\)-flux RVB spin-liquid at zero temperature [60], which the present results do not contradict in fact. However the situation is not yet settled: extension towards finite inter-chain couplings has lead to consider other candidates for the ground state, such as valence bond crystals [61, 192]. The claim for a VBC is not supported by a DMRG calculation for a spin ladder, though, [193] but may not be excluded for the infinite system [61]. Although the system would be gapped in this case, the temperature of the experiment (1.8 K) may not be small enough to detect it at present. In fact the spin gap was claimed to be extremely small from numerical studies [194]. It is also consistent with the idea that the system could be nearly critical: there are Neel states away from the special line \(J' = 2J_2\) but very close to it in the parameter space \(J' - J_2\) [61, 192]. Accordingly, the ground state of \((\text{NO})\text{Cu(NO}_3)_3\) could be a two-dimensional gapless spin liquid. This does not contradict to results of thermodynamic and resonant measurements. However such a gapless spin liquid state could be unstable to additional interactions (unfrustrated interplane interactions, Dzyaloshinskii-Moriya interactions) which can result in three-dimensional long-range magnetic order at lower temperatures.
6.7 Conclusion

Nitrosonium nitratocuprate (NO)\([\text{Cu(NO}_3]^3\) seems to be a good realization of the Nersesyan-Tsvelik model in the weak coupling regime. From analyzing the temperature dependence of the ESR intensity and static susceptibility, the main magnetic couplings of the Heisenberg model were found to be \(J = 170\) K and \(-0.05 < \alpha < 0.09\). It is clear that a precise determination of the interchain couplings deserves more studies. The temperature dependence of the ESR linewidth suggests the existence of Dzyaloshinskii-Moriya interactions. These interactions contribute to the low-temperature susceptibility and lead to departures from the Heisenberg model.

In general, thanks to the special geometry of the Nersesyan-Tsvelik model, the interchain interactions are not only weak but also strongly frustrated, thus making possible to realize an RVB or VBC state. Experimentally, indeed, no thermodynamic singularities were found down to 1.8 K despite strong antiferromagnetic couplings, and it is an interesting issue to figure whether such states are realized or not in (NO)\([\text{Cu(NO}_3]^3\).
2D honeycomb lattice InCu$_{2/3}$V$_{1/3}$O$_3$

7.1 Introduction

In planar honeycomb lattice systems a combination of nontrivial topology, strong electronic, spin and orbital correlations and degeneracies yields a reach variety of ground states, novel excitations and exotic behaviors that currently attract much attention. The recently discovered exciting phenomena range, e.g., from the quantum Hall effect in graphene [198, 199, 200, 201], superconductivity in MgB$_2$ [202] and intercalated graphite [203], to topologically driven quantum phase transitions in anyonic quantum liquids [204].

Regarding the spin degrees of freedom, an important feature of low dimensional spin systems is the presence of quantum fluctuations that inhibit long range order of the quantum spin-1/2 lattice. Such an effect essentially depends on the spin coordination number \( z \). The one dimensional (1D) Heisenberg antiferromagnetic (AFM) \( S = 1/2 \) chain with \( z = 2 \) does not show any magnetic order even at zero temperature [205], whereas long range order is possible at \( T = 0 \) K in the 2D case [12, 206] as, e.g., in the prominent \( S = 1/2 \) Heisenberg square lattice model with \( z = 4 \). The honeycomb lattice, like the square lattice, is a 2D bipartite lattice, which is not geometrically frustrated for AFM nearest neighbor interactions but it has the minimum possible coordination number of any regular 2D lattice \( z = 3 \). Thus quantum fluctuations in the honeycomb lattice are weaker than in the 1D case, but stronger than in the 2D square lattice. Hence, the AFM order for the honeycomb lattice is fragile [64, 65].

Experimentally, low dimensional spin systems described by the Heisenberg Hamiltonian

\[
\mathcal{H} = J_{afm} \sum S_i S_j
\]

are often realized in structurally three dimensional organic- or transition metal oxide (TMO) compounds where strong AFM exchange interaction \( J_{afm} \) between unpaired localized spins occurs along only one or two spacial directions. Owing to residual small 3D exchange couplings such materials usually exhibit a long range Néel order at a finite
7.2 Crystal structure and previous measurements

InCu$_{2/3}$V$_{1/3}$O$_3$ crystallizes in the hexagonal space group $P6_3/mmc$, $a = 3.3571(3)$ Å and $c = 11.9165(2)$ Å, consisting of alternating layers of [InO$_6$] octahedra and Cu$^{2+}$ and V$^{5+}$ ions in a trigonal-bipyramidal coordination as shown in Fig. (7.1) [Ref. [68]]. The Cu$^{2+}$ ($3d^9$, $S = 1/2$) ions are proposed to be arranged in a 2D network of hexagons with the nonmagnetic V$^{5+}$ ($3d^0$) ions in the middle of each hexagon. In such structure, the Cu$^{2+}$ and V$^{5+}$ ions occupy the same crystallographic site statistically in a two to one ratio, this allows in principle the formation of a honeycomb lattice for these ions.

Figure (7.2) (taken from Ref. [67]) shows the temperature dependence of the static magnetic susceptibility $\chi_{\text{stat}}(T)$ compared to the ESR intensity $I_{\text{ESR}}$. The temperature dependence of $\chi_{\text{stat}}(T)$ reveals a broad maximum at $\sim 180$ K characteristic of a low-dimensional antiferromagnet, passes through a minimum at $\sim 45$ K followed by a kink at $38$ K and shows a Curie-like upturn at lower temperatures. $\chi_{\text{stat}}(T)$ was analyzed as a sum
7.2. Crystal structure and previous measurements

Crystal structure and previous measurements

$\text{InCu}_{2/3}\text{V}_{1/3}\text{O}_3$

Figure 7.2: Magnetic susceptibility $\chi_{\text{stat}}(T)$ of InCu$_{2/3}$V$_{1/3}$O$_3$ and different contributions to it according to Eq. (7.1). The spin susceptibility of Cu$^{2+}$ ions estimated from $I_{\text{ESR}}$ is shown for comparison. From Ref. [67].

Figure 7.3: Temperature dependence of ESR linewidth $\Delta H_{pp}$ of InCu$_{2/3}$V$_{1/3}$O$_3$ powder sample. Inset: Temperature dependence of the g-factor. From Ref. [67].

of three contributions:

$$\chi_{\text{stat}} = \chi_0(T) + \chi_{\text{CW}} + \chi_{\text{spin}}$$  \hspace{1cm} (7.2)

where $\chi_0$ is the sum of the temperature independent diamagnetic and Van-Vleck susceptibilities, $\chi_{\text{CW}}$ is the Curie-Weiss contribution owing to uncompensated spins at defect structural sites which is given by

$$\chi_{\text{CW}} = \frac{C_{\text{def}}}{T - \Theta}$$  \hspace{1cm} (7.3)

$\chi_{\text{spin}}$ is the spin susceptibility of Cu$^{2+}$ ions in the (Cu/V)-O planes [67]. The analysis of the static susceptibility $\chi(T)$ has indicated $J_{\text{afm}} \approx 280$ K of the honeycomb spin lattice [67].

In the ESR experiment performed on a powder sample at standard X-band frequency $\nu = 9.47$ GHz, a strong paramagnetic Cu$^{2+}$ resonance signal was clearly visible at high temperatures. By decreasing the temperature below 80 K, ESR signal strongly broadened and shifted towards lower fields [Fig. (7.3)] and could not be detected below 50 K as shown in Fig. (7.2) [67]. The vanishing of the ESR signal, along with a 'kink' observed in the susceptibility measurement at 38 K, tentatively proposed a long range AFM ordering in InCu$_{2/3}$V$_{1/3}$O$_3$.

A later structural neutron diffraction study revealed that a structural $2^\infty\{V_1Cu_6/3\}$ order in the hexagonal planes has a finite correlation length $\xi_{\text{st}} \sim 300$ Å, and that these structural domains are randomly arranged along the $c$ axis [68]. As has been argued in
7.2. Crystal structure and previous measurements

7. D2 honeycomb lattice InCu$_{2/3}$V$_{1/3}$O$_3$

Figure 7.4: The measured static susceptibility ($\chi_{\text{meas}}(T)$), correction for paramagnetic impurities at defect sites ($\chi_{\text{meas}}(T) - \chi_{\text{CW}}(T) = \chi_{\text{corr}}(T)$, solid red line), and the calculated susceptibility from QMC methods for $J_{\text{afm}} = 240$ K (triangles, blue). Inset: A logarithmic plot of the spin-spin-correlation length in units of shortest Cu-Cu contacts from QMC calculations for two different systems. Note that $\xi$ diverges above $J/T = 1$, e.g., below 120 K and approaches a finite value below $\approx 50$ K, according to QMC calculations for a system of 32×64 spins. Imported from Ref. [68] and $\xi$ is denoted by $\xi_s$ in the present text.

Ref. [68] this structural disorder rendering finite values of the spin-spin correlation length $\xi_s \leq \xi_{\text{st}}$ concomitant with the substantial spacing between the honeycomb planes and with the low spin coordination number in the planes should effectively preclude a 3D Néel order in InCu$_{2/3}$V$_{1/3}$O$_3$.

Quantum Monte-Carlo calculations support this scenario. The calculated susceptibility $\chi_{\text{QMC}}(T)$ coincides well above 120 K with the corrected susceptibility ($\chi_{\text{corr}}(T)$) as shown in Fig. (7.2). Whereas, due to the increasing spin-spin correlation length $\xi_s$, $\chi_{\text{corr}}(T)$ differs slightly from $\chi_{\text{QMC}}(T)$ below 120 K. QMC calculations for 32×64 spins suggest that $\xi_s$ is almost constant below 50 K [inset of (Fig. (7.2)]. Thus the kink-like anomalies in $\chi(T)$-dependence at 30 K and 38 K [(Fig. (7.2)] previously identified with the transition to the long range ordered state [67] have been assigned to glasslike order of unsaturated spins in domain boundaries [68].

In this chapter, we have investigated the magnetic properties of InCu$_{2/3}$V$_{1/3}$O$_3$ using two local spin probe techniques, electron spin resonance (ESR) and nuclear magnetic resonance (NMR), to obtain insights into the nature of the ground state of this compound. These experiments were complemented by measurements of the field dependence of the static magnetization $M(B)$ and by quantum Monte-Carlo calculations (QMC). Our results reveals that, contrary to earlier expectations, structural disorder does not preclude the Néel ordered state in InCu$_{2/3}$V$_{1/3}$O$_3$ at least on a spacial scale of structural domains which, owing to their large size, has properties very similar to the long range AFM order in the infinite systems. Part of the results of this work has been published in Ref. [207].
7.3. Experiment

Clean stoichiometric powder of InCu$_{2/3}$V$_{1/3}$O$_3$ was synthesized from the respective oxides by a conventional solid-state technique as described in Ref. [68]. From it we prepared an ‘oriented’ sample by mixing the powder with epoxy and letting it harden in a magnetic field of 1 T. Owing to the specific anisotropy of the Cu$^{2+}$ g factor [67] the c axis of the powder particles in the sample was oriented perpendicular to the orientation axis (hereafter o axis) defined by the direction of the applied field, as confirmed by the x-ray diffraction.

ESR measurements were carried out with a standard X-band Bruker EMX spectrometer (Section 2.4.1) and also with the high-field/high frequency ESR spectrometer (Section 2.4.2). NMR data were collected on a Tecmag pulse solid-state NMR spectrometer with a 9.2 T superconducting magnet from Magnex Scientific. The NMR spectra were obtained by measuring the intensity of the Hahn nuclear spin echo versus magnetic field. The $T_1$ relaxation time was measured with the method of stimulated echo. Static magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer from Quantum Design.

7.4 ESR measurements at X-band frequency

In this section we discuss the ESR measurements at X-band frequency. As a starting point, we study the angular dependence of the ESR signal in the ab-plane. Then, we follow the temperature evolution of the ESR parameters for two different field directions; when the magnetic field $H$ is applied parallel to the orientation axis, $H \parallel o$-axis, and perpendicular to it, $H \perp o$-axis.

7.4.1 Angular dependence of the ESR signal

The ESR response of InCu$_{2/3}$V$_{1/3}$O$_3$ at room temperature for a magnetic field $H$ parallel to the orientation axis is characterized by a single lorentzian line profile. Whereas, when $H \perp o$-axis, a weak and narrow additional line is observed. For studying the anisotropy of the ESR signal we will focus on the main strong line and the additional line will be discussed later in the temperature dependence results.

The angular dependence of the g-factor at room temperature is presented in Fig (7.5). The anisotropy of the g-factor in the ab-plane can be fitted as:

$$g = \sqrt{g_\perp^2 \cos^2 \theta + g_\parallel^2 \sin^2 \theta}$$  \hspace{1cm} (7.4)

where, $\theta = 0$ when $H \perp o$-axis. By rotating the sample from $H \perp o$-axis to $H \parallel o$-axis, the g-factor differs from 2.16 to 2.23, which is in a good agreement with previous measurements in Ref. [67]. The anisotropy of the g-factor depends on the degree of the splitting of the d orbital states of Cu$^{2+}$ in the crystal electric field. In the most common coordinations of Cu$^2$ in oxides, such as octahedral, square-pyramidal or square-planar, the orbital ground state is $d_{x^2-y^2}$. In this case, $g_a > g_c > 2$ is expected. This is not the case of InCu$_{2/3}$V$_{1/3}$O$_3$
7.4. ESR measurements at X-band frequency

Figure 7.5: Angular dependence of the $g$-factor at room temperature. Solid red line is the fit according to Eq. (7.2).

Figure 7.6: The anisotropy of the linewidth ($\Delta H_{pp}$) at room temperature. Solid red line is the fit according to Eq. (7.3).

where, $g_a > g_c \geq 2$. Such anisotropy is expected only if the $d_{3z^2-r^2}$ orbital has the lowest energy, which is exceptional for the cuprates [67].

The anisotropy of the peak-to-peak linewidth ($\Delta H_{pp}$) is shown in Fig (7.6). For $H \perp o$-axis, the linewidth is maximum and amounts to 677 Oe. As we rotate the sample, the linewidth decreases gradually following the $\Delta H \propto (1 + \cos^2 \theta)$ angular dependence and reaches finally a minimum of 630 Oe for $H \parallel o$-axis. The linewidth anisotropy can be fitted by the equation:

$$\Delta H_{pp} = A(1 + \cos^2 \theta) + B$$  \hspace{1cm} (7.5)

where $A$ and $B$ amount to 61 Oe and 553 Oe, respectively. However, it is essential to notice that the ESR signal is clearly narrower than the signal observed in the previous measurements performed in Ref. [67] [see Fig (7.3)], this is due to the enhancement of the sample quality. By improving the homogeneity of the sample and decreasing the concentration of impurities and defects, the inhomogeneous broadening of $\Delta H_{pp}$ is reduced. In fact, the observation of the second narrow line, in this study, is possible only because of this decrease of ESR signal width.
7.4.2 Temperature dependence of the ESR parameters

- ESR intensity

The typical ESR signals at different temperatures and for \( H \parallel o \)-axis are shown in the left panel of Fig. (7.7). At room temperature, the ESR signal consists of a single Lorentzian line \( L_1 \). Below room temperature, the intensity of \( L_1 \) slowly increases and reaches a maximum at \( T \approx 200 \) K, where it starts to decrease as presented in the right panel of Fig. (7.7). At 120 K, a weak additional line \( L^* \) emerges. While \( L_1 \) intensity decreases rapidly below 120 K, \( L^* \) intensity gradually increases. Hence the relative weight of \( L^* \) increases by decreasing the temperature. These two well defined ESR lines vanish below \( T = 40 \) K, which is in agreement with Ref. [67] where the signal vanishes below 50 K. In the temperature range between \( 3.6 \) K \( \leq T < 40 \) K, the ESR response can be attributed to impurity effects. As expected for paramagnetic impurities, the intensity of the signal increases rapidly by decreasing the temperature. These impurities also present in the static susceptibility measurements and appear as a Curie-like tail at low temperatures. For \( H \perp o \)-axis, \( L_1 \) intensity has the same behavior as for \( H \parallel o \)-axis. However, in this field direction and in contrast to \( H \parallel o \)-axis, \( L^* \) is visible at room temperature. Decreasing the temperature accompanied by a slow increase of \( L^* \) intensity until reaching \( T = 200 \) K, where this increase speeds up and the intensity shows a peak at \( T = 58 \) K. Below this temperature the intensity decreases rapidly and the \( L^* \) vanishes as well as \( L_1 \) at 45 K. The intensity of the \( L^* \) at \( H \perp o \)-axis is much stronger than its intensity at \( H \parallel o \)-axis [Fig. (7.7), right panel].
The intensity of $L_1$ is two orders of magnitude stronger than that of $L^*$. Therefore, the total intensity of the ESR signal obviously follows the intensity of $L_1$. The temperature dependence of the intensity of $L_1$ line, and accordingly the total ESR intensity, is in a good agreement with the temperature dependence of the static susceptibility ($\chi_{\text{static}}$) at high temperatures (discussed later in the magnetization measurements). Whereas, $L_1$ intensity deviates gradually from $\chi_{\text{static}}$ below 200 K.

For $L^*$, the peak at $T \approx 58$ K suggests a possible relation with the finite size in-plane domains. In this case, $L^*$ line is attributed to the spins on the domains boundaries ($S_b$). Quantum Monte-Carlo calculations [68] suggested that the correlation length $\xi_s$ increases rapidly below 120 K, this associated with the decrease of the spin susceptibility and hence, $L_1$ intensity. By considering 'freelike' spins on the domains boundaries, the susceptibility of these spins is expected to follow Curie-like behavior. This is actually what we observe for $L^*$, where the intensity increases by decreasing the temperature, until reaching 58 K. However by approaching 50 K, $\xi_s$ gradually increases towards its maximum, and consequently, the spins on the domains boundaries are now strongly affected by the 'bulk' spin correlations. Below 58 K, and as the system approaches the opening of the AFM gap, the intensity of both $L_1$ and $L^*$ rapidly decreases until finally the two lines vanish. It is worth to note that the peak in $L^*$ intensity at 58 K complies with the anomaly that appears in $\chi_{\text{static}}$ at 50 K [68], which was also attributed to unsaturated spins on the domains boundaries.

- **g-factor**

The temperature dependence of the $g$-factor for $H \parallel o$-axis is presented in Fig. (7.8a). Cooling down the sample below room temperature, first, decreases the $g$-factor of $L_1$, where it reaches a minimum at $T \approx 100$ K. Whereas, for $40 < T < 100$, $g_{\parallel1}$ tends to increase gradually until the vanishing of the signal. The $g$-factor of $L^*$ shows a monotonic increase by decreasing the temperature below 128 K. Figure (7.8b) shows the temperature dependence of the $g$-factor for $H \perp o$-axis. In the temperature dependence of $g_{\perp1}$, one can again identify two regions; from room temperature down to $\approx 100$ K and $40 < T < 100$ K, where $g_{\perp1}$ decreases in these two regions but with two different rates. For $H \perp o$-axis, $g_{\perp*}$ shows a different behavior. In the beginning, $g_{\perp*}$ increases by decreasing the temperature down to 80 K, where it reaches a maximum and then decreases gradually.

The shift of the $g$-factor of $L_1$ for $H \parallel o$-axis and $H \perp o$-axis is expected for the development of short range ordering (SRO). In this case, the onset of this SRO is at $T \approx 100$ K, which is in agreement with growing correlations length $\xi_s$ below 120 K suggested by QMC calculations. In both field directions, the $g$-factor of $L^*$ has almost the same value and mounts to 2.06, which indicates that we are still dealing with Cu$^{2+}$ spins.

- **The linewidth $\Delta H_{pp}$**

The temperature dependencies of the ESR peak-to-peak linewidth $\Delta H_{pp}$ for $H \parallel o$-axis and $H \perp o$-axis are shown in Fig. (7.9). In both field orientations, the temperature
dependence of $\Delta H_{pp1}$ can be divided into three regions. For $150 \, \text{K} \leq T \leq 300 \, \text{K}$, decreasing the temperature decreases the width of $L_1$. However below $150$, $\Delta H_{pp1}$ increases rapidly and reaches a peak at $T \approx 60 \, \text{K}$ and then decreases again until the signal vanishes. Whereas, the width of $L^*$ again shows a monotonic increase when $H \parallel o$-axis. But when $H \perp o$-axis, $\Delta H_{pp}$ shows a peak at $T \approx 58 \, \text{K}$.

As mentioned before, in this study the ESR signal is narrower (almost 50 % at room temperature) than the previous study in Ref. [67]. This straightforwardly is the reason of the observation of the second ESR line $L^*$. Moreover, in the present study, the increase of the $\Delta H_{pp}$ with decreasing temperature is much smaller compared to that in Ref. [67]. In Ref. [67], $\Delta H_{pp}$ increased from 1 kOe at room temperature to about 2.8 kOe at 50 K (280 %). However, in our study, and for both field directions, the increase of $\Delta H_{pp}$ dose not exceed 50 %. The narrower signal width allow us to observe the peak in the $\Delta H_{pp}$ temperature dependence at 60 K, whereas, it is completely absence in measurements in Ref. [67].

Normally in the AFM ordered systems, the linewidth is characterized by the critical broadening as the temperature is lowered towards the ordering temperature. This critical
behavior can be identified in the case of Ref. [67]. However, in our measurements and since the signal broadening is much smaller, it is more convenient to discuss the broadening of the linewidth as a sign of the growing correlation within SRO 2D domains. According to this scenario, the peak at 60 K is the signature of the saturation of $\xi_s$. When $\xi_s$ reaches its maximum and then saturates, we now have well established 2D SRO domains.

The linewidth of $L^*$ increases almost 6 times by decreasing the temperature when $H \perp o$-axis. This would again illustrate the connection between the origin of $L^*$ and the spins on the domain boundaries ($S_b$). As the temperature is lowered, the growing spin correlation will logically affect the relaxation of $S_b$ spins. This, also, causes a ‘critical broadening like’ behavior for $L^*$ linewidth, which, indeed, we observe in our measurements.

X-band measurements reveal a characteristic temperature $T^* \approx 58$ K for the spin correlations in the InCu$_{2/3}$V$_{1/3}$O$_3$. This is in agreement with Quantum Monte-Carlo calculations and the minimum of $\chi_{static}$ at 50 K [68]. $L^*$ line, which is attributed to the spin at the domains boundaries, is more pronounced when the magnetic field is applied perpendicular to the orientation axis. This is unexpected, since our measurements were carried out in the $ab$-plane within the Cu-V-O layer. The vanishing of the ESR signal at 40 K could be indicative of an opening of the energy gap for resonance excitations, e.g., due to the establishment of the AFM order. Thus, we performed a high field / high frequency measurements in a broad frequency range extending into the sub-THz range. These measurements are presented in the next section.

### 7.5 High field ESR measurements

The high field ESR measurements performed for a magnetic field applied parallel to the orientation axis. In the beginning, we follow the temperature evolution of the ESR signal at $\nu = 332$ GHz and analyze the obtained data. Then, we present maps of the resonance absorption as a function of frequency and field at several temperatures.

#### 7.5.1 Temperature dependence of ESR signal at $\nu = 332$ GHz

The temperature dependence of the HF-ESR spectra at $\nu = 332$ GHz and for $H \parallel o$-axis is shown in Fig. (7.10). At $T = 180$ K, a single lorentzian line $L_1$ is observed with a $g$-factor $g_1 = 2.25$. This line can be easily related to the main line detected on the X-band experiment. By lowering down the temperature below to 120 K, a weak line $L_2$ appears in the left shoulder of $L_1$. For further decrease of temperatures, $L_1$ rapidly broadens and slightly shifts to lower resonance fields. Whereas, $L_2$ gains more intensity and also shifts to lower resonance fields. Below 40 K, $L_1$ and $L_2$ cross each other and inverse positions, hence, $L_1$ resonance field is smaller than $L_2$. For $T \leq 40$ K, the position of $L_1$ shifts strongly to lower magnetic fields and its width increases significantly until reaching its maximum at $T \approx 30$ K and then decreases again. Whereas, $L_2$ resonance field moves gradually towards higher magnetic fields. At $T = 8$ K, a third weak line $L_3$ is observed at low magnetic fields, this line is not shown in Fig. (7.10) and will be discussed in the frequency dependence measurements.
Figure 7.10: Temperature dependence of the ESR signal of InCu$_{2/3}$V$_{1/3}$O$_3$ at 332 GHz for $H$ $\parallel$ o-axis.

Figure 7.11: Temperature dependence of the ESR g-factor (upper panel) and linewidth (lower panel) at 332 GHz for $H$ $\parallel$ o-axis. Inset: Temperature dependence of the resonance field. Circles and triangles refer to $L_1$ and $L_2$ in Figure 6.

Figure (7.11a) illustrates the temperature dependence of both the g-factor and the resonance field ($H_{\text{res}}$). Such strong shift of the effective g-factor is typical for AFM ordered systems and originates from development of static internal fields [186] which shifts the resonance field $H_{\text{res}}$. The strong shift of $H_{\text{res}}$ begins at $T \approx 40$ K and matches very well with the vanishing of the ESR signal at X-band frequency. $L_2$ possesses a g-factor which is relatively close to the broad $L_1$ g-factor. Since the resolution of the ESR experiment to such close g-factors is decreasing at low frequencies, it is difficult to observe $L_2$ in the X-band measurements. It is also important to note the absence of $L^*$ in the high frequency measurements. Since $L^*$ is two orders of magnitude weaker than $L_1$ [see section (7.4.2)], the low microwave power at high field / high frequency measurements may result in a very small intensity of $L^*$. This accordingly makes it difficult to detect $L^*$.

The temperature dependence of ESR modes $L_1$ and $L_2$ widths ($\Delta H_1$ and $\Delta H_2$ respectively) is presented in the Fig. (7.11b). $\Delta H_1$ exhibits an abrupt variation at $T \approx 30$ K. Decreasing the temperature down to 30 K associated with the increase of $\Delta H_1$, especially
7.5. High field ESR measurements

for 30 K ≤ T ≤ 120 K where ΔH1 increases by almost one order of magnitude. Such increase is usually identified as the critical broadening of the linewidth which is caused by spin fluctuations due to the staggered magnetization in AFM correlated regions. This critical behavior can be described by:

\[ \Delta H(T) = \Delta H(\infty) + A \varepsilon^{-p} \]  

where \( \varepsilon = (T - T_N)/T_N \) and \( p \) is the critical exponent. The data is nicely fitted with \( T_N = 20 \) K and \( p = 1.05 \). We note here, that the value of \( p \) is an accepted value for 2D systems with an interplanar coupling which leads to 3D AFM fluctuations [186].

The strong shift of the \( L_1 \) resonance field and the rapid broadening of its linewidth strongly suggest the development of AFM ordering below \( T \approx 20 \) K, which is consistent with the kink in the static susceptibility measurements near to this temperature.

7.5.2 Frequency dependence of ESR signal

Now, it is rather interesting to study the frequency evolution of the these ESR lines. Since the signs of AFM ordering are present in the temperature dependence at both X-band frequency and 332 GHz measurements, it is expected to observe the antiferromagnetic resonance (AFMR) below the suggested ordering temperature (\( T_N \approx 20 \) K). Hence, the frequency dependence of the ESR signal at three different temperatures was studied. First, we investigated the development of the signal deeply in the AFM region at \( T = 8 \) K. Then, we move to \( T = 20 \) K at the ordering temperature. Finally, in the temperatures, we followed the frequency evolution of the signal at 60 K.

- AFMR at \( T = 8 \) K

Selected ESR spectra at various frequencies collected at \( T = 8 \) K for a magnetic field applied parallel to the orientation axis (\( H\parallel o \) axis) are shown in Fig. (7.12a). Several resonance modes are visible. At high frequencies three modes can be detected, \( L_1, L_2 \) and \( L_3 \). These modes shift towards higher fields by increasing the excitation frequency. At lower frequencies, the \( L_4 \) absorption mode can be observed which, in contrast, moves towards lower fields by increasing the frequency.

The evolution of \( L_1 - L_4 \) is summarized in the frequency-field (\( \nu \) vs. \( H \)) diagram in Fig.(7.12b). Notably, non of \( \nu(H)_{L_i} \) branches correspond to a paramagnetic resonance condition \( h\nu = g\mu_BH_{res} \). Resonance modes \( L_1, L_3 \) and \( L_4 \) are obviously gapped. Extrapolation of \( L_3 \) and \( L_4 \) branches to zero field yields an estimate of the gap value \( \Delta \approx 190 \) GHz. Mode \( L_4 \) softens with increasing the field strength revealing a specific critical field \( H_c \sim 5.5 - 6 \) T where \( \nu_{L4} \rightarrow 0 \). Above \( H_c \) mode \( L_2 \) emerges. In fact, taking the above estimate of \( \Delta \) and the value of the \( g \) factor for \( H\parallel o \) axis \( g = 2.23 \) obtained from the X-band measurements at high temperatures it is possible to reasonably model the \( L_1 - L_4 \) branches with the AFM resonance (AFMR) relations for a uniaxial two-sublattice antiferromagnet [208]. \( L_3 \) and \( L_4 \) can be represented as

\[ h\nu_{L3,L4} = \Delta \pm g\mu_BH_{res} \]  

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7.5. High field ESR measurements

Figure 7.12: Frequency dependence of the ESR signals at $T = 8$ K: (a) Selected spectra at different excitation frequencies $\nu$. Open circles, solid circles, triangles and squares indicate the resonance field $H_{\text{res}}$ of the resonance lines $L_1 - L_4$; (b) The $\nu$ vs. $H$ diagram of the resonance modes. The symbols correspond to respective lines in panel (a). Solid lines are model dependences.

where the plus and minus signs correspond to $L_3$ and $L_4$, respectively. $L_1$ and $L_2$ can be described as:

\[
\hbar \nu_{L_1}/g\mu_B = \sqrt{\Delta^2 + H_{\text{res}}^2} \quad (7.8)
\]

\[
\hbar \nu_{L_2}/g\mu_B = \sqrt{H_{\text{res}}^2 - \Delta^2} \quad (7.9)
\]

Apart from some systematic discrepancy for the $L_2$ branch the model agrees well with the experimental data. The behavior of $L_2$, $L_3$ and $L_4$ is typical for the situation when a magnetic field is applied parallel to some 'easy' axis of an antiferromagnet whereas $L_1$ corresponds to a 'hard' direction [208]. The field $H_c$ at which $\nu_{L_2}, \nu_{L_4} \to 0$ is the spin-flop field $H_c$ related to $\Delta$ as [208]

\[
H_c = (h/g\mu_B)\Delta \quad (7.10)
\]

With the above estimate of $\Delta$ one obtains $H_c \sim 6$ T. Since the magnetic field was applied in the honeycomb plane of InCu$_{2/3}$V$_{1/3}$O$_3$, there must be therefore some 'easy' direction in the plane that defines the AFM vector of two sublattices. Obviously the direction of this in-plane 'easy' axis of each powder particle is random in the sample, because specific in-plane crystallographic directions in our oriented sample are not defined. Therefore both 'easy' and 'hard' AFMR modes are present.

• AFMR at $T = 20$ K

The frequency-field diagram measured at $T = 20$ K is illustrated in Fig.(7.13). A clear signature of AFMR is present. At low frequencies, $L_4$ is much weaker comparing to that
7.6. NMR measurements

Further evidence for the occurrence of the AFM sublattices and related staggered magnetization has been obtained from the NMR measurements of $^{51}$V ($I = 7/2$) and $^{114}$In ($I = 9/2$) nuclei in InCu$_{2/3}$V$_{1/3}$O$_3$ [measured performed by E. Vavilova]. The V site is symmetric with respect to the Cu sites. Therefore the staggered fields from the honeycomb spin lattice should be compensated at this position. On the other hand, the In is positioned outside the hexagonal (Cu,V)-plane asymmetrically with respect to the Cu honeycomb ring. One could expect therefore an uncompensated staggered field at this position.

NMR signals from both type of nuclei have been experimentally detected. At high temperatures both spectra consist of a main line and a typical satellite structure arising...
due to the quadrupole interaction. Below 20 K, where AFMR modes are observed in the ESR experiment, the $^{51}$V NMR spectrum does not change qualitatively as shown in Fig. (7.15a,b). However, the $^{114}$In NMR signal experiences a remarkable change if measured in a magnetic field $H_{NMR}$ smaller than $H_c$. In Fig. (7.15c,d) the satellite line corresponding to the NMR transition between the quadrupole split nuclear levels $|\frac{1}{2}\rangle$ and $|\frac{3}{2}\rangle$ of $^{114}$In is shown for $T = 35$ K and 10 K. At $T = 35$ K the satellite is unsplit regardless the field of the measurement.

However, at $T = 10$ K the signal splits in two components for $H_{NMR} < H_c$ whereas it remains unsplit for $H_{NMR} > H_c$. This observation strongly supports the scenario of compensated collinear AFM sublattices at $H < H_c$ which turn into the spin flop state at $H > H_c$. Remarkably, though the $^{51}$V NMR lines remain unsplit at low temperature the longitudinal nuclear relaxation rate $^{51}T_1^{-1}$ shows a substantial field dependence. As can be seen in Fig. (7.15e) it decreases by a factor of 7 by approaching the $H_c$ and shows no field dependence at $H_{NMR} > H_c$. The sensitivity of $^{51}T_1^{-1}$ to the spin structure may be related to magnetic anisotropy that defines a specific ‘easy’ orientation in the honeycomb spin plane and possibly produces a small uncompensated fluctuating field at the V nuclei in the collinear phase that become ineffective for the longitudinal relaxation after the spin reorientation has occurred.
7.7 Magnetization measurements

Motivated by the findings of the local ESR and NMR techniques we have carried out the temperature and field dependences of the magnetization on an oriented powder sample of \( \text{InCu}_{2/3}V_{1/3}\text{O}_3 \) for a magnetic field applied parallel to the \( o \)-axis.

7.7.1 Temperature dependence of the static susceptibility

The temperature dependence of static susceptibility was performed at three different magnetic fields; \( H = 0.3 \) T similar to resonance field at X-band measurements, \( H = 1 \) T the field of the measurements introduced in Ref. [68] and \( H = 7 \) T which is above the spin reorientation field suggested by the HF-ESR measurements.

The temperature dependences of the static susceptibility \( \chi(T) \) at different fields are shown in Fig. (7.16) and normalized to the susceptibility at room temperature. These measurements are compared to the ESR intensity which is represented by open circles. In general, our results agree with the measurements in Ref. [68]. However, the present measurements are more sensitive to the kinks which appear at low temperatures. The temperature derivative of \( \chi(T) \) clearly spots the two kinks \( k_1 \) and \( k_2 \) as shown in Fig. (7.16 inset). At \( H = 0.3 \) T, \( k_1 \) and \( k_2 \) are observed at \( T \approx 26 \) K and \( T \approx 48 \) K respectively. Increasing the magnetic field smears gradually \( k_1 \). The second kink \( k_2 \) matches very well with vanishing of the ESR signal and can be identified as a signature of the domain boundaries suggested in Ref. [68]. This kink becomes more pronounced by increasing the applied magnetic field.

7.7.2 Field dependence of the magnetization

The field dependence of the magnetization \( M(H) \) up to \( 7 \) T at different \( T \) is presented in Fig. (7.17). The curvature of the \( M(H) \) at low fields is likely due to a small amount of free-like spins, which also yield a Curie-like tail in the \( T \) dependence of \( \chi(T) \). The \( M(H) \) dependence at the lowest temperature \( T = 2 \) K is characterized by a pronounced step-like
increase of $M$ at $H \approx 5.7$ T. It can be straightforwardly interpreted as a critical field $H_c$ for
the spin reorientation, in a nice agreement with ESR and NMR data. The derivative of the
field dependence of the magnetization is shown in Fig. (7.18). The spin reorientation field
is clearly expressed by a peak at $H_c \approx 5.66$ T for $T = 2$ K. By increasing the temperature
the peak continuously broadens, slightly shifts towards higher fields [Fig. (7.18 inset)] and
finally smoothly vanishes above $\sim 20$ K.

7.8 Discussion

In the X-band measurements, we observed two ESR lines, $L_1$ and $L^*$. $L^*$ can only be
observed at the X-band measurements because it has a small intensity. We found a character-
istic temperature $T^* \approx 58$ K for the $L^*$ line [see Fig.(7.7) and Fig.(7.9)]. This tempera-
ture can be related to the spin correlations in the finite size in plane domains suggested by
the Quantum Monte-Carlo calculations [68], which imply an in-plane structural disorder.
However, the vanishing of the ESR signals at 40 K is an important indicator of the opening
of the AFM gap.

The temperature dependence of the ESR signal at $\nu = 332$ GHz gives another evidence
on the AFM ordering. The strong shift of ESR resonance field along with the rapid
increase of the linewidth by decreasing the temperature towards $T_N$ are quite typical for
the LRO systems. Indeed, the observation of AFMR in the frequency dependence of
the ESR signal below $T_N$ is a decisive sign of the establishment of the antiferromagnetic
ordering. Moreover, the softening of the AFMR, [see $L_4$ mode in Fig.(7.12)], reveals a
spin reorientation at $H_c \sim 6$ T. The ESR measurements are strongly supported by the
$^{114}$In NMR results. The splitting of the $^{114}$In NMR signal below the $T_N$ is in agreement
with the compensated collinear AFM sublattices scenario. The field dependence of the
7.8. Discussion

7. 2D honeycomb lattice InCu$_{2/3}$V$_{1/3}$O$_3$

Figure 7.19: $T$-dependence of the staggered magnetization $m_{st}$ of the honeycomb lattice with interplane couplings $J_z = 0.1, 0.2, 0.3$ and $0.4J_{afm}$ for the system size $14 \times 28 \times 14$. Inset: $m_{st}$ vs. $T/J_{afm}$ for $J_z = 0.4J_{afm}$ for different system sizes. Calculated by U. Löw.

The magnetization is in agreement with ESR measurements and straightforwardly suggests a spin reorientation at $H_c \sim 5.66$ T when $T \leq T_N$. Thus, the results of three different techniques strongly suggest the formation of collinear AFM Néel sublattices in the $S = 1/2$ honeycomb plane in InCu$_{2/3}$V$_{1/3}$O$_3$ at a finite temperature $T_N \sim 20$ K.

Generally, the reported absence of the magnetic anomaly in the specific heat $C_p$ in Ref. [68], does not exclude the occurrence of the magnetic phase transition in a low-dimensional system due to residual interactions in the third dimension. If the ordering temperature $T_N$ is substantially smaller than $J_{afm}/k_B$, most of the magnetic entropy $S_{mag}$ is already gone at $T \sim J_{afm}/k_B$ due to the 2D in-plane AFM correlations, just as it happens in InCu$_{2/3}$V$_{1/3}$O$_3$ [68]. Thus an additional change of $S_{mag}$ at $T_N$ might be small and not visible in the $C_p$ owing to a substantial phononic background.

The question arises if this 3D situation is realized in InCu$_{2/3}$V$_{1/3}$O$_3$ despite the occurrence of disordered finite size structural domains. To address this issue we have performed a computational study of a finite size spin-1/2 clusters on the honeycomb lattice by means of a continuous Euclidean time Quantum-Monte-Carlo algorithm that includes the coupling in the third dimension [66]. We find that the Néel type structure and the staggered magnetization $m_{st}$, otherwise present in the 2D case only at $T = 0$, develops in a rather narrow interval at a finite temperature that depends on the strength of the interlayer coupling $J_z$ [calculation performed by U. Löw]. As shown in the main panel of Fig. (7.19) a temperature interval where $m_{st}(T)$ exhibits a step-like increase is mainly determined by the value of $J_z$ whereas the sharpness of this step increases with the increase of the cluster size [inset of Fig. (7.19)]. Note that in InCu$_{2/3}$V$_{1/3}$O$_3$ the size of in-plane structural domains amounts to $\sim 300$ Å, (Ref. [68]) which corresponds to $\sim 90 \times 90$ spin sites, i.e.
a much larger number than in our model calculation. Thus one should expect quite a sharp set up of the two-sublattice collinear AFM Néel spin structure and the occurrence of the staggered magnetization in InCu$_{2/3}$V$_{1/3}$O$_3$ that experimentally would be difficult to discriminate from a true magnetic phase transition expected in the thermodynamic limit.

Finally, regarding modelling of the finite size systems, it is appropriate to mention here that a theoretical calculation in the framework of the (anisotropic) Heisenberg model of the ESR response of the AFM cluster comprising 8 spins only already yields AFMR modes of a substantial intensity that for the ‘easy’ axis direction have qualitatively similar properties as those shown in Fig. (7.12) [188].
7.9 Conclusion

In summary, by studying ESR, NMR and static magnetization of the oriented powder sample of the honeycomb spin-1/2 lattice compound InCu$_{2/3}$V$_{1/3}$O$_3$ we have found strong experimental evidence for the formation of the Néel type collinear AFM spin structure at temperatures below $\sim 20$ K and a respective development of the staggered magnetization. A reorientation of spin sublattices in a magnetic field of $\sim 5.7$ T has been clearly identified in the magnetization and magnetic resonance measurements.

Quantum Monte-Carlo calculations of the spin clusters of the coupled layers with the honeycomb topology reveal a sharp development of the staggered magnetization at a finite temperature that in the thermodynamic limit would correspond to a phase transition to the AFM long-range ordered Néel state. This explains the robustness of the low temperature AFM spin structure despite the low spin coordination number, the pronounced structural two dimensionality as well as the occurrence of the finite size incoherent structural domains in InCu$_{2/3}$V$_{1/3}$O$_3$. In view of the present results, neutron diffraction experiments addressing the magnetic structure of InCu$_{2/3}$V$_{1/3}$O$_3$ would be highly desirable.
Summary

The main focus of this thesis is the investigation of the magnetic properties of the low dimensional spin systems using electron spin resonance (ESR) spectroscopy. A tunable high-field / high-frequency (HF) ESR in static fields up to 15 T was used to obtain insights into the complex and rich physics of these systems. Throughout the thesis, we systematically studied one dimensional, quasi-one dimensional and two dimensional spin systems.

A detailed analysis of temperature, field and frequency dependences of the ESR spectra allowed to highlight the low dimensional behavior, the nature of the ground state and magnetic anisotropy in the studied systems. To achieve a better understanding of the different features observed in our ESR measurements, further experimental techniques such as nuclear magnetic resonance (NMR), magnetization, specific heat and conductivity measurements were employed. The obtained results from these various methods were analyzed in the framework of theoretical models.

The complex transition metal oxide Ir2V5O15 contains well-defined zigzag vanadium $S = 1/2$ chains. An unusual anisotropic thermal contraction of the lattice changes significantly the overlap integrals and the character of magnetic intra- and interchain interactions. Our experimental results reveal that the interplay of structural and electronic changes induces a transition from a semiconducting behavior with ferromagnetic correlations at high temperatures above a crossover temperature $T^* \sim 120$ K to the insulating regime with predominantly antiferromagnetic interactions between vanadium localized moments at low temperatures.

The magnetic resonance data clearly indicate the slowing down of the spin-spin correlations by approaching a characteristic temperature $T_{SRO} \sim 20$ K and suggest a frustrated glassy-like magnetic ground state without long-range order. Furthermore, transitions between different spin configurations give rise to an additional gapped ESR mode which is not expected in a spin-1/2 chain without frustration. The ESR gap value corresponds to an energy separation $\Delta \sim 5$ K between the ground state $S = 1/2$ configuration of a frustrated spin triangle and its excited $S = 3/2$ state.
The spin-chain spin ladder compound Sr$_{14}$Cu$_{24-x}$Zn$_x$O$_{41}$ ($0 \leq x \leq 0.75$) was studied using ESR, static magnetization and conductivity measurements. ESR measurements reveal a remarkable influence of the hole dynamics on the Cu-spin relaxation for all values of $x$. Surprisingly, the temperature dependence of the ESR linewidth suggests a gradual increase of the hole mobility upon Zn doping.

This is consistent with the conductivity measurements $\sigma(T)$ which imply a significant increase of $\sigma$ with increasing Zn content. The ESR intensity and the static magnetization show the conservation of a spin-gap like feature for all Zn concentrations, which may reflect the survival of the dimerized ground state upon Zn doping. These results emphasize the crucial role of the interplay between the chain and ladder subsystems on the physical properties of this quasi-1D system.

Copper nitrate monohydrate Cu(NO$_3$)$_2$·H$_2$O is a new low dimensional $S=1/2$ system, which shows a significant interplay between structure and magnetism. The temperature dependence of the ESR response for different field directions indicates a substantial magnetic anisotropy and occurrence of different exchange paths in the Cu layers. The anisotropy of the ESR measureables reveals a two dimensional nature of the Cu$^{2+}$ layers in this material. At low fields, a phase transition of antiferromagnetic nature can be identified.

However, ESR and NMR studies reveal a broad $(T,H)$-parameter range above the AFM ordering phase boundary $T_N(H)$ where pronounced quasi-static magnetic correlations dominate the magnetic resonance response. Various spin gap excitations have been observed using high field ESR and NMR. These features are discussed by considering the ground state and magnetic excitations of random spin clusters which are realized in Cu(NO$_3$)$_2$·H$_2$O.

In nitrosonium nitratocuprate (NO)[Cu(NO$_3$)$_3$], the topology of the magnetic interactions of the copper spins suggests that it could be a realization of the so called ‘confederate flag model’ (Nersesyan-Tsvelik model). Indeed, the constant ESR resonance field over the whole temperature range, 3.4 K $\leq T \leq 300$ K, clearly indicates the absence of long range magnetic ordering down to 3.4 K, which is in agreement with the specific heat measurements down to 1.8 K. Also, the ESR intensity and the static susceptibility reveal a pronounced low dimensional character of the spin susceptibility. Furthermore, the temperature dependence of width of the ESR signal manifests a considerable influence of Dzyaloshinskii-Moriya interactions in this system.

InCu$_{2/3}$V$_{1/3}$O$_3$ is the experimental realization of the two dimensional $S=1/2$ honeycomb model. Our experimental results give evidence for a Néel-like antiferromagnetic ground state below $T_N \sim 20$. In the ESR measurements, the signal vanishes at the X-band frequency (9.5 GHz) below 40 K. Whereas, at high frequencies (332 GHz), we find a strong shift of the resonance field and a rapid increase of the linewidth by decreasing the temperature down to $T_N$. Finally, in the frequency - field diagram we clearly observe antiferromagnetic resonances at $T \leq T_N$. In agreement with our ESR results, the $^{114}$In NMR signal splits below $T_N$. Both the AFMR and the field dependence of the magnetization suggest a spin reorientation at a magnetic field $\sim 5.7$ T for $T \leq T_N$. 

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Consistent with our experimental observations, Quantum Monte-Carlo calculations reveal the formation of the staggered sublattices with substantial sublattice magnetization at a finite temperatures due to the interlayer coupling in a finite-size honeycomb spin domain. Thus, the results of three different techniques strongly suggest the formation of collinear AFM Néel sublattices in this material despite the low spin coordination number, the structural two dimensionality and in-plane structural disorder.

The results of this thesis clearly show that ESR is a very informative technique for the investigation of low dimensional spin systems. Not only it has the ability to distinguish between the paramagnetic and the ordered states but also it is a powerful and extremely sensitive tool for probing magnetic excitations. It enables to study spin correlations and their temperature and field dependence, as well as to determine energy gaps in the studied systems.
Bibliography


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Publication List

1. *Insulator to semiconductor transition and magnetic properties of the one-dimensional $S = 1/2$ system In$_2$VO$_5$.*

2. *Interplay between structure, transport and magnetism in the frustrated $S = 1/2$ system In$_2$VO$_5$.*

3. *High Field ESR Study of the new low dimensional $S = 1/2$ system: Cu(NO$_3$)$_2$·H$_2$O.*

4. *Finite size effects and magnetic order in the spin-1/2 honeycomb lattice compound InCu$_{2/3}$V$_{1/3}$O$_3$.*
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