Experimental study of clean and dirty quantum magnets

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The only true voyage of discovery [...] would be not to visit strange lands but to possess other eyes.

Marcel Proust, In Search of Lost Time
Vol. V: The Captive (1923)
Abstract

Quantum many-body physics is one of the most active topics in modern solid state physics. While the fundamental laws governing the physics in condensed-matter scale are well known, when enough interacting particles are put together, the emergent physics is usually different. In many cases it leads to unconventional ground states and exotic excitation spectra. Despite the development of new computational techniques and vast improvements in the sheer computational power, the Hilbert space expands exponentially and quickly becomes intractable. Moreover, even if the computational studies can be carried out, they often provide just the final result but no intuitive understanding of the complex problems. Therefore, smart effective theories together with a pocketful of tricks are needed to understand, explain and predict the many phenomena observed. In order to validate such theories, experimental studies are crucial. Additionally, new phenomena observed experimentally often lead way to new theoretical ideas and a better understanding of the complex physics.

This thesis aims to provide experimental traction to the study of many body physics in magnetic insulators. It is concentrated on magnetic systems in low dimensions. A number of well-known theoretical models are realized in condensed matter systems. The ones studied here range from one dimensional models — spin chains and spin ladders — to two dimensional lattices. When such models are realized in real life materials, they often lend themselves well to perturbations. In this thesis, such an opportunity is often taken either by chemical substitution or external pressure.

As a first model system, a Heisenberg Antiferromagnetic (HAF) $S = 1/2$ chain is studied. The compound SrCuO$_2$ is one of the best realizations of this model. Even then, it orders at low temperatures due to residual three dimensional interactions. A very sensitive muon spin rotation technique is employed to study the ordering. The nature of the magnetic ground state and the ordering temperature is determined as a prerequisite to studying the effects of perturbations. Then, some of the Cu$^{2+}$ ions with $S = 1/2$ are replaced by Ni$^{2+}$ ions with $S = 1$. This procedure fragments the spin chains and leads to drastic changes in the ground
state and a reduction of the ordering temperature. A range of impurity concentrations is studied to complete the picture.

Having established the effects of disorder on the ground state of the HAF $S = 1/2$ chain, the spectral properties are investigated. It has been theoretically predicted that fragmenting the chains leads to a gapped spin excitation spectrum. Use of inelastic neutron scattering allows investigation of such effects. First, a simplest realization of a HAF $S = 1/2$ chain Sr$_2$CuO$_3$ is studied. It is found that the depletion of the low energy states indeed occurs in a form of a pseudogap, magnitude of which scales with the number of broken links in the chain. Surprisingly, it is also found that the pseudogap appears even when impurities are introduced outside of the chain, when Sr$^{2+}$ is replaced by Ca$^{2+}$. This suggests that the gapless state is very delicate and can be affected by various perturbations. Similar results are obtained by studying the SrCuO$_2$ spin chain system. It is found that the pseudogap also develops upon introduction of impurities but has a magnitude which is almost doubled compared to the expected number of chain link brakes. It is attributed to the particular structure of SrCuO$_2$ where two chains are in the vicinity of each other and a defect in one acts as a scattering centre for the other one as well.

As a second model system, Heisenberg $S = 1/2$ two leg ladder is investigated. The magnetic excitations in a strong-rung ladder model system — an organometallic compound Cu(C$_8$H$_6$N$_2$)(Cl$_{1-x}$Br$_x$)$_2$ — are studied using Raman spectroscopy. By measuring the two-magnon scattering it is found that the spectral properties can be tuned when chloride is replaced by bromide. Additionally, an alternative method to modify the system — external pressure — is employed. It opens the opportunity to extend the tuning range.

Another spin ladder — a strong-leg model system (C$_7$H$_{10}$N)$_2$CuBr$_4$ is also investigated using Raman technique. At low temperatures, excitations are found to appear at an energy transfer much higher than the exchange interaction in this ladder material. They are identified as unconventional phonon-assisted magnetic excitations and allow studying magnetic properties by measuring high energy excitations.
Finally, a quasi two dimensional gapped quantum paramagnet \((C_4H_{12}N_2)Cu_2Cl_6\) is studied. Recently, pressure induced phase transitions were reported to take place in this compound. Raman spectroscopy allows probing a wide range of pressures. The experiments reveal a marked change in the excitation spectrum as the system undergoes the two phase transitions.
Kurzfassung


Als erstes Modellsystem wird die Heisenberg antiferromagnetische (HAF) $S = 1/2$-Kette untersucht. Die bekannte Verbindung SrCuO$_2$ ist eine der besten Verfügbaren Realisierungen dieses Modells. Aufgrund eines Rests dreidimensionaler Wechselwirkungen ordnet dieses System bei tiefen Temperaturen. Um
diesen Übergang zu einem geordneten Grundzustand zu untersuchen wird die sehr empfindliche Myonenspinrotation verwendet. Als Grundvoraussetzung für die Untersuchung des Einflusses von Störungen wurde zunächst die Art des magnetischen Grundzustands und die Ordnungstemperatur bestimmt. Als Störung werden einige der Cu$^{2+}$-Ionen, welche $S = 1/2$ tragen durch Ni$^{2+}$ mit $S = 1$ ersetzt. Dies fragmentiert die Spinketten und führt sowohl zu einer drastischen Veränderung des Grundzustands als auch zu einer Reduktion der Ordnungstemperatur. Um den Einfluss dieser Art der Störung systematisch zu untersuchen, wurde eine Reihe verschiedener Konzentrationen von Ni-Störstellen untersucht.


Um auf SrCuO$_2$ zurückzukommen, wurde zwar festgestellt, dass sich ebenfalls eine Pseudolücke öffnet, deren Magnitude jedoch fast doppelt so gross ist wie aufgrund der Zahl der Störstellen erwartet. Dies wird auf die spezielle Struktur von SrCuO$_2$ zurückgeführt, bei der zwei Ketten jeweils sehr nahe sind und eine Störstelle in der einen auch als Streuzentrum für die andere agiert.

Als zweites Modellsystem wurde die Heisenberg $S = 1/2$-Zweiholmenleiter untersucht. Das Spektrum der Organometallischen Verbindung Cu(C$_8$H$_6$N$_2$)(Cl$_{1-x}$Br$_x$)$_2$ wurde mittels Ramanspektroskopie untersucht. Die Untersuchung des Zweimagnonen-Spektrums führte zutage, dass die spektralen Eigenschaften durch die Ersetzung von Cl durch Br gestimmt werden können. Als alternativer Weg, um das System zu verändern, wurde externer Druck verwendet, was die Möglichkeit
eröffnet, den Stimmbereich zu vergrößern.

Eine weitere Spinleiter \((\text{C}_7\text{H}_{10}\text{N})_2\text{CuBr}_4\) wurde mittels Raman-Spektroskopie untersucht. Obwohl die Energieskala in diesem System zu klein ist, um magnetische Anregungen direkt zu beobachten, wurden von Phononen assistierte magnetische Anregungen beobachtet, was es erlaubte, die magnetischen Eigenschaften durch Messung hochenergetischer Anregungen zu untersuchen.

Zum Schluss wurde der quasi-2D-Quantenparamagnet \((\text{C}_4\text{H}_{12}\text{N}_2)\text{Cu}_2\text{Cl}_4\) untersucht. Kürzlich wurde in dieser Verbindung ein druckinduzierter Quantenphasenübergang entdeckt. Durch Ramanspektroskopie ist es möglich, eine größere Bandbreite von Drücken zu untersuchen. Diese Experimente zeigten eine kontinuierliche Veränderung des Anregungsspektrums, was einer erheblichen Modifikation der Austauschkonstanten entspricht.
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Chapter 1

Introduction

1.1 There is Plenty of Room in Low Dimensions

Magnetic insulators have been essential model systems in the study of physics, from the field of phase transitions, to ordering into intricate magnetic structures [1–3]. While it is an interesting and fruitful field in higher dimensions, the most fascinating processes happen for small spin values in low dimensions [4, 5]. For many years, the low dimensional quantum magnets have been a domain of mainly theoretical work [6–9] with a number of exciting properties predicted, such as quantum spin liquid behavior [7] and fractional excitations [10] as well as spectral gap dependence on the spin number [11, 12]. Over the last few decades, advances in the technology of crystal growth have allowed for designing and growing materials which are good realizations of fundamental quantum models [13–17] and enabled the field to be shifted to the experimental realm. Moreover, novel instrumentation has recently allowed performing previously inaccessible experiments, such as direct measurements of whole excitation spectra using modern time-of-flight neutron spectrometers [18, 19].

At the moment of writing, many of the predictions for pure quantum magnets have been experimentally observed and well established. Additionally, new computational techniques have allowed direct quantitative comparison between the experiments and the theory. Present state of the field allows taking the next step — perturbing such systems to reveal new phenomena. In this thesis, such approach is taken and many of the archetypical model systems are modified.
1.2 Outline of the Thesis

In the first part of thesis, spin chains are fragmented and the effects on the static and dynamic properties are studied. Attention is then shifted to the spin ladders and the effect of altering the exchange constants along the relevant directions by chemical substitution and hydrostatic pressure is explored. Finally, a complex two dimensional lattice of spins with dimer elements is pressurized in order to drive it through a quantum phase transition and study the effects on the spectrum. The detailed structure of this thesis is described in the following paragraphs.

1.2 Outline of the Thesis

The present thesis reports on a series of experiments on selected model quantum magnets, probing previously unexplored properties. While the bulk of the thesis concerns with the new research findings, a few introductory chapters are included in order to increase the readability of the work and to set the stage for the results of the present work. In chapter 2, several main concepts of quantum spin systems in low dimensions are presented followed by a few remarks on quantum phase transitions in chapter 3.

Chapter 4 introduces the main experimental techniques that were used in the present work. Neutron scattering is presented first, since it is arguably the most powerful technique to study magnetism in the solid state. However, it requires a neutron source and rather large crystals which are not always available. Therefore, a large part of the measurements were performed using muon spin rotation techniques (to probe the magnetic ordering) and Raman spectroscopy (to study the excitations). These techniques are described in the second half of the chapter.

The principal part of this work starts with chapter 5. The magnetic ordering in a model spin chain material SrCuO$_2$ is investigated. First, a clean system is investigated to establish the nature of the ordering and to get an estimate on the extent of one-dimensionality. While it has been studied before, some of the reports in the literature are inconsistent. A careful study using very clean samples allows attributing previous inconsistencies to the quality of the samples and completes a coherent picture of the static properties of SrCuO$_2$. The attention is then shifted to the previously unstudied effect of site dilution in this system. A highly inhomogeneous magnetic ordering is observed upon
introduction of a very small amount of impurities. The ordering temperature is found to decrease drastically in the diluted system.

Dynamic properties of diluted spin chains are discussed in chapter 6. Two different spin chains are investigated — Sr$_2$CuO$_3$ and SrCuO$_2$. As the chains are diluted, the low energy excitations are found to be suppressed and a spin pseudogap opens up. This is due to the fragmentation of the spin chains and the confinement of spinons within the fragments. As the chains get fragmented, the universal scaling behavior predicted for such chains breaks down. However, by taking into account the pseudogap, the scaling can be restored and a good data collapse is found for both spin chains over a wide temperature range.

Chapter 7 focuses on a different model system — a spin ladder. First, a whole substitution series of spin ladder material Cu(C$_8$H$_6$N$_2$)(Cl$_{1-x}$Br$_x$)$_2$ is investigated using Raman spectroscopy. Recent studies have suggested that by replacing the halogen ions responsible for some of the exchange paths, the magnetic properties can be tuned continuously. In the present work, the excitations are probed directly. It is found that the spectral properties are modified continuously by the halogen substitution. Moreover, hydrostatic pressure allows the range of tunability to be extended and to move the system from the strong-rung regime towards an isotropic ladder. In addition, a very well characterised strong-leg ladder (C$_7$H$_{10}$N)$_2$CuBr$_4$ is studied. The energy scale is too low to access the magnetic excitations directly but due to an unconventional phonon-assisted magnon scattering, magnetic excitations can be also probed in this system. This opens an opportunity to study the coupling between the lattice and magnetic moments in quantum spin ladders.

A quasi two dimensional quantum spin system (C$_4$H$_{12}$N$_2$)Cu$_2$Cl$_6$ is studied in chapter 8. Motivated by the recent discovery of the pressure-induced quantum phase transition in this material, excitations at different pressures are probed using Raman spectroscopy. The magnetic scattering changes markedly as the pressure is increased. The spin gap is reduced and subsequently closed upon applying pressure. The excitation spectrum is observed to have different lineshapes in the different magnetic phases.

Finally, the results and conclusions of this thesis are summarized in chapter 9. This work is finalised by discussing possible future directions and follow-up studies, which would expand our understanding of quantum magnets even further.
1.2 Outline of the Thesis
Chapter 2

Magnetism in Low Dimensions

The behavior of magnetic systems changes dramatically when the number of dimensions becomes smaller than the familiar three. Here, an introduction to the low dimensional magnetism is provided, together with a few example lattices relevant for the present thesis.

2.1 What Happens to Magnetism at Low Dimensions

In common magnets, the magnetic moments arrange themselves to form long-range magnetic structures upon lowering the temperature. Probably the most well-known magnet is lodestone Fe$_3$O$_4$, an iron ore which has an ordering temperature of 858 K and therefore is magnetic at room temperature [20]. The spontaneous magnetization that appears in lodestones has been harnessed in technology for centuries. Spontaneous magnetization appears in ferromagnets, such as nickel and cobalt, as well as in ferrimagnets, such as the lodestone.

The issue is different in the case of antiferromagnets. While a phase transition takes place and there is magnetic ordering, no spontaneous magnetization exists. The ground state of alternating up and down arrangement, proposed by Néel [21] explains most of the properties of classical antiferromagnets, such as MnF$_2$. However, it turns out that it is not a true ground state of an antiferromagnet
2.1 What Happens to Magnetism at Low Dimensions

Figure 2.1: Schematics of the lattices studied in this thesis. A spin chain (a) has only one relevant exchange constant, whereas in both, two dimensional lattice (b) and spin ladder (c) more exchange paths are present.

[22–24]. A ground state has, however, a large projection onto the Néel state. This leads to an appearance of magnetic Bragg peaks at the antiferromagnetic zone center, as seen in neutron diffraction experiments [25]. Therefore, in three dimensions, especially for systems with large spin values, the Néel state is usually an adequate description of a ground state.

The magnetic properties become increasingly more complicated as the number of dimensions is lowered. It has been rigorously shown by Mermin and Wagner that Heisenberg systems with finite-range interactions cannot spontaneously break symmetry at finite temperatures in one and two dimensions [26]. Therefore such systems do not develop long range order.

The fact that the systems do not order at low temperatures does not make them less interesting. On the contrary — the excitations become more exotic than the usual spin waves.

In this thesis, three types of systems are studied — spin chains, spin lattices with dimer elements and spin ladders, schematics of which are shown in Fig. 2.1. The main aspects of these systems are introduced in the next few paragraphs.
2.2 Spin Chain

The Heisenberg antiferromagnetic spin $S = 1/2$ chain is one of the most well known models in magnetism. It is defined by only one exchange constant $J$ and is described by the following Hamiltonian:

$$H = J \sum_j S_j S_{j+1}. \quad (2.1)$$

Here, $S_j$ is the spin operator acting on the $j$’th spin. The ground state was shown to have no long range order already in 1931 [6]. The basic excitation in a spin chain has an $S = 1/2$ unlike the conventional $S = 1$ spin wave [10]. A handwaving picture of such an excitation, called a spinon, can be constructed by first thinking of an Ising chain. In an Ising chain, the fundamental excitations are kinks — domain walls in the chain. A spinon can be thought of as an isotropic limit of the domain wall in the Ising chain.

In a neutron scattering experiment, only the $S = 1$ transitions can be induced, and therefore, the spinons are only observed in pairs, with the spectrum consisting of a continuum, bounded by kinematic limits, which have been shown to be [27]:

$$\frac{\pi}{2} J |\sin(q)| \leq \hbar \omega(q) \leq \pi J |\sin(q/2)|, \quad (2.2)$$

where the momentum transfer along the chain $q$ defines the energy extent of the scattering $\hbar \omega(q)$. The exact dynamical structure factor for the two spinon continuum has been calculated in [28]. Additionally, the contribution of four-spinons has been estimated by Caux et al. [29]. It was shown that it is important to use the exact solutions for the high energy part of the scattering continuum [30, 31]. However, the expressions for the exact solutions are cumbersome and therefore for low energies, the semi-empirical Müller ansatz [32], provides an accurate description which allows using it for comparison with neutron scattering experiments [33]. It can be expressed using the upper ($\omega_U$) and lower ($\omega_L$) boundaries of the scattering continuum and two Heaviside step functions, denoted by $\theta$. In order to scale the ansatz to absolute value of the dynamical structure factor, the scaling constant $A$ also needs to be introduced which is obtained from the sum rules of magnetic scattering [32]. The full expression reads:
2.3 Dimer Lattice

\[ S_{MA}(q, \omega) = \frac{A}{2\pi\hbar} \frac{\theta(\omega - \omega_L(q))\theta(\omega_U(q) - \omega)}{\sqrt{\omega^2 - \omega_L(q)^2}}. \] (2.3)

As a final note on the spin chains, it is worthwhile mentioning that they host universal scaling properties due to quantum criticality [34]. This property will be described in the following chapter.

2.3 Dimer Lattice

Another example of a quantum magnet is a network of spin dimers — antiferromagnetically coupled pairs of \( S = 1/2 \) spins. A completely isolated spin dimer has a singlet ground state and an excitation gap separating it from the triplet. If a dimer is coupled to other dimers, it can be described by the following Hamiltonian [35]:

\[ H = J_D \sum_j \left( S_{j,1} S_{j,2} \right) + \sum_{j \neq k, m, n} J_{jkmn} \sum_j S_{j,m} S_{k,n}, \] (2.4)

where \( J_D \) is the intradimer exchange constant and \( J_{jkmn} \) is the interdimer exchange constant. \( j \) and \( k \) enumerates the dimers, whereas \( m \) and \( n \) correspond to the spin within the dimer. The isolated dimer would have no dispersion, but due to interdimer exchange, the excitations (often called triplons) can hop along the lattice. Assuming a square lattice of dimers with a uniform interdimer exchange constant \( J_{ID} \), the dispersion can be written as:

\[ \hbar \omega(q) = J_D + J_{ID} \left( \cos(q_x) + \cos(q_y) \right). \] (2.5)

Weakly coupled dimers have been a fertile ground for solid state physics, since a dimer lattice is one of the simplest toy models, which under certain conditions exhibits very interesting physics, such as Bose-Einstein condensation of magnons [36] and pressure-induced quantum criticality [37, 38].
2.4 Spin Ladder

Another model system which is easy to present but exhibits a series of non trivial phenomena is a quantum spin ladder. It consists of two chains coupled together via rungs. It is therefore defined by two exchange constants — \( J_\parallel \) for coupling along the leg of the ladder and \( J_\perp \) for coupling perpendicular to the ladder. The Hamiltonian is expressed as:

\[
H = J_\parallel \sum_j \left( S_{j,1} S_{j+1,1} \right) + J_\perp \sum_j S_{j,1} S_{j,2}. \tag{2.6}
\]

The physics of a spin ladder depends on the strength of the exchange constants \( J_\parallel \) and \( J_\perp \). The absolute values of coupling only set the energy scale, but the ratio of the two exchange constant alter the fundamental properties of the system, such as the nature of the excitations.

In the strong-rung case, the ladder is a weakly coupled one dimensional dimer lattice - the excitations are triplons, which are hopping along the leg of the ladder. In the case of the leg exchange being much stronger, the spin ladder resembles a spin chain with spinon excitations. However, due to rung exchange, the spinons are confined. In both cases, the excitation spectrum is gapped.

While for both limiting scenarios, there are exact solutions [40–43], the intermediate cases are more difficult to treat. Nevertheless, recent progress in computational physics has enabled calculations of spectral properties of the ladders using density matrix renormalization group (DMRG) methods [39, 44, 45]. A set of numerical results are shown in Fig. 2.2 corresponding to an asymmetric channel of ladder excitations, where the highly-dispersive magnon excitations are observed for the strong-rung case.
2.4 Spin Ladder

Figure 2.2: Calculated dynamic structure factors for different ratios of leg and rung exchanges ($x = J_{||}/J_{\perp}$). Panel a) corresponds to weakly coupled dimers, whereas d) shows the spinon continuum of a spin chain. Panels b) and c) correspond to intermediate cases. In fact, b) shows the dynamic structure factor for an isotropic ladder, whereas c) corresponds to a particular case of (C$_7$H$_{10}$N)$_2$CuBr$_4$. Adapted from [39].
Chapter 3

Quantum Phase Transitions

Phase transitions are introduced with the emphasis on quantum phase transitions. Two examples of quantum phase transitions relevant to this thesis are described.

A major part of the research in modern physics is directed to understanding the many different phases of matter. The study of how the different phases change into one another has led to many developments in statistical and solid state physics. This chapter introduces the main ideas about the thermal and quantum phase transitions that are relevant for the thesis. An in-depth treatment of classical phase transitions can be found in many staple textbooks [46, 47]. Quantum phase transitions are covered in [48, 49].

3.1 Classical and Quantum Phase Transitions

Any physical system aims at reducing its internal energy. At the same time, however, it tries to maximize its entropy. The configuration that optimizes these two requirements is selected and is called a phase. This competition can be formalized by defining the free energy $F$ which needs to be minimized for a stable phase [50]:

$$F = U - TS,$$  \hspace{1cm} (3.1)
3.2 Spin Chain as a Quantum Critical System

where $U$ is the internal energy, $T$ is temperature and $S$ is entropy. By inspecting eqn. 3.1 it is clear that at high temperatures, entropy is the more relevant variable and therefore high temperature phase has no structure. At low temperatures, however, the internal energy becomes dominant and long range order of some parameter can occur if it minimizes the internal energy [51].

These ideas can be generalized and applied to many different systems. Many powerful concepts stem from the study of phase transitions, such as Landau theory of phase transition, spontaneous symmetry breaking and scale invariance [1, 52, 53].

The most widely known example of a thermally-driven (classical) phase transition is the ordering of a two dimensional Ising lattice. A handwaving argument can be made to estimate the transition temperature, which is rather close to the extensive Onsager’s solution [54]. Additionally, many computer simulations allow visualizing such phase transition and appreciate aspects such as a divergent coherence length [55].

If, however, the phase transition takes place at zero temperature, entropy no longer plays a role and the phase transition is driven by quantum fluctuations. The textbook example of a quantum phase transition is the Ising model in a transverse field [49]. At zero field, it is ordered ferromagnetically, with the direction identified by the anisotropy axis. At very high transverse field, the spins are pointing parallel to the field. At a critical field value $B_C$, the system undergoes a quantum phase transition into a quantum paramagnet [49].

In the following paragraphs, two different types of quantum phase transitions will be introduced, which are directly related to the physics studied in this thesis.

3.2 Spin Chain as a Quantum Critical System

As described in the previous chapter, the Heisenberg Antiferromagnetic $S = 1/2$ chain is one of the archetypical models in quantum magnets. Additionally, it is an example of a quantum critical system at the brink of a phase transition.

As illustrated in Fig. 3.1, the generic spin chain configuration lies in a multi-parameter space. The anisotropy axis is defined as the ratio of the relevant energy scales for different spin components, i.e. $\Delta = J_z/J_{xy}$. For $\Delta < -1$ and $\Delta > 1$, the system is an Ising ferromagnet and antiferomagnet, respectively.
Figure 3.1: Phase diagram of spin chain depicting the quantum critical nature. The anisotropy can force the system to order at zero temperature into an Ising ferromagnet or antiferromagnet, while the interchain coupling leads to ordering at finite temperatures. Adapted from [34].
For the intermediate values of $\Delta$ the system is in an XY phase with an easy-plane anisotropy and a gapless excitation spectrum [56]. The spin chain systems studied in this thesis are at the isotropic Heisenberg point of $\Delta = 1$, with the arrow showing the region where the experiments were performed.

If the chain is coupled to its neighbors (with $z$ being the number of the neighboring chains), the coupling can be either ferromagnetic or antiferromagnetic with coupling strength $J_\perp$. The value $zJ_\perp$ defines the second axis in Fig. 3.1. At a coupling strength $J_\perp = 0$, the system is at a critical state.

An equally valid way to describe the quantum criticality in the chain is to describe it as being an alternating chain with exchange constants $J$ and $J + \delta$ and the tuning parameter $\delta$. As it goes through 0, the system undergoes a transition [57, 58].

Since the system on the verge of a quantum phase transition is at a critical state, the only relevant energy scale is the temperature. This allows expressing the dynamical structure factor as a function of $\omega/T$ in a universal scaling form. Quantum critical scaling in such spin chains has been studied theoretically [59] and confirmed experimentally [60, 61]. In chapter 6 we investigate how impurities affect this behavior.

### 3.3 Quantum Phase Transition in a Dimer Lattice

Another example of a quantum phase transition is illustrated in Fig. 3.2. A ground state in the case of a weakly coupled dimer system is approximately a product of valence bond spin singlets on dimers [62]. However, if the ratio of exchange constants between intradimer and interdimer is altered, the system can transform into a lattice (for example, a square lattice) of equally coupled spins. Such a system can have long range order.\(^1\)

While in the theoretical sense, the obvious tuning parameter is the ratio of

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\(^1\)A two dimensional square lattice only orders at $T = 0$ with a reduced ordered moment [63]. Since the quantum phases transitions are considered here, this poses no problem. Moreover, in experimental realizations, at low-enough temperatures, the magnetic ordering takes place due to stabilization by residual interlayer interactions [64].
Figure 3.2: Phase diagram of a dimer lattice where the strength of the exchange constants can be tuned using applied pressure. Dimers form singlets which do not exhibit a long range order. On the other hand, if the exchange constants are tuned in such a way that the interdimer coupling constants become comparable to intra dimer coupling, a long range order develops. $P_C$ and $T_N$ correspond to critical pressure and Néel temperature, respectively. Based on [65].
inter- and intradimer exchange constants, it is very difficult to achieve such tuning in real solid state systems. However, in some rare cases, hydrostatic pressure can change the orbital overlap in precisely such a way as to force a quantum phase transition. Up until very recently only one realization of such phase transition was known — TlCuCl$_3$, which is in fact a system of dimers, weakly coupled in three dimensions. Progress in material synthesis and increased availability of high-pressure techniques have enabled the discovery of a second material where a similar phase transition takes place — (C$_4$H$_{12}$N$_2$)Cu$_2$Cl$_6$. It is potentially a much more interesting system, since it is a lattice spins linked by a complex network of interactions, yet still dominated by dimer interaction. The spins in (C$_4$H$_{12}$N$_2$)Cu$_2$Cl$_6$ are interacting predominantly in two dimensions (at ambient pressure) and the system was found to host both quantum critical and multi-critical points upon application of pressure [66]. In chapter 8, the spin excitations are studied as the system undergoes these transitions.
Chapter 4
Experimental Methods

Experimental techniques used in the present thesis are described. The main features of neutron scattering, muon spin rotation techniques and light spectroscopy are introduced together with their strong and weak points.

In order to tackle complex problems arising in the field of quantum magnetism, a set of complimentary techniques is needed. Since the physics of interest is realized in real-life samples, a series of material characterisation methods are employed in the initial stages of the investigation. They include X-ray diffraction, magnetic susceptibility and heat capacity measurements. However, for a more detailed understanding of magnetism, additional experiments are often needed that address the specific properties of interest. In the case of this thesis, neutron scattering, muon spin rotation and raman spectroscopy techniques were employed. In this chapter, the main aspects of these techniques are introduced with emphasis on the details relevant for the research performed in the thesis.

4.1 Neutron Scattering
Neutron scattering is the prime technique to study magnetic ground states and excitations in bulk condensed matter systems, and as such has been well documented. There is a large number of excellent textbooks which describe the
technique in detail [67–71]. Here, only the basic theory is summarized with particular aspects selected which are relevant for the present work.

Since neutrons have no charge and hence are immune to Coulomb interactions, they can penetrate deep into the sample as well as go through complex sample environment [71]. Moreover, they scatter both off nuclei, due to short range nuclear interaction, as well as off magnetic moments — since neutron has a magnetic moment corresponding to spin $S = 1/2$, it interacts via dipole interaction. Finally, because both the momentum and energy transfer is resolved, it allows mapping the whole reciprocal space and accessing dispersion relations and density of states of the various excitations [67].

Some drawbacks of the technique need to be mentioned. First, since neutrons are hard to produce, such experiments cannot be done in-house and require obtaining beamtime at a large scale facility — at a reactor or a spallation source. Secondly, due to weak interaction, large samples are needed (grams) which ideally should be single crystals if detailed dispersion measurements are to be performed. In addition, some of the nuclei are strong absorbers of neutrons (such as Ir) while some others have strong incoherent scattering (H) which limits the selection of materials that can be studied [67].

### 4.1.1 Basic Principles

A neutron scattering experiment, sketched in Fig. 4.1 probes the probability that incoming neutron prepared in a state $|k_i, \sigma_i \rangle$ with wavevector $k_i$ and spin $\sigma_i$ interacts with the sample under consideration and scatters into the final state $|k_f, \sigma_f \rangle$ with wavevector $k_f$ and spin $\sigma_f$. The sample undergoes a transition between state $|\lambda_i \rangle$ and state $|\lambda_f \rangle$. The measured quantity is the double differential cross section, which represents the probability of a neutron being scattered in a particular solid angle for an energy transfer. Since the process can be treated as a small perturbation, the cross-section can be expressed using Fermi’s golden rule [67, 70]:

$$
\frac{d^2\sigma}{d\Omega d\omega} = \frac{\hbar k_f}{k_i} \left( \frac{m}{2\pi \hbar^2} \right)^2 \sum_{\lambda_f,\sigma_f \lambda_i,\sigma_i} p_{\lambda_i} p_{k_i,\sigma_i} |< k_f, \sigma_f, \lambda_f | V | k_i, \sigma_i, \lambda_i >|^2 
\times \delta(\hbar \omega + E_{\lambda_i} - E_{\lambda_f}).
$$ (4.1)
with $p_{\lambda_i}$ and $p_{k_i\sigma_i}$ being the probabilities of the sample and neutron being in a particular initial state, $V$ describing the interaction potential and $\delta(\hbar\omega + E_{\lambda_i} - E_{\lambda_f})$ ensuring the energy conservation.

Two different types of neutron scattering are typically differentiated depending on the interaction potential, which can be due to the nuclear or magnetic interaction. The two cases are briefly described in the following sections.

**Nuclear scattering**

When neutrons are scattered of nuclei, they interact via a short range nuclear interaction, which is called a Fermi pseudopotential and can be written as [67]:

$$V_{\text{nuc}}(\mathbf{r}) = \frac{2\pi\hbar^2}{m} \sum_j b_j \delta(\mathbf{r} - \mathbf{R}_j).$$  \hspace{1cm} (4.2)

The $b_j$ is known as the scattering length off the nucleus $j$ and gives the interaction strength. It is a complex quantity, real part of which is related to the scattering strength whereas the imaginary part is related to the absorption
4.1 Neutron Scattering

The samples studied in the present thesis had very little absorption which could be ignored. By taking into account the interaction potential, the cross section of nuclear scattering can be expressed as [67]:

\[
\frac{d^2\sigma}{d\Omega d\omega} = \hbar \frac{k_f}{k_i} \left( \frac{m}{2\pi \hbar^2} \right)^2 \sum_{j,j'} b_j b_{j'} \int_{-\infty}^{\infty} <e^{-iqR_j'(t)}e^{-iqR_j(t)}> e^{-i\omega t} dt. \tag{4.3}
\]

The eqn. 4.3 is the starting point to deriving the special cases of scattering that give information about the structure and vibrations in crystals. It can be shown that the scattering cross-section depends on two separate correlation functions — coherent scattering and incoherent scattering. The coherent scattering depends on the correlations between the positions of different nuclei, while the incoherent scattering is governed by the correlations of the same nuclei at different times. While the latter can be used to extract the phonon density of states [72], coherent scattering is usually the one that is more relevant to solid state physics, since it provides the crystal structure and dispersion relations.

As a closing remark on nuclear scattering, it is worthwhile to introduce an alternative, more intuitive representation of the scattering cross section:

\[
\frac{d^2\sigma}{d\Omega d\omega} = \hbar \frac{k_f}{k_i} S(q, \omega). \tag{4.4}
\]

Here, \(S(q, \omega)\) is called the scattering function (also known as the dynamical structure factor). By moving into continuum for the nuclear density, it can be defined as the space and time fourier transform of the correlation function of the scattering length density [67]:

\[
S(q, \omega) = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} < b(0,0)b(x,t) > e^{-i(qx-\omega t)} dt dx. \tag{4.5}
\]

The scattering length density in turn is a particle density operator, weighted by the corresponding scattering lengths [67].

**Magnetic scattering**

Since a neutron has a magnetic moment \(\mu_n\), it also interacts with the magnetic field in the sample. The interaction potential depends on the spin of the neutron \(\sigma\) and the magnetic field distribution in the sample \(H\) [67, 70]:

\[
\frac{d^2\sigma}{d\Omega d\omega} = \hbar \frac{k_f}{k_i} S(q, \omega). \tag{4.4}
\]
The relevant constants are the nuclear magneton $\mu_n = e\hbar/2m_p$ and the gyromagnetic ratio for neutron $\gamma = 1.913$. In general, the magnetic field distribution in the sample $H$ is a complicated quantity which arises due to orbital and spin angular momentum of the electrons. If the magnetism is of itinerant nature, the field distribution depends on the band structure of the sample and on the population dependence on the spin value.

For all the systems studied in the present thesis, the magnetic moments are localized, which simplifies the problem. Furthermore, in all the materials presented here, the magnetism is due to Cu$^{2+}$ ion, where the orbital momentum is quenched and the scattering cross-section depends only on the scattering due to electron spin. In such a case, the magnetic scattering cross section can be written as [67]:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\hbar k_f}{k_i} (\gamma r_0)^2 e^{-2W(q)} |F(q)|^2 \sum_{\alpha,\beta} \left( \delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2} \right) S_{\alpha\beta}(q,\omega).$$

In addition to previously introduced constants, $r_0 = 2.82 \times 10^{-15}$ is the classical radius of the electron. The sum runs over the three indices of the space dimensions. The polarization factor $\left( \delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2} \right)$ defines a very fundamental property of neutron scattering experiment — neutrons only interact with the magnetic moments perpendicular to the momentum transfer [70].

For the purpose of the present thesis, the most important factor is the dynamic structure factor $S_{\alpha\beta}(q,\omega)$. Similarly to the case of nuclear scattering, the dynamic structure factor in magnetic scattering provides information about spin correlations [67, 70]:

$$S_{\alpha\beta}(q,\omega) = \frac{1}{2\pi \hbar} \sum_{j,j'} \int_{-\infty}^{\infty} <S_\alpha^0(j,0)S_\beta^\beta(j',t)> e^{iq(r_j-r_{j'})} e^{-i\omega t} dt.$$

The quantity that is represented by $S_{\alpha\beta}(q,\omega)$ is the space and time Fourier transform of spin-spin correlation function. It effectively provides a probability that there is a spin component $S_\alpha^\alpha$ on ion $j$ at time $t = 0$ and a spin component $S_\beta^\beta$ on ion $j'$ at time $t$.  

$$V_{\text{mag}}(r) = \mu_0 \mu_n H = -\gamma \mu_0 \mu_n \sigma H.$$  

(4.6)

(4.7)

(4.8)
4.1 Neutron Scattering

The dynamical structure factor $S_{\alpha\beta}(q,\omega)$ is the quantity that bridges the experiments and theory. The strength of neutron scattering is that the theoretically calculated correlation functions can be directly compared with the experimental results. Additionally, $S_{\alpha\beta}(q,\omega)$ is related to the imaginary part of the generalized susceptibility, which means that neutron spectroscopy reveals the linear response of the system upon application of wavevector and frequency dependent magnetic field [67–69].

The two remaining factors of eqn. 4.7, $e^{-2W(q)}$ and $|F(q)|^2$ relate to the attenuation of the scattering intensity with momentum transfer. The former factor is known as the Debye-Waller factor, which depends on the mean displacement of the nuclei due to thermal fluctuations and it is usually a small correction. More importantly, the latter term, called the magnetic form factor arises due to the fact that the magnetic moment of the neutron interacts with the unpaired electron cloud, which unlike in the nuclear scattering, has a finite extent and may lead to significant attenuation at higher momentum transfers [69].

Magnetic form factor

The magnetic form factor is the Fourier transform of the unpaired electron density [68, 69]:

$$F(q) = \int \rho(r)e^{iqr}dr. \quad (4.9)$$

Since the magnetic spin systems studied in the present thesis are based on Cu$^{2+}$ ions, the electron distribution is anisotropic. Consequently, the form factor is also anisotropic and the attenuation of scattering intensity depends on the direction of the momentum transfer [73]. In the case of Cu$^{2+}$ ions, the electron responsible for the magnetism lies in the $3d_{x^2-y^2}$ orbital. In the materials studied in this thesis by neutron scattering, the copper ions are linked by oxygen 2p orbitals.

Because the electron wavefunction is spread out in the $x$-$y$ plane (defined by the copper-oxygen plaquette), the form factor decays rather quickly if the momentum transfer orientation is within this plane. On the other hand, the electron wavefunction decays very fast in the $z$ direction and the form factor will decay slower. These general observations can be quantified by expressing the form factor in terms of Bessel functions and spherical harmonics [73]:
Experimental Methods

\[ F(q, \theta) = \langle j_0(|q|) \rangle + C_2(1 - 3 \cos^2(\theta)) \langle j_2(|q|) \rangle + C_4 \left( 1 - 10 \cos^2(\theta) + \frac{35}{3} \cos^4(\theta) \right) \langle j_4(|q|) \rangle, \]  

(4.10)

where \( C_{2,4} \) are coefficients which are tabulated for the \( \text{Cu}^{2+} \) ion [74] and \( \theta \) is the angle between the momentum transfer and the normal to the plane of the plaquette. The functions \( j_n(q) \) are the radial integrals, quantifying the wave function. The numerically calculated radial integrals for most magnetic atoms and ions are tabulated in the *International Tables for Crystallography* [74]. The resulting form factor decay for different orientations is plotted in Fig. 4.2. There are two implications arising from the anisotropy of the form factor.

The first implication is important in the process of experimental planning. In order to obtain the maximum signal at high energy transfers, one needs to align the sample in such a way that most energy transfer arises from the momentum transfer along the direction where the form factor decay is the slowest. In the case of \( \text{Sr}_2\text{CuO}_3 \), for example, in the time-of-flight experiments the sample was mounted with the incoming wavevector \( k_i \) parallel to the crystal \( c \) axis, which in turn is perpendicular to the copper-oxygen plaquette.

The second implication is related to data analysis. In one-dimensional systems, the intensity is integrated with respect to the other two dimensions. However, the form factor decay is anisotropic. Therefore, in order to apply the appropriate correction for different energy transfers, the momentum-dependence of the intensity needs to be deconvoluted for each energy cut and calculated separately.

4.1.2 Experimental Aspects

**Neutron production and detection**

Since neutrons are unstable particles with a lifetime of about a quarter of an hour, producing them for experiments is a challenge. There are two ways neutrons are produced for condensed matter research — using a reactor running at critical conditions, and accelerator-based spallation, where neutrons are peeled off from a heavy nucleus [71].
Figure 4.2: Form factor squared for Cu\(^{2+}\) ion. The black line shows the commonly used dipole approximation. However it is clear from the figure that already at a few Å\(^{-1}\) momentum transfer, there is a significant difference between the form factor decay within the plane of the plaquette (blue line) and perpendicular to it (red line).
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In a reactor, like the one at the Institute Laue-Langevin in Grenoble (ILL), a chain reaction takes place. Enriched $^{235}\text{U}$ absorbs neutrons to form $^{236}\text{U}$ which then follows a series of decays releasing thermal energy and surplus neutrons. These neutrons are then moderated by heavy water held at room temperature or liquid deuterium at 20 K for thermal and cold neutrons respectively, which allows tailoring neutron energies to the particular physics problem [71].

In a spallation source, an elaborate accelerator system creates a pulsed high-energy proton beam which hits a heavy target, such as liquid mercury in the case of Oak Ridge’s Spallation Neutron Source (SNS). For every proton, a few tens of neutrons are peeled off, which are then moderated in a similar manner as in the reactors [75].

Since neutrons are uncharged, detecting them requires using a nuclear reaction. A most common method is to use $^{3}\text{He}$ gas detectors and make use of the following reaction:

$$n + ^3\text{He} \rightarrow p + ^3\text{H} + 0.77\text{MeV}. \quad (4.11)$$

A neutron is absorbed by the $^3\text{He}$ nucleus which then splits into a proton and a tritium, releasing 0.77 MeV of kinetic energy. The ionization from recoiling particles is detected. In the case of three-axis spectrometers, it is an effective point detector. However, in the case of time-of-flight spectrometers, there are many tubes, which allow for a position sensitivity in the in-plane angular distribution. Moreover, $^3\text{He}$ is stored in long tubes which allow out-of-plane spatial resolution due to charge division. The centre of the detector tube has an anode wire which collects the electrons from the ionized gas. The wire has a large resistance and high voltage. The proportion of charge collected at each end of the wire allows determining the position of the neutron detection event [76].

Three-axis method

The key to the neutron spectroscopy experiment is having a well-defined neutron energy and momentum before the scattering event and measuring them after the interaction with the sample. One of the ways to perform this task is to employ the technique of three-axis spectroscopy. The basic setup is shown in Fig. 4.3. The spectrometer has three independent arches, which are rotated to achieve the
4.1 Neutron Scattering

required position in the reciprocal space [70].

After the neutrons have been moderated, they have energies distributed according to the Maxwell-Boltzmann law [77]. The first axis of the spectrometer selects neutrons of the required energy and is called a monochromator. It consists of large single crystals such as copper or pyrolytic graphite. Neutrons with a certain energy are selected by Bragg reflections from the crystal. The angle of the monochromator ($\theta_M$) and hence the direction of the reflected beam ($2\theta_M$) are adjusted so that the Bragg condition is fulfilled for the neutrons of required energy (wavelength).

The second axis allows moving the analyzer around the sample stage and rotating the sample. This enables varying the scattering angle of the sample. The third axis hosts the analyzer. It is equivalent to the monochromator, since by modifying the angles $\theta_A$ and $2\theta_A$ it selects the neutrons of the desired energy and passes them to the detector. Usually, the final energy is kept constant, so that the variation of the monitor efficiency would not influence the measured scattering intensity.

Three-axis spectrometers are very powerful for studying specific points in reciprocal space. They allow for very well controlled measurements of the quantities upon varying external parameters (e.g. temperature, magnetic field). However, the technique is naturally limited in intensity, since most of the neutrons are lost at the monochromator and analyzer stages.

**Time-of-flight method**

An alternative method of obtaining momentum and energy dependent dynamical structure factor is by using a time-of-flight technique. It solves half of the intensity problem indicated above, by registering all the scattered neutrons.\(^1\) The basic setup is shown in Fig. 4.4 and it relies on having a sharp pulse of incident neutrons. Such pulses can be naturally created in a pulsed spallation source (such as ISIS\(^2\) or SNS) or rotating beam choppers can be used to create the

---

\(^1\)The actual number of detected neutrons is limited by the spacial extent of the detector but the increase of efficiency is nevertheless significant since neutrons with all energies are analyzed.

\(^2\)An accelerator based neutron and muon source, which is part of the Rutherford Appleton Laboratory in Didcot, UK

40
Figure 4.3: Three-axis spectrometer consists of three, separately controlled rotational arch stages. The monochromator angle defines the incident energy, whereas the analyzer angle defines the energy of the neutrons to be measured. The angle between the incoming and the analyzed beam is adjusted by rotating the analyzer and detector around the sample stage axis.
4.1 Neutron Scattering

time structure (as is the case for the time-of-flight spectrometers in ILL). The main difference from three-axis spectrometers is that the neutrons are monochromated only once. All of the scattered neutrons are analyzed and their energy is determined from the time it took them to reach the detectors [78].

An incoming beam of neutrons usually first passes through a time-resetting chopper, marked as $T_0$ in Fig. 4.4. Since it is open just for a very short time, it also blocks the fast, undermoderated neutrons and in this way significantly reduces the background. Incident neutrons are then monochromated.\footnote{Here, direct geometry time-of-flight spectrometers are described, which were used in this thesis. There is an alternative technique — indirect time-of-flight spectroscopy — where neutrons with a fixed final energy are studied and the initial energy is determined by the time of flight.} The most common way of performing energy selection is by using a Fermi Chopper (FC in Fig. 4.4). It consists of sheets of neutron absorbers with curved slits to allow the neutron passage. The ratio between energy resolution and intensity can be varied by adjusting the slit widths or by changing the rotational frequency. The energy is selected by setting the phase of the rotation with respect to the neutron pulse.

After the interaction with the sample, the neutrons then propagate to the detector banks. They are usually a few meters away to optimize the energy and momentum resolution. Often, the beampath is evacuated to avoid any unwanted scattering. The detectors have both position and time sensitivity. Angle in the scattering plane is resolved due to the fact that an array of vertical tubes is present in the spectrometers. The out-of-plane angle is obtained by making use of the charge-division. The energy of the neutrons is calculated by measuring the time it takes for them to reach the detectors. The task is made simple since the neutrons at the energy scales of interest are rather slow due to their mass and hence non-relativistic. Therefore the energy transfer to the sample is given by [78]:

$$\omega = \frac{1}{\hbar} \left( E_i - \frac{m}{2} \frac{L^2}{(t-t_{int})^2} \right), \quad (4.12)$$

with $E_i$ corresponding to the initial energy of the neutron. $L$ is the distance from the sample to the detector bank. Since it takes finite time for neutron to
Figure 4.4: Schematics of a time-of-flight spectrometer. The energy of the incoming neutrons is set by the choppers and the energy of the scattered neutrons is determined from the time taken to arrive at the detector.
travel distance \( L_0 \) from the \( T_0 \) chopper to the sample, this time \( t_{\text{int}} \) needs to be subtracted from the total measured time. It is given by \( t_{\text{int}} = L_0 \sqrt{m/2E_i} \).

The main advantage of the time-of-flight method is that a large portion of the dynamical structure factor \( S(q, \omega) \) is obtained simultaneously. This large amount of data needs to be treated and sensible projections have to be calculated to extract the relevant information about the studied system. A Python-based Mantid software package [79] was used for the initial reduction of the scattering data. Analysis of the data was performed using Matlab library set Horace [80].

The time-of-flight method is especially well applicable in low-dimensional systems. If dispersion only takes place in one direction, the scattering can be integrated in the other directions to improve the statistics. In the case of high-J cuprate chains studied in this thesis, this is an essential tool, that allows obtaining high quality data from low-S and large-bandwidth systems \( \text{Sr}_2\text{CuO}_3 \) and \( \text{SrCuO}_2 \).

**Absolute normalization of the spectrum**

One of the strengths of neutron scattering is that in some of the cases, the neutron scattering cross-section can be calculated in absolute units for comparison with the experiment. One of such cases is the HAF \( S = 1/2 \) chain studied in this thesis. In order to make use of this prediction, it is important to have the measured scattering cross-section in absolute units as well. This requires that in addition to measuring the sample under investigation, a well-characterised sample of known cross-section, such as vanadium, is also measured. Comparing the values of the two measurements puts the data from the studied crystal on an absolute scale [81].

The measured quantity in the experiment is partial neutron current \( \delta J_{\omega}(k_f) \) — a number of neutrons per time in a solid angle \( d\Omega \), with final energy \( \omega_f \). The first manipulation of data by a reduction algorithm performs a conversion of the current into a double-differential cross-section according to eqn. 4.13 by normalizing the data by the solid angle, the energy interval and the flux \( \Phi \) [73, 79]:

\[
\frac{d^2\sigma(q, \omega)}{d\omega d\Omega} = C \frac{d^2I(q, \omega)}{d\omega d\Omega} = \frac{\delta J_f(k_f)}{\Phi(k_i) d\omega d\Omega} \tag{4.13}
\]

There are two more important steps that are being performed by the reduction
algorithm. The sensitivity of the detector array is cross-calibrated by using incoherent scattering from vanadium sample and a 'white beam' of neutrons. This cross-calibration is then applied to the data. It is important that the 'white beam' data are obtained under the same configuration as the data from the sample. The final manipulation by a reduction algorithm is the correction for the $k_i/k_f$ factor so that the resulting 'reduced' data are proportional to the dynamic structure factor. It is however still in arbitrary units and gives information about the intensity as a function of energy and momentum transfer $\frac{d^2I(q,\omega)}{d\omega d\Omega}$, which is related to the absolute scattering cross section by the constant $C$.

In order to obtain $C$ and express the scattering cross-section in absolute units, incoherent scattering intensity of Vanadium is measured, using the same incident energy and identical instrument configuration as for the actual experiment. Since incoherent scattering is smeared in energy by the resolution of the spectrometer, an energy-integrated scattering from Vanadium $I_V$ is used in the normalization. To obtain the scattering per Cu$^{2+}$ ion (which is equivalent to normalization per formula unit in the case of the compounds studied here), the number of Vanadium atoms $N_V$ in the standard sample must be known as well as the number of copper ions $N_{Cu}$ in the studied crystal. Then $C$ can be expressed as [81]:

$$C = \frac{1}{I_V N_{Cu}} \frac{N_V}{4\pi} \sigma(V).$$

(4.14)

Having expressed the data in such a form allows direct comparison with models.

### 4.2 Muon Spin Rotation

One of the most sensitive techniques to observe static magnetic moments in a solid is by the use of muon spin rotation techniques. Spin-polarized muons are implanted in the sample under investigation and the time evolution of their polarization is measured. Such measurement allows learning about the magnetic properties of the matter surrounding the muon. Here, a concise introduction is given into the technique which is described in detail elsewhere [82–84].
4.2 Muon Spin Rotation

4.2.1 Experimental Aspects

Muon production

The muon spin rotation measurements are possible due to the parity violation in nature [85, 86]. At a first stage it is exploited to create spin-polarized muons from the decay of pions. The creation of pions is a well-known process which is achieved by bombarding a target with protons. In the case of experiments at PSI, the protons of 590 MeV are directed onto a graphite target, leading to collisions with stationary neutrons and protons which result in production of pions. Since pion is an unstable particle with a lifetime of 26 ns, it decays into a muon and a muon neutrino [84]:

\[
\pi^+ \rightarrow \mu^+ + \nu_\mu
\]  

At the rest frame of the pion, neutrino and muon are emitted in opposite directions. This is where the parity violation comes into play, since it implies that only left-handed neutrinos exist in nature. Therefore due to the conservation of angular momentum, the muon has to have its spin antiparallel to its linear momentum. This allows a fully polarized beam of muons to be created. Sometimes pions of high energy are used in order to create muons that penetrate specific sample environment. However in such a case, due to movement of pion, the muons are partly depolarized in the laboratory frame.

Polarization measurement

The muon itself is unstable and after being implanted into the sample, decays into a positron and two neutrinos:

\[
\mu^+ \rightarrow e^+ \nu_e + \bar{\nu}_\mu
\]  

The positrons resulting from this reaction are detected. Due to parity violation, the probability of the flight direction of the emitted positron is not isotropic, but reflects the muon spin orientation. The angular probability distribution is also dependent on the energy of the positron which in this three-body decay can vary from zero to 52.3 MeV (mass of the pion). Since a typical experiment collects

\footnote{Paul Scherrer Institute in Villigen, Switzerland}
a vast number of positrons, an energy-integrated distribution can be considered, which is \[84\]:

\[
W(\Theta) \propto [1 + \frac{1}{3}\cos(\Theta)]
\]  

(4.17)

Therefore, the distribution of the positron emission direction relays the information about the orientation of the muon spin at the time of the decay. By measuring the time-dependence of the positron emission distribution, the time evolution of muons in the sample can be probed \[83\].

Usually, scintillator detectors are positioned parallel and anti-parallel to the muon spin, called forward and backward detectors, respectively. A sketch of the experimental setup, demonstrating the main principles is shown in Fig. 4.5. When a field perpendicular to the muon spin is applied, it leads to the precession of implanted muon and hence to the oscillating response of the positron detectors. The muons decay and the number of positrons decrease as a function of time. Therefore the number of positrons detected in the forward detector is \[84\]:

\[
N_{FW}(t) = N_0 \exp\left(\frac{-t}{\tau_\mu}\right)[1 + \alpha_0 \cos(\gamma_\mu B t)]
\]  

(4.18)

The parameter \(\alpha_0\) is a number close to 1/3 as in eqn. 4.17 but is in fact dependent on the experimental conditions, such as solid angle coverage of the detectors and the range of energy of the positrons that are detected. Usually, the exponential decay is taken out of the consideration, by combining measurements from two opposing detectors to account for normalization conditions. In a general case, the experiment can be performed in zero external field or with an applied field either longitudinal or transverse to the muon spin orientation. The quantity that is analysed is the observed asymmetry:\(^5\)

\[
A(t) = \frac{N_{FW}(t) - \alpha N_B(t)}{N_{FW}(t) + \alpha N_B(t)}
\]  

(4.19)

where in addition to the detector counts, an additional parameter \(\alpha\) is introduced to take into account the deviations from perfect experimental geometry

---

\(^5\)The asymmetry is proportional to the polarization of the muons at time \(t\).
4.2 Muon Spin Rotation

Figure 4.5: An example of a muon spin rotation setup with an applied transverse field. The muon is precessing around the magnetic field, before decaying into positrons.

and different efficiencies of the detectors. Experimentally, it is obtained by performing measurements at a weak transverse field in the disordered phase of the sample.

4.2.2 Information About Magnetism

Having a tool to measure the polarization of the muon as a function of time allows studying the effect of local magnetism on the muon. The experiments can be performed with no external field or in applied field. The different cases are discussed below.

Zero field measurements

In a zero field measurement, the observed asymmetry depends on the muon precession frequency at its position. The precession frequency in turn depends on the local magnetic field $B_{loc}$ which is a combination of static and fluctuating
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fields arising from the magnetic moments of the electrons as well as nuclear spins [84].

A most well known case is the response of a muon implanted in a sample that has nuclear moments that are static on the time scale probed by muons. Since the moments are randomly oriented, the muons effectively see magnetic field centered around zero with a Gaussian distribution with a finite width \( \Delta_G \). The observed positron decay asymmetry is then described by the Kubo-Toyabe function (Fig. 4.6a), with the 1/3 tail corresponding to the muon spin components parallel to the local field [87]:

\[
\frac{A(t)}{A(0)} = \frac{1}{3} + \frac{2}{3} \left(1 - \gamma^2 \mu^2 \Delta_G^2 t^2\right) \exp\left(-\frac{\gamma^2 \mu^2 \Delta_G^2 t^2}{2}\right) \tag{4.20}
\]

If the electronic spins are ordered and the muons experience identical non-zero field, a uniform cosine will be observed:

\[
\frac{A(t)}{A(0)} = \frac{1}{3} + \frac{2}{3} \cos(\gamma \mu B t), \tag{4.21}
\]

as seen in Fig. 4.6b. A more realistic scenario is that there is a distribution of fields, centered around a non-zero value, which leads to the decay of the asymmetry. Assuming static fields with a Gaussian distribution, the asymmetry can be expressed as a following damped cosine function:

\[
\frac{A(t)}{A(0)} = \frac{1}{3} + \frac{2}{3} \cos(\gamma \mu B t) \exp\left(-\frac{\gamma^2 \mu^2 \Delta_G^2 t^2}{2}\right), \tag{4.22}
\]

which is shown in figure 4.6c. Another commonly observed asymmetry evolution is the sinc function:

\[
\frac{A(t)}{A(0)} = \frac{1}{3} + \frac{2}{3} \sin(\gamma \mu B_{\text{max}} t) \frac{1}{\gamma \mu B_{\text{max}} t}, \tag{4.23}
\]

also known as the zeroth-order spherical Bessel function \( J_0 \). Such an asymmetry evolution is shown in figure 4.6d and is observed when the magnetic structure is ordered incommensurately, since the local field distribution is modulated. Finally, it is important to mention that in the case of the distribution of local fields (such as in inhomogeneous ordering), the asymmetry evolution will be effectively a sum of many relaxation functions with different periodicity and will appear as
4.2 Muon Spin Rotation

Figure 4.6: A few example muon polarization functions showing a) Gaussian Kubo-Toyabe, with $\Delta = 10$ G, b) cosine function arising from a single muon site experiencing local field $B = 40$ G, c) a damped cosine function arising from a distribution of fields experienced by muons ($B = 40G$, $\Delta = 5$ G) and d) a Bessel function with $B_{\text{max}} = 40$ G. There is an apparent $\pi/4$ phase shift between the maxima of the asymmetry curve between c) and d).
Experimental Methods

an exponential decay, which in principle could have an exponent different from unity [83].

Longitudinal field measurements

In the case when magnetic field is applied parallel to the spin of the muon, studying the change of the asymmetry evolution allows extracting additional information. Often, such setup is used to study the dynamic properties of the magnetic systems [88]. For the purpose of the present thesis, it serves a different function — it allows differentiating between the asymmetry decrease due to static moments and magnetic fluctuations. If the decrease of the asymmetry is due to static magnetic moments, the application of longitudinal field forces the asymmetry to recover. For some field distributions, simple expressions can be used to reproduce the experimental data. If however, the decrease of asymmetry is due to dynamic fluctuations, the evolution of the asymmetry remains unchanged upon application of such a field [84].

Transverse field measurements

When a small magnetic field is applied to a non-magnetic sample perpendicular to the spin of the muon, the muons precess coherently at a frequency given by the applied field. If the temperature is lowered below the ordering transition, the muons will sense the local field in the sample due to the frozen spins, in addition to the applied field. This causes dephasing of the precession and can be used to estimate the magnetic and non-magnetic volume fractions in a sample and how their ratio changes across the phase transition. This technique additionally allows accurately pinpointing the transition temperature.

4.3 Raman Spectroscopy

Neutron scattering is usually the technique of choice to study magnetic excitations in solids, but it has strict experimental limitations. The samples have to be of a large size due to the weak interaction of neutrons with matter. In addition, certain isotopes are unsuitable due to their high absorption or incoherent scattering. In such cases, light spectroscopy can be used. Furthermore, due to high
4.3 Raman Spectroscopy

yield, many measurements can be performed as a function of a varied parameter (e.g. substitution level or pressure) allowing a more detailed study compared to the neutron experiments. Unfortunately, Raman scattering also suffers from drawbacks, the main two being (i) that only $q = 0$ sector corresponding to zero momentum transfer is probed and (ii) that the absolute cross-section is often hard to estimate.

The basic principles of the technique are described below. Several good books and monographs are available on Raman spectroscopy for studies of excitations in solid state [89–92]. Unlike neutron spectroscopy and muon spin rotation measurements, Raman spectroscopy experiments were performed in-house at Neutron Scattering and Magnetism (NSM) laboratory in Hönggerberg. A Raman spectrometer, optimized for low energy studies was commissioned during the early stages of the project. Subsequent development was performed to tailor the spectrometer for the studies presented here. The results presented in this thesis are from the first set of experiments obtained using this particular Raman setup. Therefore, a more detailed description of the specifics of the spectrometer will be given towards the end of the chapter.

4.3.1 Basic Principles

Being a scattering process, Raman spectroscopy can be sketched using the same Fig. 4.1 as for neutrons. In the case of Raman spectroscopy, however, the incident particle is a photon and the interaction takes place via electromagnetic interaction. Incident laser light is absorbed by the sample causing polarization $P$, which then irradiates light at the same or different frequency. The generic cross-section can be expressed as [89, 90]:

$$\frac{d^2\sigma}{d\Omega d\omega_f} = \frac{\omega_i \omega_f^3 n_f V}{(4\pi\epsilon_0 c^2)^2 n_i |E_i|^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} <[e_f P(0,0)]|e_f P(r, t)] > e^{-i(qr - \omega t)} dt dr.$$  \hspace{1cm} (4.24)

Here, $\omega_i$ and $\omega_f$ are the angular frequencies of the incoming and irradiated light. In practice, since visible light phonons have energy of a few eV, whereas the excitations are of the order of 1–100 meV, the incoming and outgoing photon energies are almost the same. The prefactor therefore is usually written as $\omega_L^4$, setting the scale of intensity, as in Rayleigh process [89].
Factors $n_i$ and $n_f$ are the refractive indices of the media where light travels and interacts, respectively. They are usually left out of the consideration since it is something that is not varied in experiment and only gives a small correction to the absolute scattering intensity. $V$ is the scattering volume, $\epsilon_0$ is the permittivity of free space and $E_i$ is the amplitude of the electric field of the incident light. The factors $e_i$ and $e_f$ are the unit vectors defining the direction of the polarization of incoming and outgoing light.

The key factor in the cross-section is the polarization $P(r, t)$, that is induced by the incoming light with particular polarizability. Each component of the polarization vector can be written as [90, 91]:

$$P^\mu(r, t) = \epsilon_0 \sum_\nu \chi^{\mu\nu}(r, t) E^\nu_i(r, t). \quad (4.25)$$

Using this definition, the cross-section can be rewritten in a similar fashion to the neutron case [90, 91]:

$$\frac{d^2\sigma}{d\Omega d\omega_f} = \frac{\omega_L^4 n_f V}{(4\pi c^2)^2 n_i} \sum_{\alpha,\beta,\mu,\nu} e_\alpha^i e_\beta^f e_\mu_i e_\nu_f S^{\alpha,\beta,\mu,\nu}(q, \omega), \quad (4.26)$$

where the scattering function $S^{\alpha,\beta,\mu,\nu}(q, \omega)$ is expressed as the space and time Fourier transform of the polarizability correlation function [90, 91]:

$$S^{\alpha,\beta,\mu,\nu}(q, \omega) = \int \langle \chi^{\alpha\beta}(0, 0) \chi^{\mu\nu}(r, t) \rangle e^{-i(qr - \omega t)} dt dr. \quad (4.27)$$

Equation 4.27 shows the key quantity measured in the Raman spectroscopy experiment. As will be described in the later paragraphs, expanding the polarizability with respect to elastic or magnetic fluctuations allows connecting the observed signal with physically meaningful properties. A note must be made about the kinematic restriction. Since visible light is used (for example, $\lambda = 532$ nm), the wavelength is about $10^3$ times longer than the interatomic distance (few Å). Hence, only excitations very close to the Brillouin zone centre are excited in Raman experiment. Second order processes, however, allow combining excitations with opposite momenta and therefore allow accessing the whole Brillouin zone [89].

Finally, it is important to mention that due to the strength of the electromagnetic interaction, light scattering is prone to surface-related effects. The
4.3 Raman Spectroscopy

corollary of this statement is that the surfaces must be clean and of high quality for a successful Raman experiment.

**Scattering of phonons**

Raman scattering is most commonly used in studying phonons. In order to obtain the scattering cross section for the phonons, the polarizability is usually expressed as Taylor series with respect to normal modes $Q(r, t)$:

$$
\chi^{\alpha\beta}(r, t) = \chi_0^{\alpha\beta}(r) + \sum_{j=1}^{3N-3} \frac{d\chi^{\alpha\beta}(r, t)}{dQ_j} Q_j(r, t)
$$

(4.28)

Here the expansion is only made up to the first term which corresponds to single-phonon scattering. The crucial element is that the derivative of polarizability $\frac{d\chi^{\alpha\beta}(r, t)}{dQ_j}$ has to be non-zero in order for the $j^{th}$ mode to be Raman-active (contribute to the scattering). This is the basis of the Raman scattering selection rules. If the crystal structure and symmetry is known, a group-theory analysis can be performed to identify all the normal modes and determine if they are Raman-active. The methods to obtain the selection rules can be found in standard books [93, 94], but in practice, the results for different crystal structures are tabulated [95]. Moreover, this information has been digitized and computer codes can perform the analysis [96–100].

**Magnetic light scattering**

In the case of magnetic scattering, similar expansion can be made in terms of spins of the system. Following [101], the first three terms are written out as:

$$
\chi^{\alpha\beta}(r, t) = \chi_0^{\alpha\beta}(r) + \sum_{\mu} K_{\alpha\beta\mu}(r, t) S_\mu^r + \sum_{\mu, \nu} G_{\alpha\beta\mu\nu}(r, t) S_\mu^r S_\nu^r
$$

$$
+ \sum_\delta \sum_{\mu, \nu} H_{\alpha\beta\mu\nu}(r, \delta, t) S_\mu^r S_\nu^r S_{r+\delta}^r
$$

(4.29)

The first term of the expansion is independent of spins and can be ignored. The term proportional to $S_\mu^r$ corresponds to one-magnon scattering. The strength of the scattering is set by the prefactor $K$. It has been shown in [101] that the
prefactor is non-zero only in the magnetically ordered state. Its magnitude can be related to the Faraday rotation coefficient [102]. There are also constraints in the scattering geometry in which the one-magnon scattering can be observed. In the backscattering geometry with linearly polarized incoming and outgoing light, which is used at the NSM laboratory, only $\Delta S = 0$ transitions are probed, therefore one-magnon scattering cannot be accessed. The third term in eqn. 4.29 is the second order of the same effect, since two excitations on the same spin are considered. This type of scattering is usually very weak, even in geometrically optimized experiments [91, 101] and inaccessible in the $S=1/2$ systems.

The last term of the eqn. 4.29 is related to two-magnon scattering. Two different spins in the system, separated by distance $\delta$ are involved and the process is referred to as exchange-scattering [103]. The two-magnon scattering is observable in state with no long range order, therefore it is this process that is of the most interest when studying quantum magnets. Additionally, since it proceeds with the change of spin $\Delta S = 0$, it is observable in the backscattering geometry. It is this term that all the magnetic light scattering studied in this thesis originates from. The details of the intensity and lineshape of scattering depends on the microscopic properties of the system and in some cases can be calculated exactly to within scale factors [104–106]. Finally, it is worth noting that by inserting the last term of the eqn. 4.29 into eqn. 4.27, the $S(q, \omega)$ can be expressed in terms of spin operators as in the case for neutron scattering. This shows also the physical interpretation — the magnetic scattering studied in this thesis is related to the four-spin correlation function.

### 4.3.2 Experimental Aspects

The experimental setup used in this thesis is schematically shown in Fig. 4.7. The photons used for exciting the sample were generated by using a laser with a narrow energy spread. Two different lasers are installed in the NSM laboratory, with wavelengths of $\lambda = 532$ nm and $\lambda = 660$ nm. By default, the green laser is used due to the $\omega^4_L$ factor in the cross section. However, in certain cases, such choice leads to additional background. An example is materials with small electronic bandgap, where electronic scattering takes place if high enough energy photon is used for the excitation. This leads to a broad scattering signal which
4.3 Raman Spectroscopy

masks the weaker magnetic quasiparticle excitations invisible. In such cases, using lower energy red laser allows overcoming this problem.

The light coming out of the laser is linearly polarized. As seen in Fig. 4.7, \( \lambda/2 \) plate is installed after the laser which allows either to rotate the polarization by a right angle or to keep it in its original polarization. For low temperature measurements, the full power of laser may be too large and therefore various filters \( F \) can be used to attenuate the beam power. The laser beam goes through a beam splitter and is then focused onto a sample using a microscope \( M \). The sample is placed in a helium flow cryostat from Cryovac [107]. Additionally, for high-pressure studies, a diamond anvil cell can be used, which is described at the end of the chapter.

After the interaction with the sample, the outgoing light is directed to the diffraction gratings for spectral analysis. Before entering the series of diffraction gratings, the light polarization is selected using an analyzer \( A \). Since the diffraction gratings are anisotropic, the efficiency of the grating depends on the polarization of the light. In order to correct for this efficiency difference, a \( \lambda/4 \) plate is installed after the analyzer to change linearly polarized light to circularly polarized light.

The heart of the Raman setup are the three stages of diffraction gratings. The first two stages act as a band-pass filter which cuts off the light which is Rayleigh scattered. The first diffraction grating \( G_1 \) splits the scattered light and the second diffraction grating \( G_2 \) is positioned in an opposite sense to recombine it. In between them, a physical barrier blocks the stray light. It can be done either using the edge of the slit \( S_2 \) or by placing a pin in the centre of the slit. The final diffraction grating \( G_3 \) is used for spectral analysis and it disperses the light onto the liquid nitrogen cooled charge-coupled-detector (CCD) camera which records the intensity of light as a function of position, which can be translated into energy.

The configuration of the spectrometer is highly flexible. In each of the stages, there are three different diffraction gratings, which allow optimizing the resolution and intensity as well the observable spectral range. For example, for a broad spectral overview with high intensity and low resolution, a setup with low density of grooves is used — 300 per mm for \( G_1 \) and \( G_2 \) and 500 for \( G_3 \). A high resolution setup uses gratings with 1800 and 2400 grooves per mm.
Figure 4.7: The schematics of the Raman setup used in the thesis. The laser light with a defined polarization (using $\lambda/2$ plate) and intensity (using filters F) is focused on the sample using a microscope (M). The sample is positioned in a cryostat and can also be mounted in a pressure cell. The three grating system is used for stray light suppression and spectral analysis. The slits $S_1$ and $S_3$ are used to define the physical width of the beam, which can be related to resolution and the background level. Slit $S_2$ defines the spectral window to be analyzed. Mirrors $M_1$ to $M_{10}$ guide the beam through the stages to the CCD camera where the signal is recorded. Based on [108, 109].
4.3 Raman Spectroscopy

Figure 4.8: Raman spectra of BaMg$_{1/3}$Ta$_{2/3}$O$_3$ obtained using a series of scans with limited spectral region, together with corresponding reference spectra obtained from a standard light source (a). When the data are normalized with respect to the standard source, an overlapping, well-behaved spectrum is obtained (b) which can be used for analysis of physical properties of the sample.

Normalization procedure

The spectrometer has a complicated efficiency dependence on the wavelength of the outgoing light which is different for different configurations. This effect can distort the spectrum, cause difficulties in interpreting the spectral lineshapes and may lead to an apparent disagreement between data and detailed balance principle. The effect is most pronounced, however, when several frames are taken and need to be joined for an analysis of complete spectrum as seen in Fig. 4.8a. In order to overcome this issue, the spectra need to be normalized using a standard light source. In our laboratory, a halogen lamp was used, spectrum of which is also displayed in Fig. 4.8a. The data need to be divided by the reference spectrum in order to obtain the real scattering spectrum. Additionally, the spectrum of the halogen light has an intrinsic intensity dependence, which needs to be taken into account (it is almost flat in the energy range studied in this thesis). The resulting spectrum (for example, one in Fig. 4.8b) can then be used for analysis.
Sources of background

In order to perform a successful experiment, various sources of background have to be minimized. As already mentioned, the surface quality of the sample is of paramount importance. Often, as-grown surfaces are the best. Other times, a natural cleavage plane provides an alternative surface. If these two methods do not yield desired results, the surfaces can be polished. Polishing, in particular, works very well with hard crystals. However, when treating soft organometallic compounds, often too much damage is done to the sample. Additionally, strain can be induced in the sample which lead to poor quality of the spectrum.

Additional source of background comes from the cosmic rays. Since the CCD camera is extremely sensitive, it can register high energy cosmic rays incident on the detector. They show up as spikes in intensity at one or a few pixels. While potentially disruptive, they can be easily removed by taking several spectra with the same configuration and removing features that appear only in one frame.

There are two more cases of background that are easy to identify and mitigate. They are shown in Fig. 4.9. The first one is the scattering from air, displayed in Fig. 4.9a. It is due to the rotational spectrum of water molecules. When part of the beampath is flushed with Argon gas, the background can be suppressed as shown in the figure. Additionally, the reference spectrum without any sample can be carefully measured and subtracted from the sample spectrum.

The second source of background is the light contamination from the room. In Fig. 4.9b, no scattering from the sample is observed since it is overwhelmed by the background. It is therefore important to have good light isolation during the experiment. A note must be made that it is more important when using the green laser since accidental photons close to the center of the visible light spectrum are more abundant.

Pressure cells

An important part of the Raman setup used in NSM laboratory is the diamond anvil pressure cell. Due to the fact that there is no phononic background at low energies, it offers high yield and allows measuring multiple pressures per sample. The basic cell design is shown in Fig. 4.10. It consists of two opposing diamonds with supporting backing plates made from a copper-beryllium alloy.
4.3 Raman Spectroscopy

Figure 4.9: Two sources of Raman background displayed. Panel a) shows the scattering from the air, whereas b) shows the spectrum of the light in the room.

(2% beryllium). The diamonds with the support are placed in between plates made of nickel-copper alloy Monel-400. The high pressure is reached by applying force by the screws.

The sample space is created by using a copper-beryllium gasket in between the two diamond tips. In order to create hydrostatic pressure, a pressure transmitting medium has to be used. All the measurements reported in this thesis have been done using Daphne Oil 7373 as the transmitting medium. It is easy to handle and has high hydrostaticity at the required pressures. It has limitation and can only be used to about 22 kbar, since at this pressure it solidifies at room temperature [110]. Therefore, an upgrade to our setup is now being commissioned to liquify Argon and use it as transmitting medium to reach higher pressures.

In order to measure the pressure, ruby spheres are introduced into the sample space as shown in Fig. 4.10c. The pressure is determined by measuring the position of R1 ruby fluorescence line, shown in Fig. 4.10d for ambient pressure and 17 kbar. The position of the peak depends on the pressure and temperature [111]. At low temperature, an empirical function has been obtained in [112] which is expressed as:
Experimental Methods

Figure 4.10: Diamond anvil pressure cell used in this thesis to achieve high pressure in Raman experiments. Panel a) shows the side view and b) shows the top view. The inside of the cell is shown in c) where the sample (green slab) and rubies (red spheres) are visible. The diameter of the sample space is 600 µm. The pressure measurement is performed by measuring the position of R1 ruby fluorescence lines as shown in d) for ambient pressure and 17 kbar.

\[ P[kbar] = 17620 \times \ln \left( \frac{\lambda}{\lambda_0} \right), \]  (4.30)

where \( \lambda \) is the measured wavelength of the emitted fluorescence line at the elevated pressure. The reference wavelength \( \lambda_0 \) is measured at ambient pressure. At every pressure, the fluorescence measurements are obtained from several ruby spheres in the vicinity of the sample to gauge the homogeneity of the pressure throughout the sample space. The average value of the observed positions is taken for the nominal pressure. The spread of the values is independent on the absolute pressure and is usually within 1 kbar.
4.3 Raman Spectroscopy
Chapter 5

Magnetic Ordering in Intact and Depleted Spin Chain SrCuO$_2$

Weakly coupled chains are expected to order magnetically at low temperatures due to residual interactions. Here this effect is studied in one of the best realizations of HAF $S=1/2$ chain SrCuO$_2$. The ordering in a clean system is revisited before dwelling into the more interesting problem of effects of site-dilution.

It has been known since the Bethe’s work in the 1930s that an ideal HAF $S=1/2$ chain has no long range order even at zero temperature [6]. However, in real materials the magnetic ordering is stabilized by three-dimensional interactions and the long range order develops at very low temperatures [113–115]. This has been shown experimentally for a number of HAF $S=1/2$ chains [116–118] as well as more generally, for an odd-leg spin ladder [119].

It is natural to ask how the magnetic ordering is affected when imperfections and defects are introduced into the system. The simplest situation would be to remove some of the spins from the chain. In fact, the effect of such site-dilution on the magnetic ordering has been studied in a great detail theoretically [120, 121], but detailed experimental studies have been lacking up to now. Combining the very sensitive $\mu$SR probe [84] with the recent advances of ultra-pure crystal growth [122] has allowed for a systematic study of the disorder effects. In this chapter, the spin chain material SrCuO$_2$ is introduced followed by the
5.1 Spin Chain System SrCuO$_2$

As a model system to tackle this issue, SrCuO$_2$ was chosen due to its exceptional one-dimensionality. The dominant intra-chain exchange constant $J_\parallel$ is very large at 226 meV [33] and the material exhibits excellent one-dimensional behavior across a broad range of temperatures [124]. While the system does order antiferromagnetically in three dimensions at low temperatures due to residual interchain interactions, the ordered moment remains very small [125, 126]. There exists a slight complication in this system in a form of a neighboring chain as seen in Fig. 5.1. It arises due to the fact that two chains are weakly coupled via a weak coupling which is expected to be ferromagnetic from Goodenough-Kanamori rules [127]. Little is known about this coupling, but it is expected to

![Figure 5.1: Structure of the spin chain compound SrCuO$_2$. The exchange interaction between $S = 1/2$ from Cu$^{2+}$ is mediated by O$^{2-}$ ions. The dominant interaction $J_\parallel$ define the spin chains. The neighboring chains are additionally coupled via weak ferromagnetic interaction $J_Z$. Because of the two neighbouring chains, such structure is sometimes referred to as a zigzag spin chain.](image-url)
be very weak [114]. Indeed, all the experiments so far have shown that the role of the two-chain structure in terms of magnetism is negligible and the chains can be treated as well isolated entities [33, 126]. Nevertheless, as will be shown later in chapter 6, this complication does play a role for the dynamic properties of diluted-chains.

The crystals were grown using the floating-zone method as described elsewhere [122, 123]. They crystallize in a space group Cmcm, with lattice constants $a = 3.556 \text{ Å}$, $b = 16.27 \text{ Å}$, and $c = 3.904 \text{ Å}$. In order to probe the magnetic fields in all muon sites, the crystals were crushed and then pressed into pellets.

## 5.2 Magnetic Ordering in the Pure SrCuO$_2$

The measurements of magnetic ordering reported in this chapter were performed using GPS, LTF and GPD muon spectrometers at PSI. While they all allow similar measurements and can be described in terms of $\mu$SR principles outlined in chapter 4, they have different sample environments and therefore different levels of background, as described later in the chapter.

To establish the procedure and obtain reference measurements, $\mu$SR experiments were first performed on the clean parent compound. Whereas an earlier study has reported an increase of relaxation at low temperatures [125] suggesting glassy behavior, present measurements have revealed well-defined oscillations below the transition temperature as shown in Fig. 5.2, unambiguously demonstrating a homogeneous magnetic ordering. Above the phase transition the muon decay asymmetry could be well described by a standard Gaussian Kubo-Toyabe equation (eqn. 5.1) usual for the disordered materials, with relaxation included to approximate the dynamic effects.

\[
A(t) = G_{KT}(t, \Delta) \times \exp(-\lambda t) \quad (5.1)
\]

where

\[
G_{KT}(t, \Delta) = \frac{1}{3} + \frac{2}{3}(1 - \gamma^2 \Delta^2 t^2) \exp(-\frac{\gamma^2 \Delta^2 t^2}{2}) \quad (5.2)
\]

The asymmetry below the phase transition was reproduced by an oscillatory function with two frequencies, corresponding to two different muon positions.
5.2 Magnetic Ordering in the Pure SrCuO$_2$

Figure 5.2: Muon decay asymmetry for the pure SrCuO$_2$ above and below the ordering temperature. The low temperature data could be reproduced by fitting a sum of two Bessel functions whereas the high temperature data can be represented by a static Kubo-Toyabe function corresponding to the magnetic fields arising from the nuclei. The inset shows the temperature dependence of the extracted average internal field in two muon stopping sites when the system is in the ordered state. The dashed lines are to guide the eye.
Magnetic Ordering in Intact and Depleted Spin Chain SrCuO$_2$

with corresponding magnetic fields. Initial attempts to fit the spectrum with sum of two cosine functions have yielded reasonable result, but the phase drifted towards 45 degrees. A fit using Bessel function shown in eqn. 5.3 provided a better agreement with the data. Such functional dependence is suggestive of an incommensurate magnetic structure [84]. This is consistent with an earlier neutron scattering study, which reported incommensurate ordering [126].

$$A(t) = \frac{2}{3}[A_1 J_0(\omega_1 t) \exp(-\lambda_1 t) + A_2 J_0(\omega_2 t) \exp(-\lambda_2 t)]$$

$$+ \frac{1}{3}(A_1 + A_2) \exp(-\lambda_{tail} t) \quad (5.3)$$

Two distinct precession frequencies occur in the $\mu$SR spectra, corresponding to the local magnetic fields of 80 G (three quarters of the signal) and 16 G (a quarter of the signal). The development of the local magnetic field at these sites is shown in the inset of Fig. 5.2. The ordering in the samples studied here was found to take place at higher temperature than reported in the past [125]. This and the presence of oscillations can be explained by the fact that the sample quality was much better in the present work. In fact, the results previously reported in [125] of the 'clean' sample has shown asymmetry spectrum which is very similar to the one seen in 0.1% Ni-substituted compound in the present study.

5.3 Site-Dilution and the Effect on the Ordering

Even though the removal of some spins from the system is a natural theoretical approach, experimentally it is not so straightforward. Often, the simplest way to dilute such spin chains is by replacing the $S = 1/2$ Cu$^{2+}$ ion by an $S = 0$ ion Zn$^{2+}$. However, it is known that Zn enters these compounds very poorly [128]. Therefore an alternative method to achieve the same effect had to be pursued by implanting an $S = 1$ Ni$^{2+}$ ion. This leads to the chain fragmentation due to the fact that the spin of Ni impurity is screened and acts effectively as two $S = 1/2$ particles [129], which in turn dimerize with spins at the end of the chains as sketched in Fig. 5.3. The remaining relevant actors for magnetism are the spin chains of finite lengths which we want to study.
5.3 Site-Dilution and the Effect on the Ordering

![Diagram showing spin chain and impurity interaction](image)

Figure 5.3: AN effect of an $S = 1$ impurity in a spin chain. When a spin chain shown in a) is implanted with an $S = 1$ impurity b), the impurity $S = 1$ is screened and acts as two $S=1/2$ items which dimerize with the neighboring spins within the chain c) leaving the chains of finite length as described in [129].

In order to make sure that the chain fragmentation proceeded as expected, the magnetic susceptibility was measured and compared with theoretical predictions. This problem has been studied in detail by Sirker et al. in [130, 131] and the complete expression of the susceptibility per mole reads:

$$\chi(x, T) = \frac{N_A (g\mu_B)^2}{k_B} \left[ \frac{x}{4T} \frac{1-x}{2-x} [1 - (1 - x)^2] \right] + (1 - x)^2 \left[ (1 - x + \frac{xJ}{T}) \chi_{\text{bulk}} + x\chi_{\text{bound}} \right].$$

In the above equation, $\chi_{\text{bulk}}$ is the contribution from the bulk spin chains [132, 133], $\chi_{\text{bound}}$ corresponds to the boundary susceptibility and is expressed as $1/\chi_{\text{bound}} = 12 T ln(2.9J/T)$ [134]. The first term is the dominant one, arising from the contribution to the susceptibility due to the free $S = 1/2$ spins[129] at the ends of the odd-length chains.

The obtained data shown in Fig. 5.4 are described by this picture very well. A discrepancy at very low temperatures is observed, where the measured susceptibility is below the expected one. This effect has been noted in previous studies [135] and interpreted as resulting from three-dimensional interactions. The number of chain breaks $x$ can be fitted to the expression above and compared to the nominal composition as shown in the inset of Fig: 5.4. While small deviations persist, generally the desired amount of spin breaks is obtained by Ni-substitution. Therefore, the Ni-substituted SrCuO$_2$ can be described as a system of fragmented spin chains.

In terms of $\mu$SR measurements, the introduction of impurities into the sample
Figure 5.4: Magnetic susceptibility multiplied by temperature for samples with different impurity concentration. The thin solid line shows the theoretical prediction of [131]. The measured susceptibility follows the prediction very well down to about 10 K, whereupon there are some deviations due to three-dimensional interactions. The fitted impurity concentration is shown in the inset for fit using the complete data set (black circles) and data only above 10K (blue squares). The case of fitted number of impurities equal to the nominal concentration is shown by the black solid line.
5.3 Site-Dilution and the Effect on the Ordering

Figure 5.5: a) Muon spin rotation asymmetry for the pure SrCuO₂ and the Ni-substituted compounds. When as little as 0.1% Ni impurities are introduced, the oscillations are suppressed. However, at least for the mildly compounds with small amount of impurities, there is still a reduction of asymmetry which is a signature of either a slowing down of spin fluctuations or of static but inhomogeneous order. b) When rather weak longitudinal field is applied, the asymmetry is found to recover, signaling that the nature of the asymmetry reduction is due to static ordering.

destroys the asymmetry oscillations as seen in the Fig. 5.5a. The spectra can be reproduced using an empirically chosen simple exponential relaxation. The spectra of 0.5% and 1% Ni-substituted samples show no change as a function of temperature. On the other hand, spectra of the samples with more modest impurity levels reveal an increase of relaxation rate upon cooling as shown in Fig. 5.6.

An increase in the relaxation rate is indicative of slowing down of the spin-fluctuations or static ordering. These two cases can be separated by performing measurements with magnetic field applied parallel to the initial muon polarization. The decay asymmetry was found to recover when longitudinal field was applied as shown in Fig. 5.5b, which suggests that the sample has static order. The absence of oscillations in the spectrum can be explained by the magnetic ordering with a distribution of different magnetic moments in different sites. In such a case, different muons precess at different frequencies which does not result in oscillations in the asymmetry spectrum.
To determine the transition temperature more accurately, weak transverse field of 30 G was applied and measurements were performed for pure samples as well as samples with low impurity level (0.1% and 0.25%) that showed increase of relaxation upon cooling. Additionally, the decay asymmetry was measured for a sample with moderate levels of impurities (0.5%) that displayed no sign of ordering in zero field measurements. The spectra were fitted throughout the temperature range with a weakly damped oscillating function (eqn. 5.5). To obtain the transition temperature, the obtained asymmetry parameter was then fitted to a sigmoidal function (eqn. 5.6). The asymmetry as a function of temperature was then converted into a nonmagnetic volume fraction and is shown in Fig. 5.7a.

\[ A(t) = A(T) \cos(\omega_{ext} t + \phi) \exp(-\lambda_1 t) \]  
\[ A(T) = A_{para} + \frac{A_{mag}}{1 + \exp\left(\frac{I_T - T}{\Delta T}\right)} \]  

It is worth noting that the values plotted in the figure are arising both from the samples and the sample environment, hence the magnetic fraction is always...
5.3 Site-Dilution and the Effect on the Ordering

lower than unity. In principle this could be corrected to absolute values by measuring a fully magnetized reference system of identical dimensions as the sample and using the paramagnetic part of such measurement as a background. Since the aim of the project has been to investigate the nature of the ordering and the transition temperatures, the detailed volume fraction determination was not pursued. Nevertheless, certain inferences could still be made as discussed below.

Two nominally pure samples were measured which were grown in different batches. The first one, that was used for the zero field measurements described above was measured in transverse field in the very low background GPS instrument. Even in this setup, some residual paramagnetic fraction is observed as seen in Fig. 5.7a. This, however, arises not from the phase separation but from the fact that one of the muon sites experiences very small internal magnetic field and the applied field is comparable to the internal field. Therefore, the implanted muons get polarized and appear in a paramagnetic site. It can be inferred from the zero-field measurements, that about a quarter of muons sit in the low field site which is consistent with the size of residual asymmetry observed in transverse field scans. The second pure sample was measured using GPD spectrometer in a pressure cell, therefore unsurprisingly, the observed paramagnetic fraction is even larger. The obtained ordering temperatures for the two samples were 3.63(6) and 2.78(5) K respectively.

The weakly disordered materials (0.1% and 0.25% Ni-substitution) showed qualitatively similar behavior. Since the measurements were performed in a dilution refrigerator of LTF instrument, a large part of the remaining paramagnetic response at low temperatures is of instrumental origin. However, as the number of impurities is increased to 0.25%, the observed magnetic volume fraction seems reduced. This, however is most likely due to the fact that the weight of the distribution of magnetic moments in the ordered sample is shifting to very low values and hence an extremely small probing field would be needed to get an accurate estimate of magnetic volume fraction. The ordering temperature can still be obtained accurately because the nonmagnetic volume fraction stays approximately constant at low temperatures as seen in Fig. 5.7a. The obtained ordering temperatures for samples with 0.1% and 0.25% of Ni impurities were found to be 1.47(3) and 1.03(4) K respectively.
Figure 5.7: a) Measurements of the muon decay asymmetry under applied transverse field allow extraction of the nonmagnetic volume fraction as a function of temperature for the pure and the site-diluted SrCuO$_2$. The pure SrCuO$_2$ was measured using the low background GPS instrument as well as the higher-background GPD instrument. The compounds with impurities were measured using the LTF spectrometer which also has a considerable background. The lines are fits to the sigmoid function which allow extracting the transition temperature, which is plotted in b). The points corresponding to the "0" value of 0.5 % and 1% Ni-substituted compounds are plotted since no increase of decay asymmetry was observed in the zero-field measurements. The solid line is the prediction from [121].
5.4 Discussion and Conclusions

The muon decay asymmetry in the sample with 0.5% Ni impurities shows very little temperature dependence. There is a small decrease of the nonmagnetic volume fraction at low temperatures but it keeps decreasing as the temperatures are lowered and does not stabilize. Since there is no bending of the sigmoid curve, no transition temperature can be defined.

Using the obtained transition temperature for the pure compounds, interchain coupling can be calculated using empirical equation developed for weakly coupled single chains [115]. This can be used to calculate the theoretically expected ordering temperature for the site-diluted chain [120] and compared to the observed values. The obtained transition temperatures are shown in Fig. 5.7b together with the prediction of [120].

5.4 Discussion and Conclusions

Previous studies of the ordering in pure SrCuO$_2$ have left many unanswered questions, notably why the oscillations in the muon spectrum were absent [125] as well as why there was more than one characteristic temperature observed in the neutron study [126]. The present experiments suggest that both of these issues can be explained by the lower quality samples used in the past studies. The obtained results decidedly show that in the pure sample the muons precess coherently around the static local magnetic fields in two different locations in the crystal lattice. The system however is extremely sensitive to even very low levels of impurities. Even using the optimized growth procedure, two nominally pure samples from different batches have been found to have slightly different transition temperatures. The previously reported muon decay asymmetry [125] looks very similar to the one that was presently obtained using a 0.1% Ni-substituted sample. Therefore, it is most likely that the previous study was affected by a small amount of impurities. The reasoning behind explaining the neutron scattering results is very similar. In the experiment reported in [33], the sample that was used for measurements had two crystallites. It is only natural that in such a sample there were areas with different concentrations of impurities which led to the slow uprise of the Bragg peak with an unusual rate for an order parameter.

The effect of very small site dilution on the magnetic ordering has been con-
Magnetic Ordering in Intact and Depleted Spin Chain SrCuO$_2$

sidered theoretically [120] and the inhomogeneous magnetic moment distribution has been predicted. The present measurements show no oscillations in the disordered materials even at the lowest temperatures. This is indeed consistent with the theoretical prediction of [120] since a distribution of frequencies results in a spectrum that shows no oscillations. The suppression of oscillations has also been shown previously in a related spin-chain compound Sr$_2$CuO$_3$ [128]. It is noteworthy that the magnetic moment distribution is not only inhomogeneous, the largest weight is in the very low moments. The ordered moment distribution is also found to shift to lower values upon increasing the site dilution level.

The magnetic ordering temperature is also found to be strongly affected. It decreases as the level of impurities is increased. The rate of temperature decrease is generally consistent with the predictions [120]. The ordering temperature of the 0.1% and 0.25% Ni-substituted samples behaves according to the theoretical predictions, as seen in Fig. 5.7b.

The biggest surprise of this study is that the samples with 0.5% and 1% Ni impurities show no magnetic ordering. This is in stark contrast to the theoretical predictions that estimated the maximal decrease of the ordering temperature to be fivefold [120]. There are several possibilities for such behaviour. Firstly, as discussed in the theoretical study, only odd-length chain fragments contribute to the magnetic ordering whereas the even-length segments assume spin singlet state. Therefore, if the introduction of Ni-impurities was to lead to preferential creation of even-length segments, magnetic ordering would be suppressed rather quickly. This assumption is unlikely due to low statistical probability of such configuration. Secondly, it is possible that the two-chain structure in SrCuO$_2$ plays a role in this situation. Due to weak interchain coupling, a singlet ground state could be formed between spins in the neighboring chains which would in turn prevent long range order. This possibility could in principle be examined if more careful experiments were performed on the related spin chain Sr$_2$CuO$_3$ with no second spin chain nearby. The third possibility is that the average ordered moment is reduced to values that become too small for the achievable sensitivity.

To summarize, magnetic ordering in pure and site-diluted model spin chain SrCuO$_2$ was studied using $\mu$SR techniques. The previously unresolved issues of the ordering in this particular system were settled by using ultra-pure samples. Upon site-dilution, the magnetic ordering becomes inhomogeneous as predicted.
5.4 Discussion and Conclusions

theoretically. Moreover, for modest levels of site-dilution, the ordering temperature decreases at the predicted rate. For site dilution of 0.5 % and higher, the ordering is found to be completely suppressed.
Chapter 6

Impurity-Induced Spin Pseudogap in Spin Chains $\text{Sr}_2\text{CuO}_3$ and $\text{SrCuO}_2$

Heisenberg $S = 1/2$ chains are famous for their gapless excitation spectrum. Here, the spectrum is measured after an introduction of impurities and a spin pseudogap is found to open. This phenomenon is explained by considering fragmented chains. Temperature-dependence measurements reveal that the universal scaling behavior present in the pure chains persists even in the presence of impurities, albeit masked by the pseudogap.

When disorder is introduced in the spin chains, in addition to changes in the static properties discussed in the previous chapter, the dynamic properties are altered as well. A spin gap has been predicted to open when the chain is site-diluted [129] but up until now there have been no experimental observations. Recently, some indirect hints of this phenomenon have been reported in the high-J cuprate chains. The spin-lattice relaxation rate, measured by Nuclear Magnetic Resonance (NMR) experiments, has been observed to drop at low temperatures in samples with impurities [136–138]. Additionally, the magnetic heat transport was found to be greatly reduced and the ballistic nature compromised upon introduction of disorder [139, 140].

In this chapter, direct measurements of low energy excitations by neutron
scattering in such spin chains are reported. Most of the work was performed on a single spin chain material Sr$_2$CuO$_3$, which is presented in the beginning of the chapter. Different ways to introduce disorder are then described. Results of the neutron scattering experiments are reported for different systems followed by a discussion and theoretical interpretation of the outcome. Part of the results presented in this chapter have been published in [141].

6.1 Spin Chain System Sr$_2$CuO$_3$

The cuprate materials SrCuO$_2$ and Sr$_2$CuO$_3$ are among the best realizations of HAF $S = 1/2$ chain. The main difference between them is that SrCuO$_2$ has a
double chain structure as discussed in chapter 5 which, as will be shown, leads to additional scattering of spinons. On the other hand, Sr$_2$CuO$_3$, shown in Fig. 6.1 has only one isolated chain. The dominant intrachain exchange constant $J_\parallel$ is 241 meV [31]. It displays one dimensional behavior over a large range of temperatures and the pure system orders only at 5 K [117, 124].

The crystals were grown using the floating-zone method [138, 140]. They crystallize in a space group Immm, with lattice constants $a = 12.69$ Å, $b = 3.91$ Å, and $c = 3.49$ Å.

The Sr$_2$CuO$_3$ samples studied with neutron spectroscopy were made of a few co-aligned crystals with crystal a axis perpendicular to the scattering plane. The 1 % Ni-substituted sample consisted of three co-aligned single crystals with total mass of 8.6 g and a Full Width Half Maximum (FWHM) mosaic of 0.4° as measured at 020 and 002 peaks. The 2 % Ni-substituted sample consisted of two single crystals with a mass of 4.6 g and mosaic of 0.7°. The 3.5 g 5 % Ca-substituted sample was made of two crystals with a mosaic of 0.3°.

For the study of the double chain material SrCuO$_2$ with Ni impurities, four single crystal samples of a total mass of 4.0 g and a mosaic spread of 0.9° were used.

### 6.2 Effect of Impurities

There are several ways to introduce disorder into the spin chain as discussed in chapter 5. Here, in addition to the breaking of the chains by implanting Ni$^{2+}$, another way to perturb the system is explored. Ca$^{2+}$ is used to replace part of the Sr$^{2+}$ ions which leads to slight local disruption of the lattice due to the different sizes of the ions. As will be shown later, this leads to additional scattering of spinons. The different types of disorder are shown in Fig. 6.2.

The effect of the impurities can be seen in the susceptibility measurements in Fig. 6.3. To a first approximation, the breaking of the chains introduces effective $S = 1/2$ paramagnetic response coming from the odd-length chains. However, it is known that the even-length chains also contribute to the magnetic response due to susceptibility of the singlets within the finite-length chains. Therefore the susceptibility curve deviates from Curie behavior as already seen in the previous chapter.
6.2 Effect of Impurities

Figure 6.2: Different ways to introduce disorder in the studied compounds. The cleanest way is to implant a different ion in the place of Cu$^{2+}$ in a single chain material Sr$_2$CuO$_3$ as shown in a). Implantation of such type was also performed in the double chain material SrCuO$_2$, displayed in b). A significantly less direct way is to replace Sr$^{2+}$ with an ion of a different type as seen in panel c).
Figure 6.3: Magnetic susceptibility multiplied by temperature for the studied compounds. The highest response is observed in the 2% Ni-substituted system where the largest amount of broken links in the chains is expected. The sample with Ca impurities shows small response as expected for a substitution outside of the chain. The extracted impurity concentration of Ni-substituted samples is shown in the inset for fit using all the data (black circles) and measurements only above 10K (blue squares). The solid black line corresponds to the number of impurities equal to the nominal concentration.
6.3 Spin Pseudogap in Sr$_2$CuO$_3$ with Ni impurities

By using the same fitting equation as in previous chapter, the number of impurities can be extracted and is shown for Ni-substituted compounds in the inset of Fig. 6.3. The extracted values show that the number of broken links correspond to the level of substitution and confirms that introducing Ni impurities is a clean way to fragment the chains. As previously discussed in the case of SrCuO$_2$, at very low temperatures, there are deviations since three-dimensional coupling begins to play a role [123, 135].

In the case of Ca-substitution, the Ca$^{2+}$ ions are expected to replace Sr$^{2+}$ due to the similar ionic radii of the two ions. The magnetic susceptibility measurements in Fig. 6.3 show that this is the case. Even though a large amount of Ca impurities is introduced to the sample, the magnetic response is very low. The functional form of the susceptibility is slightly different than that of Ni-substituted system, but from the magnitude of the response, the maximum number of links broken in the chain can be estimated to be less than 0.5%.

6.3 Spin Pseudogap in Sr$_2$CuO$_3$ with Ni impurities

In order to study the excitations, neutron spectroscopy measurements were performed. Most of the measurements were done at SEQUOIA time-of-flight spectrometer at ORNL with sample kept at $T = 6$ K and using incident energies of 12, 20 and 50 meV for the Sr$_2$CuO$_3$ compound and 25 meV for the SrCuO$_2$. Additional preliminary and temperature dependence three-axis measurements were performed at 4F2 spectrometer at LLB facility, PUMA spectrometer at FRM-2 facility, IN 8 and IN 20 instruments at ILL and TASP spectrometer at PSI. Additional time-of-flight data were obtained at MERLIN spectrometer at ISIS.

The high energy part of the two-spinon continuum has already been studied in the pure compound in a great detail before [31]. In the current study, much lower energies were probed, effectively only accessing the bottom of the two-spinon continuum. Due to the very steep dispersion, they appear as vertical stripes of intensity in the dynamical structure factor as seen in Fig 6.4a. The additional features visible in that plot are the phonons, appearing as a complicated structure of different branches. They interfere with the study of magnetic excitations, but
Figure 6.4: The measured dynamical structure factor of 1% Ni-substituted Sr$_2$CuO$_3$. Spectrum obtained using initial energy of the neutrons of 50 meV is shown in a) as a function of energy transfer and momentum transfer along the chain direction. The intensity is integrated along the other two directions. This can be justified by inspecting b) and c) where the scattering between energies of 4 and 10 meV is plotted as a function of momentum transfer along and perpendicular to the chain. The latter figures are obtained from experimental runs with initial neutron energy of 20 meV due to lower background in the low energy region.

A few pockets of phonon-free parts of the dynamical structure factor can be found at energies around 25 and 44 meV as well as the whole spectrum below 12 meV. The spectrum at high energies shows no effect of impurities.

Before concentrating on very low energies and the effect of impurities, it is worth examining the magnetic scattering as a function of momentum transfer perpendicular to the chain. As seen in Fig 6.4b and c, where the scattering due to excitations in the energy range of 4 to 10 meV are displayed, the spinons are indeed located only at the antiferromagnetic point of the momentum transfer along the spin chain. The other directions are irrelevant. This feature makes the
6.3 Spin Pseudogap in Sr$_2$CuO$_3$ with Ni impurities

time-of-flight technique especially attractive for the study of one-dimensional systems. A big gain in signal can be achieved by integrating the scattering intensity over the momentum transfer perpendicular to the chain direction.

Momentum transfer in the vertical direction mainly allows increasing the data quality whereas the momentum transfer parallel to the neutron flux is the determining factor in the energy transfer too. These are great advantages, but caution related to the magnetic form factor needs to be taken when interpreting the data quantitatively. Since neutrons scatter of electrons which are extended in space, there is an effective loss of scattering at higher momentum transfers. As discussed in chapter 4, Cu 3$d_{x^2−y^2}$ orbitals lead to an anisotropic form factor as sketched in Fig. 4.2. Therefore, when the scattering is momentum-integrated, track needs to be kept of both the magnitude and direction of the momentum transfer.

Having covered the more subtle points about the data, attention can now be directed to the main question posed in this chapter. What happens to the low energy excitations when impurities are introduced in the spin chain? Fig. 6.5 shows the low energy part of the spectrum for the Sr$_2$CuO$_3$ with two different concentrations on Ni impurities. In both cases there is a suppression of low energy states that will be referred to as a pseudogap for the reasons that will be explained in the following paragraphs. One can infer that the energy scale associated with this pseudogap is larger for the system that has higher concentration of impurities.

In order to quantify this dependence more precisely, the dynamical structure factor can be integrated over momentum and expressed as a function of energy. This is shown in Fig. 6.6 for two concentrations: 1 % and 2 %. Indeed, the size of the pseudogap scales with the number of impurities but it can be directly compared with the prediction based on fragmented chains as described below.

An intact spin chain has a well defined scattering dependence on energy [32, 33]:

$$S_{\infty}(\omega) = (\gamma r_0)^2 \frac{k_f^2 g_s^2}{k_i} 4 \frac{A n(\omega) + 1}{\pi J} \tanh \left( \frac{\hbar \omega}{2 k_B T} \right) .$$

(6.1)

Here, the main factor is the exchange constant that gives the scale to the scattering — $A/\pi J$, which is obtained by integrating the Müller ansatz, introduced in eqn. 1.3 with respect to momentum in the low energy region. The other
Figure 6.5: Dynamical structure factor of the two Ni-substituted samples as measured by time-of-flight neutron spectroscopy. The vertical rods at the antiferromagnetic wavevector are the bottom of two-spinon continuum. The suppression of low energy states gives rise to a pseudogap which scales in energy with increasing number of broken links.
contributions include $(\gamma r_0)^2 = 0.290$ barn, $k_i$ and $k_f$ are the incident and final neutron wave vectors, and $A = 1.34$ is the Müller ansatz normalization [32]. In the calculations g factor of $g^2 = (2.12)^2$ was used, which is the average value for the spin components probed in the current experiments. The g factor was calculated based on the Electron Spin Resonance (ESR) measurements of related compounds [142]. Since the data are normalized to absolute units, the extracted result can be directly compared with the calculated structure factor.

It can be seen that the dynamical structure factor in eqn. 6.1 is constant with respect to energy at low temperatures. It is plotted for $T = 0$ as a dashed line in Fig. 6.6. Since measurements were performed at 6 K, the scattering above $\sim 2$ meV is not affected by the finite temperature. Clearly the measured spectrum does not correspond to this line. In order to account for the decrease of low energy degrees of freedom, spinon confinement needs to be considered. In the case of Ni-substitution, it is due to straightforward chain fragmentation as discussed earlier.

Since the spinons are confined to within a fragment of a chain, the momentum of the spinons is quantized. Due to the fact that the dispersion is linear in this low energy region, the quantized energy levels are spaced equidistantly. In fact, such problem has been studied theoretically in [129] for a single chain of finite length. It was found that the spacing between the levels in a fragment of length $L$ is $\Delta_L = 3.65 \times J/L$.

Therefore a spectrum for a single chain fragment can be described as a series of delta functions $S_L(\omega) = \sum_{n=1}^{L} S^\omega_n \Delta_L \delta(\hbar \omega - \hbar \omega^\omega_L)$, where $n$ corresponds to the $n$th energy level. Each energy level has a certain spectral weight $S^\omega_n$. If the total scattering is assumed to remain the same, it can be expressed as $S^\omega_L = S^\omega_\infty(\omega^\omega_L)$.

Since in a solid state system, the defects will be distributed, a distribution of spin gaps will be observed. Assuming a random distribution, a probability of having a fragment of length $L$ is given by $P_L = x^2(1 - x)^L$, where $x$ is the concentration of impurities. Combining the probability of each spectrum with the spectral function allows calculating the dynamical structure factor:

$$S(\omega) = \sum_{L=2}^{\infty} S_L \times P_L = \sum_{L=2}^{\infty} x^2(1 - x)^L \sum_{n=1}^{L} S^\omega_n \Delta_L \delta(\hbar \omega - \hbar \omega^\omega_L). \quad (6.2)$$

Since the low energy properties are studied in this work, only the long chains
Impurity-Induced Spin Pseudogap in Spin Chains $\text{Sr}_2\text{CuO}_3$ and $\text{SrCuO}_2$

contribute to the observed scattering. Therefore the first sum can be approximated as an integral. Additionally, since the number of delta functions that contribute to the low energy scattering is much smaller than the total number of them, the upper limit of the second sum does not matter and it can be set to infinity. By making use of these observations, the spectral function can be rewritten as [143]:

$$ S(\omega) = S_\infty(\omega) \times \sum_{n=1}^{\infty} n(\frac{\Delta}{\hbar \omega})^2 \exp(-n\frac{\Delta}{\hbar \omega}). $$  \hfill (6.3)

This sum can be evaluated analytically, giving:

$$ S(\omega) = S_\infty(\omega) \times F(\omega), $$  \hfill (6.4)

where by setting $\Delta = 3.65 \times J \times x$, $F$ is expressed as:

$$ F(\omega) = \left(\frac{\Delta}{2\hbar \omega}\right)^2 \sinh^{-2}\left(\frac{\Delta}{2\hbar \omega}\right). $$  \hfill (6.5)

This means that the dynamical structure factor can be factorized into the infinite-chain dynamical structure factor and a defect-induced envelope function. The envelope function due to the spin gap depends only on the concentration of impurities $x$ and the strength of the exchange constant $J$.

As can be seen in Fig. 6.6, the experimental data are reproduced by the eqn. 6.4 without any adjustable parameters. This suggests that for the single-chain material $\text{Sr}_2\text{CuO}_3$, introducing $\text{Ni}^{2+}$ impurities is a very clean way to fragment the chains and the size of the pseudogap indeed scales with the number of impurities as can be inferred from theoretical considerations.

6.4 Spin Pseudogap in Ni-substituted $\text{SrCuO}_2$ and Ca-substituted $\text{Sr}_2\text{CuO}_3$

The situation becomes more complicated for different impurity types. As seen in Fig. 6.2, when $\text{Ni}^{2+}$ is introduced into the double-chain material $\text{SrCuO}_2$, in addition to braking a chain, it also lies in the vicinity of the neighboring chain. The main consequence arising from such complication is that the impurities may
**6.4 Spin Pseudogap in Ni-substituted SrCuO$_2$ and Ca-substituted Sr$_2$CuO$_3$**

![Momentum integrated dynamical structure factor](image)

Figure 6.6: Momentum integrated dynamical structure factor of the 1% Ni-substituted (squares) and 2% Ni-substituted (circles) samples. The dashed line shows the prediction for an intact chain, whereas the solid lines show the scattering for spin chains with 1% (black) and 2% (blue) broken links.
act as additional scattering centers for the spinons. Impurities lead to the formation of the pseudogap as shown in Fig. 6.7b. But a more quantitative analysis shows that there is a rather poor agreement between the data and the predicted dynamical structure factor assuming nominal concentration of impurities (1 %). However, if the effective amount of impurities is allowed as a fitting parameter, a value of 1.7(1)% is found to reproduce the data very well. This suggests that indeed the proximity of the two chains in the crystal leads to additional scattering centers.

In the case of the single-chain material Sr$_2$CuO$_3$ with Ca$^{2+}$ impurities, the impurities break very few chains if any, as evidenced by the susceptibility measurements (Fig. 6.3). The pseudogap, however is observed again suggesting that breaking of the chains is not a necessary condition for the formation of the pseudogap — instead, what matters is the confinement of the spinons. In order to reproduce the momentum integrated data shown in Fig. 6.7a, the effective number of the chain breaks is fitted and found to be 2.1(3)%, assuming that the exchange constant is not modified.

### 6.5 Temperature Dependence of the Scattering

When measured at different temperatures, the dynamical structure factor allows learning about the universal scaling properties arising from the quantum critical nature of a spin chain. Fig. 6.8 shows the data in such a form. By including the exchange constant along the chain, this quantity can be expressed in a way that allows comparison between different chains. In the present case, both the single-chain material Sr$_2$CuO$_3$ and the double-chain system SrCuO$_2$ could be presented in the same plot.

When impurities are introduced into spin chain and the pseudogap opens, a new energy scale is introduced. This has the largest consequences at low temperatures but the effect extends throughout all temperatures, as can be seen in Fig. 6.8a, no scaling can be observed in the as-measured data from the systems with impurities. However, if the data are corrected by the envelope function of eqn. 6.5, the collapse and scaling is restored.

The fact that the data can be described effectively in a large temperature range for two different chains, provide additional confidence in the proposed model.
Figure 6.7: a) Momentum integrated dynamical structure factor of the 5% Ca-substituted Sr$_2$CuO$_3$ samples. The dashed line shows the prediction for an intact chain, whereas the solid line shows the best fit of 2.1% broken links. Panel b) displays the dynamical structure factor of the 1% Ni-substituted SrCuO$_2$. The data in this case are best reproduced using an effective number of broken links of 1.7%.
Figure 6.8: a) The as-measured dynamical structure factor expressed in a universal scaling form. (b) The dynamical structure factor corrected by the pseudogap function. The empty and full symbols correspond to time-of-flight and three-axis measurements respectively. The solid line is the theoretical prediction for the \( S = 1/2 \) chain.
6.6 Conclusion

When impurities are introduced into spin chains, the dynamic properties change significantly. The study reported in this chapter provides an understanding of the disorder-induced phenomena. A number of seemingly different cases can all be described in a single framework.

The key concept is that once the chain is severed in any way, it can no longer be treated as an infinite system. Spinons, that would otherwise propagate freely in the chains are confined within finite segments of the chains. This leads to momentum quantization and in turn, energy quantization. A statistically weighted sum of spectra from finite-length chains can reproduce the measured spectrum from a crystal sample.

When transferring this picture to an experimental realization, several cases need to be considered separately. A simplest case is when the defects are introduced into a single, well isolated spin chain. Then the number of defects can be directly taken as the number of broken chain links. Indeed, Sr$_2$CuO$_3$ with Ni impurities can be described in such a way.

When the impurities do not directly cut the chain, they can still influence the spectral properties by confining the spinons. Two such cases were described here. In the case of Ni-substituted double chain compound SrCuO$_2$, the effective number of chain-breaks was found to be close to double that the number of impurities, arising from the vicinity of the second chain. In the case of Ca-substituted single chain compound Sr$_2$CuO$_3$, where the Ca is implanted away from the chains, a sizeable spin gap was still observed.

The results presented here show that the low energy dynamic properties of the spin chains with impurities are governed by the level of spinon confinement.
Chapter 7

Magnetic Excitations in Spin Ladders Cu(C_8H_6N_2)(Cl_{1-x}Br_x)_2 and (C_7H_{10}N)_2CuBr_4

The excitations in spin ladders are rather unusual and depend on the ratio between the leg and rung exchanges. In this chapter, the excitations in two families of materials are studied using Raman spectroscopy. Interesting spectral tunability is found in one of the materials, whereas the second one exhibits phonon-assisted magnetic scattering.

Quantum spin ladders are among the best model systems for studying low-dimensional many body physics. The limiting cases of non-interacting dimers and non-interacting spin chains have exact solutions, and the physical properties of the system changes as a function of the ratio between the exchange along the leg ($J_\parallel$) and along the rung ($J_\perp$) [39, 114, 144]. The very nature of the excitations changes from triplons hopping along the leg in the strong-rung case to confined spinons in the strong-leg case.

By now, there are several good materials realizing the spin ladder model. Usually, a newly synthesized ladder model material falls into either of the two categories with a fixed ratio of the exchange constants. However, an intriguing option of continuously varying the leg to rung ratio, albeit in a small range, has been recently suggested in a family of materials Cu(Qnx)(Cl_{1-x}Br_x)_2 (Qnx = C_8H_{6}N_{2})
7.1 Raman Scattering in Spin Ladders

[145–148], where by varying the ratio of the halide ions in the exchange path, both the exchange along the rung as well as along the leg is modified. Therefore it would be very interesting to explore how the excitations change when the system is tuned. Unfortunately, neutron scattering experiments are not very feasible since only small crystals have been synthesized up to now. The only neutron study was performed on the Br-end compound using 27 g of deuterated powder [149] which is extremely expensive and yielded limited results.

Fortunately, Raman measurements can be performed on these compounds and allows extracting quantitative data for the whole family of compounds. Theoretical prediction exist for the spectra of ladders with different ratio of the exchange constant and is introduced in the first paragraph of this chapter. It is followed by the description of the spin ladder system Cu(Qnx)(Cl_{1-x}Br_x)\_2. The Raman spectroscopy results are then presented and compared with theoretical predictions as well as calculations based on previous bulk measurements.

The second part of this chapter deals with a very different system — a strong-leg ladder (C\_7H\_10\_N)\_2CuBr\_4, which is very well understood and many experimental results position it as one of the best realizations of a spin ladder. Unfortunately, the energy scales involved in direct scattering are too low to be accessed by the Raman spectroscopy. However, as will be found, an interesting process of phonon-assisted magnetic scattering allows studying magnetic excitations. After introducing the material, results are presented and discussed in the context of the interaction between phonons and magnons. Part of the results presented in this chapter have been published in [150].

7.1 Raman Scattering in Spin Ladders

Magnetic Raman scattering is often difficult to interpret since various contributions can be relevant. For materials with no long range order only two-magnon scattering is generally allowed which is easier to interpret. The total transfer of the spin is zero as well as the total momentum transfer. In the case of the spin ladder, a further simplification exists — the spectrum can be calculated to within a single scale factor, because the contributions of interactions on the rungs and legs are proportionate [104]. Detailed calculations of the spectra have been performed for various ratios of leg and rung exchanges [105, 106], which can be
Magnetic Excitations in Spin Ladders $\text{Cu}(\text{C}_8\text{H}_6\text{N}_2)(\text{Cl}_{1-x}\text{Br}_x)_2$ and $(\text{C}_7\text{H}_{10}\text{N})_2\text{CuBr}_4$

used directly to compare with our measurements.

7.2 Strong-Rung Spin Ladder $\text{Cu}(\text{Qnx})(\text{Cl}_{1-x}\text{Br}_x)_2$

The $\text{Cu}(\text{Qnx})(\text{Cl}_{1-x}\text{Br}_x)_2$ spin ladder was chosen due to the suggestions that it can be tuned by chemically substituting the halogen ions, which provide the exchange path for the rung. Previous bulk measurements yielded the following estimates of the exchange parameters: $J_\parallel = 1.61 \text{ meV}$, $J_\perp = 2.95 \text{ meV}$ ($J_\perp/J_\parallel = 1.83$) and $J_\parallel = 1.99 \text{ meV}$, $J_\perp = 3.26 \text{ meV}$ ($J_\perp/J_\parallel = 1.64$) for $x = 0$ and $x = 1$, respectively.

In terms of structural properties, they crystallize in the monoclinic $C 2/m$ space group, with lattice parameters $a = 13.237 \text{ Å}$, $b = 6.935 \text{ Å}$, $c = 9.775 \text{ Å}$, $\beta = 107.88^\circ$ for pure $\text{Cu}(\text{Qnx})\text{Cl}_2$ [145] and $a = 13.175 \text{ Å}$, $b = 6.929 \text{ Å}$, $c = 10.356 \text{ Å}$, $\beta = 107.70^\circ$ for pure $\text{Cu}(\text{Qnx})\text{Br}_2$ [146].

The crystals used in this study were grown by using a method of slow diffusion in methanol solution as described in [147]. Since a clean, well-defined surface is needed for precise Raman measurements, as-grown crystals were used with a surface plane that included a well-defined crystallographic $b$ axis and a combination of the other two directions. A typical size of the samples studied was $2 \times 1 \times 1 \text{ mm}^3$.

7.3 Raman Scattering in $\text{Cu}(\text{Qnx})\text{Br}_2$

The Raman spectra reported in this chapter were obtained using the in-house spectrometer described in chapter 4. A green laser with $\lambda = 532 \text{ nm}$ was used. The power of the laser beam hitting the sample was set to 0.5 mW to minimize heating of the sample.

A typical Raman spectrum of the Br-end compound is shown in Fig. 7.2a. At high temperatures, the scattering is dominated by phonons but upon cooling down, a broad feature is found to develop. Based on the temperature dependence, it is assigned to two-magnon scattering. Additional confirmation can be drawn from the fact that the observed spectrum is consistent with a lineshape predicted by the theoretical calculations of [105]. The polarization-dependence of the spec-
Figure 7.1: A sketch of the structure of the Cu(C₈H₆N₂)(Cl₁₋ₓBrₓ)₂ spin ladder with the principal exchange paths indicated by arrows. The interaction along the leg and the rung of the ladder proceeds through quinoxaline (Qnx) molecules and halogen ions respectively.
Magnetic Excitations in Spin Ladders Cu(C₈H₆N₂)(Cl₁₋ₓBrₓ)₂ and (C₇H₁₀N)₂CuBr₄

Figure 7.2: a) Temperature dependence of the spectrum for the Br-end compound. At low temperatures a broad continuum develops which is interpreted as two-magnon scattering. b) The polarization-dependence of the spectrum shows that the most intense scattering appears with the electric field vector parallel to the ladder direction.

Figure 7.2b reveals that the scattering is strongest when the electric field of the incoming and outgoing light is parallel to the ladder direction.

7.4 Tuning the Ladder Using Chemical Substitution

Having identified the scattering in the ladder, it is now possible to discuss the effect of chemical substitution. The spectra of the two-end compounds is shown in Fig. 7.3. It is immediately visible from the figure, that the Br-end compound has a higher energy scale as expected from previous bulk measurements [146–148]. Another visible feature is that the width of the scattering continuum is increasing faster than the onset. This indicates that the bandwidth is increasing faster and in turn suggests that the exchange along the leg is increasing faster than along the rung.

In order to extract the information about the spin excitation gap and the magnon bandwidth for the whole substitution series, the spectral region close to
Figure 7.3: Raman scattering from the two end compounds. The sharp features are due to lattice vibrations with the most intense phonons shaded. The broad continuum is due to two-magnon scattering. The magnetic scattering in the Br-end compound is associated with a higher energy scale.
Magnetic Excitations in Spin Ladders Cu(C$_8$H$_6$N$_2$)(Cl$_{1-x}$Br$_x$)$_2$ and (C$_7$H$_{10}N)_2$CuBr$_4$

Figure 7.4: a) The onset and b) the cutoff regions for selected different concentrations. The spectra are offset for a clearer presentation of the data. The fitted straight lines are presented as dotted lines with the intersection providing the estimates of the threshold. The sharp phonons for the $x = 0$ compound are truncated for the visual clarity of the data.

The onset and cutoff of the continuum was studied. As shown in Fig. 7.4, two straight lines were fitted below and above the thresholds with the intersection taken as the onset or cutoff threshold value. For the onset, the linear fit covered an energy range of ±7 cm$^{-1}$ around the onset, excluding the data in its immediate vicinity (0.6 cm$^{-1}$ on either side). For the cutoff, the linear fitting range was 15 cm$^{-1}$ below the onset and up to 30 cm$^{-1}$ above it, excluding 1.2 cm$^{-1}$ in the immediate vicinity. The obtained values for the upper and lower continuum thresholds are plotted in Fig. 7.5.

The extracted values of the onset and cutoff can be used to compare the present results with previous studies. By making use of the fact that the onset of the scattering is twice the size of the gap [105], 2$\Delta$ obtained from neutron scattering experiments on the Br-end compound [149] can be compared with the Raman data. Analogously, the same quantity can be estimated from bulk magnetic measurements of the series, reported in [148]. The estimates from all the methods are plotted in Fig. 7.5b for comparison.

Similarly, cutoff values can be used to learn about the bandwidth of the scattering. The width of the magnetic scattering continuum can be related to the

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Figure 7.5: Extracted values of the onset (shown in panel b) and cutoff (panel a) of magnetic scattering for different concentrations (black triangles). The estimates using the results from previous studies are also plotted. Red circles represent values estimated by using bulk measurements of [148] and extrapolating DMRG calculations of [39]. The blue triangles are taken from inelastic neutron study of Br-end compound [149]. The dashed lines are to guide the eye.
Magnetic Excitations in Spin Ladders $\text{Cu(C}_8\text{H}_6\text{N}_2)\text{(Cl}_{1-x}\text{Br}_x)_2$ and $(\text{C}_7\text{H}_{10}\text{N})_2\text{CuBr}_4$

spread in energies of two-magnon scattering calculated from single-magnon dispersion relation. This has been calculated in detail in [39] for several values of the ratio $J_\perp/J_\parallel$. Since $\text{Cu(Qnx)(Cl}_{1-x}\text{Br}_x)_2$ is a strong-rung ladder, close to the isotropic case, the calculated values for ratios of $J_\perp/J_\parallel = 2$ and $J_\perp/J_\parallel = 1$ can be used which give cutoff values in terms of the leg exchange constant to be $6.28J_\parallel$ and $4.08J_\parallel$, respectively. In order to obtain the cutoff for each member of the substitution series, a linear interpolation of these values can be calculated. The interpolation was done with respect to $J_\perp/J_\parallel$. As a final step, the exchange constants obtained in [148] were used to obtain the cutoff value for comparison with the observed data. The resulting estimates are plotted in Fig. 7.5a together with the data obtained in the present study and the neutron scattering results of [149].

The trend of the increasing energy scale as more Br is introduced is consistent with the earlier predictions of tunability [148]. However, both the onset and cutoff are observed at consistently lower energies by about 10%. While the exact origin of this discrepancy is unclear, the most likely cause is the additional terms in the Hamiltonian. If a weak inter-ladder interaction is present it may have not been observed by the powder neutron scattering measurements. Similarly, assuming an ideal ladder in the analysis of bulk magnetization data, the extracted gap would be not the real bottom of the three-dimensional dispersion that is probed in the present experiments. The discrepancy would propagate to the estimation of the cutoff as well. Therefore the Raman spectroscopy experiments reported here suggest that additional interactions are present in $\text{Cu(Qnx)(Cl}_{1-x}\text{Br}_x)_2$.

### 7.5 Tuning the Ladder with Hydrostatic Pressure

Since $\text{Cu(Qnx)(Cl}_{1-x}\text{Br}_x)_2$ is an organometallic compound, it is expected that the crystal structure would be susceptible to the external pressure. Since the magnetic exchange energy depends on the orbital overlap between electrons from different ions, the application of pressure is expected to change the magnetic properties as well. Raman spectra of the Br-end compound, shown in Fig. 7.6, demonstrate that it is indeed the case.
7.5 Tuning the Ladder with Hydrostatic Pressure

Figure 7.6: Raman scattering of from Cu(Qnx)Br$_2$ with applied pressure. The onset of the scattering stays constant, whereas the cutoff shifts to higher energies. Inset shows the extracted values with the dashed line to guide the eye.

The onset of the magnetic scattering does not change significantly, but the cutoff is moved to much higher energies. Following the reasoning described above, this means that the gap value does not change, but the bandwidth increases markedly. Consequently, this hints that the main change with hydrostatic pressure is the increase of the leg exchange constant and therefore, the pressure pushes the system towards the isotropic ladder case even more.

This has very interesting consequences. Provided the structure is not altered too much with application of pressure, there is a possibility of shifting the ladder from the strong-rung regime to the strong-leg regime. If this is achieved, the Raman spectrum would exhibit an unusual two-peaked lineshape, as suggested
by theoretical studies [105]. The rate of change of the leg to rung ratio is however rather small. Therefore such transformation to a strong-leg regime is currently not achievable by using the NSM Raman setup. However, the planned upgrades, as indicated in chapter 4 may open such opportunities.

7.6 Strong-Leg Spin Ladder \((C_7H_{10}N)_2CuBr_4\)

The impetus for studying a strong-leg spin ladder is to observe qualitatively different excitations than in the strong rung case. While the direct observation as predicted by [105], could not be observed in the most ideal realization of strong-leg model — \((C_7H_{10}N)_2CuBr_4\), higher order processes have delivered interesting excitations of new type as described in the following few paragraphs.

Crystallographically, \((C_7H_{10}N)_2CuBr_4\) forms a monoclinic structure with the space group \(P2(1)/n\) and lattice constants \(a = 7.504 \text{ Å}, b = 31.61 \text{ Å}, c = 8.202 \text{ Å}, \beta = 98.98^\circ\) [16]. The ladders are formed by Cu\(^{2+}\) ions connected by superexchange interaction via bromide ions as shown in Fig. 7.7. The exchange constants have been measured to be \(J|| = 1.42 \text{ meV}\) and \(J\perp = 0.82 \text{ meV}\) [45, 151].

The samples that were used for the study consisted of slabs of material with dimensions of a few millimeters. Geometrically, the surfaces used for the study had the \((ac)\) plane available for the studies. Since \(a\) direction is parallel to the leg of the ladder, it was aligned with one of the electric field orientation. Similarly, \(c\) direction was aligned to the other light polarization, but only approximately so, due to the monoclinic angle.

7.7 Phonon-Assisted Magnetic Excitations

Typical Raman spectra from \((C_7H_{10}N)_2CuBr_4\) at different temperatures are shown in Fig. 7.8. At high temperatures, the Raman scattering is dominated by scattering from phonons. At low temperatures, emergence of magnetic scattering is expected at low energies.

Based on the theoretical calculations of [105] and the previously described results on \(Cu(Qnx)(Cl_{1-x}Br_x)\) spin ladder, the scattering is expected to be present in the range from a few cm\(^{-1}\) to about 40 cm\(^{-1}\). The predicted onset of the con-
Figure 7.7: A Sketch of the structure of the (C\(_7\)H\(_{10}\)N)\(_2\)CuBr\(_4\) spin ladder with the principle exchange paths indicated by the arrows. The interaction along the leg and the rung of the ladder proceeds through halogen ions. The rest of the structure acts as a very effective isolator.
Magnetic Excitations in Spin Ladders $\text{Cu}(\text{C}_8\text{H}_6\text{N}_2)(\text{Cl}_{1-x}\text{Br}_x)_2$ and $(\text{C}_7\text{H}_{10}\text{N})_2\text{CuBr}_4$

Figure 7.8: Temperature dependence of Raman scattering in $(\text{C}_7\text{H}_{10}\text{N})_2\text{CuBr}_4$ in the $\sim$(ca) polarization.

Since the absolute value of the magnetic cross section is dependent on the material properties, the most probable explanation is that the signal is simply too weak to be observed. In fact, this is not an unusual case — for many potentially interesting compounds, no magnetic Raman scattering has been observed.

However, in the case of Raman scattering in $(\text{C}_7\text{H}_{10}\text{N})_2\text{CuBr}_4$, new features do appear at low temperatures, but they are located in the very high energy part of the spectrum, as shown by the arrows in Fig. 7.8. These features appear
7.7 Phonon-Assisted Magnetic Excitations

at temperatures comparable to the relevant exchange constants and therefore they are likely to arise from magnetic excitations. Moreover, the width of the two highest energy excitations is comparable to that expected from two-magnon continuum and therefore the observed scattering is most likely related to two-magnon scattering. Nevertheless, the energies at which the scattering takes place are too high for a direct magnetic scattering process discussed earlier. Therefore, another mechanism must play a role here.

The most likely explanation for this scattering is that the magnetic excitations are assisted by a phonon and a composite process of exciting a phonon and two magnons takes place. Such a phonon might modify the lattice in such a way that one of the bonds, responsible for the principle exchange in the ladder, is affected. Experimental observations of anomalously broad infrared absorption lineshapes for two magnons were interpreted as a result of a coupling between magnons and phonons [152]. Similar suggestions were made for Raman spectroscopy, suggesting that the phonons act like sinks of momentum [153]. However, neither of the two cases correspond to the observations described here, because in this case, the energy of the magnetic excitation is shifted by a substantial amount.

An interesting feature of this scattering is seen in Fig. 7.9. It is only strong in one of the polarizations, with the electric field set to cross-polarized configuration. This could be related to the polarization properties of the phonon that induces such magnetic scattering. However, on closer inspection, it is evident that the phonon next to the strongest magnetic scattering peak is present in all polarizations with approximately equal intensity. This, therefore, poses deeper questions on the nature of phonon-magnon coupling in this material and a program of follow up experiments are planned as described in chapter 9.
Magnetic Excitations in Spin Ladders Cu(C\textsubscript{8}H\textsubscript{6}N\textsubscript{2})(Cl\textsubscript{1-x}Br\textsubscript{x})\textsubscript{2} and (C\textsubscript{7}H\textsubscript{10}N\textsubscript{2})CuBr\textsubscript{4}

Figure 7.9: Raman spectra of (C\textsubscript{7}H\textsubscript{10}N\textsubscript{2})CuBr\textsubscript{4} at different polarizations of the incoming and outgoing light.
7.8 Conclusion

Raman spectroscopy measurements were used for an in-depth study of magnetic excitations in quantum spin ladders. In the case of light scattering in Cu(Qnx)(Cl\textsubscript{1−x}Br\textsubscript{x})\textsubscript{2}, a large degree of tunability was demonstrated. While the Cl-end compound is firmly in the strong-rung regime, the ladder approaches the isotropic case with increasing Br content. Moreover, hydrostatic pressure increases the exchange constant along the leg even more.

Even though the observed spectra suggest that the Cu(Qnx)(Cl\textsubscript{1−x}Br\textsubscript{x})\textsubscript{2} ladders have additional interactions, the present measurements represent the cleanest Raman study of organometallic quantum spin ladders. Promising extensions of the study can be made with an upgrade of the high-pressure setup.

An even more interesting result has been the observation of phonon-induced magnetic scattering in the strong-leg spin ladder (C\textsubscript{7}H\textsubscript{10}N)\textsubscript{2}CuBr\textsubscript{4}. This observation will open a new direction of research by allowing the study of interaction between magnetic and lattice excitations.
Chapter 8

Magnetic Excitations in 
\( (C_4H_{12}N_2)Cu_2Cl_6 \) Under Pressure

Spin excitations in a quasi two dimensional spin system 
\( (C_4H_{12}N_2)Cu_2Cl_6 \) were investigated using Raman spectroscopy. The 
excitation spectrum as a function of hydrostatic pressure exhibits 
significant changes as the phase transitions take place.

Quantum phase transitions are fascinating phenomena which have recently attracted a lot of attention in the field of magnetic insulators, since they allow well-controlled studies of critical phenomena. Perhaps the most well-known example is the field induced phase transition in gapped quantum magnets, which can be interpreted as Bose-Einstein condensation of magnons [35]. In such cases, since an external field is applied, one of the directions in space is predefined. The subsequent phase transition breaks rotational SO(2) symmetry in the plane perpendicular to the applied field [35, 49, 154, 155]. The gapped quantum magnets can also undergo a transition in the absence of the applied field, leading to an SO(3) symmetry breaking, if the ratios of exchange constants are varied. While theoretically it is a natural approach [65], experimentally it is a difficult task. A certain amount of luck is needed to discover materials where the application of external pressure, has the desired effect of modifying the exchange constants in a way needed to induce a phase transition.

Up until recently, only one compound exhibiting such a phase transition has
been found — TlCuCl₃ [156, 157]. Extensive studies of the phase transition in TlCuCl₃ has brought to light many interesting physical phenomena, including a longitudinal excitation mode, which can be interpreted as a Higgs quasiparticle in magnetic insulators [37, 38].

A new system hosting a pressure-induced quantum phase transition has been discovered recently. It is an organometallic compound (C₄H₁₂N₂)Cu₂Cl₆, described in more detail in the following chapter. Muon spin rotation experiments have indicated that long range order develops at a pressure of $P_{c1} \approx 4.4$ kbar. Moreover, a second phase transition was suggested to take place at $P_{c2} \approx 13.4$ kbar, switching the magnetic structure from a helical to a collinear one [66].

Subsequent neutron scattering experiments of (C₄H₁₂N₂)Cu₂Cl₆ under pressure have revealed that indeed the spectrum is also modified and the magnetic excitation gap is closed above the critical pressure [158]. Interestingly, no change was observed at the second phase transition, raising more interest in the pressure-induced phenomena in this material. Unfortunately, only two pressures could be studied in [158] due to limited time available at a neutron source.

Therefore, Raman spectroscopy is employed here to study the change in the dynamics as a function of pressure with a finer step in pressure. Additionally, the second phase transition is investigated in more detail to reveal whether or not significant changes in the excitation spectra are present.

### 8.1 Two Dimensional System (C₄H₁₂N₂)Cu₂Cl₆

The organometallic spin compound (C₄H₁₂N₂)Cu₂Cl₆ has been extensively studied in the past, revealing that the magnetic properties are dominated by a system of spin dimers [159, 160], with an exchange constant of $J_1 = 1.3$ meV. The dimers are connected in an intricate two-dimensional lattice, with at least five more different bonds that could be identified by neutron scattering experiments [161]. The three main exchange pathways are shown in Fig. 8.1.

Structurally, (C₄H₁₂N₂)Cu₂Cl₆ crystallizes in the P̅₁ triclinic space group, with lattice parameters $a = 7.984$ Å, $b = 7.054$ Å, $c = 6.104$ Å, $α = 111.23°$, $β = 99.95°$, $γ = 81.26°$ [161].

The crystals for this study were grown in the NSM laboratory using a thermal gradient method [17]. The cleanest spectra were obtained from crystals with as-
Figure 8.1: Structure of the (C_4H_{12}N_2)Cu_2Cl_6 compound. The magnetic lattice is formed by $S = 1/2$ spins from copper ions. The main exchange interactions mediated by chloride ions are indicated.
8.2 Raman Spectrum of ($C_4H_{12}N_2$)$_2$Cu$_2$Cl$_6$ at Ambient Pressure

Figure 8.2: Raman spectra of ($C_4H_{12}N_2$)$_2$Cu$_2$Cl$_6$ compound at various temperatures. The incoming and outgoing polarization of the electric field is approximately along the crystallographic c direction.

grown surfaces. A large amount of crystals had to be examined using an X-ray diffractometer to find crystals with desired surfaces. The initial ambient pressure study was performed on large crystals with an extent of a few millimeters in all the characteristic dimensions. The high-pressure experiments were carried out using much smaller crystals with an extent of about 0.3 $\times$ 0.1 $\times$ 0.2 mm.

8.2 Raman Spectrum of ($C_4H_{12}N_2$)$_2$Cu$_2$Cl$_6$ at Ambient Pressure

Despite the large interest in the magnetic properties of ($C_4H_{12}N_2$)$_2$Cu$_2$Cl$_6$, no Raman spectroscopy studies have been performed up to now. Here, the NSM
Raman spectrometer is used to obtain the data and elucidate the nature of the phase transitions. In order to limit the background, the red laser of $\lambda = 660$ nm was used to obtain the results presented in this chapter. The laser power hitting the sample was set to 3 mW.

Typical spectra obtained at different temperatures are shown in Fig. 8.2. At high temperatures the spectrum is dominated by the scattering of phonons, but as the sample is cooled down, a broad continuum appears, which is assigned to two-magnon scattering based on its temperature dependence and the energy range.

The samples used for the initial studies had faces that were only approximately corresponding to the magnetic exchange paths. For the high-pressure study, a sample with a b-c face was used. This allows checking polarization properties more carefully as shown in Fig. 8.3a. The signal is strongest when the light is polarized parallel to the c direction. The perpendicular direction was marked x, which contains a combination of a and b directions. No scattering is observed in the perpendicular direction. A note must be made here about the difference between the spectrum in figures 8.2 and 8.3a. They are obtained from different crystals which have a slightly different orientation. More importantly for the signal quality is that the former is from a large crystal, with a very clean face. The latter was obtained from a crystal upon which high pressure was applied and then released. This results in some layers of Daphne oil on the surface as well as some other dirt which sticks to it, therefore the signal quality is not as good as in Fig. 8.2.

### 8.3 Spin Excitations at High Pressures

The main result of this part of the study are the Raman spectra of $(C_4H_{12}N_2)Cu_2Cl_6$ under different pressures, shown in Fig. 8.4. The sharp phonon peaks are gradually shifted to higher energies with increasing pressure. No broadening of the peaks is observed, suggesting a uniform pressure and no strain at least in the measurement volume.

The magnetic scattering is, in contrast, shifted towards lower energies. At low pressures, the shape of the spectrum does not change, but is only shifted to lower energies. At pressures above the critical pressure indicated by muon...
8.3 Spin Excitations at High Pressures

experiments of [66], the scattering continuum becomes broader and tends to get more asymmetric as seen in the lineshape of the spectrum between 6 and 12 kbar. Starting with 14 kbar, the magnetic scattering shape changes drastically and becomes increasingly broad. This pressure approximately corresponds to the second phase transition observed in the muon experiments [66]. At 15 kbar, the centre of the peak is at very low energies, unresolved in these experiments, while at even higher pressures the peak centre moves up in energy again. Thus, it is evident that significant changes take place at the second phase transitions and there is possibly another characteristic pressure of 15 kbar, where the properties of the system are markedly altered again.

It is also interesting to dwell upon the polarization properties of the scattering at high pressures shown in Fig. 8.3b. While neutron scattering experiments of [158] have shown that the system becomes three-dimensional at elevated pressures, the magnetic Raman scattering is still confined to the selection rules present at ambient pressure.

8.3.1 Quantitative Analysis of the Spectrum

Ideally, the observed Raman spectra could be connected to a microscopic model of the system which allows tracing the changes in magnetic interactions as a
Figure 8.4: Raman spectra of (C₄H₁₂N₂)Cu₂Cl₆ compound at elevated pressures. The data were collected at temperature of $T = 2.6$ K. The spectra obtained at different pressures are offset for visual clarity.
8.4 Conclusion

function of pressure. However, such calculations are generally very complicated [106, 162] and the obtained lineshapes are very sensitive to small perturbations of the Hamiltonian [163]. For the case of the studied system such calculations do not exist, and an empirical interpretation needs to be employed.

One of the ways to empirically study such lineshapes is to calculate the moments of the scattering distribution. Unfortunately, since not the whole scattering peak can be observed in the experiment, such method could not be used in the present case. Alternatively, extrapolated onset and cutoff values can give an indication about the excitation gap and the bandwidth, as seen in chapter 7. In the case of scattering in \((C_4H_{12}N_2)Cu_2Cl_6\), the onset and cutoff are not as sharp and as a result it is difficult to pick an unbiased range of fitting for the determination of such quantities.

In the light of the above, a different method of quantification was employed. A set of indicative quantities, directly read off the spectra are presented in Fig. 8.5. The peak position and half maxima positions are plotted in the top panel, which shows that all the values decrease with pressure up to 10 kbar. As the pressure is increased further, the higher-energy side of the continuum starts moving up. The center of the peak reaches the lowest value at 15 kbar, where the spectrometer can no longer resolve the position of the peak. It then shifts back up in energy.

By considering the extracted quantities, the lineshape of the scattering in the three different phases can be considered. In the first phase, the peak moves to lower energies, but remains rather symmetric. As soon as the boundary is crossed into the first ordered phase, the asymmetry increases and a high energy shoulder develops. The changes in the spectrum exhibited around the second phase transition are even more pronounced. The lineshape acquires a broad structure which suggests that a different type of scattering takes place.

8.4 Conclusion

The evolution of magnetic excitations in \((C_4H_{12}N_2)Cu_2Cl_6\) across the quantum phase transitions was probed using Raman spectroscopy. A continuous evolution of the exchange constants due to the applied pressure resulted in changes of the spectrum. The onset of the continuum shifted to lower energies with moderate pressures, as expected from earlier neutron studies. No dramatic changes in the
Figure 8.5: Extracted values of the pressure dependence of the magnetic scattering in \((C_4H_{12}N_2)Cu_2Cl_6\). Top panel shows the positions of the maximum of the peak as well as the positions where the intensity drops to half the maximum value. The horizontal dashed line shows the lower limit observed in our configuration and therefore the peak position at 15 kbar has large errorbars. The lower panel shows the difference between the upper and the lower half maximum position (FWHM). Since the FWHM is not accessible in the whole range, additionally, a difference between the peak position and the position of the half maximum on the higher energy side is also plotted (HWHM). The vertical dashed lines in both panels correspond to the critical pressures suggested by the muon experiments.
8.4 Conclusion

lineshape of the spectrum are observed as the material is pressurized moderately and stays in the first phase. As the system goes through the first phase transition, the spectrum becomes markedly asymmetric with the lineshape acquiring a high-energy shoulder. Recent theoretical calculations have suggested that such spectral shape might be a signature of the Higgs mode contribution to the magnetic scattering [162].

Close to the pressure where the second phase transition was reported earlier, the scattering continuum abruptly broadens suggesting a stark change in the excitations. Interestingly, the earlier neutron study did not observe any change between the scattering in the first and the second phase [158]. The most likely reason is that the pressure applied in the neutron study was not high enough, because it involved a complicated loading procedure with no way to check the pressure directly. There is an alternative possibility that, accidentally, the spectra are the same at 9 kbar and 18 kbar that were used in the neutron study. Indeed, the peak position of the scattering observed in the present study is at the same energy for these two pressures. Either way, the present study motivates repeating the neutron scattering experiment, possibly including an intermediate pressure.

One of the values of the present study is the demonstration that Raman spectroscopy can be used to study quantum phase transitions. While not as conclusive as neutron scattering, being an in-house technique, it enables obtaining datasets, with a fine step in the driving parameter, which in this case is pressure.

Similarly, it is evident that to maximise the usefulness of such a technique, theoretical calculations would be very beneficial. Therefore it is expected that Raman studies presented in this thesis will motivate theoretical and computational studies of Raman spectra, which in turn will enable obtaining quantitative understanding of the spectra as is the case in neutron spectroscopy.
Chapter 9

Conclusions and Future Work

The main results of the present thesis are summarized, describing the impact of the findings on the understanding of quantum magnetism. Directions of promising future research are indicated.

9.1 Overview and Conclusions

In this thesis, the physics of clean and dirty quantum magnets was examined experimentally. Two distinct directions were taken in the research program: i) an in-depth study of static and dynamic properties of HAF $S = 1/2$ chains with impurities and ii) an exploratory study of quantum magnets using light spectroscopy. Both approaches yielded significant new findings that are summarized in the next few paragraphs.

In the case of HAF $S = 1/2$ chains, the role of impurities was explored in detail. While the importance of the impurities was clearly shown before [136, 139, 164], no unified explanation of the experimental results existed. In this thesis, all the experimental observations of two different model systems — Sr$_2$CuO$_3$ and SrCuO$_2$, could be described in one framework. The susceptibility measurements allowed estimating the level of chain fragmentation. The reduction of magnetic phase transition temperature and the shift to inhomogeneous ordering could be accounted by the chain fragmentation [123].
9.1 Overview and Conclusions

The effect of impurities on the magnetic excitations were also investigated, revealing that a pseudogap develops in the severed chains. In the case of direct breaking of the chains, the spectrum could be reproduced with no adjustable parameters using the arguments of fragmented chains. Additionally, the spin pseudogap was found to open also in the case where no direct fragmentation took place. This observation promotes the idea that the relevant criterion in the formation of a pseudogap is the confinement of the spinons in finite-length chain segments [141, 165].

The flurry of experimental work, including the results reported in this thesis as well as the heat transport studies of [139, 140] has already motivated theoretical work on spin-phonon coupling in spin chains. A recent theoretical study of [166] has described such phenomena using an intuitive picture of phonons acting thermally populated defects. Such defects in turn can influence the fast spin excitations [166].

The second direction, namely employing light scattering in studying quantum magnets proved to be very useful. It is a strong complimentary technique to neutron scattering. In can be particularly useful when no large crystals are available or when getting many data points as a function of a tuning parameter, such as chemical substitution level or pressure, is important.

In the first light spectroscopy study described in this thesis, a large data set from different versions of Cu(Qnx)(Cl_{1-x}Br_x)2 was collected that demonstrated the tunability of the spectral properties of this spin ladder. Additional tuning was demonstrated using hydrostatic pressure.

A dedicated pressure dependence study of excitations in (C_4H_{12}N_2)Cu_2Cl_6 was also carried out using Raman spectroscopy. A strong effect of hydrostatic pressure on the magnetic scattering was observed. Many pressure points were collected in order to complement the previous neutron spectroscopy study. Significant changes in the excitation spectra around the second critical pressure were detected which were not seen by the earlier measurements. This confirmed the existence of the second phase transition and has motivated follow-up neutron experiments which are currently being planned.
9.2 Future Work and Outlook

The first direction of the thesis regarding the impurity effects in spin chains has answered most of the questions that were open at the beginning of the project, therefore there is little planned in terms of experiments to elucidate physical properties. Of course, many studies could be performed in terms of material properties and chemistry, such as why the Zn substitution is inefficient in these materials [167] whereas it works well in spin ladders with similar structures, such as SrCu$_2$O$_3$ [168, 169]. Additionally, there are still several interesting experiments that could be performed to showcase the physics of such chains with impurities. Magnetic diffraction could be performed to elucidate on the inhomogeneous magnetic ordering in the samples with impurities. Furthermore, even though magnetic heat transport is now well understood in such systems, a thorough study of spin transport is still missing as well as studies of the impurity effects in such cases.

On the other hand, the light spectroscopy measurements reported in this thesis is just the showcase of the many results to come from using such an approach.

With an improvement of the high pressure setup, the study of magnetic excitations in Cu(Qnx)(Cl$_{1-x}$Br$_x$)$_2$ will be extended in the hope of forcing the system to go into the strong-leg regime. While the success is uncertain, positive result would encourage a number of follow up studies. One direction that is particularly tempting is to use very high pressure and rather high magnetic field to tune the system into a Luttinger liquid phase where the sign of interaction could be altered between the attractive and repulsive regimes [170].

Light scattering in the (C$_7$H$_{10}$N)$_2$CuBr$_4$ is also very promising. While we have identified that the magnetic excitations observed in the Raman spectrum are assisted by phonons, the interaction between lattice and magnetic excitations has not yet been addressed. It is planned to study this issue by modifying the phonons and observing the change in the magnetic excitations. Two approaches to modify the phonons will be taken. First, the isotope effect will be studied, where the difference in the spectra between hydrogen and deuterium versions of the compound will be inspected. Secondly, hydrostatic pressure will be applied to invoke more gradual changes.

In addition to continuing the research on the materials already studied in this
thesis, the Raman spectroscopy setup will be used for a number of different compounds. One of the directions is natural minerals, which are often difficult to grow in large crystals. As a first test material, malachite, a gapped $S = 1/2$ dimer system [171] will be investigated, magnetic properties of which have been predicted to alter with pressure [172].

On the other hand, a number of well-known materials with predictions of pressure and substitution effects will be investigated. An example is a planned study of pressure and substitution effects in SrCu(BO$_3$)$_2$. The pressure has already been shown to have significant influence in the magnetic properties [173]. Theoretical predictions also exist for the effect of nonmagnetic impurities, suggesting low energy states below the spin gap [174].

To summarize, the light scattering study presented in this thesis is just the tip of the iceberg, with many more exciting discoveries bound to take place.
Bibliography


[107] KONTI for Microscopy and Electro-Optical measurements.


[135] K. Karmakar and S. Singh, Finite-size effects in the quasi-one-dimensional quantum magnets Sr$_2$CuO$_3$, Sr$_2$Cu$_{0.99}$M$_{0.01}$O$_3$ ($M = \text{Ni, Zn}$), and SrCuO$_2$, Phys. Rev. B 91, 224401 (2015).


$S = \frac{1}{2}$ Heisenberg spin chain compound $\text{Sr}_2\text{CuO}_3$: From clean to dirty limits, Phys. Rev. B 89, 104302 (2014).


List of Publications

- [8] Magnetic ordering in the ultra-pure site-diluted spin chain materials SrCu$_{1-x}$Ni$_x$O$_2$
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- [6] Spin pseudogap in Ni-doped SrCuO$_2$

- [5] Effect of oxygen on tuning the TiN$_x$ metal gate work function on LaLuO$_3$

- [4] On the nature of the interfacial layer in ultra-thin TiN/LaLuO$_3$ gate stacks
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• [3] Study of interfaces and band offsets in TiN/amorphous LaLuO$_3$ gate
  stacks
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  I. Alexandrou, Q. Wang, J.M.J. Lopes, J. Schubert
  Microelectronic Engineering 88 1495 (2011)

• [2] Surface oxidation of the icosahedral Ag-In-Yb quasicrystal
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