

INELASTIC LIGHT SCATTERING IN LOW-DIMENSIONAL SPIN SYSTEMS

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Chapter 1

Introduction

A considerable amount of research has been carried out on low-dimensional quantum spin systems since the discovery of high- T_c superconductivity in layered cuprates. This is owed to the proposal of the RVB (Resonating Valence Bond) state as a possible origin of exotic properties of high- T_c superconductors [1]. The dimension of the spins and the spin value determine strongly the nature of ground states and elementary excitations of quantum spin systems. In contrast to a classical three-dimensional system, low-dimensional spin systems with exotic exchange topology and/or geometrical frustration show a variety of peculiar phenomena like spin-Peierls transition, formation of a spin gap, degenerated ground states, magnetic bound states of elementary triplets, chirality and so on. Magnetic materials realizing the corresponding systems are quite often found in transition metal oxides such as cuprates, vanadates and titanates. In these compounds the on-site Coulomb interaction U is much larger than the width W of the energy band, that is, the ratio of U/W is large. Thus, spin dynamics is expected to be closely related to charge, orbital, and lattice degrees of freedom.

A powerful tool for studying low-dimensional spin systems is Raman spectroscopy which is sensitive to nearly all possible types of collective excitations as well as the interplay among them. The successful application of Raman spectroscopy to low-dimensional spin gap systems should be attributed to the effectiveness of the spin-conserving exchange process on a short-range singlet ground state. This magnetic light scattering can provide information about exchange paths and coupling constants, spinon excitations, spin gaps, and triplet-triplet interactions.

In this thesis a number of compounds which have a unique exchange topology have been studied. The main aim of this work is to broaden and deepen

the understanding of a generic feature of spin dynamics in low-dimensional spin systems. In particular, the relation between the presence of new elementary excitations and the spin topology is pursued. The main aspect of light scattering measurements in dimerized spin systems can be summarized as follows. Quite generally, two-magnon/four-spinon continua have been observed in dimerized spin systems. It delivers a direct information about spin gaps as well as a clue to inter-dimer interactions. In addition, the significance of spin-phonon coupling is very frequently evidenced by a renormalization of phonon frequencies. For special cases, some optic modes should be treated in a nonadiabatic limit. This *dynamic* spin-phonon coupling can even renormalize the spin gap and the strength of dimerization. The lattice instabilities coupled to spins can lead to fluctuations of the magnetic energy of the system seen as quasielastic scattering. For frustrated spin systems magnetic bound states of triplets arise from strong triplet-triplet interactions. Near quantum criticality pronounced spin singlet dynamics can lead to the presence of longitudinal magnons in a long-range ordered state with reduced sublattice magnetization. In the following, a detailed discussion will be given on specific compounds in view of the above-mentioned physics.

The organization of this thesis is as follows. In chapter 2 theoretical results of well-studied low-dimensional spin systems will be summarized together with corresponding experimental results. This chapter will lay the background for discussions of the measured spectra. In chapter 3 the basic mechanism and experimental setup of inelastic light scattering will be presented. Starting from phononic excitations the microscopic origin of the double exchange mechanism as well as of the quasielastic scattering in a magnetic system is explained. In chapter 4 we deal with the frustrated double-chain system LiCu_2O_2 which is intrinsically doped by magnetic/nonmagnetic impurities. The coexistence of long-range ordering with a dimerized state has been found. In chapter 5 low-energy excitations in the two-dimensional Heisenberg spin system $\text{K}_2\text{V}_3\text{O}_8$ will be addressed. Special focus lies on anomalies of two-magnon scattering compared to the undoped cuprates. Chapter 6 is devoted to the three-dimensional networked spin-dimer systems TlCuCl_3 and KCuCl_3 . Dynamic spin-phonon coupling and a three-magnon process are reported. In chapter 7 the influence of a structural phase transition on magnetic properties will be discussed in the quasi-two-dimensional orthogonal dimer system $\text{SrCu}_2(\text{BO}_3)_2$. In chapter 8 the observation of a longitudinal magnon in the spin tetrahedra system $\text{Cu}_2\text{Te}_2\text{O}_5(\text{Br},\text{Cl})_2$ is reported near a quantum critical point. Finally, chapter 9 gives a summary on general aspects that have been highlighted in this work.

Chapter 2

Low dimensional spin systems

In this chapter we shall give a brief overview of low-dimensional quantum spin systems with emphasis on key concepts related to experimental results. Strictly speaking, there are no exact realizations of one- and two-dimensional magnetic systems in the solid state. In practical cases, however, a theoretical description of the ideal system provides a good starting point in understanding experimental results for quasi-one and quasi-two-dimensional systems. Up to now, model systems such as one-dimensional Heisenberg antiferromagnets (HAF), the frustrated alternating Heisenberg chain, and the spin ladder system have been theoretically well studied. Furthermore, a lot of examples have been recently realized in actual compounds and investigated experimentally. In the following we will briefly discuss them one by one. Before presenting detailed results let us introduce the Mermin-Wagner theorem [2].

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

The above conditions are precisely satisfied by the Heisenberg model. To clarify the implication of the Mermin-Wagner theorem we will make several annotations:

- Even in the isotropic Heisenberg model low dimensional ferromagnets exhibit LRO at $T = 0$, but antiferromagnets do not.
- When interactions are of infinite range, *e.g.* the dipolar interactions, one might find a finite critical temperature even in low dimensions.
- Anisotropic interactions can lead to LRO at finite temperature.

- For square and hexagonal lattices a ground state with LRO exists for spin $S \geq 1$ [3, 4].
- A ground state with LRO exists for the 3d HAF model for spin $S \geq 1/2$ [5].

2.1 One-dimensional HAF chains

Much information about the 1D Heisenberg AF chain comes from the Bethe-Ansatz solution for the ground state and excitation spectrum [6]. Furthermore, the Lieb-Mattis theorem¹ shows that the ground state of the $S=1/2$ HAF with an even number of spin is a singlet [7]. According to the Lieb-Schultz-Mattis theorem, for a half-integer spin chain an excitation spectrum is either gapless or degenerate [8]. In contrast, for an integer spin chain, Haldane made the conjecture that its spin excitation spectrum is gapped [9]. Now this conjecture is well established [10].

We will now consider the Heisenberg model on a one-dimensional chain of N sites

$$H = J \sum_{n=1}^N \vec{S}(n) \cdot \vec{S}(n+1), \quad (2.1)$$

where $J > 0$. By using the Jordan-Wigner transformation the Heisenberg Hamiltonian is written as follows [11]:

$$H = \frac{J}{2} \sum_{j=1}^N (c^\dagger(j)c(j+1) + h.c.) + \gamma J \sum_{j=1}^N (n(j) - \frac{1}{2})(n(j) + \frac{1}{2}), \quad (2.2)$$

where γ represents an anisotropy² and the creation (destruction) operator $c^\dagger(j)$ ($c(j)$) for a fermion at site j is defined as $c^\dagger(j) \equiv S^+(j)K^\dagger(j)$ ($c(j) \equiv K(j)S^-(j)$) with the kink operator $K(j) = \exp(i\pi \sum_{i=1}^{j-1} S^+(i)S^-(i))$. The kink operator $K(j)$ rotates the spin configuration by π about the z -axis for all sites up to the $(j-1)$ th site:

$$K(j)|\frac{1}{2}, \dots, \frac{1}{2}\rangle = i^{j-1}|\overbrace{-\frac{1}{2}, \dots, -\frac{1}{2}}^{j-1}, \frac{1}{2}, \dots, \frac{1}{2}\rangle. \quad (2.3)$$

¹For general spin and all dimensions and also for a bipartite lattice, the entire eigenvalue spectrum satisfies the inequality $E_0(S) \leq E_0(S+1)$ where $E_0(S)$ is the minimum energy corresponding to total spin S .

²For $\gamma = 1$ the isotropic Heisenberg model is recovered. The case $\gamma = 0$ corresponds to the XY model.

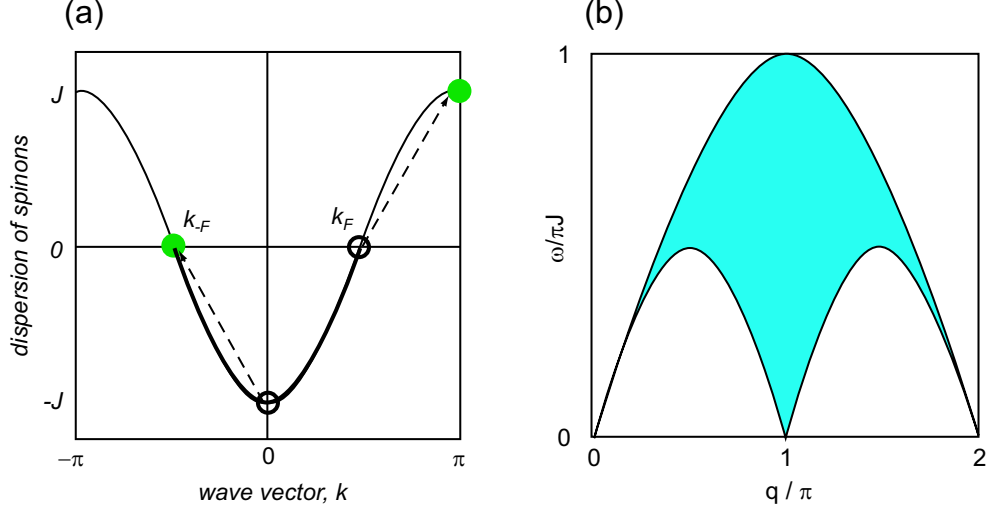


Figure 2.1: (a) Dispersion of spinons with a description of particle-hole excitations (b) The spinon continuum spectrum for the spin-1/2 HAF chain. The upper (lower) edge of the spectrum is given by $\omega_q^l = \frac{\pi}{2}J|\sin(q)|$ ($\omega_q^u = \pi J|\sin(q/2)|$) [13, 14].

The nonlocal nature of the kink operator destroys the long-range ordered state. The eigenvalues for an isotropic system with periodic boundary conditions are given by the Fourier transformation

$$H_0 = \int_{-\pi}^{\pi} \frac{dk}{2\pi} \epsilon(k) c^\dagger(k) c(k) \quad (2.4)$$

where

$$\epsilon(k) = -J \cos k. \quad (2.5)$$

The negative energy states lie in $0 \leq |k| < \frac{\pi}{2}$. Two Fermi points, $k_F = \pm \frac{\pi}{2}$ are obtained by filling up the negative energy modes (Fig. 2.1(a)). This disconnection of the 1D Fermi surface is the origin of the peculiar behaviors which are not seen in higher dimensions. In 1D systems quantum fluctuations are sufficiently strong to prevent true long-range AF order, giving instead a slow decay of the spin correlations at a rate that varies algebraically with the

separation between spins

$$\lim_{|j| \rightarrow \infty} \langle S^+(i) S^-(i+j) \rangle \approx (-1)^j \frac{const}{|j|} \rightarrow 0. \quad (2.6)$$

This $1/r$ -decay law has an immediate consequence on the staggered susceptibility defined as

$$\chi_{stag} = \chi(q = \pi) \propto \sum_{m=1}^{\infty} e^{im\pi} \langle S_i^z S_{i+m}^z \rangle \propto \sum_{m=1}^{\infty} \frac{1}{m} \rightarrow \infty. \quad (2.7)$$

The divergent response to a staggered field gives an explanation why an arbitrarily small interchain coupling can establish a long-range order [12].³

Ground state and excitation spectrum

The ground state of 1D HAF chain is given by a spin-singlet with total spin zero characterized by a "spin liquid". In the thermodynamic limit with "periodic boundary conditions" the excitations are described as massless $S=1/2$ spinons. Such excitations can be created only in pairs because a total spin must be either integer or half-integer. Thus, in the Heisenberg chain the conventional magnons are deconfined into spin-1/2 spinons, giving rise to a two-spinon continuum. Des Cloizeaux and Pearson [13] calculated the low-lying excitation spectrum which is given by

$$\omega_q^l = \frac{\pi}{2} J |\sin(q)|. \quad (2.8)$$

Later, a rigorous result was derived by Faddeev and Takhyatan [14]. The energy of the low-lying excited states can be written as $\omega(q_1, q_2) = \omega(q_1) + \omega(q_2)$ with $\omega(q_i) = \frac{\pi}{2} J |\sin(q_i)|$ and total momentum $q = q_1 + q_2$. Here note that a spinon pair has the energy ω and the momentum q as a whole. This means that the relative motion of the spinon pair is not fixed. Moreover, the additivity of energy and momentum of spinons implies that they do not interact with each other, that is, they are *asymptotically free*. This motivates us to interpret the lower bound known as des Cloizeaux and Pearson states in terms of a superposition of two spinons, one of which carries zero momentum. The upper

³It is controversial whether there is a nonzero critical coupling ratio between in-chain and interchain interactions ($J'/J = R_c$) below which the system retains a singlet ground state. For this issue we refer to [12] and references therein.

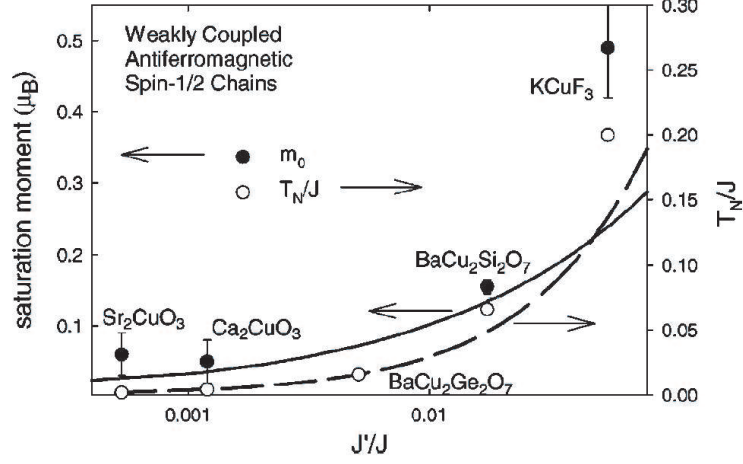


Figure 2.2: Ordered moment and T_N/J for weakly coupled spin-1/2 Heisenberg antiferromagnetic chain compounds as a function of J'/J [15]. The lines are the prediction of a chain mean field theory [16].

bound corresponding to two spinons with each momentum $q/2$ is given by ⁴

$$\omega_q^u = \pi J |\sin(q/2)|. \quad (2.9)$$

Real compounds

We will now discuss real materials found in the nature. Apparently, the perfect 1D HAF is a physical abstraction. However, almost ideal systems with weak interchain interactions are realized in KCuF_3 , Sr_2CuO_3 , Ca_2CuO_3 , $\text{BaCu}_2\text{Ge}_2\text{O}_7$ and $\text{BaCu}_2\text{Si}_2\text{O}_7$ [15]. Fig. 2.2 displays the ordered moment and the ratio of Néel temperature to in-chain interactions (T_N/J) as a function of the ratio of interchain to in-chain interactions (J'/J). Due to quantum fluctuations the ordered moment per Cu site is strongly reduced compared to the saturation value of $\sim \mu_B$ in 3D. Here note that orbital moments are quenched.

⁴The dispersion relation in the classical case is given by $\omega_q^{cl} = 2J |\sin(q/2)|$. The quantum effect then seems to be a renormalization of the excitation by a factor of $\pi/2$. As pointed out in the text, this has its root in a fundamental difference between the corresponding excitations.

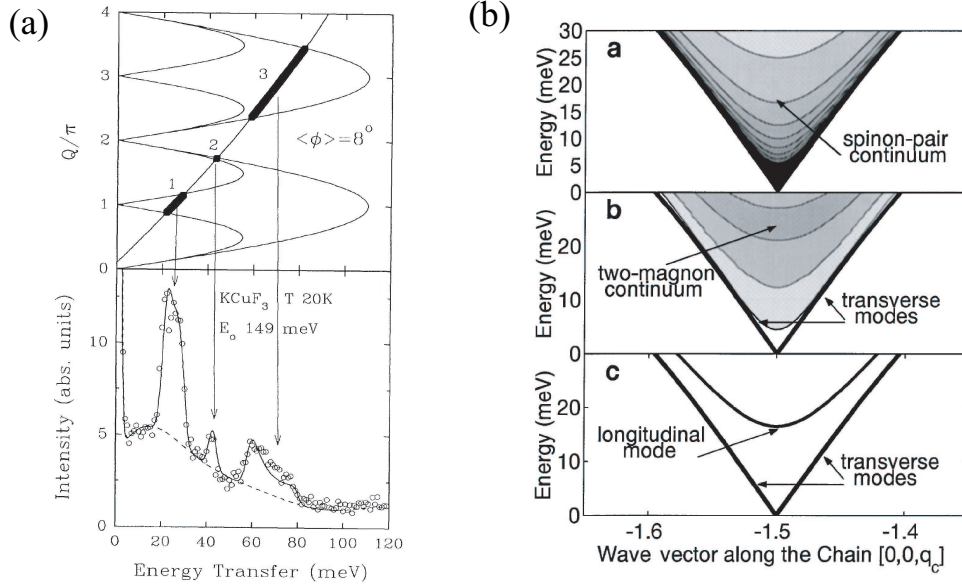


Figure 2.3: (a) (upper panel) Scattering trajectory for a detector at an angle of 8° with respect to the crystallographic axis and an incident energy of $E_o = 149\text{ meV}$ as well as scattering intensity when the trajectory intersects with the continuum (lower panel); scattering measured at $T=20\text{ K}$ and a fit (solid line). (b) Three calculations of magnetic correlations in KCuF_3 [20]. The shading of the contours denotes the intensity of the scattering. For the detailed explanations see the text.

The remaining sizable ordered moment is ascribed to weak interchain interactions which restore partially long-range order. Thus, in such weakly coupled chain systems the excitation spectrum is expected to be described by both classical dynamics of the Néel ordered state and critical dynamics of the quantum disordered state [16]. The Goldstone modes of the former state are well-defined transverse spin waves obeying a linear dispersion relation. This arises because the magnon dispersion perpendicular to the chain leads to a softening of the gap for transverse excitations.⁵ In contrast, the excitation spectrum

⁵For an isolated Néel ordered chain magnons have an energy gap Δ in a staggered field. For the isolated chain, the transverse and longitudinal components cannot be defined since components of the dynamical correlation function are identical.

of the quantum disordered state corresponds to the two-spinon continuum at higher energies [17]. This separation of single-particle and continuum dynamics has been observed in $\text{BaCu}_2\text{Si}_2\text{O}_7$ using inelastic neutron scattering measurements [18].

Excitation spectrum of KCuF_3

More specific, we will discuss the spin dynamics of the well-studied system KCuF_3 . The Bethe-Ansatz solution cannot provide a direct information about correlation functions. Instead, much information comes from the Müller ansatz [19] for the correlation function at $T=0$

$$S^{\alpha\alpha}(q, \omega) = \frac{1}{\sqrt{\omega^2 - (\omega_q^l)^2}} \Theta(\omega - \omega_q^l) \Theta(\omega_q^u - \omega), \quad (2.10)$$

where $\alpha = x, y$, or z and $\Theta(\omega) = 1$ if $\omega > 0$, and 0 otherwise. This analytic form has a square-root singularity at the lower bound which is characteristic for a 1D system. The upper panel of Fig. 2.3(b) illustrates the two-spinon continuum given by the Müller ansatz at $[0,0,-3/2]$ in KCuF_3 . Scattering is expected within the V-shaped region. The middle panel exhibits the scattering intensity calculated from spin-wave theory with two-magnon terms. The magnon branches are well-defined transverse modes while the two-magnon signal is a longitudinal mode, forming a broad continuum with a maximum at 23.5 meV. Even though classical theory can explain the presence of substantial spectral weights at higher energies, it fails to reproduce the exact form as well as temperature dependence of the observed spectra [20]. Rather, the spinon based theory gives full agreement with experimental observations [20, 21, 22] (see Fig. 2.3(a)). The lower panel of Fig. 2.3(b) displays a longitudinal mode corresponding to a magnon excitation polarized parallel to the direction of static staggered magnetization in the crossover from 1D to 3D physics upon ordering [17]. Here note that excitations in conventional 3D magnets are single-particle spin waves which are polarized perpendicular to the order parameter. In contrast, in the $S=1/2$ HAF chain the spectrum is a polarization-independent multi-spinon continuum. A longitudinal mode is a quasi-long-lived spin wave polarized parallel to the direction of ordered moment and contributes to the dynamics only when the ordered moment is suppressed by zero-point fluctuations. Actually, this novel excitation was observed by neutron scattering measurements as a single symmetric broad peak in the longitudinal spectrum in KCuF_3 [23]. A similar study of $\text{BaCu}_2\text{Si}_2\text{O}_7$ for longitudinal polarization shows ill-defined longitudinal magnons as a single

broad continuum feature [24].

Longitudinal magnons

According to spin chain-mean-field theory [16, 17], each spin chain is considered in an effective staggered field which induces an attractive potential between spinons. This staggered field leads to a formation of two-spinon bound states. Two components of them are polarized perpendicular to the staggered field while one of them is parallel to the staggered field. The former components correspond to conventional spin waves while the latter is a longitudinal mode with a gap of $\Delta_{\parallel} = \sqrt{3}\Delta$. For each polarization there is a multimagnon continuum with a gap of $\Delta_c = 2\Delta$. Thus, one expects a sharp longitudinal magnon and a broad longitudinal continuum for longitudinal polarization. However, the width of the longitudinal magnon is strongly damped in $\text{BaCu}_2\text{Si}_2\text{O}_7$ so that the distinction between the longitudinal magnon and the continuum is impossible. Another interesting system for the discussion of the longitudinal magnon is the spin-1 chain compound CsNiCl_3 [25]. In the paramagnetic phase this compound is characterized as a quantum-disordered Haldane system. However, because of non-negligible interchain interactions 3D long-range order develops below 4.4 K. The Néel temperature is much smaller than the energy of the Haldane gap ($k_B T_N / \Delta \sim 1/3$) and only half the full magnetic moment condenses due to quantum fluctuations. This indicates that the system is close to a quantum critical point which separates a singlet Haldane phase from the Néel phase. In this case, the characteristic Haldane triplet dynamics persists into the 3D long-range ordered state. This requires a release of the constraint on the magnitude of the staggered spin density along the chain. Thus, this leads to increased degrees of freedom and to new modes arising from the longitudinal fluctuations of the staggered spin density [26]. Actually, polarized inelastic neutron scattering measurements have detected the mixing of longitudinal and transverse fluctuations due to a damping of the longitudinal magnon through interactions with transverse modes [25]. Therefore, we can regard strong longitudinal quantum fluctuations in the long-range ordered state as a signature of the presence of triplet excitations.

Optical and Raman spectroscopy study of 1D spin systems

Complementary to neutron scattering, optical and Raman spectroscopy can probe higher order magnetic excitations in the singlet sector such as multimagnon continua and bound states. Fig. 2.4(a) shows the midinfrared optical

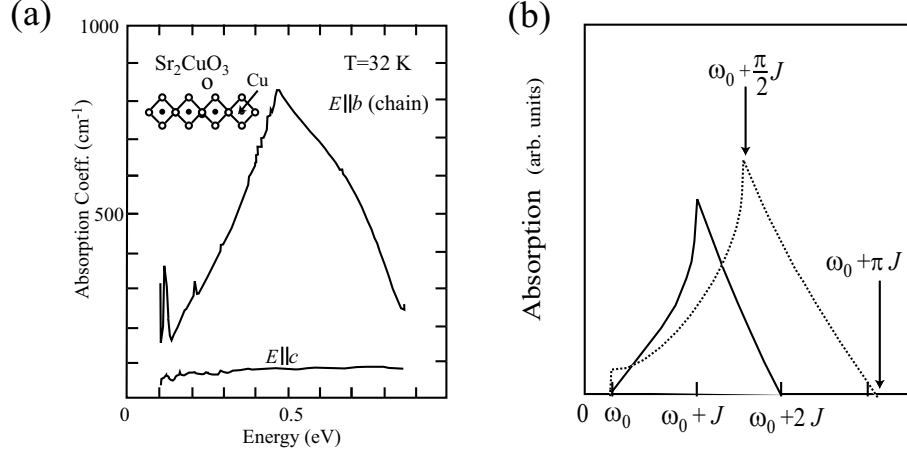


Figure 2.4: (a) Midinfrared absorption spectra of Sr_2CuO_3 [27] (b) Theoretical prediction of absorption coefficient due to phonon-assisted processes for the XY model (solid line) and the Heisenberg model (dotted line) [27].

absorption spectra of Sr_2CuO_3 [27]. A broad absorption band extending to 0.9 eV with a cusplike singularity at 0.48 eV was observed along the chain axis. This frequency range is far above the energy of one- and two-phonon modes and far below the onset of a charge-transfer gap excitation band at 2 eV. The broad band was interpreted in terms of a phonon-assisted absorption mechanism involving particle-hole excitations of spinons. The theoretical results for the XY (solid line) and Heisenberg model (dotted line) displayed in Fig. 2.4(b) reproduce well the main features of the experimental data. The XY model describes the noninteracting spinon. In the Heisenberg model, an Ising type coupling $S_n^z S_{n+1}^z$ induces repulsive interaction between spinons, making the absorption spectrum different from the XY model. The absorption band of the XY (Heisenberg) model extends from ω_0 to $\omega_0 + 2J$ ($\omega_0 + \pi J$) and has a cusp at $\omega_s = \omega_0 + J$ ($\omega_0 + \pi J/2$). Note that the position of the cusp lies in agreement with the top of the lower boundary of particle-hole excitation. In addition, the total spectral weight extends up to the cut-off energy of the spinon-wave continuum. The singular behavior around the cusp is due to the square-root divergence in the single-particle density of states at the top and bottom of the spinon band.

Up to now, there are two reports on inelastic light scattering measurements of Sr_2CuO_3 [28] and KCuF_3 [29]. The former shows anomalies in integrated

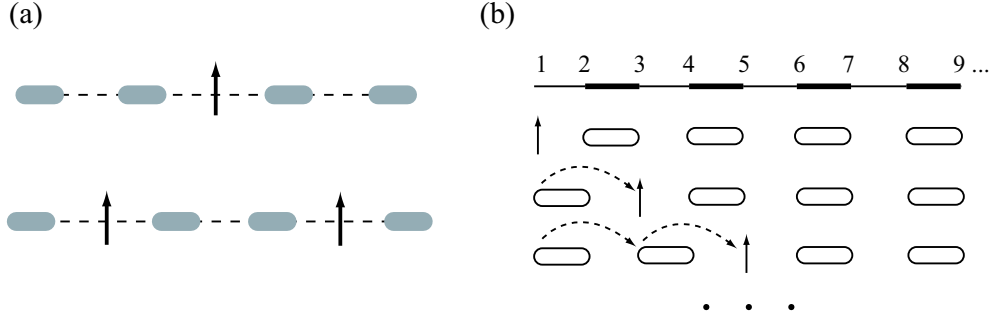


Figure 2.5: (a) Sketch of a spinon (upper line) and a spinon pair (lower line) as a domain wall in the RVB-picture (b) Possible configurations in the dimerized chain. The thick (thin) solid lines represent strong (weak) bonds and the open eyelets stand for singlets, the arrows for spinons. After few hops of the free spinon the number of misaligned singlets at the strong bonds are increasing linearly [38].

intensity of phonon modes due to a coupling of phonons to singlet pairs. The latter exhibits quasielastic Raman scattering originating from magnetic energy fluctuations. However, there is no clear evidence for the existence of unbound spinons. For the non-resonant case the Raman operator $\mathcal{R} \sim S_i \cdot S_j$ [30] commutes with the Hamiltonian of Eq. 2.1 in a strict 1D HAF system. This may be the reason why one cannot observe magnetic Raman scattering in weakly coupled chain systems.⁶

2.2 Frustrated alternating chains

The interest in one-dimensional systems with frustration and dimerization has been boosted by the discovery of inorganic quasi 1D compounds like the spin-Peierls system CuGeO_3 [31], the quarter-filled spin ladder NaV_2O_5 [32] and the alternating chain $(\text{VO})_2\text{P}_2\text{O}_7$ [33]. The excitation spectrum of these compounds is always gapped and low-lying excitations consist of triplets and bound states. The generic Hamiltonian for dimerized and frustrated spin chains reads

$$H = J \sum_i ((1 + (-\delta)^i) \vec{S}_i \vec{S}_{i+1} + \alpha \vec{S}_i \vec{S}_{i+2}) \quad (2.11)$$

⁶In a resonating case, however, the selection rule can be broken. Possibly, one has a chance to observe spinons.

where δ is the parameter of the dimerization and $\alpha = J'/J$ is the relative frustration by next-nearest neighbor coupling. The first insight into the excitation spectrum is obtained from a renormalization group approach [34]. In the case of $\delta = 0$, corresponding to the frustrated Heisenberg chain, the model is characterized by a critical frustration $\alpha_c = 0.2412$ [35]. For $\alpha < \alpha_c$ the system renormalizes to the Heisenberg fixed point, that is, the ground state is a spin liquid with "elementary" excitations as massless spinons. At α_c the spinons have a finite mass with a quadratic minimum in their dispersion. Moreover, a spontaneous symmetry breaking of the translational symmetry occurs, that is, spontaneous dimerization takes place. For $\alpha > \alpha_c$ the effective interaction renormalizes to large values, generating an exponentially small gap ($\exp[-c(\alpha - \alpha_c)]$). The excitation spectrum is created by breaking singlet bonds. Each broken bond produces a pair of decoupled spins (massive spinons) on neighboring sites which can propagate coherently along different sublattices.⁷ For $\delta \neq 0$ the ground state is dimerized with a spin gap, but the elementary excitation is a magnon. For the special case $2\alpha + \delta = 1$ the ground state is exactly a product wave function of independent singlet dimers [36]. Here note that this relation includes the Majumdar-Ghosh point $\alpha = 0.5$ where the ground state is a doubly degenerate resonating valence bond (RVB) given by $\phi_1 \equiv [12][34] \dots [N-1 N]$ and $\phi_2 \equiv [23][45] \dots [N1]$ with a singlet spin configuration $[lm]$ at the sites l and m [37].

For the sake of concreteness, let us explain the effect of dimerization using the spinon motion in the RVB picture. Without dimerization both spinons are asymptotically free because the left and right state of the spinon is energetically equal (Fig. 2.5(a)). With dimerization the spinon has a weak bond to the left (right) and a strong bond to the right (left) as seen in Fig. 2.5(b). After few hops of the free spin away from the original configuration the singlet to the left of the spinon is no longer at the strong bonds. This means an energy loss due to an attractive potential which ties the free spinon to its origin. Dimerization localizes a spin singlet at the strong bonds. They can be interpreted as spinons trapped by a confining potential. The confining potential is linear, that is, $V(i) \propto \delta \cdot J \cdot i$ where i denotes an up-spinon at site $2i + 1$. This linearity can be understood as the loss of total n singlets on the strong bonds if the spinon hops n times. Furthermore, if one considers frustration, above the critical frustration value energies are proportional to $\delta^{2/3}$ if δ measures the potential strength [38]. This results from a quadratic kinetic energy and a

⁷A spontaneous dimerization leads to the distinction between weak and strong bonds, forming two sublattices.

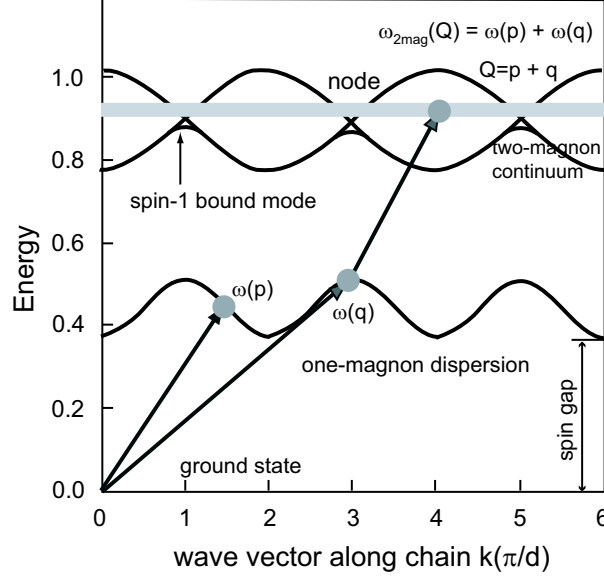


Figure 2.6: The $S=1$ excitation spectrum of the spin-1/2-alternating Heisenberg chain with moderately strong dimerization [41].

linear potential due to dimerization. For subcritical frustration the confining potential follows a square root behavior, that is, $V(x) \propto \sqrt{x}$ where x is the separation of the spin from the strong bond [39].

Magnetic excitations in a dimerized spin chain

In the following we will discuss magnetic excitations in dimerized Heisenberg chains. The one-magnon $S=1$ triplet has a gap energy $\Delta = J - \alpha J/2$ and dispersion $\omega_{1mag}(k) \approx J - \alpha J/2 \cos(kd)$ with the chain periodicity constant d [40, 41]. The wavefunction for the one-magnon state can be approximately thought of as a localized wavepacket of magnetic polarization along x , y , or z direction travelling through a featureless singlet background with the gap energy Δ . The wavefunction of the two-magnon states behaves like free particles at large separations. However, when they come close the scattering and interference occurs each other. In 1D antiferromagnets such a scattering conserves particle number, energy, and momentum up to a lattice wavevector since a finite-range interaction gives a zero matrix element between delocalized two-particle states. Thus, the energy of two-magnon states is approximated by

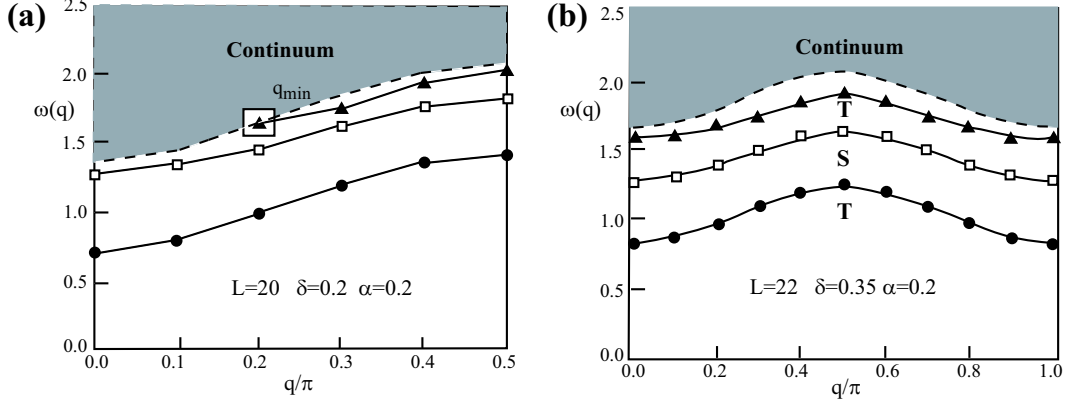


Figure 2.7: (a) Dispersion of the lowest excitations for $\alpha = 0.2$ and $\delta = 0.2$ and (b) for $\alpha = 0.35$ and $\delta = 0.2$ [42, 43].

$\omega_{2mag}(k) \approx \omega_{1mag}(k_1) + \omega_{1mag}(k_2)$, where $k = k_1 + k_2$. As Fig. 2.6 displays, a range of allowed two-magnon energies is constructed by a simple vector addition. In addition, bound states can be formed. Their physical origin can be explained as follows. Consider two dimers in excited states. If there is no coupling between them, all the double excited states $S=0, 1$, and 2 will be degenerate with the energy $2J$. Turning on interdimer coupling αJ , an $S=2$ quintuplet will have a higher energy of $2J + \alpha J/4$ while an $S=1$ triplet and an $S=0$ singlet will have a lower energy of $2J - \alpha J/4$ and $2J - \alpha J/2$, respectively. The $S=0$ mode gains the largest energy and has the bound states at all wavevectors. In contrast, the $S=1$ mode has them around the node points ($|n\pi - kd| \leq \pi/3$ with an odd integer n) where the kinetic energy is small compared to the binding energy.

Magnetic excitations in frustrated and alternating chains

In the following we will address alternating spin systems with frustration. Although universal features can be captured by analytic methods, the detailed picture of elementary excitations as a function of parameters (α, δ) is obtained by numerical studies [42, 43]. As pointed out above, dimerization binds spinons pairwise to each other. Thus, the total spin can be $S=0$ (singlet) or $S=1$ (triplet). Binding leads to a lowering of energy below twice the triplet excitation gap Δ_{01} . This means that the elementary excitation is a

bound state of singlet and triplet rather than spinon. Fig. 2.7 displays the dispersion of the lowest excitations in two different parameter regimes. The continuum arises from a decay of excited bound states by producing a pair of spinons.

We focus on the singlet and triplet energy gap ratio $R(\alpha, \delta) = \Delta_s/\Delta_t$. In the absence of frustration $\alpha = 0$ and for any dimerization $R=2$ is found. This means that there is no long wavelength singlet excitation branch. At the critical frustration one obtains $R = \sqrt{3}$. For $\alpha < \alpha_c$ one obtains $R(\alpha, \delta) > \sqrt{3}$ where R is insensitive to the dimerization parameter. When the parameters α and δ increase towards stronger dimerization a second triplet branch splits from the continuum. This second triplet can be interpreted as a bound state between a triplet and a singlet excitation. For a given δ , the momentum range for which the second triplet is split from the continuum is centered around $q = \pi/2$ and increases continuously with increasing α . The minimal frustration α_{min} for the second triplet to be a well-defined excitation over the entire Brillouin zone is approximated by a simple linear function of δ , $\alpha_{min} \approx (1 - \delta)/3$. In the limit $\delta \rightarrow 0$, $\alpha_{min} \rightarrow 1/3$. The most well-known example of a frustrated and alternating spin chain system is the spin-Peierls system CuGeO_3 [31]. The best model parameters which describe thermodynamic and neutron scattering data are found to be $J \approx 160$ K, $\alpha = 0.36$ and $\delta = 0.012$ [42]. In neutron scattering measurements [44] an evolution of a triplet branch from a spinon continuum upon cooling through $T_{SP} = 14.3$ K was observed. For $T > T_{SP}$ Raman scattering measurements show a broad continuum arising from "frustration-induced scattering".⁸ In the spin-Peierls regime $T < T_{SP}$ a singlet bound state at 30 cm^{-1} and a broad continuum above $2\Delta_{01} \approx 34 \text{ cm}^{-1}$ have been observed [45, 46, 47, 48].

2.3 Spin ladder systems

Spin ladder systems are ideally suited for the study of the crossover from a 1D chain to a 2D AFM. In general, the excitation spectrum of the n -leg ladder shows a drastic difference, depending on whether n is even or odd. For an even-leg ladder, the excitation spectrum has a spin gap with exponentially decaying two-spin correlations [49, 50]. The gap should decrease as n increases so that

⁸The Raman operator is given by $\mathcal{R} \sim \sum_i (S_i \cdot S_{i+1} + \gamma S_i \cdot S_{i+2})$. Here the second term arises as a result of frustration. This operator does not commute with the Hamiltonian (2.11). Thus, magnetic Raman scattering is observable in contrast to isotropic spin chain systems.

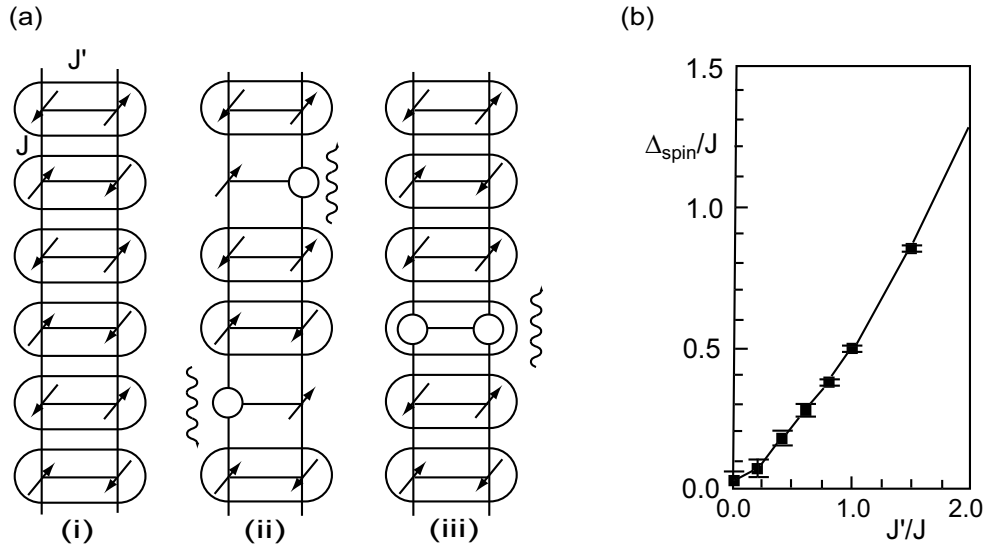


Figure 2.8: (a) A sketch of the ground state of a two-leg ladder and hole bound-states; (b) spin gap as a function of the ratio J'/J for a two-leg ladder. Here note that the alternative notation $J_{\perp} = J'$ and $J_{\parallel} = J$ is used [54].

the gapless square lattice limit is reached when n goes to infinity. In contrast, for an odd-leg ladder, physical properties are equivalent to those of a single chain [51]. That is, the excitation spectrum is gapless with power-law decaying correlations. The difference between the even- and odd-leg ladder has a similarity to that between integer and half-integer spin chains. Khveshchenko [52] has shown that for the odd-leg ladder a topological term governing the dynamics at long wavelengths appears in the effective action whereas for the even-leg ladder it cancels out. For an extensive review of the real ladder materials and their experimental results we refer to Ref.[53].

Ground state and elementary excitations in the two-leg ladder

In the following we will restrict our interest to the two-leg ladder. The Hamiltonian can read

$$H = \sum_i [J_{\parallel}(S_{1,i} \cdot S_{1,i+1} + S_{2,i} \cdot S_{2,i+1}) + J_{\perp} S_{1i} \cdot S_{2i}] \quad (2.12)$$

where $J_{\parallel}$ and $J_{\perp}$ are the leg and rung couplings and i denotes the rungs and

1, 2 the two legs. When $J_{\perp} = 0$, two decoupled AFM chains are recovered. When $J_{\parallel} = 0$, the exact ground state consists of the direct product of spin singlets $|\Psi\rangle_S = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ where $\uparrow$ and $\downarrow$ are the spin-up and spin-down eigenvectors of the spin operator S_z . In the strong coupling limit local triplet excitations propagate along the chains and their energy acquires a momentum dependence with a dispersion law

$$\omega(k) = J_{\perp} + J_{\parallel} \cos(k). \quad (2.13)$$

The spin-gap is defined as the minimum excitation energy at $k = \pi$

$$\Delta_{spin} = \omega(\pi) \approx J_{\perp} - J_{\parallel}. \quad (2.14)$$

In this limit the spins spend most of the time in singlets. Such a "spin liquid" state is well described by a short-range RVB state [50]. The actual spin gap behavior as a function of the ratio of $J_{\perp}/J_{\parallel}$ is shown in Fig. 2.8. Due to a power-law decay of correlations the spin gap of a two-leg ladder opens immediately upon turning on the rung coupling [54].

Next, we will think about what are the proper elementary excitations of the two-leg ladder system. Two pictures are thinkable: (i) If rung coupling is dominant, the excitations are local triplets on each rung (rung triplets) dressed by the magnetically polarized environment. (ii) If the rung coupling is weak, it binds two fractional $S=1/2$ spinons on either chain to an integer $S=1$ triplet [55]. For an arbitrary ratio of $x = J_{\parallel}/J_{\perp}$ spectral densities are calculated in terms of the number of rung triplets (integer excitations)⁹ using a continuous unitary transformation (CUT) [56]. For large x the triplet is dressed and the quasiparticle weight is reduced while a considerable spectral weight of multiparticle continuum is present. They also found a midband square-root singularity (MBS) within the two-triplet continuum at an energy of about $3.4J_{\perp}$. The presence of the MBS is due to the pure triplet-triplet interactions and divides the continuum into two bands. The lower band which lies below the MBS possesses a large part of the spectral weight. The momentum dependence of this line has a similarity to the upper edge of the two-spinon continuum (see the eq. 2.9). The description of the two-spinon feature in terms of a two-triplet picture shows that integer dressed excitations describe the physics of spin ladder without resorting to the fractionality of the

⁹Here the number of rung triples is a good quantum number in the sense that it remains constant.

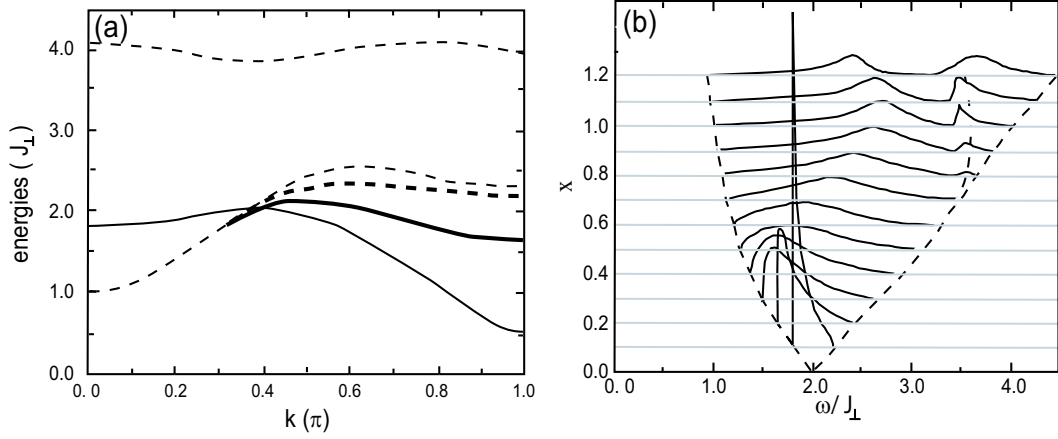


Figure 2.9: (a) Dispersion of excitations of the two-leg ladder in the isotropic limit: Elementary triplet (thin solid line), lower and upper boundary of the two-magnon continuum (thin dashed line), bound state for $S=0$ (thick solid line), and $S=1$ (thin dashed line) are shown. (b) Raman spectral density as a function of the ratio $x = J_{\parallel}/J_{\perp}$. The dashed lines depict the lower and upper boundary of the two-triplet continuum [57].

excitations.

Raman response of the two-leg ladder

Let us discuss the Raman response of the two-leg ladder calculated by using the CUT method [57]. Fig. 2.9(a) displays the dispersion of the rung triplet, the lower and upper boundary of the two-triplet continuum, and bound states in the $S=0$ and the $S=1$ sector. As usual, Raman spectroscopy can probe total spin-zero excitations near the Brillouin zone center.¹⁰ Thus, the leading contribution to the spectral densities arises from the two-triplet and four-triplet continuum.¹¹ In Fig. 2.9(b) the spectral density from the two-triplet sector is shown for the ratio of $x = J_{\parallel}/J_{\perp}$. For small x the Raman spectrum exhibits a strong resonance near the lower boundary while the spectral weight is shifted

¹⁰This is valid only for one-particle scatterings. For multi-particle scatterings, Raman spectroscopy can scan the total Brillouin zone.

¹¹The spectral weight of the four-triplet sector amounts to only 7% of that of the two-triplet sector even in the isotropic limit. Thus, the two-triplet contribution is considered in the following.

toward the lower boundary. The bare two-triplet spectrum in a 1D magnetic system has a symmetric form with van-Hove singularities of one-over-square-root type at the lower and upper boundary. This resonance results from the two-triplet attraction of neighboring triplets. As seen in Fig. 2.9(a), this leads to a bound state of two-triplets at a finite momentum. On increasing x the kinetic energy of the relative motion of the triplets increases whereas the attractive interactions diminish. The resulting Raman spectrum broadens while the resonance peak shifts toward the center of the continuum. Noticeably, the second peak appears for $x > 0.6$. The existence of this feature depends on the one-triplet kinetics and two-triplets interaction. At first, a dip in the triplet-dispersion near $k = 0$ (see Fig. 2.9(a)) leads to an additional van-Hove singularity at $2\omega(0)$ contributing to additional spectral weight. Secondly, the separation of the second peak from the main one by $2\omega(0)$ implies the orthogonal relation between excited triplets. This orthogonality is induced by triplet-triplet interactions.

Optical and Raman experimental results

We will present here results of an optical study of $\text{Ca}_{14-x}\text{La}_x\text{Cu}_{24}\text{O}_{41}$ [58]. This is a layered compound consisting of CuO_2 1D spin chains and Cu_2O_3 two-leg spin ladders [59]. A nominal undoped sample is expected for $x = 6$ which lies beyond La solubility limit [60]. An almost undoped ladder is realized in the sample with $x = 5$ which contains $1/24$ holes per Cu ion on average. This is because most of them are located on the chains [61]. In this compound the singlet bound state has been observed in the optical conductivity $\sigma(\omega)$ via phonon-assisted two-magnon absorption as displayed in Fig. 2.10. Two peaks at 2140 and 2800 cm^{-1} are assigned to 1D van-Hove singularities in the density of states of the singlet bound state. The lower peak corresponds to the singlet energy at $k = \pi$ while the higher one to the maximum of the singlet dispersion at about $k \approx \pi/2$ (see Fig. 2.9(a)). The broad feature at 4000 cm^{-1} is due to the two-magnon continuum. The exchange constants $J_\perp$ and $J_\parallel$ can be determined by calculating the maximum and the minimum of the singlet bound state dispersion. One obtains the two magnetic parameters as $J_\parallel \approx 1020 - 1100 \text{ cm}^{-1}$ and $J_\parallel / J_\perp \approx 1$. The difference of the line shape between the leg and the rung is due to a selection rule originating from the reflection symmetry about the a axis.

Fig. 2.11 exhibits high-energy magnetic Raman spectra of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ and $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$ for the leg and the rung polarization together with a theoretical fit in the inset [62, 63]. Two-magnon scattering of $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$ with

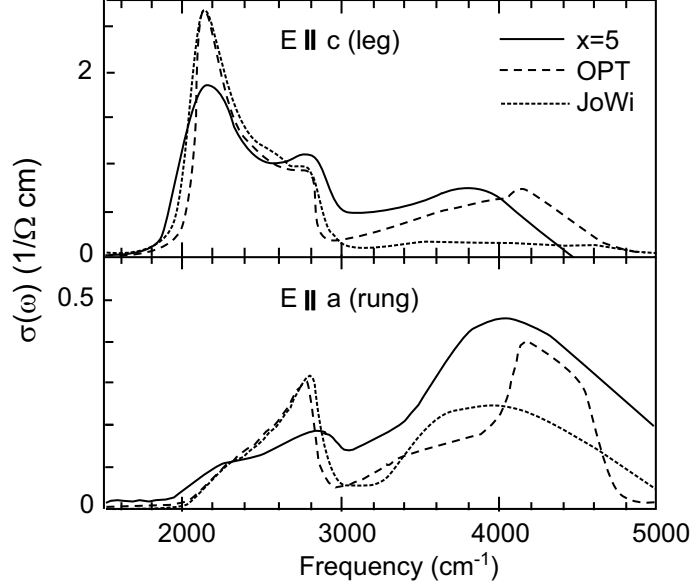


Figure 2.10: Experimental data of optical conductivity $\sigma(\omega)$ of $\text{Ca}_{14-x}\text{La}_x\text{Cu}_{24}\text{O}_{41}$ for polarization of the electrical field parallel to the legs and to the rungs after subtracting the electronic background at $x = 5$. They are compared with two different theories: optimized perturbation and Jordan-Wigner transformation [57, 58].

no charge carriers is characterized by a rather broad peak around 2948 cm^{-1} with a tail to higher energies. In contrast, an intrinsically hole-doped material $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (0.25 holes per Cu atom) shows a very sharp asymmetric feature with a peak at 3003 cm^{-1} . A possible origin for the sharpness lies in the modulation of the triplet by a periodic pinning potential of holes in the chains [64]. Taking into account that for a spin ladder most of the two-magnon Raman spectral density arises from the combination of triplets near the Brillouin zone center [55], one can estimate $J_{\perp}/J_{\parallel} = 0.8 \pm 0.1$ and $J_{\parallel} = 880 \pm 160 \text{ cm}^{-1}$ [63]. The discrepancy between the experimental data and the theoretical fit (see the inset of 2.11) may be attributed to four-spin cyclic exchange interaction. An inclusion of the cyclic exchange constant $J_{\text{cyclic}}/J_{\perp} \approx 0.20 - 0.27$ can explain the disappearance of the second peak and the sharpness of the main peak [65]. The effect of cyclic interaction is twofold: (i) it induces a repulsive interaction between triplets on neighboring rungs. (ii) it renormalizes the coupling constants, leading to a reduction of the triplet on-site energy. As a result, the spin

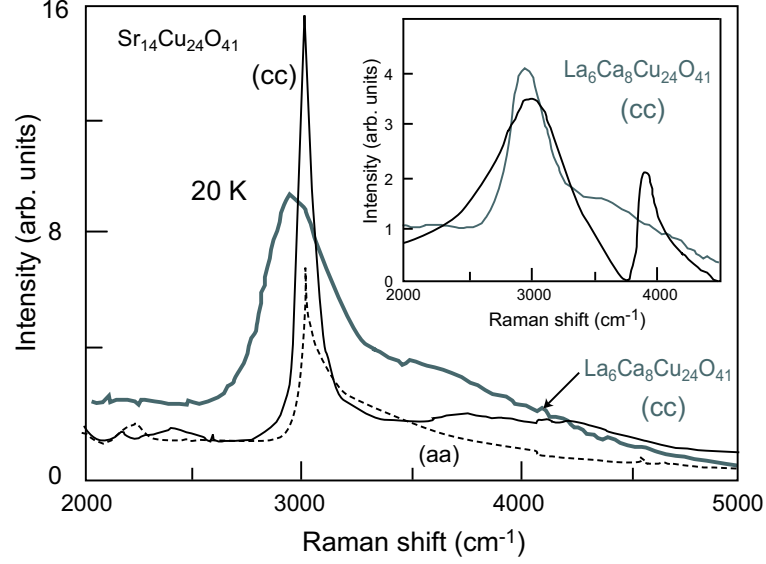


Figure 2.11: Raman spectra of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ in leg (solid black line) and rung (dashed black line) polarization in high energy region. For comparison Raman spectrum of $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$ in leg (solid gray line) polarization is shown at 20 K [62].

gap and the bandwidth of the one-triplet dispersion are reduced. Furthermore, the contribution from bound state for $S=0$ should be also considered. Unfortunately, this contribution to Raman spectrum has not been included in the theoretical calculation. In particular, the large difference around 3700 cm^{-1} might be ascribed to it.

Chapter 3

Raman spectroscopy

In this chapter we will recapitulate the theoretical basis of Raman scattering on phonons and magnetic excitations in solids. The main goal is to provide a background which is helpful for understanding our experimental observations. Firstly, we will formulate light scattering for a general situation. Secondly, the microscopic theory of light scattering by phonons and magnons will be outlined. Finally, the experimental setup will be described.

3.1 Phononic Raman scattering

A typical situation of a light scattering experiment is schematically depicted in Fig. 3.1(a): monochromatic light with frequency ω_I and polarization $\mathbf{e}_I$ is incident on the medium, and the medium scatters light, and finally the spectral density of the scattered light with ω_S and $\mathbf{e}_S$, that is, intensity as a function of the frequency change, is measured using the detector. The scattered light consists of elastic scattering ($\omega_S = \omega_I$), the Stokes component ($\omega_S < \omega_I$) and the anti-Stokes component ($\omega_S > \omega_I$). Let us consider a response relation between the polarization $P(\omega, \mathbf{r})$ and the external electric field $E(\omega, \mathbf{r})$:

$$P(\omega, \mathbf{r}) = \chi(\omega)E(\omega, \mathbf{r}), \quad (3.1)$$

where $\chi(\omega)$ is the susceptibility tensor. In the real medium $\chi(\omega)$ shows always spatial and temporal fluctuations due to quantum and thermal motion of particles. One thus expects a spectral density from light scattering :

$$\rho(q, \omega) \sim \int \langle \delta\chi^*(q, t)\delta\chi(q, 0) \rangle e^{i\omega t} dt, \quad (3.2)$$

where $q = k_I - k_S$ and $\omega = \omega_I - \omega_S$ are the change of wave vector and number, respectively. In solids the fluctuations of $\chi(\omega)$ originate from two sources.

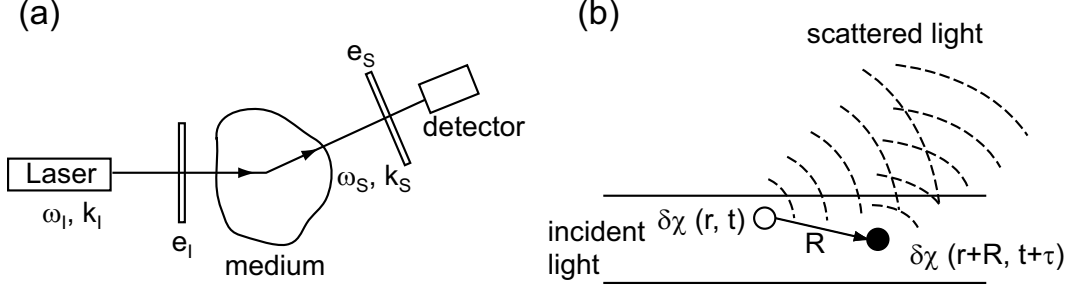


Figure 3.1: (a) Schematic description of light scattering geometry (b) Interference of secondary waves from different points inside the incident beam.

One of them is density fluctuations leading to a scattering continuum. This is because an energy transfer from the electromagnetic field to low-energy electronic states has no well-defined eigenfrequency. The other is due to internal degrees of freedom like phonons and magnons. This leads to peaks in $\rho(\omega)$ at frequencies corresponding to the energy of low-lying collective excitations. There is another approach toward a description of light scattering based on the differential cross section. For inelastic scattering one can write the differential cross section in terms of the matrix elements of the transition susceptibility operator [66]:

$$\frac{d^2\sigma}{d\omega d\Omega} \propto \sum_{i,f} P(E_i) |\hat{e}_s \cdot \langle f | \chi_{\alpha\beta} | i \rangle \cdot \hat{e}_I|^2 \delta[\frac{1}{\hbar}(E_i - E_f) - \omega], \quad (3.3)$$

where $P(E_i)$ is the probability of finding the crystal in the initial state and Ω is the solid angle. Using a perturbation theory one gets the susceptibility:

$$\begin{aligned} \chi_{\alpha\beta}(\omega, k) &= 2 \sum_{i,f} \int \langle ik | \hat{M}_\alpha | fk \rangle \langle fk | \hat{M}_\beta | ik \rangle \\ &\times \left[\frac{1}{\omega_{fi}(k) - \omega} + \frac{1}{\omega_{fi}(k) + \omega} \right] \frac{d^3k}{(2\pi)^3}. \end{aligned} \quad (3.4)$$

Here $\langle fk | \hat{M}_\beta | ik \rangle$ is the dipole matrix element of $\hat{M}_\alpha = er_\alpha$ between the occupied and empty band states, $\omega_{fi} = [E_f(k) - E_i(k)]/\hbar$, and 2 is the spin factor.

One phonon scattering in an adiabatic approximation

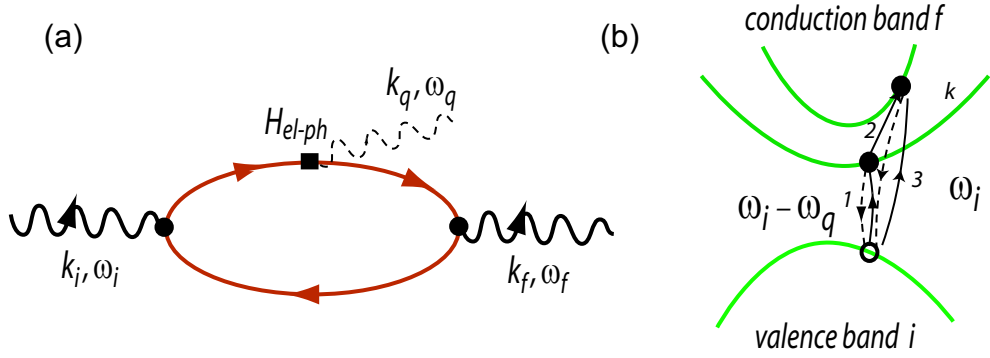


Figure 3.2: (a) Feynman diagram representation of a first-order phonon scattering process which makes the largest contribution to the cross section (b) Schematic electronic energy bands of a crystal showing electronic transitions corresponding to third-order light-scattering process for Stokes process. The pair state created in the first transition can lead to a second transition within the conduction band before the recombination in the final transition. Here note that this is one of possible processes which contribute to the scattering intensity.

Here we will address how to calculate phonon Raman intensity within the adiabatic approximation following Ref. [67]. Suppose that the eigenvector Q_ν of a Γ -point optical mode $\nu (= 1, \dots, 3N_c)$ is known where N_c is the number of ions per the unit cell. In the adiabatic limit the phonon can be treated as a very slow ionic displacement leading to a *static* potential within the unit cell $\delta U_\nu(r)$. This slow varying potential will (i) shift the energy of the $|ik\rangle$ state by $\delta E_{i,\nu}(k) = \langle ik | \delta U_\nu(r) | ik \rangle$ and (ii) change the band wave function as $\delta | ik \rangle = \sum_{f \neq i} \frac{\langle ik | \delta U_\nu(r) | fk \rangle}{E_f(k) - E_i(k)} | fk \rangle$. Thus, the susceptibility tensor in (3.4) will be changed:

$$\delta \chi_{\alpha\beta}^\nu = \sum_{a=1}^{N_c} Q_{a,\nu} \frac{\partial \chi_{\alpha\beta}(\omega)}{\partial Q_a}. \quad (3.5)$$

Consequently, Raman scattering intensity at the phonon frequency Ω_ν will be

observable:

$$\rho(\omega) = \frac{1}{\pi} I_R \frac{\gamma_\nu}{(\omega - \Omega_\nu)^2 + \gamma_\nu^2}, \quad (3.6)$$

where γ_ν is the phonon linewidth and $I_R \sim \omega^4 < (e_I^\alpha \delta \chi_{\alpha\beta}^\nu e_S^\beta)^2 >$ is the integrated intensity. Note that the ω^4 term arises from dipole radiation. By inserting (3.4) into (3.5) one sees that the integrated intensity of phonons is determined by two contributions. The first one is due to the dependence of band energy on ion configuration, $\partial \omega_{fi}(k) / \partial Q_a$. The second one can be ascribed to the polarization of band wave functions and the change in interionic distances $\partial < f k | \hat{M}_{\alpha,\beta} | i k > / \partial Q_a$. Note here that one-phonon scattering arises from third order time-dependent perturbation theory rather than a direct light-phonon interaction because of a large difference of the photon energy ($\hbar \approx 1.5 - 2.5$ eV) and the phonon energy (< 100 meV). As depicted by the Feynman diagram in Fig. 3.2, the scattering process includes three virtual electronic transitions which are treated as independent:

- (i) An incident photon excites an intermediate electron-hole pair state via the electron-radiation coupling.
- (ii) The electron-phonon interaction causes a transition of the electron (Stokes process) or hole (anti-Stokes one) to a different state.
- (iii) The transition to the electronic ground state occurs via a recombination of the virtual electron-hole pair emitting a scattered phonon.

We can write the relevant Hamiltonian involving phonon excitations as

$$H_R = -\frac{e}{mc} p \cdot A + \sum_{ijk} g_{ij}(k) (\hat{a}^\dagger + \hat{a}) \hat{c}_{ik}^\dagger \hat{c}_{jk}, \quad (3.7)$$

where $g_{ij}(k)$ is the electron-phonon coupling between the band i and j , while $\hat{a}^\dagger(\hat{a})$ and $\hat{c}_{ik}^\dagger(\hat{c}_{jk})$ are the phonon and electron creation (annihilation) operators, respectively. The first term in (3.7) is the electron-radiation interaction of step (i) and (iii) describing a scattering process via an intermediate state resulting in an interband transition. The second term in (3.7) is a contribution which is linear in terms of the electron-phonon interaction. This term involves step (ii) by coupling phonons to electron states in two ways: (i) phonons couple to electron states with the same occupancy (both are empty or occupied) and (ii) phonons couple to occupied and unoccupied states. Finally, we briefly mention selection rules for Raman scatterings. A rigorous argument can be provided using a group theory. However, a qualitative understanding can be achieved if one considers the requirement that the derivative $\partial U / \partial Q_a$ should follow the symmetry properties of the crystal lattice. Specifically speaking, in the presence of inversion symmetry the Raman intensity is nonzero for phonons

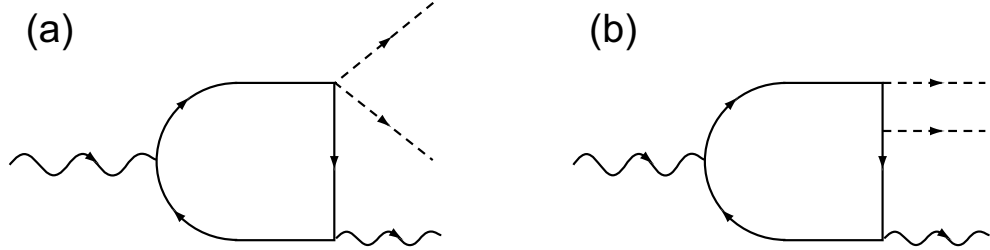


Figure 3.3: (a) Feynman diagram representation of the second-order phonon scattering process arising from the anharmonic electron-phonon interaction (b) Feynman diagram of the second-order process in terms of the linear electron-phonon interaction. The wiggly lines stand for photon propagator, the solid lines for electron propagator, and the dashed lines for phonon propagator.

whose displacements are inversion symmetric.

Two-phonon scattering

Before proceeding to discuss two-phonon scattering we will consider the kinematics of an inelastic light scattering process. For transparent crystals the conservation of energy and momentum can be written as

$$\begin{aligned}\omega &= \omega_I - \omega_S \\ q &= k_I - k_S.\end{aligned}\tag{3.8}$$

Phonon wave vectors are typically three orders of magnitude larger than the light wave vectors over the major part of the Brillouin zone. Thus, one-phonon scattering is restricted to a regime near the Γ -point of the Brillouin zone. The situation is different in the case of two-phonon scattering. When the two phonons are created, then energy and momentum conservation gives

$$\begin{aligned}\omega_{\sigma q} + \omega_{\sigma' q'} &= \omega_I - \omega_S \\ q + q' &= k_I - k_S.\end{aligned}\tag{3.9}$$

Here σ and σ' denote the branch of phonons. Thus, one can see that only the total momentum of a pair of the emitted phonons $q + q' = 0$ should vanish. The frequencies are the same at wave vectors q and $-q$, and the energy conservation can be written $\omega_{\sigma q} + \omega_{\sigma' q} = \omega_I - \omega_S$. To first approximation, the second-order

light-scattering spectrum of phonons is provided by the combined density of states of phonon pairs

$$\rho_2(\omega) = \sum_{\sigma, \sigma'} \sum_q \delta(\omega - \omega_{\sigma q} - \omega_{\sigma' q}). \quad (3.10)$$

To understand the microscopic origin of the two-phonon process let us expand the electron-phonon interaction up to quadratic term [68]:

$$\begin{aligned} H_{e-p} = & \sum_q g_1(q) (\hat{b}_{-q}^\dagger + \hat{b}_q) \hat{c}_{k+q}^\dagger \hat{c}_k \\ & + \sum_q g_2(q) (\hat{b}_{q_1}^\dagger \hat{b}_{q_2}^\dagger + \hat{b}_{q_1}^\dagger \hat{b}_{q_2} + \hat{b}_{q_1} \hat{b}_{q_2}) \hat{c}_{k+q}^\dagger \hat{c}_k. \end{aligned} \quad (3.11)$$

Here g_2 is anharmonic interaction constant. The Feynman diagram in Fig. 3.3 displays the main mechanism. The processes are the extension of the first-order process to higher order. The first term represents simultaneous emission of two phonons due to the lattice anharmonicity, that is, due to the second term of Eq. (3.11). In contrast, the diagram in Fig. 3.3(b) shows that two phonons are created separately in a pair of first-order electron-lattice interactions corresponding to the first term in Eq. (3.11). This process contains an additional virtual electron state besides the emission of two-phonons. This state can be in *resonance* when the energy of the incident light is suitably selected. Thus, this process gives a dominant contribution to the two-phonon scattering near a resonance. In a simple model the second-order scattering intensity depends on the frequency of the incident photon with $(\omega - \omega_{fi})^{-4}$ for the anharmonic process while the resonating process gives $I_2 \sim (\omega - \omega_{fi})^{-6}$, where ω_{fi} is the interband energy.

3.2 Magnetic Raman scattering

Light scattering through magnetic excitations in crystals is based on the same physical mechanism as phonon excitations. It does not occur through the magnetic dipole interaction between spin fluctuations and the magnetic vector of light. Rather, it is caused by the electric dipole interaction. The magnons induce a spatially periodic modulation of the susceptibility tensor. This fluctuation of the susceptibility tensor, in turn, scatters light. In usual, magnetic Raman scattering has smaller light scattering cross sections than light scattering by phonons. Fig. 3.4 displays a typical magnetic Raman spectrum of NiF_2 . NiF_2 is an antiferromagnetic ordered system with a Néel temperature

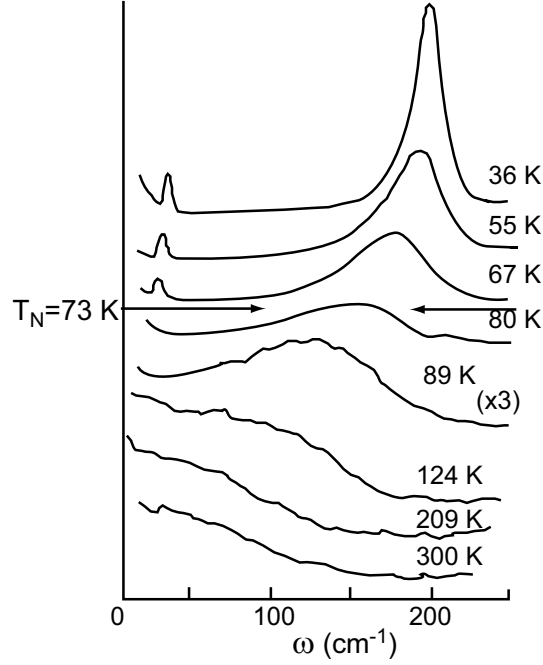


Figure 3.4: Temperature dependence of the first- and second-order magnetic scattering in NiF_2 [69].

$T_N=73$ K [69]. The small peak around 30 cm^{-1} is attributed to one-magnon scattering while the intensive maximum around 200 cm^{-1} originates from two-magnon scattering. The temperature dependence of the scattering intensity shows different behaviors for the one- and two-magnon spectrum: the one-magnon scattering disappears near at T_N while the two-magnon scattering persists to several times T_N . With increasing temperature the former does not undergo a large shift in the frequency while the latter strongly softens and dampens. Furthermore, the one-magnon line is split under a magnetic field, but the two-magnon line is not affected for moderate fields. The surprising thing is that the two-magnon Raman scattering cross section is larger than the first-order one. If the second-order mechanism results from a higher order process of the first-order one, perturbation theory predicts several orders of magnitude smaller intensity in the second-order process. This suggests that the second-order magnetic scattering is of different origin.

Magnetic-optic coupling mechanism

From now on, we will discuss the mechanism of light scattering by magnons on a phenomenological level following Ref. [70]. The effective Hamiltonian which describes the interaction of light with a magnetic system is given as:

$$\begin{aligned} H_{p-mag} &= \sum_{r,\gamma} P^\gamma(r) \cdot E_S^\gamma(r) \\ &= \sum_r \sum_{\alpha,\beta} E_I^\alpha \chi^{\alpha\beta}(r) E_S^\beta. \end{aligned} \quad (3.12)$$

This arises from the electric dipole interaction between the polarization P and the scattered electric field E_S . For magnetic materials the susceptibility tensor will be spin-dependent. Thus, the modulation of $\chi^{\alpha\beta}(r)$ can be expressed in Taylor series in terms of spin operators:

$$\begin{aligned} \chi^{\alpha\beta}(r) &= \chi_0^{\alpha\beta}(r) + \sum_\mu K_{\alpha\beta\mu}(r) S_r^\mu + \sum_{\mu,\nu} G_{\alpha\beta\mu\nu}(r) S_r^\mu S_r^\nu \\ &\quad + \sum_\delta \sum_{\mu,\nu} H_{\alpha\beta\mu\nu}(r, \delta) S_r^\mu S_{r+\delta}^\nu + \dots \end{aligned} \quad (3.13)$$

Here the coefficient tensors K , G , and H denote the strength of the coupling between light and the magnetic system. The constant term $\chi_0^{\alpha\beta}$ corresponds to an elastic scattering contribution. The linear term in S_r^μ can be written as a combination of the terms S_r^+ and S_r^- which describe one-magnon creation and annihilation, respectively. The combinations of electric field vectors with these terms determine the polarization selection rules: For systems with cubic symmetry one-magnon scattering is present only if $E_I^z E_S^+ - E_I^+ E_S^z \neq 0$. The quadratic term in spin operators at a single ionic site r also gives rise to one-magnon scattering. This is because this term can be effectively rewritten as being proportional to $S_r^+ S_r^z$, $S_r^z S_r^+$, $S_r^- S_r^z$, and $S_r^z S_r^-$. Note that these are all linear in a transverse spin operator. The selection rule is satisfied if $E_I^z E_S^+ + E_I^+ E_S^z \neq 0$ for the cubic system. The quadratic spin term at different sites also has a contribution to the one-magnon scattering due to the terms proportional to $S_r^+ S_{r+\delta}^z$, $S_r^z S_{r+\delta}^+$, $S_r^- S_{r+\delta}^z$, and $S_r^z S_{r+\delta}^-$. However, such a contribution will be negligible because it arises from higher order perturbation. Up to now, we have presented the mechanism for one-magnon scattering following the Elliott-Loudon process. Within this mechanism, in order to obtain two-magnon scattering one needs to go to higher order. Then, the resulting two-magnon scattering cross section would be hardly observable. However, in antiferromagnets two-magnon scattering is frequently more intense than

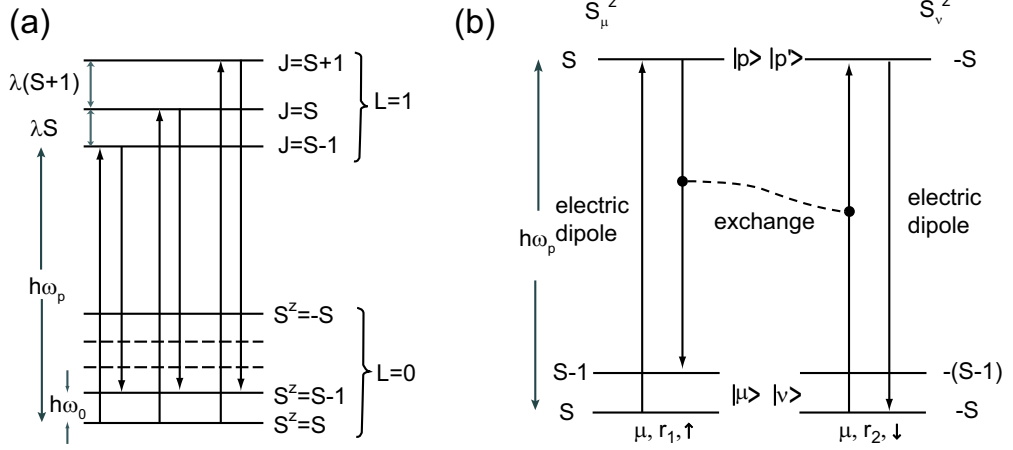


Figure 3.5: (a) Schematic illustration of the one-magnon scattering mechanism (b) Schematic illustration of the exchange scattering mechanism.

one-magnon scattering as seen in Fig. 3.4. This discrepancy can be resolved by an alternative mechanism known as the exchange scattering mechanism. A two-sublattice antiferromagnet has two magnon branches with frequencies $\omega^\pm(k)$. There is the extra possibility of having two-magnon excitations with $\Delta S^z = 0$ besides $\Delta S^z = 2$: spin deviations are created at a pair of exchange-coupled magnetic sites on opposite sublattices states through virtual electronic transitions to higher states. This mechanism allows for terms proportional to $S_r^+ S_{r+\delta}^-$ and $S_r^- S_{r+\delta}^+$. Here note that the physically different origin of the one- and the two-magnon scattering does not impose the restriction on the relative scattering intensity between one- and two-magnon scattering.

One-magnon scattering due to spin-orbit coupling

We will now discuss the microscopic mechanism of one-magnon scattering based on spin-orbit coupling [71]. Consider the magnetic ionic energy level diagram with zero orbital angular momentum and with spin S in the ground state as displayed Fig. 3.5. The effective magnetic field will split this state into $(2S+1)$ components. The ion is supposed to have an excited orbital state with $L = 1$ and the same S as the ground state. Then, this will be split into three components corresponding to $J = S + 1, S$, and $S - 1$ by spin-orbit interaction $\lambda L \cdot S$, where λ is the spin-orbit coupling constant with an order

10^2 cm^{-1} . Each excited state $|J, J^z\rangle$ is expressed as a linear combination of the unperturbed $|L^z, S^z\rangle$ states. The transition from $S^z = S$ ground state to $S^z = S - 1$ takes place by a successive electric dipole transition via the $L = 1$ virtual intermediate state. The coupling constant K can be calculated in terms of the spin-orbit coupling λ . For the case that magnetic ions do not have $L = 0$ ground state, the lifting of a degenerated ground state by the crystal field can give rise to magnetic excitations by changing both orbital and spin components.

Two-magnon scattering due to exchange mechanism

As pointed out, the spin-orbit coupling cannot be extended to higher order to give account for second-order magnetic Raman scattering. Rather, the two-magnon scattering is based on a new mechanism known as "the exchange scattering mechanism" [30]. This mechanism arises from third-order perturbation theory: second-order in the electric dipole interaction and first-order in the exchange interaction between two electrons via Coulomb interaction. The main scattering mechanism is illustrated in Fig. 3.5(b). The ground state of ion μ has an electron r_1 with $S^z = \frac{1}{2}$ (denoted by $\uparrow$) in an orbital $|\mu\rangle$, while ion ν has an electron r_2 with $S^z = -\frac{1}{2}$ (denoted by $\downarrow$) in an orbital $|\nu\rangle$. The total Hamiltonian for the electric dipole interactions and the Coulomb interaction is

$$H = e(E_I + E_S) \cdot (r_1 + r_2) + \frac{e^2}{r_{12}}, \quad (3.14)$$

where $r_{12} = |r_1 - r_2|$ is the distance between two electrons. The initial two-ion state is $|\mu r_1 \uparrow\rangle \otimes |\nu r_2 \downarrow\rangle$. The final state corresponds to $|\mu r_2 \downarrow\rangle \otimes |\nu r_1 \uparrow\rangle$. A dominant contribution describing the simultaneous change of the spin components of ions μ and ν is given by

$$\langle \nu r_1 \uparrow | eE_S \cdot r_1 | \mu r_1 \uparrow \rangle \quad (3.15)$$

$$\begin{aligned} & \times \langle \mu r_2 \downarrow | \frac{e^2}{r_{12}} | \nu r_2 \downarrow \rangle \otimes \langle \mu r_1 \uparrow | \\ & \times \langle \nu r_1 \uparrow | eE_I \cdot r_1 | \nu r_1 \uparrow \rangle / \hbar^2 (\omega_I - \omega_P)^2. \end{aligned} \quad (3.16)$$

The essential feature of this process is the double spin-flip caused by the matrix element of the Coulomb interaction conserving the total z component of spins. The total matrix element can be written as

$$\langle S_\mu^z = S - 1, S_\nu^z = -(S - 1) | H_{2-mag} | S_\mu^z = S, S_\nu^z = -S \rangle \quad (3.17)$$

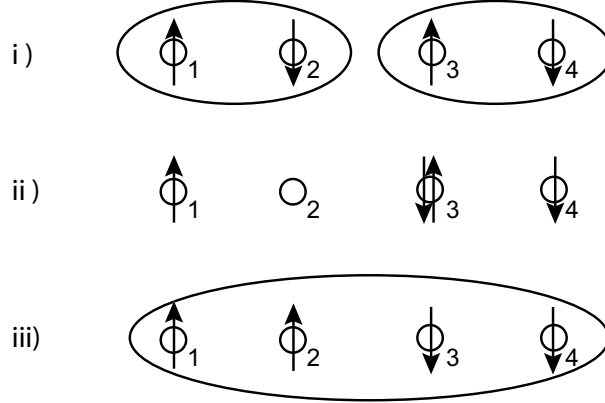


Figure 3.6: Schematic illustration of the exchange scattering mechanism for the alternating spin chain with frustration: two triplet states iii) result from the ground state i) through the exchange mechanism ii) [73].

by means of a spin Hamiltonian

$$H_{2-mag} = \sum_{ij} F^{ij} E_S^i E_I^j S_\mu^- S_\nu^+. \quad (3.18)$$

Note that the two-magnon Hamiltonian (called Fleury-Loudon Hamiltonian) is proportional to the Heisenberg Hamiltonian owing to the same exchange mechanism through Coulomb interaction. Because of the short range of exchange coupling, the scattering mechanism is effective within nearest neighbors on the opposite sublattices. This restriction leads to a reduction in the energy of the two-magnon state by $2J(2zS - 1)$ in the Ising model. Here note that for higher-dimensional antiferromagnetic systems the bare spectrum of two-magnon spectrum typically has a peak near the zone-boundary where the two-magnon density of state $\rho_2(\omega) = \sum_q (\omega - 2\omega_q)$ is largest.

Exchange mechanism in low dimensional system

In quasi-one dimensional systems with dimerization and frustration two-magnon scattering has been observed with polarization of E_I and E_S both parallel to the chain direction [75]. For an alternating spin chain the Raman operator is derived from Eq. (3.18) as follows [48]:

$$\mathcal{R} = \sum_i (1 + \gamma(-1)^i) S_i \cdot S_{i+1}. \quad (3.19)$$

Here γ comes from the dimerization of the spin system. For $\alpha = 0$ this operator commutes with Hamiltonian (2.11). Thus, magnetic Raman scattering is expected in the presence of competing antiferromagnetic interactions, that is, $\alpha \neq 0$. In the strong dimerization limit an exchange light scattering process can easily be illustrated as shown in Fig. 3.6. Two spins at neighboring sites form a dimer. There is no spin correlation between dimers. Thus, the ground state is a tensor product of singlet states. Without loss of the generality, we will consider four spins at sites, 1,...,4. The ground state is $|s_{1,2} > \otimes |s_{3,4} >$ where $s_{i,i+1} = \frac{1}{\sqrt{2}}(|\uparrow_i \downarrow_{i+1} > - |\downarrow_i \uparrow_{i+1} >)$ with $i = 1, 3$. The singlet state can be promoted into three triplet states:

$$\begin{aligned} t_{i,i+1}^0 &= \frac{1}{\sqrt{2}}(|\uparrow_i \downarrow_{i+1} > + |\downarrow_i \uparrow_{i+1} >), \\ t_{i,i+1}^1 &= |\uparrow_i \uparrow_{i+1} >, \\ t_{i,i+1}^{-1} &= |\downarrow_i \downarrow_{i+1} >. \end{aligned} \quad (3.20)$$

In the strong dimer limit the Raman operator simplifies to $\mathcal{R} = S_2 \cdot S_3$. Applying this to the singlet ground state one obtains

$$\mathcal{R} |s_{1,2} > \otimes |s_{3,4} > = \frac{1}{4}(-|t_{1,2}^0 > \otimes |t_{3,4}^0 > + |t_{1,2}^1 > \otimes |t_{3,4}^{-1} > + |t_{1,2}^{-1} > \otimes |t_{3,4}^1 >). \quad (3.21)$$

This process corresponds to the creation of two triplets on neighboring dimers while conserving the z-component of a total spin in agreement with the Fleury-Loudon model.

For finite temperatures the lowest triplet state can be thermally populated. This state can be described as $|t_{1,2}^0 > \otimes |s_{3,4} >$. This effect should be considered when the gap ratio to the transition temperature $2\Delta/T_{dimer}$ is not too large. Applying the Raman operator one expects the following final states:

$$\begin{aligned} \mathcal{R} |t_{1,2}^0 > \otimes |s_{3,4} > &= \frac{1}{4}(-|s_{1,2} > \otimes |t_{3,4}^0 > + |t_{1,2}^1 > \otimes |t_{3,4}^{-1} > \\ &\quad - |t_{1,2}^{-1} > \otimes |t_{3,4}^1 >). \end{aligned} \quad (3.22)$$

The last two terms include two triplets. Thus, this Raman process ("three magnon scattering") induces a transition from one- to two-magnon states. Actually, such a process was observed in CuGeO₃ [72].

3.3 Quasielastic Scattering

Frequently, quasielastic scattering has been reported in Raman scattering measurements of magnetic systems. Based on the exchange mechanism, its origin is explained in terms of either spin diffusion or spin-energy fluctuations. The former leads to a broad Gaussian lineshape in conventional magnetic systems. In contrast, the latter often results in a Lorentzian profile of scattering intensity in low-dimensional systems. This quasielastic scattering gives information on exchange constants and/or magnetic specific heat. In the following, we will restrict our interest on a coupling of light to the magnetic energy of the system in the mechanism of two-magnon scattering. For an extensive review on quasielastic scattering in low-dimensional spin systems we refer to Ref. [75].

Spin-energy fluctuations

According to Reiter and Halley [76, 77], the scattering intensity above a critical temperature can be written as follows

$$I(\omega) \propto \int_{-\infty}^{\infty} e^{-i\omega t} \langle E(k, t) E^*(-k, 0) \rangle dt, \quad (3.23)$$

where $E(k, t)$ is magnetic energy density given by the Fourier transform of $E(r) = - \langle \sum_{i>j} J_{ij} S_i \cdot S_j \delta(r - r_i) \rangle$ with the position of the i th spin r_i . Introducing the hydrodynamic form given by Halperin and Hohenberg [78] and applying the fluctuation-dissipation theorem, the above equation is simplified to

$$I(\omega) \propto \frac{\omega}{1 - e^{-\hbar\omega/k_B T}} \frac{C_m T_T D k^2}{\omega^2 + (D_T q^2)^2}. \quad (3.24)$$

Here D_T is a thermal diffusion constant given by $D_T = K/C_m$, where K is the magnetic contribution to the thermal conductivity. q is approximated as $|k_0| \sin \theta / 2$, where k_0 and θ are the wave vector of the incident light and the scattering angle, respectively. In the high-temperature limit the scattering intensity has a Lorentzian lineshape

$$I(\omega) \propto C_m T^2 \frac{D_T k^2}{\omega^2 + (D_T q^2)^2}. \quad (3.25)$$

This equation implies that the magnetic specific heat and thermal diffusion constant can be estimated from the integrated intensity and the half-width at half maximum of the quasielastic scattering.

For temperatures below the magnetic ordered temperature one should also consider the contribution of the magnetization to the scattering intensity:

$$I(\omega) \propto \int_{-\infty}^{\infty} e^{-i\omega t} [\langle E(k, t) E^*(-k, 0) \rangle + J^2 \langle m_z(k, t) m_z^*(-k, 0) \rangle] dt. \quad (3.26)$$

Using the hydrodynamic form the final result is summarized as follows

$$I(\omega) \propto \frac{\omega}{1 - e^{-\hbar\omega/k_B T}} \left[\frac{C_m T D_T k^2}{\omega^2 + (D_T q^2)^2} + J^2 \frac{\chi_{\parallel} D_{\parallel} k^2}{\omega^2 + (D_{\parallel} q^2)^2} \right]. \quad (3.27)$$

where $D_{\parallel}$ is the diffusion constant for the component of the magnetization parallel to the sublattice magnetization, $\chi_{\parallel}$ is the parallel susceptibility and J is the exchange interaction.

3.4 Experimental setup

In the following a brief description of experimental setup will be presented. Fig. 3.7 illustrates schematically Raman spectroscopy. Conventional Raman spectroscopy makes use of a continuous wave laser as a light source. The argon laser is widely used because it is not so susceptible to an instability due to pressure changes in the tube and provides a wide range of lines as well as a high power. In particular, an argon laser is of most value in the blue (488 nm) and green (514.5 nm) regions of spectrum. To perform resonance Raman studies the argon laser should be combined with a krypton laser which has most value for the red and yellow spectrum.¹ However, one of the disadvantage of ion lasers is the presence of plasma lines arising from many atomic transitions. These plasma lines are much weaker than the main laser line, but are comparable with, or even stronger in intensity than typical Raman signals. Thus, these should be removed before reaching the sample. This can be done in two successive steps: firstly, one can use a pre-monochromator in which a series of prisms disperses the light coming in. The dispersed light is then passed through an aperture sufficiently wide to take the light of the wavelength required but too narrow to take at the same time, the plasma lines which are spatially separated from the wavelength of interest. After that, the laser beam is further passed through a series of pinholes which blocks isotropic radiation from spontaneous emissions.

¹Unfortunately, our laboratory is equipped only with the argon laser. Thus, the detailed resonant scattering has not been done.

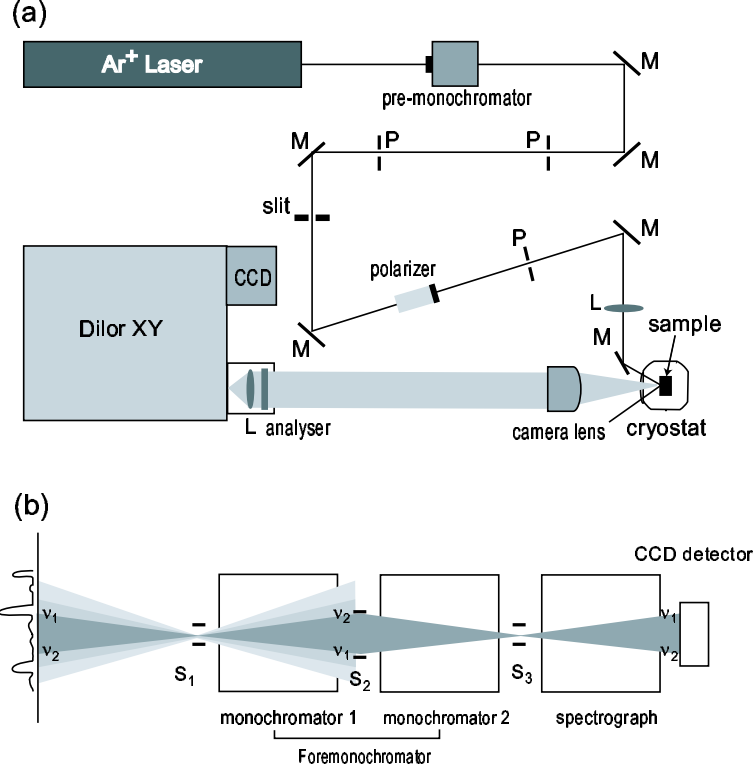


Figure 3.7: (a) Schematic experimental setup of Raman spectroscopy. M stands for mirror, P for pinhole, and L for lens. (b) Scheme of a triple spectrometer.

After filtering the plasma lines the laser beam is focused onto the sample with collecting lens of a focus length $f = 10$ cm. The focused light is incident on the sample in quasi-back scattering geometry. The scattered light is collected using a commercial camera lens of a focus length $f = 8$ cm and is sent to the spectrometer.²

A schematic diagram of a triple monochromator is shown in Fig. 3.7(b). It consists of a double subtractive monochromator with a spectrograph. Light from the sample is focussed on an image in the plane of the entrance slit (S₁) which lies in the focal plane of a concave mirror. This mirror directs

²The camera lens can effectively capture the spectrum in the visible region which is sufficient for this work.

the light to the diffraction grating. The different wavelengths of light are dispersed into parallel beams travelling in slightly different direction. The slit width ($S_1=100\text{ }\mu m$) determines the resolution of the spectrometer. Then, the light is passed through a wide central slit ($S_2= 2000\text{ }\mu m$) between the first and second element and the gratings are set that the entire spectral range of interest passes through this slit, but most of the Rayleigh scattered light is blocked. The first and second stages are arranged so that the dispersions of the two gratings are opposed. That is, the first element disperses the light in the normal manner, but the second element acts to recombine the light, after spatial filtering. In this way, the double element effectively acts as a very sophisticated filtering device for the spectrograph by reducing stray light. The final stage (the spectrograph) uses a slit ($S_3=100\text{ }\mu m$) and a grating which disperses this light once more with the required resolution and now the exit slit can be replaced by an array detector located in the focal plane. With a multichannel charge coupled device (CCD) detector one can measure roughly the spectral region of 600 cm^{-1} at one time in the green line. For a complete study of phononic and magnetic excitations, the grating should be scanned several times.

Chapter 4

Frustrated alternating spin chain system LiCu_2O_2

In this chapter we will present Raman scattering study of the frustrated spin chain system LiCu_2O_2 . The prototype example of low dimensional spin systems with frustration and dimerization is the inorganic spin-Peierls system CuGeO_3 [31]. Extensive theoretical and experimental investigations of such a system have unveiled a variety of exotic magnetic excitations [75] as well as a rich phase diagram including a gapless phase, a gapped dimer liquid phase, and a quasi-long-range ordered spiral phase [79], depending on the dimerization and the relative frustration by next-nearest neighbor coupling. Most interestingly, in a dimer phase doping with nonmagnetic impurities can lead to a Néel ordered state coexisting with the dimerized state due to the resonating-valence-bond character of spin correlations [80, 81, 82]. LiCu_2O_2 is a good candidate for addressing this issue because the dimerized phase of LiCu_2O_2 is intrinsically contaminated by magnetic and nonmagnetic impurity phases.

4.1 Crystal structure and magnetic properties

LiCu_2O_2 has an orthorhombic crystal structure of space group $Pnma$ with the lattice parameters $a=5.72$, $b=2.86$, and $c=12.4$ Å [83]. There exist monovalent and divalent copper ions in the crystal structure. As displayed in Fig. 4.1(a), chains of Cu^{2+} ions propagate along the b axis. There are two such parallel Cu-chains which run along the a axis and which are connected along the c axis by a nearly 90° oxygen bond. Therefore, magnetic Cu^{2+} ions form a double-chain along the b axis which is separated from each other by both Li ions and planes with nonmagnetic Cu^+ ions. The distance between the magnetic

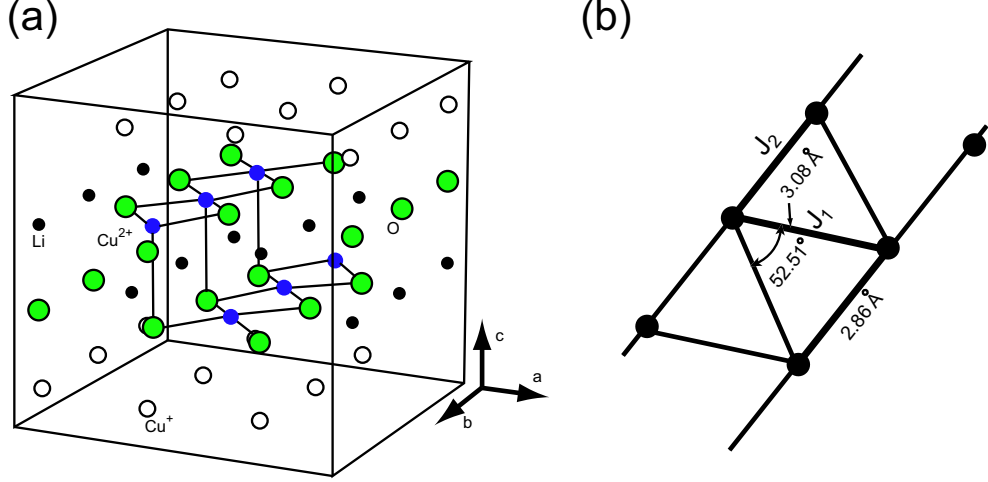


Figure 4.1: (a) Crystal structure of LiCu_2O_2 showing the double Cu^{2+} chains [84]. (b) Sketch of exchange paths and distances between Cu^{2+} ions in the double-chain structure.

next-nearest-neighbor Cu^{2+} ions along the double-chain is about of $2.86 \text{ \AA}$, and between the nearest-neighbor Cu^{2+} ions is about $3.08 \text{ \AA}$ (see Fig. 4.1(b)). Thus, depending on the ratio of the nearest- to the next-nearest-neighbor exchange coupling constants, one can consider LiCu_2O_2 as being either a frustrated spin chain or an asymmetric zigzag spin ladder [83, 84, 85].

As displayed in Fig. 4.2(a), the magnetic susceptibility $\chi(T)$ shows a broad maximum around 35 K which is typical for low-dimensional antiferromagnets [85]. A transition to a long-range-ordered state is clearly seen in its derivative, occurring at 23 K and 9 K. In particular, a second transition is evidenced by a sharp drop in $\chi(T)$ when $B \parallel c$. Specific measurements [85] show a large asymmetric peak around 9 K and a small and broad doubly peaked anomaly at 22.5 K and 24.2 K as displayed in Fig. 4.2(b). The origin of the double-peak structure around $T_{c1} \sim 23 \text{ K}$ is not clear at present. Recent neutron diffraction measurements [86] evidence a helimagnetically ordered state at $T_{c1} \sim 23 \text{ K}$ while thermodynamic measurements [85] suggest a collinear AFM state at $T_{c2} \sim 9 \text{ K}$. Both transitions are attributed to an intrinsic non-stoichiometry and the effect of nonmagnetic and/or magnetic impurities [85, 86]. However, the exact origin is not yet clear. At elevated temperatures high-field electron spin resonance (ESR) gives evidence for a spin singlet state with spin gap

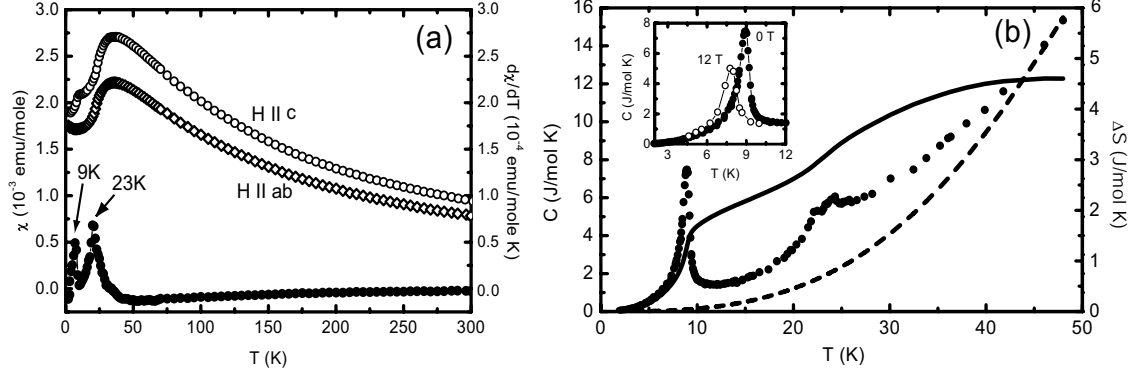


Figure 4.2: (a) Temperature dependence of the magnetic susceptibility $\chi(T)$. The bottom curve describes the temperature dependence of $d\chi/dT$ when $B \parallel c$. (b) Temperature dependence of the specific heat (full circles); the dashed line denotes the estimated phonon contribution. The solid line denotes the entropy removed after subtracting the phonon contribution. The inset shows the shift of low-temperature peak under an external field [85].

of $\Delta \sim 72$ K [85]. In addition, with decreasing temperature a reduction of orthorhombic strain has been observed [84]. These magnetostructural peculiarities of LiCu_2O_2 provide a good opportunity to investigate the influence of a variety of magnetic and nonmagnetic impurities on magnetic property of a frustrated spin chain system.

4.2 Experimental setup

The single crystals were grown using a self-flux method and characterized by a microstructural analysis and thermodynamic measurements as described in Ref. [85]. The single crystals are microscopically twinned and contain LiCuO -impurity phase. Raman spectra were measured in a quasi-backscattering geometry with the excitation line $\lambda = 514.5$ of Ar^+ laser with the power of 10 mW and were analyzed by a DILOR-XY spectrometer and a nitrogen cooled CCD detector.

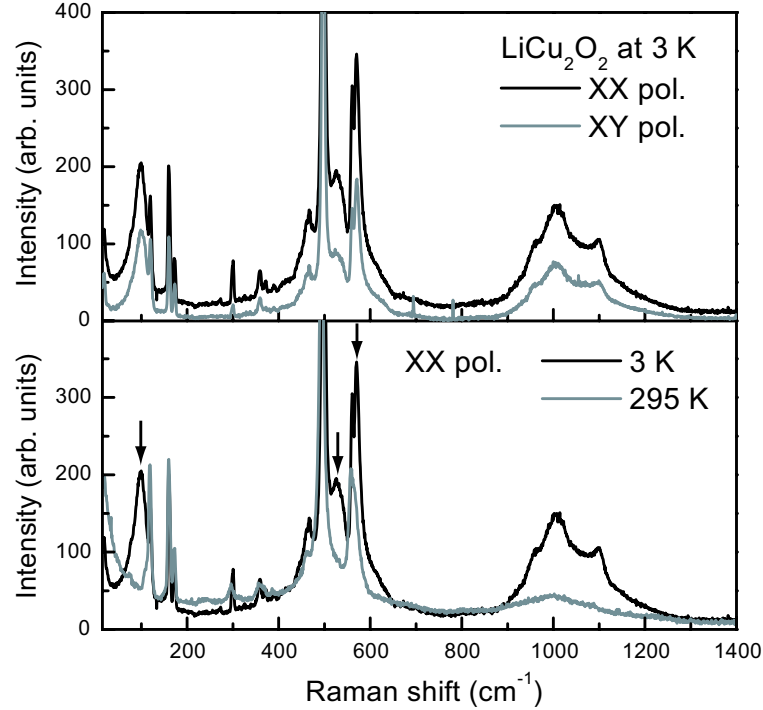


Figure 4.3: Raman spectra of LiCu_2O_2 in parallel (xx) and crossed polarizations (xy) at 3 K (upper panel) as well as at low and room temperature in parallel polarization (lower panel). The arrows indicate additional phononic and magnetic signals which appear at low temperature.

4.3 Phononic excitations

Fig. 4.3 displays Raman spectra in parallel (xx) and crossed (xy) polarizations at 3 K as well as at 5 K and room temperature in xx polarization. Here the x -axis is an arbitrary direction in ab -plane. Noticeably, Raman spectra in crossed polarization exhibit the same behavior as those in parallel polarization with weaker intensity. This is ascribed to a twinning of the single crystal on a microscopic level. Thus, the observed spectra can be regarded as an average over all ab -plane polarizations. LiCu_2O_2 has a space group $Pnma$. The site symmetry of all atoms is $4c$. Subtracting the acoustic ($B_{1u} + B_{2u} + B_{3u}$) modes the factor group analysis yields the following Raman- and infrared-active modes; $10 A_g(\text{aa,bb,cc}) + 5 B_{1g}(\text{ab}) + 10 B_{2g}(\text{ac}) + 5 B_{3g}(\text{bc}) + 5 A_u + 9 B_{1u} + 4 B_{2u} + 9 B_{3u}$. At room temperature we observe 12 Raman-active

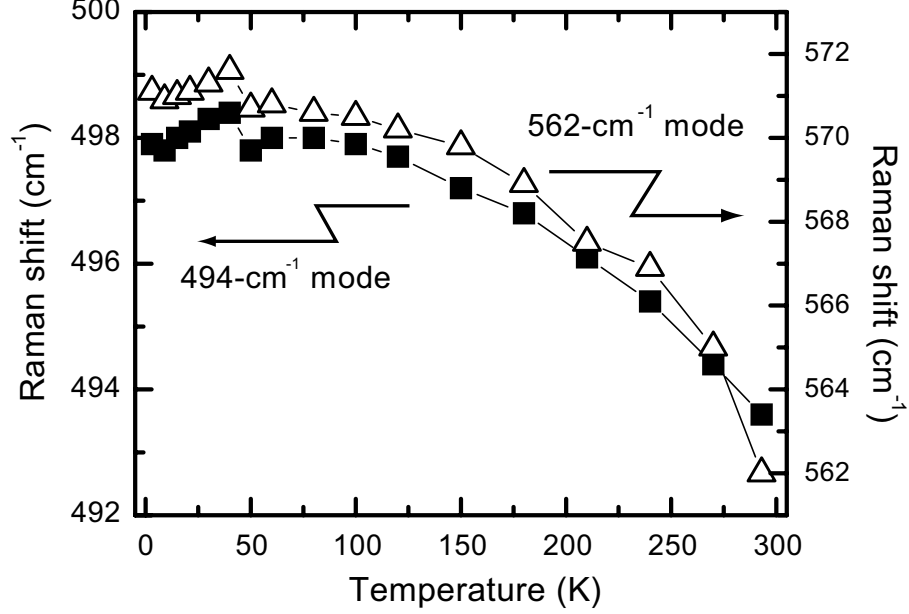


Figure 4.4: Temperature dependence of the 494-cm⁻¹ and 562-cm⁻¹ phonon modes.

modes out of the maximally expected 15 modes for the *ab*-plane polarizations. Here note that a broad band extending from 850 cm⁻¹ to 1300 cm⁻¹ is second order scattering of the first order signals between 400 cm⁻¹ and 650 cm⁻¹ which correspond to bending and stretching modes of Cu-O. The observed two-phonon scattering should be attributed to lattice anharmonicity and/or resonant scattering as higher-order Raman scattering of 3d transition metal oxides usually does.

With decreasing temperature several distinctive features show up. First, upon cooling new phonon modes appear. In addition, almost all phonon modes become sharp and more intense. In particular, several phonon modes undergo a substantial shift in energy. Second, a low frequency scattering background as well as magnetic continua develops in an intriguing manner. We concentrate firstly on phonon anomalies which reflect changes of the local symmetry and bond strengths. Significant changes are observed in the bending and stretching modes of Cu-O. The temperature dependence of the 494- and 562-cm⁻¹ modes is plotted in Fig. 4.4. Upon cooling from room temperature both modes undergo an appreciable hardening by 5-8 cm⁻¹ and then saturate around $T = 50$

K. Upon further cooling they soften slightly while showing a tiny jump at 50 K. It should be noted that a softening takes place for temperatures whose energy scale is comparable to the exchange constant $J \sim 44$ K [85]. Such an anomalous evolution of phonon modes has been observed in the alternating spin chain system $(\text{VO})_2\text{P}_2\text{O}_7$ [87, 88] and interpreted in terms of strong spin-phonon coupling. This suggests the significance of a coupling of spin to lattice degree of freedom in LiCu_2O_2 . Therefore, a softening below 50 K should be attributed to a renormalization of phonon energy via spin-phonon coupling. The smallness of the observed softening can be understood if one considers the big difference in energy scale between the exchange constant $J \sim 44$ K [85] and the optical phonon energy of ~ 700 K which mediates the exchange paths along the double-chain. High-resolution x-ray diffraction measurements [84] show a substantial increase of orthorhombic strain $(a - b)/(a + b)$ upon heating. Transition metal oxides may show a decrease of the orthorhombicity with increasing temperature, since thermally activated lattice vibrations reduce the strain. Normally, phonon frequencies shift to higher energy, linewidths broaden, and integrated intensity of some phonon modes decreases. The studied system follows the behavior expected for usual systems despite the opposite behavior of the orthorhombicity as a function of temperature. To clarify the seemingly inconsistency between local and bulk properties detailed studies of structure as a function of temperature are needed.

4.4 Magnetic excitations

We will now concentrate on distinctive features observed at low temperatures and frequencies. As Fig. 4.5 displays, at 3 K a broad asymmetric continuum around 100 cm^{-1} is seen. With increasing temperature the continuum shifts to lower energy while damping increases. At the same time, a quasielastic scattering response and a weak continuum around 110 cm^{-1} develop. Although the crystals are twinned, the dynamics of low-dimensional spin system can be well resolved by Raman spectroscopy. This is because magnetic Raman scattering of low-dimensional systems contributes selectively to the polarization direction in which the incident and scattered light is parallel to the dominant exchange paths. Thus, twinning does not add an essential difficulty to interpreting magnetic signals. To clarify the relation between the magnetic excitations and the structure of magnetic ordering observed in the bulk material we will distinguish three phases following Ref. [85]; I: magnetic ordered phase ($T < 9$ K, presumably with collinear AFM structure), II: helimagnetic ordered phase (9

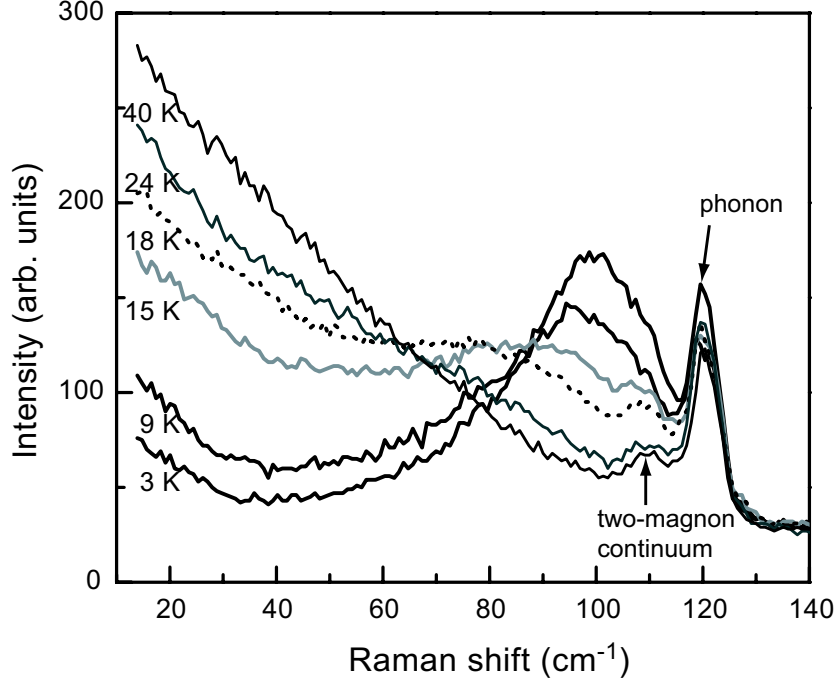


Figure 4.5: Low frequency Raman scattering of LiCu_2O_2 . Quasielastic scattering and two different kinds of two-magnon continua have been observed.

$K < T < 23 \text{ K}$), and III: dimerized phase ($T > 23 \text{ K}$).

In phase I the broad continuum extending from 40 cm^{-1} to 130 cm^{-1} is observed. This continuum persists as a wing feature of quasielastic scattering up to $T=21 \text{ K}$ ($2.3 T_{c_2}$). This feature is typical for two-magnon (2M) scattering originating from double spin-flip processes via the exchange mechanism in antiferromagnets with collinear structure [30]. Therefore, we identify phase I to be Néel ordered with $T_N=T_{c_2} = 9 \text{ K}$.

The evolution of the 2M spectrum reflects mainly the temperature dependence of short-wavelength magnon energies and lifetimes because the 2M density of states is largest at the zone boundary and long-wavelength magnons renormalize more rapidly with temperature than short-wavelength magnons [70]. Thus, the persistence of 2M scattering to several T_N can be interpreted in terms of the presence of short-range magnetic fluctuations damped by thermal fluctuations. In Fig. 4.6 its temperature dependence of the normalized 2M frequency and the full width at half-maximum is presented together with

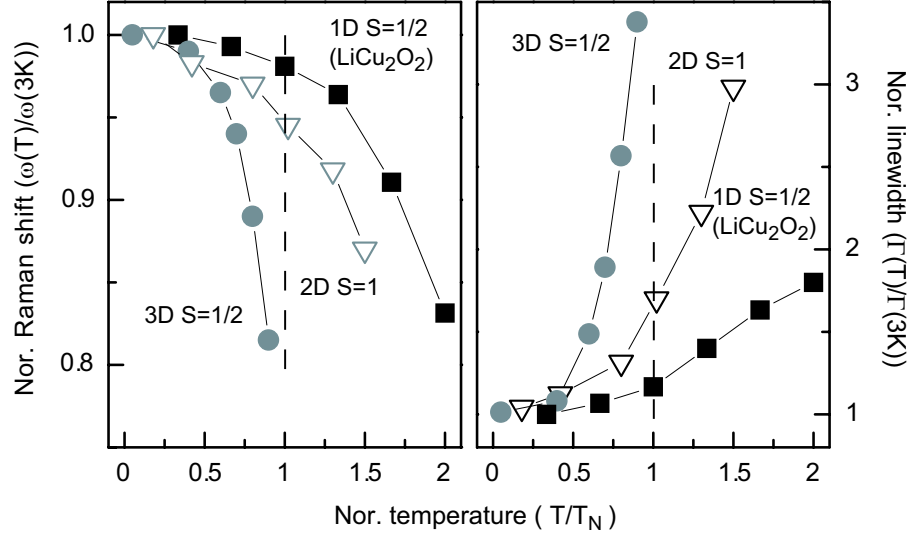


Figure 4.6: Comparison of renormalized frequency (left panel) and damping (right panel) of two-magnon continuum as a function of spin number and dimensionality. The higher dimensional data are taken from Ref. [70]. The dashed vertical line marks a Néel temperature.

higher dimensional results [70, 89]. Magnon-pair energies of LiCu₂O₂ (1D S=1/2) are renormalized only by 3%¹ at T_N . In contrast, the magnon-pair spectral weight is renormalized by 25 % at T_N for 3D S=1/2 systems and by less than 5% for 2D S=1 systems [70, 89]. The damping does scarcely take place at T_N for LiCu₂O₂. However, it strongly increases as the dimension and spin number increase as the right panel of Fig. 4.6 displays. The higher dimensionality and spin number are, the larger are changes of spectral weights at an energy scale comparable to the Néel temperature. This is related to the fact that the Néel temperature is not an appropriate energy scale for magnetic excitations in low-dimensional systems. Compared to higher dimensional systems, the robustness of spin-fluctuation dynamics on the energy scale of T_N confirms the low-dimensional character of the studied system.

The frequency of the 2M peak allows an estimate of the unrenormalized AFM exchange constant between copper spins. The exact determination of the exchange constant in the studied system is impossible because no the-

¹This is determined by the ratio of the peak position $\omega(T_N)/\omega(3K) \approx 0.97$.

oretical calculation for a double-chain system is known. However, one can make a reasonable estimation using not too stringent assumptions. Because of frustrations, the magnetic behavior of LiCu_2O_2 lies between 1D and 2D antiferromagnet. In the 2D case, the peak energy of $2.7J$ imposes a lower boundary of the exchange constant [90]. In frustrated chain systems the one-magnon dispersion is given by $\omega(k) = J(1 - \alpha \cos(kd)/2)$ with the frustration parameter α and the chain repeat vector d [91]. In the noninteracting case 2M scattering is given by twice the magnon density of states. Thus, the peak energy corresponds to $J(2 + \alpha)$. If we assume a renormalization of the peak energy due to magnon-magnon interactions by the order of $J\alpha$, then an upper boundary of the peak energy is roughly given by $2J$. To conclude, one obtains $52 \text{ K} < J < 70 \text{ K}$ from the peak energy of 140 K ($\approx 100 \text{ cm}^{-1}$). This value encompasses $J = 66 \text{ K}$ obtained by a fit of a frustrated chain model to the static susceptibility in the high-temperature regime [86].

In the following we will discuss the phase II and III. Quasielastic scattering develops in the respective temperature interval. In addition, a weak continuum extending from 102 cm^{-1} to 120 cm^{-1} becomes clearly distinguishable from the broad 2M continuum. This continuum persists up to 200 K , that is, into the dimerized phase III. We thus assign the observed signal to a 2M continuum which corresponds to a double spin-flip process of two singlets into a higher singlet state [75]. Since the onset of the continuum corresponds to twice the spin gap, one obtains a spin gap of $\Delta \approx 73 \text{ K}$. This value is in excellent agreement with $\Delta \approx 72 \text{ K}$ from high-field ESR measurements [85].

However, we find no evidence for the presence of additional magnetic excitations in the magnetic long-range ordered state II. The silence of magnetic Raman scattering seems to be related to the incommensurate helimagnetic structure suggested in Ref. [86]. In contrast to the 2M continuum from the Néel ordered state, the 2M continuum from singlet states shows no noticeable change in peak position as well as intensity as a function of temperature. This is due to the narrow bandwidth of triplet excitations compared to the magnitude of the spin gap. Moreover, two 2M continua are simply superposed to each other independently. This indicates that in phase II short-range singlet correlations and the helimagnetic ordered state coexist *coherently*. Furthermore, the simultaneous observation of magnetic excitations from Néel order and singlet correlations in phase I can be interpreted as the coherent coexistence of an antiferromagnetic long-range ordered and a dimerized state which are mutually exclusive. Note here that the dimerized state is robust in the course of the evolution of magnetic structures and their corresponding magnetic correlations. Until now, such a coexistence has only been reported in two different classes

of systems. First one can be found in the Oxo-Cu-vanadate $\text{KCu}_5\text{V}_3\text{O}_{13}$ which is a *geometrically frustrated* tetrahedra spin ladder system [92]. This frustrated spin topology results in an antiferromagnetic spin ordering of only 1/5 of all the copper spins while the other spins form singlet states with a spin gap. The other has been reported in the impurity-doped spin-Peierls system CuGeO_3 [80] and the highly hole-doped quasi-1D cuprate $\text{Sr}_{0.73}\text{CuO}_2$ [81]. The introduction of nonmagnetic impurities to dimerized states produces a local moment by breaking up dimers. With aid of higher dimensional interactions long-range ordering occurs at low temperature [82]. This disorder-order transition scenario might be applicable to the studied system as the dimerized phase of LiCu_2O_2 is intrinsically contaminated by a LiCuO impurity phase which has copper ions in a nonmagnetic Cu^+ oxidation state. The LiCuO phase is estimated to be less than 10% of the total volume. It is arranged almost regularly in the form of platelets with the dimension of $100 \times 7 \times 100 \text{ nm}^3$ (Ref.[85]). It is thus natural to expect that similar to a single-site dopant, such nanostructural nonmagnetic inclusions break Cu^{2+} - Cu^{2+} bonding along the chains, enhance three-dimensional interactions and eventually promote AFM long-range order at low temperatures.

However, within this mechanism it is difficult to capture the following features. First, the presence of a helimagnetic state is not explainable because for the introduction of dopants the interaction between local moments has an alternating sign. That is, its sign relies on whether the two local moments belong to the same or to opposite sublattices. As a result, frustrations are lifted and an AFM ordering is favored. Second, the transition of an incommensurate phase into the Néel ordered one at 9 K is driven by the presence of the magnetic Li_2CuO_2 -impurity [86]. Third, the 2M signal from a long-range ordered state is much stronger than that from a dimerized phase (see Fig. 4.5). All these observations indicate the predominance of a long-range ordering over a dimerization as well as the dependence of the magnetic structure on the kind of impurities, signaling the significant role of magnetic impurities. In the following we present a possible scenario.

Upon cooling dilute magnetic impurities which lie most probably between spin chains undergo long-range ordering via 3D interactions. Then, the long-range ordered impurities can be regarded as effective magnetic fields inducing long-range ordering in spin chains. The observed helimagnetic state might be due to the compromise of AFM order with strong in-chain frustration. Furthermore, two successive transitions at 22.5 K and 24.2 K [85] reflect an intriguing interplay of magnetic impurities between chains and nonmagnetic in-chain impurities on the background of the incommensurate spin structure.

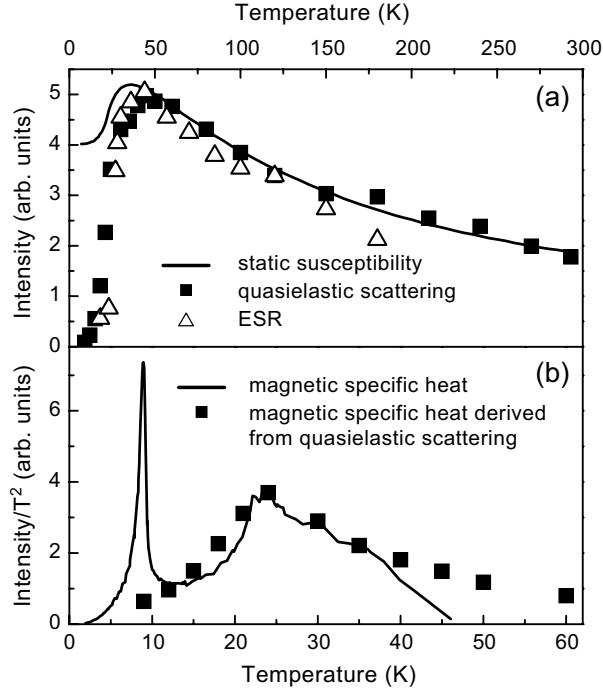


Figure 4.7: (a) Comparison of the intensity of quasielastic scattering (full rectangle) and ESR (open triangle) to static susceptibility (solid line) taken from Ref. [85]. (b) Mapping of the magnetic specific heat derived from quasielastic scattering (full rectangle) on the magnetic specific heat obtained by subtracting the phonon contribution (solid line).

Upon further cooling, depending on the presence of the Li_2CuO_2 -impurity, the Néel ordered phase will appear at about 9 K. This indicates that the collinear magnetic structure of the Li_2CuO_2 -impurity promotes the transition of the incommensurate phase to the commensurate one.

4.5 Quasielastic scattering

Finally, we will discuss quasielastic Raman response which shows a strong increase up to 45 K and then decreases slowly. Our experimental setup is suitably adjusted so that Rayleigh scattering is suppressed nearly completely above $\omega > 15 \text{ cm}^{-1}$. Quasielastic scattering arises from spin diffusion or fluc-

tuations of the energy density of the system. In the latter case the energy of the magnetic system fluctuates about the average value determined by the lattice temperature. Spin-phonon coupling leads to an enhancement of the spectral weight of fluctuations by reducing their time scale. This mechanism has been proven to be successful in describing quasielastic scattering in low-dimensional systems with spin-phonon coupling, for example, the spin-Peierls system CuGeO_3 [94], the alternating spin chain system $(\text{VO})_2\text{P}_2\text{O}_7$ [87], and the frustrated 2D spin dimer compound $\text{SrCu}_2(\text{BO}_3)_2$ [95]. Non-negligible spin-phonon interactions evidenced by phonon anomalies at low temperatures (see Fig. 4.4) strongly suggest that the quasielastic scattering in LiCu_2O_2 originates from energy fluctuations.

According to the theory of Reiter [76] and Halley [77], the scattering intensity is given by the Fourier component of the correlation function of the magnetic energy density: $I(\omega) \propto \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle E(k, t) E^*(k, t) \rangle$, where $E(k, t)$ is the magnetic energy density. In a hydrodynamic ansatz for the correlation function in the high-temperature limit [78] the above equation is simplified to a Lorentzian profile $I(\omega) \propto \frac{C_m T^2 D_T k^2}{\omega^2 + (D_T k^2)^2}$, where k is the scattering wave vector, D_T the thermal diffusion constant, and C_m the magnetic specific heat. In this case, the magnetic specific heat is proportional to the integrated intensity divided by T^2 . Using this relation one can map the scattering intensity on thermodynamic quantities. Fig. 4.7(a) displays the integrated intensity of quasielastic scattering as a function of temperature. There is a good correspondence between integrated ESR and quasielastic intensity with a peak at 45 K.² Here note that ESR probes excitations within excited states which originate from the low-dimensional character of interactions in LiCu_2O_2 as the drastic drop of its intensity below 45 K shows. Thus, one can see that ESR and Raman spectroscopy are selectively sensitive to disordered short-range correlations. In contrast, the static susceptibility becomes dominated by 3D short-range-order antiferromagnetic correlations below 45 K. In Fig. 4.7(b) the magnetic specific heat derived from the quasielastic scattering is shown together with the magnetic part of specific heat obtained after subtracting a calculated phonon contribution from the measured specific heat. In the temperature interval $12 \text{ K} < T < 40 \text{ K}$ there is a reasonable matching between them. However, a discrepancy shows up below the Néel temperature as well as above 40 K. The latter can be attributed to an overestimation of the phonon contribution to the specific heat at high temperatures by choosing only one Debye function.

²It is noteworthy that a mapping of the intensity of quasielastic scattering on the magnetic susceptibility (ESR intensity) implies a substitution of a four-spin correlations to a two-spin function. Up to now, however, there is no theoretical explanation for this.

The former discrepancy below 12 K comes from the suppression of fluctuations of spin energy density in the Néel ordered phase. Possibly, this is related to chiral spin fluctuations [93].

A maximum of C_m can also provide information on the exchange constant. In the case of a 1D AF chain the magnetic specific heat has a broad maximum at $k_B T \approx 0.481J$. The frustration shifts the maximum of C_m to lower temperature. At $\alpha < 0.3$ a maximum lies at $k_B T < 0.38J$ [94], resulting in the lower boundary of $J \sim 62$ K. This is consistent with the value obtained from the peak position of the two-magnon scattering.

4.6 Conclusion

Two different magnetic excitations with peaks at 100 and 110 cm^{-1} are observed in LiCu_2O_2 . The broad continuum with a peak at 100 cm^{-1} seen below $T_{c_2} \sim 9$ K is ascribed to two-magnon (2M) scattering from the Néel ordered state. In contrast, the narrow and weak continuum with a peak at 110 cm^{-1} arises from 2M scattering from the dimerized state with a spin gap $\Delta \sim 73$ K. It appears around 200 K and remains present well below the long-range magnetic ordering temperature while being superimposed on the former broad 2M continuum. To our present knowledge, this is the first observation of the coexistence of dimerization and antiferromagnetic long-range ordering using Raman spectroscopy. Its origin should be attributed to intrinsic chemical disorder and/or geometrical frustration. In addition, pronounced quasielastic scattering arises from fluctuations of the energy density of the spin system. This is accompanied by a softening of phonon modes which mediate exchange paths for temperature below the exchange constant of 44 K. Thus, the studied system can be considered as low-dimensional spin gapped system with substantial spin-phonon coupling and intrinsic disorder. Furthermore, our study indicates that the coherent coexistence of long-range and short-range ordered state appears to be a generic feature of low-dimensional spin-gapped system with nonmagnetic impurities. In addition, in such systems substantial spin-phonon couplings frequently lead to phonon anomalies and a quasielastic response.

Chapter 5

2D HAF $\text{K}_2\text{V}_3\text{O}_8$

The motivation to understand magnetic properties of two-dimensional spin-1/2 Heisenberg antiferromagnets (HAF) has been driven by the discovery of high T_c superconductivity in the cuprates which contain layers of $S=1/2$ Cu^{2+} ions. The undoped cuprates such as La_2CuO_4 show strong antiferromagnetic intraplanar interactions with $J \sim 1500$ K [96]. Despite the low dimensionality and the low spin number collective magnetic excitations can be largely understood within spin wave theory. In particular, the dispersing peaks observed in inelastic neutron scattering measurements can be described adequately in terms of renormalized spin waves [97]. However, Raman and optical spectroscopy exhibits anomalous features in the magnetic spectrum suggesting a significance of quantum fluctuations [98, 99]. The position of a primary peak of two-magnon scattering observed by Raman spectroscopy agrees well with calculations based on spin wave theory. However, there appear severe deviations: a broadened lineshape and an asymmetry about the peak position in B_{1g} , the existence of spectral weight at high energies and even more a second peak at $4J$, the appearance of a nominally forbidden two-magnon signal also in A_{1g} and B_{2g} geometry, and finally the dependence of the Raman intensity on the incoming photon energy [90, 100, 101, 102].

To highlight the observed anomalies in the cuprates let us briefly recapitulate the expected two-magnon scattering in 2D HAF. As discussed in section 3.2, two-magnon scattering originates from the exchange mechanism described by the coupling Hamiltonian $H_R = \sum_{\langle i,j \rangle} (E_i \cdot u_{ij})(E_j \cdot u_{ij})(S_i \cdot S_j)$ where E_i (E_j) is the electric field of the incident (scattered) photons and u_{ij} is the unit vector connecting spin sites i and j . Here note that the summation runs only over the nearest neighboring spin pairs. The lineshape of two-magnon scattering is determined cooperatively by a two-magnon density of states, geometric

factors, and magnon-magnon interactions. The two-magnon density of states corresponds to twice the one-magnon density of states. The geometric factors come from the polarization-dependence of the incident and scattered light. Thus, the selection rule due to a symmetry of the order parameter restricts magnetic Raman scattering only into B_{1g} geometry while the bare spectral weights are largest at the higher cut-off energy of $4J$. Magnon-magnon interactions shift spectral weights to lower energies, leading to the peak energy at $\sim 2.7J$.

The observed anomalies are partially explained by the resonant enhancement of two-magnon intensity as well as magnon-phonon interactions [103, 104, 105]. Especially, the former gives account for the existence of the second peak around $4J$ and resonant behavior by considering the interplay between two-magnon peak and triple resonance in the phonon-magnon vertex function in a diagrammatic approach. In contrast, the latter explains a significant broadening of the magnon spectrum due to the damping of the zone boundary magnons. However, the resonant effect in the cuprates hinders the unambiguous understanding of the nature of magnetic excitations. Thus, the study of other $S=1/2$ 2D HAF with much smaller exchange interactions is promising. $K_2V_3O_8$ $S=1/2$ is the realization of square lattice antiferromagnet with small exchange constant $J \sim 13$ K. Hence, Raman scattering study on this compound is highly desirable in order to shed light on the nature of magnetic excitations and the role of quantum fluctuations in 2D $S=1/2$ HAF.

5.1 Crystal structure and magnetic properties

$K_2V_3O_8$ has the fresnoite (tetragonal) structure with space group $P4bm$ and the lattice parameters $a=8.87$ Å and $c=5.215$ Å [106]. As shown in Fig. 5.1(a), the vanadium layer consists of slabs of corner-sharing VO_5 square pyramids and VO_4 tetrahedra with K ions between the layers. Separation of magnetic ($S=1/2$) V^{4+} - O_5 pyramids by nonmagnetic ($S=0$) V^{5+} - O_4 tetrahedra is the origin of a small exchange constant of $J = 12.8K$. As Fig. 5.1(b) displays, the temperature dependence of magnetization shows very isotropic behavior for temperatures above 8 K, indicating the Heisenberg nature of the interactions. Upon cooling below 4 K the rapid decrease (increase) of magnetization along the c-axis (the basal plane) has been observed. This indicates antiferromagnetic ordering with an easy axis along c and the existence of a small canted moment in the basal plane. Below the Néel temperature the magnetization for fields applied along c shows a spin-flop transition at a magnetic field of 8.5 kOe.

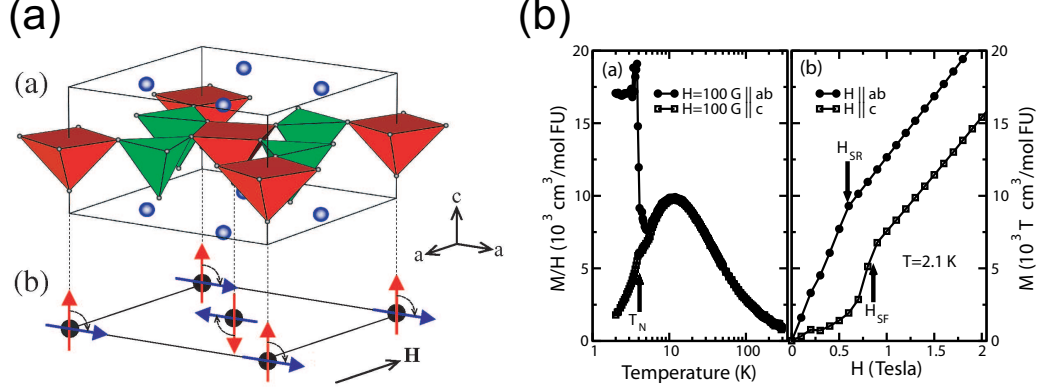


Figure 5.1: (a) The crystal structure of $K_2V_3O_8$ and arrangement of the magnetic moments. The light gray arrows stand for the zero field spin configuration and the dark gray arrows represent the magnetic behavior for a basal plane magnetic field. (b) Magnetization as a function of temperature and external field [107].

In addition, for fields within the basal plane a field-induced phase transition takes place at a magnetic field of 6.5 kOe. Neutron diffraction measurements unveil that this transition corresponds to a spin-reorientation from the c -axis to the basal plane while remaining perpendicular to the external field direction (see Fig. 5.1(a)).

The exotic magnetic behavior is well described by a model consisting of Heisenberg Hamiltonian, Dzyloshinskii-Moriya (DM) interaction and an additional c -axis anisotropy as follows [107]:

$$H = 8JS_1 \cdot S_2 + 8D_z(S_1 \times S_2)_z + 8E_zS_{1z}S_{2z} - g\mu_B H \cdot (S_1 + S_2) \quad (5.1)$$

where the factor of 8 comes from the four nearest neighbors and two sublattices. The exchange constant and values for D_z/J and E_z/J are given by $J = 12.6 \text{ K}$, $D_z/J = 0.04$ and $E_z/J = 1.2 \times 10^{-3}$, respectively. Interlayer couplings and anisotropies lead to an antiferromagnetic ordering at $T_N = 4 \text{ K}$. Using this Hamiltonian the spin-flop transition along the c -axis can be understood in terms of a competition between Zeeman energy and the c -axis anisotropy. For field applied in the basal plane, the Zeeman energy and DM interactions favor an arrangement of spins in the basal plane. This competes with the c -axis

anisotropy. With increasing field strength the spins rotate continuously from the c-axis to the basal plane while remaining normal to the applied field to minimize Zeeman energy. Recently, a chiral cycloid magnetic structure with a modulated weak ferromagnetic moment has been suggested [108]. In this case, the spin reorientation is related to a suppression of the modulated state by a magnetic field.

In addition to exotic low-temperature magnetic behavior, transport and thermodynamic measurements show anomalies around 110 K [109]. Optical spectroscopy spectra display a splitting of a vanadium/apical oxygen stretching mode of the VO_5 square pyramids for temperatures below 110 K [110]. In contrast, the ab-plane phonon modes are not sensitive to lattice distortions while showing anomalous thermal contraction. This indicates the presence of a local and weak distortion of the VO_5 square pyramids which can influence the magnetic and lattice dynamics.

5.2 Experimental setup

Single crystals of $\text{K}_2\text{V}_3\text{O}_8$ were grown in a platinum crucible by cooling appropriate amounts of VO_2 in a molten KVO_3 flux [107]. Samples with typical dimensions $4 \times 4 \times 0.1 \text{ mm}^3$ were used for Raman scattering experiments. The Raman spectra were measured in a continuous helium flow optical cryostat by varying temperature from 1.5 K to room temperature. All spectra were taken in a standard setup described in the previous chapter. The laser power of 8 mW was focused to a $100 \text{ }\mu\text{m}$ diameter spot on the sample.

5.3 Phonon anomalies

Fig. 5.2 displays Raman spectra in aa, ab, $a'a'$ and $a'b'$ polarizations at 5 K and 295 K, respectively. Scattering geometries are specified according to the basal-plane directions of the incident and scattered light polarization vectors, with $a' = a + b$ and $b' = a - b$ rotated by 45° from the a - and b -axis, respectively. At room temperature $\text{K}_2\text{V}_3\text{O}_8$ has a space group $P4bm$ (C_{4v}^2), and two formula units ($Z=2$) possessing 26 atoms. The factor group analysis yields the following total irreducible representations

$$\begin{aligned} \Gamma_{total} = & 12A_1(aa + bb, cc, \mathbf{E} \parallel \mathbf{c}) + 8A_2 \\ & + 6B_1(aa - bb) + 10B_2(ab) \end{aligned}$$

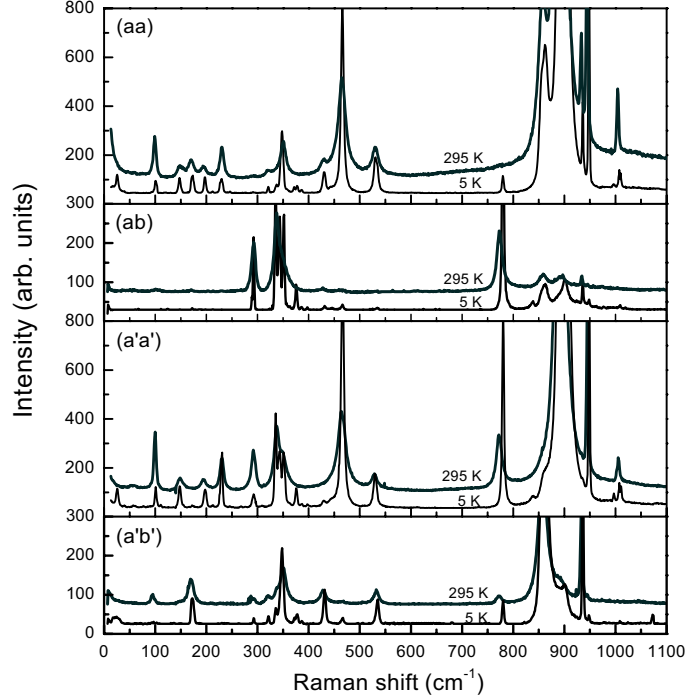


Figure 5.2: Raman spectra of $K_2V_3O_8$ in basal-plane polarizations at 5 K and 295 K, respectively.

$$+21E(ac, bc, \mathbf{E} \parallel \mathbf{a}, \mathbf{E} \parallel \mathbf{b}). \quad (5.2)$$

Subtracting the acoustic ($A_1 + 2E$) modes, 30 infrared and 54 Raman active modes are expected. Note here that the optical modes of A_1 and E symmetries are both infrared and Raman active due to a missing inversion center. We observed 19 Raman active modes at room temperature in the basal-plane polarizations. The missing modes should be ascribed to inter-plane modes and possibly weak basal-plane modes.

With lowering temperature all modes harden slightly and become sharper. Furthermore, additional new modes appear. As Fig. 5.3(a) displays, a phonon mode around 376 cm^{-1} starts to develop for temperature below 60 K. With decreasing temperature its intensity increases linearly without saturation even at very lower temperature (see Fig. 5.4(d)). This indicates that the 376 cm^{-1} -mode results from a local and continuous symmetry breaking. In addition, the largest shift of frequency is observed for the 772 cm^{-1} - and 891 cm^{-1} -

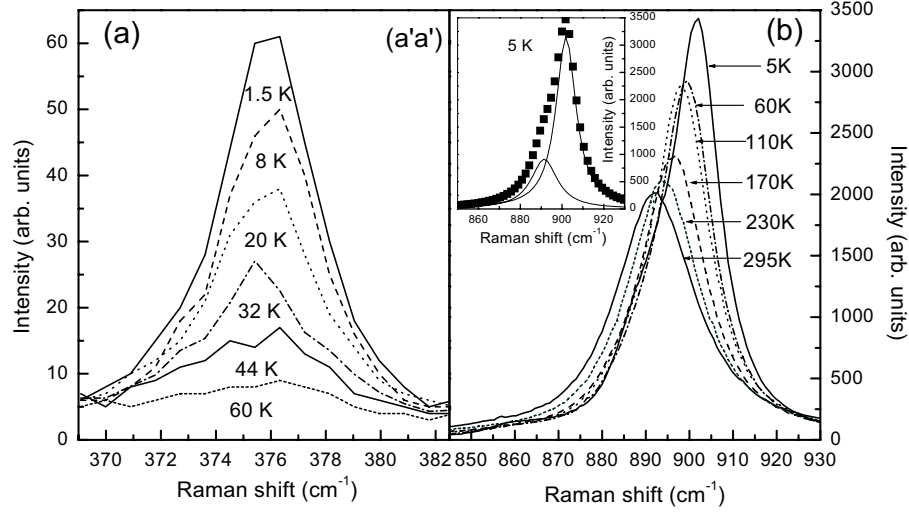


Figure 5.3: (a) An evolution of the 375 cm^{-1} mode which is sensitive to local lattice distortion for temperature below 60 K (b) An evolution of the 891 cm^{-1} mode which is sensitive to local symmetry breaking at 60 K and 110 K.

modes. These higher energy phonon bands are typical for vanadium oxides. The studied system consists of corner-sharing VO_5 square pyramids and VO_4 tetrahedra, with two different V sites and four different O sites [106]. Thus, we assign the higher energy modes to different stretching/bending modes of V-O bonds. Fig. 5.3(b) displays the detailed temperature dependence of the 891 cm^{-1} mode. At room temperature the mode consists of a single Lorentzian line. Upon cooling an additional mode turns up as a shoulder of the high temperature mode as shown in the inset of Fig. 5.3(b). The temperature dependence of the 891 cm^{-1} -mode exhibits a slight kink in slope around 110 K and a weak step by 1 cm^{-1} in the vicinity of 60 K, as displayed in Fig. 5.4(a). Below 110 K the new mode develops. Also the temperature dependence of the 772 cm^{-1} shows a change at the corresponding temperature. In the strong bonding limit the hardening can be interpreted as a shortening of V-O bond length since a reduction of V-O bond length leads to an enhancement of a covalency. Therefore, we conclude that our system undergoes a continuous thermal contraction with a local and weak symmetry breaking around 110 K and 60 K, respectively. Complimentary to our results infrared spectroscopy gives evidence that the transition at 110 K is driven by a local distortion of the VO_5 square pyramids and the local symmetry breaking takes place

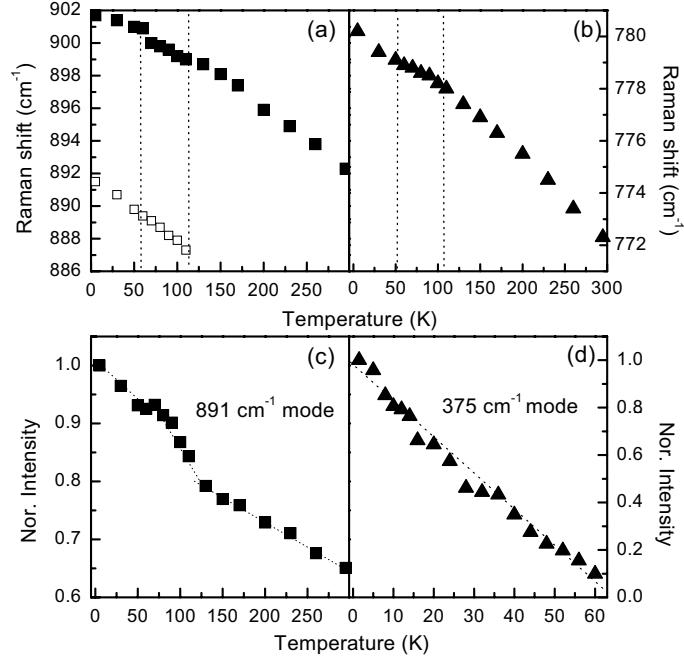


Figure 5.4: The temperature dependence of (a) the 891 cm^{-1} -mode and (b) the 772 cm^{-1} mode. The dashed line marks the local structural transition temperature of 60 K and 110 K. A change in slope has been seen around the corresponding temperatures. The temperature dependence of the integrated intensity of (c) the 891 cm^{-1} -mode and (d) the 375 cm^{-1} mode suggests a change of electronic levels.

predominantly in the basal plane [110].

Moreover, integrated intensity of the 891 cm^{-1} mode is sensitive to the 60 K and 110 K changes as shown in Fig. 5.4(c). In an overall temperature range the integrated intensity increases with three distinct temperature regime: $T \leq 60\text{ K}$, $60\text{ K} \leq T \leq 110\text{ K}$ and $T \geq 110\text{ K}$. Around 110 K and 60 K the integrated intensity exhibits a change of the slope. This is related to change of dipole matrix elements and the band energies caused by ionic displacements [67]. Optical spectroscopy shows similar temperature dependence of an inter-band excitation [110]. This suggests that the temperature dependence of the integrated phonon intensity reflects a change of crystal field energy. In order to unveil the exact nature of the local symmetry breaking neutron diffraction experiments are underway [111].

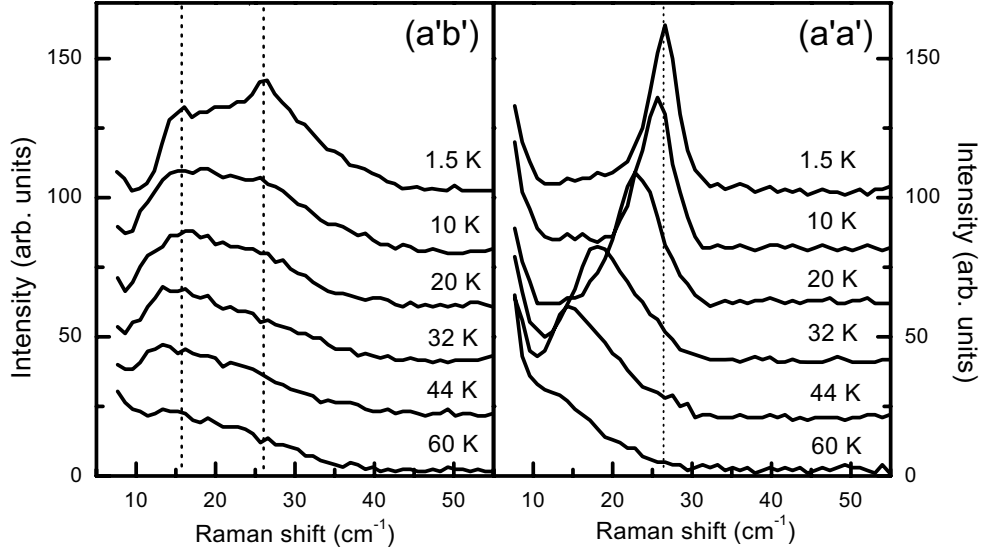


Figure 5.5: Low energy excitations of $\text{K}_2\text{V}_3\text{O}_8$ in $a'b'$ and $a'a'$ polarizations. The dashed line marks the peak position at 1.5 K. With increasing temperature the maxima are successively shifted to lower energies and persist up to $\sim 15T_N$ ($\approx 5J \approx 60\text{K}$).

5.4 Low energy excitations

With decreasing temperature new features develop at low frequencies for aa , $a'a'$ and $a'b'$ polarizations. Fig. 5.5 shows the temperature dependence of the maxima in the $a'a'$ and $a'b'$ polarizations assigned to A_1 and B_1 symmetry, respectively. The maximum in the B_1 symmetry exhibits a broad double peak structure extending from 10 cm^{-1} up to 43 cm^{-1} . The primary peak is centered at 26 cm^{-1} . In contrast, the maximum in the A_1 symmetry is sharp and rather symmetric. The peak position lies at 26 cm^{-1} and the spectral weight extends from 18 cm^{-1} to 32 cm^{-1} . With increasing temperature the peak frequency of the maxima shifts to lower frequency while the linewidth increases for both geometries.

We will assign the low energy broad continuum observed in $a'b'$ polarization to magnetic excitations. This interpretation is motivated by the energy scale of the peak energy and the selection rule. As will be discussed below, it is symmetry-allowed and satisfies the condition of the peak and cut-off energy. In 2D HAF two-magnon scattering can be detected as a double spin-flip process

via the exchange light scattering [30]. A dominant contribution comes from a symmetry-allowed B_1 geometry. Since the broad continuum is observed in a B_1 symmetry, we can extract an information about the unrenormalized AF exchange coupling between vanadium spins by analyzing its spectral weight. The two-magnon band has its peak in the frequency region where two-magnon density of states is largest. In the noninteracting case the density of states of two-magnon spectrum is given by $\rho_2(\omega) = \sum_k \delta(\omega - 2\omega_k)$ where ω_k is a one-magnon dispersion. Thus, the spectrum is dominated by zone boundary magnons [70]. The magnon energy at the zone boundary in 2D HAF is $2JzS$ where J is the exchange integral and z is the number of nearest neighbor spins. As illustrated in Fig. 5.6, in Ising limit magnon-magnon interactions lead to a reduction of the peak energy to $J(2zS - 1)$. This simple picture gives a peak position of $\omega_p = 3J$ with $z = 4$ and $S = 1/2$. With the value of the exchange coupling constant of $J \approx 13K$ [107] and the observed peak position of 26 cm^{-1} one obtains a peak energy of $2.9J$. This value lies between the classical estimate and the full quantum correction $\omega_p \sim 2.7J$ [100]. The magnon energy at the zone boundary can be directly determined from the cut-off frequency of the spectrum which corresponds to the right tail of two-magnon signal. It extends up to 43 cm^{-1} (see the left panel of Fig. 5.5). This value corresponds to $4.7J$. This is slightly larger than the classical cut-off condition of the spectral weight at $2JzS = 4J$. If one takes into account a quantum correction factor $Z_c = 1.158$, the spin wave theory gives a reasonable description to the observed broad continuum. Therefore, we arrive at the conclusion that the low energy excitations in $a'b'$ polarization are of magnetic origin.

We turn to the temperature dependence of the two-magnon frequency. The magnetic scattering can be seen up to $T=60 \text{ K}$ for both symmetries. An evolution of the spectrum reflects the temperature dependence of short-wavelength magnon energies and lifetimes [70, 89]. This is because the two-magnon spectrum is dominated by zone boundary magnons due to a flat magnon dispersion around the zone boundary. Thus, in the conventional antiferromagnets two-magnon scattering persists to several times T_N in the form of short-range magnetic fluctuations in spite of a thermal destruction of the long-range order. But the zone boundary magnon in $\text{K}_2\text{V}_3\text{O}_8$ persists anomalously to higher temperature in the energy scale set by the Néel temperature. It survives up to $15 T_N (= 5J)$. This is related to the fact that in 2D $S=1/2$ quantum spin systems magnetic excitations are scaled by the exchange coupling constant J while the classical Néel ordering is caused by the interplane interaction.

However, in spite of the success in describing the broad continuum within a magnetic origin, there exist anomalies in the line shape and selection rules: the

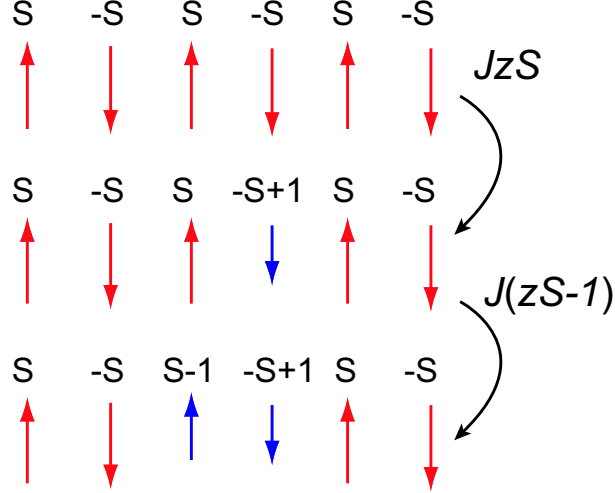


Figure 5.6: The illustration of magnon-magnon interactions in the classical picture.

double peaks in the B_1 symmetry and pronounced sharp peak in the symmetry-forbidden A_1 symmetry. In contrast to the cuprates, anomalous features should not be attributed to resonant scattering and/or magnon-phonon interactions. The former is improbable because a small magnon energy of ~ 5 meV (≈ 60 K) cannot meet the resonant condition $(2\Delta - \omega_i) \sim J$ (≈ 12 K) [105] although the incoming energy of 2.33 eV is comparable to the charge transfer gap of $2\Delta \sim 2.2$ eV [110]. Furthermore, the latter is also unrealistic due to a large difference of magnon energy of ~ 5 meV and typical phonon energy of ~ 100 meV. Actually, ESR measurements see no appreciable change of g-factor despite substantial local lattice distortions [112]. This implies that spin-phonon coupling is not substantial. In addition, the preliminary neutron scattering measurements rule out a splitting of the zone boundary magnon as the origin of the double peak feature due to a missing of a splitting in the vicinity of the zone boundary with similar magnitude [111].

Next, we will try to understand the presence of the A_1 geometry and the double peak features in terms of magnetic origin within a model Hamiltonian given by Eq. 5.1. At first glance, it seems reasonable because the renormalization and damping of the A_1 signal starts around J and persists to 60 K as Fig. 5.7 displays. Within the proposed model the presence of the A_1 signal should be attributed to DM interaction. The intensity of two-magnon scat-

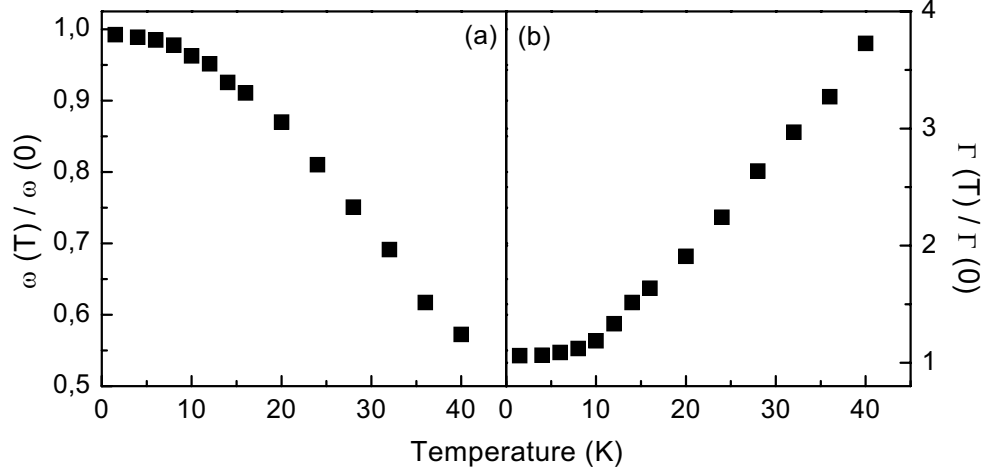


Figure 5.7: Temperature dependence of (a) the normalized frequency of the maximum in the A_1 symmetry as well as (b) the full width at half-maximum with $\omega(0) = 26 \text{ cm}^{-1}$ and $\Gamma(0) = 3.4 \text{ cm}^{-1}$.

tering corresponds to $I_2 \sim |M_\nu(\omega)|^2 \rho_2(\omega)$ where $M_\nu(\omega)$ is scattering matrix element and ν is the symmetry. Roughly, the ratio of integrated intensity is given by $I_{A_1}/I_{B_1} \sim D_z^2/J^2$. With $D_z/J = 0.04$ [107] the estimated value is negligible compared to the experimental value of $I_{A_1}/I_{B_1} \sim 0.4$. Furthermore, the width of spectral weight between the A_1 and B_1 geometries is quite different. If both are of the same magnetic origin, spectral weight should remain unchanged. It implies that DM interaction cannot account for the existence of the A_1 spectrum. Rather, another scattering mechanism is responsible for its presence. In the following we will discuss possible origins.

Firstly, we will interpret the low energy excitation observed in the A_1 symmetry in terms of a soft mode of structural origin. The studied system exhibits a local structural phase transition around 60 K and 110 K, respectively. In second-order phase transitions the crystal symmetry of the new phase is a subgroup of the old phase. Thus, below the critical temperature there will always be a Raman active A_1 component of the soft mode irrespective of the symmetry of the soft mode in the higher symmetry phase [113]. Therefore, the sharp peak observed below 60 K in the A_1 symmetry may be ascribed to a soft mode. However, the energy of the assigned soft mode is too small even if one assumes that the soft mode consists of in-phase motion of all atoms in

the unit cell, leading to the large effective mass. Therefore, we rule out this possibility.

Secondly, we will consider an electronic soft mode as a possible explanation. The ground state of V^{4+} ions in distorted pyramidal oxygen coordination is given by doubly degenerate d_{xz} and d_{yz} orbitals.¹ The local symmetry breaking can lift the degenerated orbitals as evidenced by a splitting of a doubly-degenerated E mode [110]. In this case, a continuous lattice distortion will lead to the temperature dependence of electronic levels between d_{xz} and d_{yz} orbitals. Raman spectroscopy can probe an electronic transition between the two electronic levels. In this scenario one can easily understand the sharpness of the peak shape. Probably, the double peak of the B_1 symmetry can be interpreted in terms of a mixing of magnetic excitations and electronic excitations.

Finally, we will take into account orbital excitations. In analogy to spin excitations, the aforementioned electronic soft mode corresponds to an orbital flip process. In contrast, orbital excitations are multipolar charge excitations which are possible at low energies due to a local charge neutrality. This assignment is motivated by the indication of the presence of spin-orbital wave by preliminary inelastic neutron scattering measurements [111]. To verify this possibility, measurements along interplane polarizations with thicker sample are planned in the near future. Preliminary theoretical calculations predict the presence of orbital waves in interplane polarizations, depending on the ground state configuration [115].

5.5 Conclusion

Our study of $K_2V_3O_8$ has confirmed the presence of a local symmetry breaking at 60 K and 110 K which is seen as the appearance of new phonon modes. More significantly, the small exchange constant of $J = 12.8K$ enables us to explore magnetic excitations over temperature comparable J . Two-magnon spectra observed in (a'b') polarization can be reasonably understood within the spin wave theory. In particular, zone boundary magnons persist up to $\sim 5J$ ($15T_N$). This observation suggests that in the $S=1/2$ 2D HAF system an appropriate energy scale for the magnetic excitations is the exchange constant rather than Néel temperature. In spite of some success in understanding low energy excitations in terms of magnetic excitations, there are some anomalies in the lineshape and selection rule. We have suggested an electronic soft mode and

¹This ground state is estimated by the simple consideration of the distance of V^{4+} ions from the basal plane in the vanadium pyramid [114].

orbital wave as possible origin for a sharp peak observed in (a'a') polarization. In order to reach a decisive conclusion interplane-polarization measurements are indispensable which surely rely on thicker samples.

Chapter 6

The ACuCl_3 ($\text{A}=\text{Tl}, \text{K}$) Family of Compounds

In this chapter we will present inelastic light scattering measurements of the copper halides TlCuCl_3 and KCuCl_3 . Both systems have a singlet ground state with a finite energy gap in the spin excitation spectrum. In particular, three-dimensional interdimer couplings result in the small size of the spin gap as well as the large-bandwidth of triplet excitations. This together with isotropic interactions leads to the observation of Bose-Einstein condensation of excited triplets under an external field [116]. Thus, this compound provides a chance to explore spin dynamics in the large-bandwidth limit where enhanced kinetic energy of triplets and thermally activated triplets play an important role.

6.1 Crystal and electronic band structure

The copper halides have a monoclinic structure with the space group $P2_1/c$ and four formula units per unit cell [117]. The lattice parameters for TlCuCl_3 are given by $a = 3.982\text{\AA}$, $b = 14.144\text{\AA}$, $c = 8.890\text{\AA}$ and $\beta = 96.32^\circ$, while those for KCuCl_3 are $a = 4.029\text{\AA}$, $b = 13.785\text{\AA}$, $c = 8.736\text{\AA}$ and $\beta = 97.20^\circ$. Accordingly, the TlCuCl_3 lattice is a little bit compressed along the a axis and enlarged in the bc plane compared to the KCuCl_3 lattice. The degree of monoclinicity is also somewhat different from each other. In both systems edge-sharing CuCl_6 octahedra form a $S=1/2$ double chain system running along the a axis. The double chains are separated from each other by Tl^+/K^+ ions. The CuCl_6 octahedra are highly distorted due to the strong Jahn-Teller Cu^{2+} ion with large elongation along one direction. Thus, nearly planar Cu_2Cl_6 spin-dimers are realized as shown in Fig. 6.1(a).

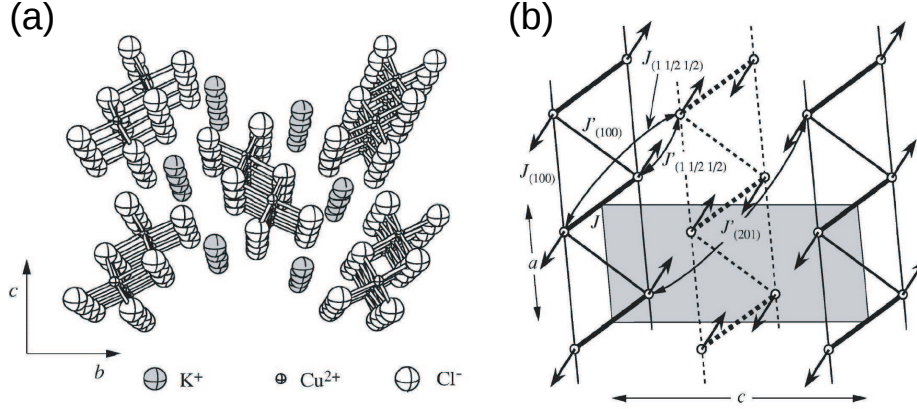


Figure 6.1: (a) Crystal structure of ACuCl_3 , with $\text{A}=\text{Tl}$ and K viewed along the a axis [128]. (b) Intradimer and interdimer exchange interactions with spin structure in the ordered phase. The shaded area is the chemical unit cell in the a - c plane [128].

In these compounds the band structures are characterized by a complex of four narrow bands close to the Fermi level formed by $\text{Cu } d_{x^2-y^2}$ orbitals admixed with $\text{Cl } p$ -states [118]. The bands are dispersive along all the symmetry directions suggesting the compounds to be three-dimensional coupled spin-dimer system. TlCuCl_3 has a somewhat larger total-bandwidth of the four-band complex than KCuCl_3 . Furthermore, the former bands are more dispersive than the latter ones. This indicates that TlCuCl_3 has the stronger intradimer and interdimer interactions than KCuCl_3 . The main origin of the differences in the strength of the intra- and interdimer couplings between two compounds does not lie in the changes of the structural parameters but in the role of the Tl^+ ion in enhancing the hopping matrix elements between the Cu^{2+} ions. Larger hybridization of Tl with the $\text{Cu } d_{x^2-y^2}$ orbitals in TlCuCl_3 originates from the proximity of the $\text{Cu } d_{x^2-y^2}$ and the $\text{Tl } 6s, 6p$ energy states and the extended nature of these orbitals in comparison to the $\text{K } 4s$ orbital in KCuCl_3 .

The Cu-Cl-Cu bond angle for both systems amounts to $\sim 96^\circ$. Note that this angle is slightly larger than 94° at which the leading isotropic exchange constant changes its sign from ferromagnetic to antiferromagnetic in the edge-

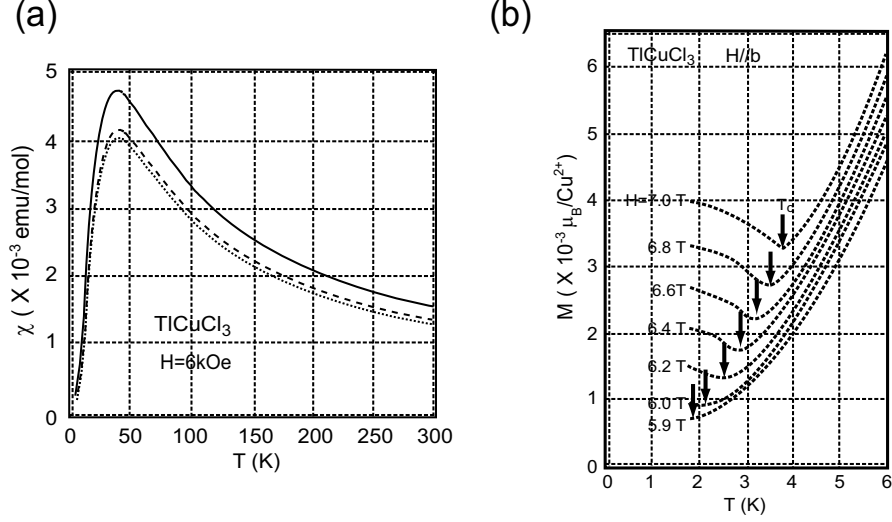


Figure 6.2: (a) The temperature dependence of the magnetic susceptibilities of TlCuCl₃ measured at $H=6$ kOe [124]. (b) The low-temperature magnetizations of TlCuCl₃ measured at various external fields for $H \parallel b$ [116].

shared cuprates [119]. Thus, the intradimer exchange coupling is expected to be weakly antiferromagnetic. In addition, the dominant interdimer couplings are given by the following interdimer hopping parameters $t'(201)$ and $t(1\ 1/2\ 1/2)$ for KCuCl₃ and the additional hopping of $t(1\ -1/2\ 1/2)$ for TlCuCl₃ (see Fig. 6.1(b)). Here $t(\mathbf{l}\ \mathbf{m}\ \mathbf{n})$ ($t'(\mathbf{l}\ \mathbf{m}\ \mathbf{n})$) denotes the hopping parameters between two equivalent (nonequivalent) sites in dimers separated by a lattice vector $(\mathbf{l}\ \mathbf{m}\ \mathbf{n})$.

6.2 Magnetic properties

The magnetic structure of TlCuCl₃ (KCuCl₃) is characterized as a strongly (weakly) and three dimensionally coupled spin-dimer system by inelastic neutron scattering (INS) measurements [120, 121, 122, 123]. As Fig. 6.2(a) displays, the magnetic susceptibility in TlCuCl₃ (KCuCl₃) shows a maximum at $T^{max} = 38$ K (30 K) and a drastic drop toward lower temperature [124]. At lower temperatures this dependence is well described by the formula $\chi(T) \approx (1/\sqrt{T}) \cdot \exp(-\Delta/k_B T)$. In TlCuCl₃ (KCuCl₃) a singlet ground state with a spin gap of $\Delta/k_B \sim 7.5$ K (31 K) arises from antiferromagnetic interac-

tion of $J \approx 61$ K (48 K) within the planar dimer Cu_2Cl_6 in the double chain [124, 125, 126, 127]. In particular, the double chain system in KCuCl_3 is very close to an alternating chain system.

The small size of the spin gap makes these compounds suitable for studying a field-induced quantum phase transition which separates a gapped singlet ground state from a field-induced magnetic ordered state. As seen in Fig. 6.2(b), this has been observed as well-defined cusp-like minima in the magnetization at $H_c = \Delta/g\mu_B = 5.7$ T and 23 T for TlCuCl_3 and KCuCl_3 [125, 128]. This transition is independent of the orientation of the magnetic field regarding the crystallographic axes. The convex magnetization and the phase boundary of the transition field were explained by mapping the triplets states to a dilute Bose gas within a Hartree-Fock approximation [116, 129]. The transition has thus been characterized as a Bose-Einstein condensation (BEC) of dilute magnons. An INS study in a magnetic field shows a linear Zeeman energy splitting of triplet states, suggesting that a softening of the lowest magnon mode drives the transition [130].

However, in spite of a success of the strongly coupled dimer model in explaining magnetic excitations, INS shows several anomalies [120]: with increasing temperature a thermally activated broadening of triplet excitations and a decrease of its spectral weight are observed. Furthermore, the spectrum is contaminated by a phonon which lies in the same energy range as the magnetic states. These effects suggest a significance of thermally-induced triplet-triplet interactions and anharmonic magnetoelastic interactions in addressing the collective dynamic properties. Raman spectroscopy can provide valuable informations about the significance of spin-phonon coupling and its influence on magnetic excitations.

6.3 Experimental setup

Single crystals used in our investigation were grown by the Bridgeman method and are cleaved along the $(0,1,0)$ and $(1,0,\bar{2})$ planes [125]. Our measurements were mainly done along the a -axis which is parallel to the double chains. Samples with typical dimension $3 \times 4 \times 0.5$ mm³ were glued on a sample holder. Raman spectra were measured with 2 mW (3 mW) of the excitation line $\lambda = 514.5$ nm of an Ar^+ laser for TlCuCl_3 (KCuCl_3). Spectra were taken in a standard experimental setup described in the section 4.2.

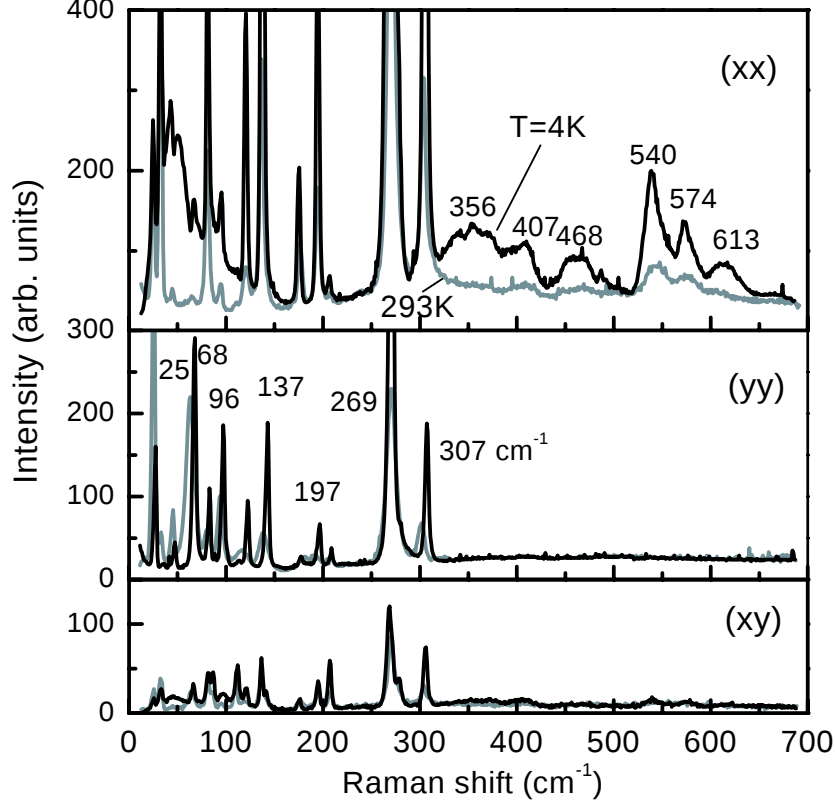


Figure 6.3: Raman scattering spectra of TlCuCl_3 in three different polarizations at $T=4$ K and $T=293$ K, respectively.

6.4 Phononic Raman scattering of TlCuCl_3

Raman spectra of TlCuCl_3 are displayed in Fig. 6.3 at high and low temperatures in aa , ab and bb polarizations, respectively. At room temperature we are able to detect 16 modes as first-order scattering below 310 cm^{-1} . Subtracting acoustic modes and infrared active modes, the factor group analysis yields the following Raman-active modes for the space group $P2_1/c$ (C_{2h}^5): $\Gamma = 15A_g + 15B_g$. The discrepancy between the number of expected and observed modes is due to a probable weakness in intensity of some phonon modes. With decreasing temperature nearly all modes become more intense while no noticeable shift of phonon frequency can be detected in xx polarization. Additional broad maxima around 46 cm^{-1} and for energies higher

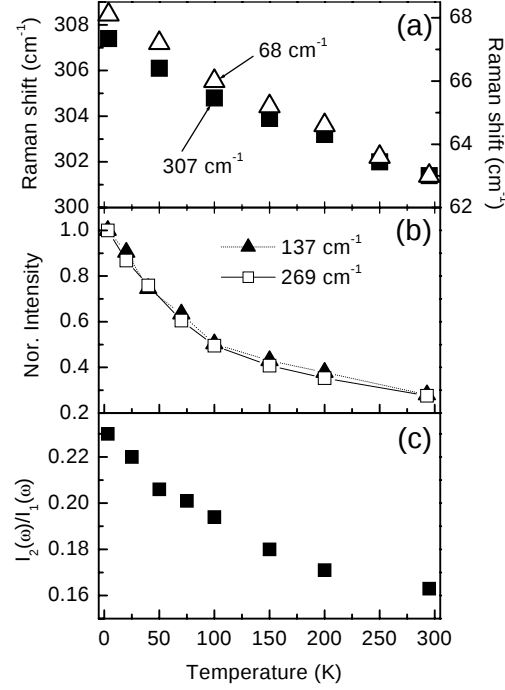


Figure 6.4: a) An evolution of the peak position at 68 cm^{-1} and 307 cm^{-1} in the (yy) scattering geometry. b) Analysis of the (xx) scattering intensity as function of temperature at 137 cm^{-1} and 269 cm^{-1} . The other modes (not shown here) exhibit a similar behavior. The intensity is normalized at 3.2 K. c) The ratio of the second- to the first-order scattering, I_2/I_1 , as a function of temperature.

than 310 cm^{-1} become more pronounced. In contrast, the modes in bb polarization show anomalies in both frequency and intensity. In Fig. 6.4(a) the frequency of the 68-cm^{-1} and 307-cm^{-1} modes in the bb polarization is plotted as a function of temperature. These modes exhibit a hardening with decreasing temperature. An appreciable hardening of $5\text{-}6 \text{ cm}^{-1}$ can be interpreted as a shortening of ionic distances in the strong coupling limit. Fig. 6.4(b) displays a strong increase of integrated intensity of the 137-cm^{-1} and 269-cm^{-1} modes upon cooling. The integrated phonon intensity consists of two main contributions [67]. One of them are the dipole matrix elements arising from a phonon-induced polarization of the wave function. The dipole momentum matrix varies exponentially with the interatomic distance. The other contribu-

tion is due to changes in the band energies caused by ionic displacements. In principle, small changes of ionic distance can lead to enhancements of phonon intensity. But the observed increase of phonon intensity is unusually strong.

We now turn to additional features observed at high frequencies. Noticeably, these modes are observed only in xx polarization. We assign them to second-order scattering due to the following reasons. Firstly, the magnetic energy scale with the strongest interaction energy of $J \approx 44 \text{ cm}^{-1}$ is too small to account for these scatterings. Secondly, these higher energy modes can be reproduced by the combination of low-energy modes. The maxima at 574 cm^{-1} can be explained by the sum of the one-phonon energy of 269 cm^{-1} and 307 cm^{-1} corresponding to bending and stretching modes of Cu-Cl. The 540-cm^{-1} and 613-cm^{-1} maxima correspond to their overtones. In a similar way, a phonon band around 356 cm^{-1} , 407 cm^{-1} and 468 cm^{-1} is ascribed to the combination of 197 cm^{-1} and 175 cm^{-1} , the overtone of 197 cm^{-1} and the combination of 197 cm^{-1} and 269 cm^{-1} , respectively. The ratio of the first- to second-order integrated phonon intensity provides information about a possible mechanism for two-phonon scatterings. The first-order intensity is $I_1 = \int d\omega S_1(\omega)$, integrated across the strongest first-order bands in the region between $250\text{-}320 \text{ cm}^{-1}$. The second-order integrated intensity of $I_2 = \int d\omega S_2(\omega)$ is determined across the corresponding double-frequency region. As displayed in Fig. 6.4(c) the Raman intensity ratio I_2/I_1 increases upon cooling. Usually, second-order scattering has its origin in an anharmonic and(or) resonant mechanism. *In an adiabatic limit* the former has the same resonance dependence of first- and second-order scattering, that is, I_2/I_1 is constant. In the latter case the first-order intensity is $I_1 \sim (\omega - \omega_{fi})^{-4}$ while second-order one is $I_2 \sim (\omega - \omega_{fi})^{-6}$ where ω_{fi} is the interband energy. As a result, one obtains $I_2/I_1 \sim (\omega - \omega_{fi})^{-2}$. Therefore, the observed temperature dependence of I_2/I_1 seems to originate from resonant scattering [67]. A hardening of optical phonon frequencies by a few cm^{-1} and two-phonon scattering have been frequently reported in quantum spin system of $3d$ transition metal oxides due to anharmonic lattice vibrations. However, in TlCuCl_3 the observed hardening is larger than what is usually expected from thermal contraction. Furthermore, as our analysis shows, the main mechanism of two-phonon scattering is not consistent with anharmonicity. Moreover, anharmonic lattice vibrations do not lead to a drastic change of the integrated phonon intensity. This indicates the presence of other mechanism. As will be discussed below, this is due to a strong coupling of phonons to spin degrees of freedom.

6.5 Magnetic Raman scattering in TlCuCl_3

We will focus now on the distinctive features found at low energies in (xx) scattering configuration. As Fig. 6.5(a) displays, there appears a broad spectrum extending from 11 cm^{-1} to 130 cm^{-1} with lowering temperature. The onset of the broad spectrum lies in the range of twice the spin gap of $2\Delta \approx 11 \text{ cm}^{-1}$. The higher cutoff energy of spectral weight is close to two times the maximum of the one magnon energy which amounts to roughly 115 cm^{-1} from INS data [120, 129]. Furthermore, the broad spectrum is observed below $J \approx 61 \text{ K} = 42 \text{ cm}^{-1}$. This motivates us to assign the observed broad spectrum to a two-magnon continuum. The two-magnon continuum corresponds to a double spin-flip process of two singlets into a higher singlet state consisting of two bound triplets. The microscopic origin of the magnon continuum is well understood within the exchange mechanism developed by Fleury and Loudon in the nonresonating limit [30]. This mechanism has been extended to a one-dimensional system with a singlet ground state [75, 131]. In TlCuCl_3 there is no hint for the presence of (i) bound states which could be formed below the energy of the two-triplet continuum due to spin frustration and/or spin-phonon coupling and (ii) quasielastic scattering which arises from fluctuations of the energy density of the spin system. This observation can be ascribed to appreciable three-dimensional interdimer interactions leading to an enhanced kinetic energy of the triplets. The increased phase volume prevents the formation of bound states and fluctuations of the magnetic energy via a coupling to lattice degrees of freedom. The observed two-magnon continuum in TlCuCl_3 is pronounced in (xx) scattering geometry, i.e. the incident and scattered electric fields are parallel to the x -axis. In contrast, there is no magnetic scattering along the y -axis while a weak signal can be seen in the (xy) configuration. Usually, magnetic light scattering is observed along the polarization parallel to the dominant exchange path between dimers. This is consistent with strong interdimer interactions along the x -direction. The existence of a magnetic scattering with weak intensity along the cross polarization should be attributed to appreciable 3D interdimer interactions itself. The effect of a strong coupling of dimers is also reflected in a broadened spectrum whose width is comparable to the intradimer coupling constant. These effects are drastically different to observations in the Shastry-Sutherland system $\text{SrCu}_2(\text{BO}_3)_2$. In this system the orthogonal coupling of spin dimers leads to a frustration of interdimer couplings and dispersionless elementary triplets. In this case, Raman scattering shows well-defined multiparticle bound states as sharp peaks and quasielastic scattering at intermediate temperatures [95]. In TlCuCl_3 the broad spectrum

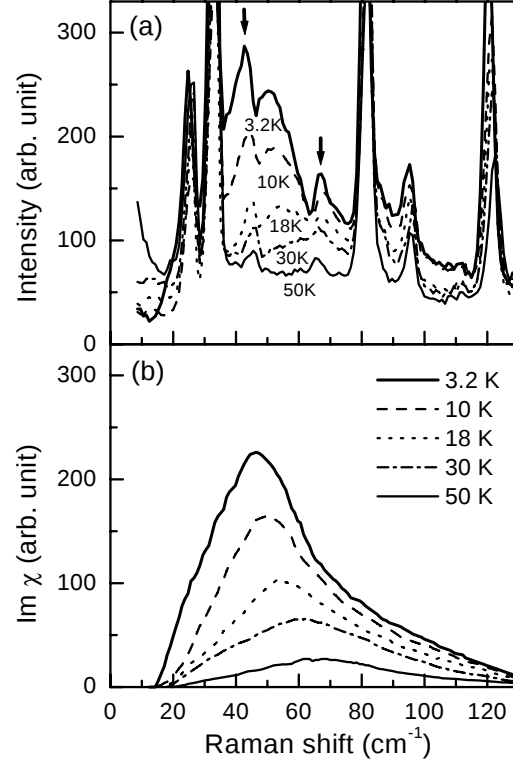


Figure 6.5: a) Two-magnon Raman spectra in (xx) polarization at different temperatures. The arrows indicate phonons with Fano lineshape. b) For clarity the spectra are presented after subtracting the phonon contributions, background and correcting by the Bose-Einstein factor.

is related to an overlap of Cu^{2+} orbitals via Tl^+ ions between dimers in a neighboring double chains. This coupling is not frustrated and thus delocalizes magnons.

Noticeably enough, a similar broad and asymmetric two-magnon continuum has been reported in the coupled tetrahedral spin system $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ [132]. This system has also strong high-dimensional inter-tetrahedra interactions. However, the main difference can be found in the evolution of spectral weights. In $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$, upon cooling, the integrated intensity of the continuum increases without noticeable changes of the spin gap and lineshape. This is typical for usual dimerized system [75]. In contrast, TlCuCl_3 shows an unusual behavior of the spectral shape with decreasing temperature: spectral

weights and peak position shift to lower energy while the lineshape becomes more asymmetric. Moreover, the spin gap is reduced. To illustrate clearly the evolution of the spectra the phonon modes on the broad maxima have been subtracted after correcting by the Bose-Einstein thermal factor. The results are displayed in Fig. 6.5(b). The depletion of the spectral weights at the lower boundary and a shift of the peak energy to higher frequency can be easily seen upon heating. This indicates a change of magnetic exchange interactions as a function of increasing temperature. Such a behavior is also contrasted to that of conventional antiferromagnetic systems: spectral weights and peak position of two-magnon scattering shift to lower energy due to a damping of zone boundary magnons upon heating [70].

Before presenting a possible explanation we will discuss the line shape of quasi-one dimensional systems including higher dimensional interaction. This is justified because the studied system has a preferential interdimer interaction along the x -axis which leads to the pronounced continuum. In a one-dimensional magnetic system the bare spectrum has a symmetric form with van-Hove singularities of one-over-square-root type at the lower and upper boundaries. Numerical and analytical analysis suggests that the two-magnon Raman spectral density results from the combination of two triplets with wave vectors q and $-q$, respectively, which lie close to the Brillouin zone center [133, 134]. Thus, the resulting spectrum has an asymmetric shape with a large spectral weight at the lower boundary. This is because a strong resonance of two neighboring magnons is caused by the attraction between magnons near the lower edge of the continuum which is nearly dispersionless [134]. That is, the resonance reflects the singularity in the bare density of state. As illustrated in Ref. [133], if turning on higher dimensional interactions, localized triplets can hop. This, in turn, smears out the van-Hove singularity while the elementary triplets become more dispersive. Thus, upon heating the spectrum broadens and becomes symmetric due to a damping of the resonance.

In this light, our spectra indicate a crossover of dimensionality of the magnetic interaction as a function of temperature. At higher temperature, a symmetric spectral shape suggests that magnetic interactions are close to a 3D valence bond state in which spin correlations are short-range and isotropic in all spatial directions [130]. Upon cooling spin correlations become more anisotropic with a preferential direction as evidenced by a rather asymmetric form with large spectral weights at the lower cut-off energy region. This is accompanied by a slight decrease of the spin gap and a large shift of the peak energy. This is ascribed to a renormalization of the magnetic energy due to spin-phonon coupling. Asymmetric Fano lines on top of and at the

right tail of the continuum (indicated by the arrow in Fig. 6.5(a)) support this [135]. They appear as an inversion of each other. Fano lines originate from the coupling between phonon and two-magnon continuum rather than the spin system to *itself*. The relative position of the Fano antiresonance is determined by the matrix element of interaction between the magnetic continuum and the phonon. Thus, it can lie on either the left or the right side of the peak. Interestingly, in our case, antiresonances are observed on both sides. Most probably, the lineshape of Fano antiresonance is related to the curvature of the phonon dispersion [136]. Phonons with different dispersion curvature will modulate the spin gap as well as the exchange constant via spin-phonon coupling quite differently. This may explain the "inversion" of the antiresonance.

Even though one cannot extract direct information about the strength of spin-phonon coupling from the asymmetric lineshapes themselves, we have good reason to assume strong spin-phonon coupling. Firstly, TlCuCl_3 has a monoclinic structure. In lattice structures with low symmetry ionic vibrations do not compensate each other in modulating the magnetic exchange. The combined effect of low lattice symmetry with low spin dimensionality will result in a very strong spin-phonon coupling. Secondly, the frequencies of Fano lines at 43 cm^{-1} and 67 cm^{-1} are comparable to the superexchange coupling constant $J \approx 44 \text{ cm}^{-1}$. The small exchange constant leads to a large density of states in the phonon energy region. This can strongly modulate the exchange constant. Our system is drastically different from, e.g., high T_C superconductors, which show weaker spin-phonon coupling. This is because the large exchange constant and higher crystal symmetry lead to a smaller density of magnon states close to the relevant phonon frequencies of Cu-O modes and the respective compensation of the phonon-modulated exchange constant.

Furthermore, the matching of low phonon energy to the magnetic energy scales in TlCuCl_3 implies that the corresponding phonons are not frozen-in with respect to the spins. However, phonons are still well-defined quasiparticles because lattice vibrations are frozen-in with respect to electronic degrees of freedom with energy of several eV. Neutron scattering measurements also exhibit a magnetic spectrum contaminated by phonons suggesting the presence of magnetoelastic interactions [120]. Recent NMR [137] and ultrasonic attenuation measurements [138] also evidence strong spin-phonon coupling leading to a first-order contribution to the BEC transition.

In a *nonadiabatic* regime with respect to spin degrees of freedom the magnetic excitations are accompanied by local lattice distortions. Moreover, with a dynamic spin-phonon coupling, $g(T)$, the lattice requires a multiphonon picture due to a nonlinear local distortion of the lattice. This provides a con-

sistent explanation for the strong temperature dependence of the one-phonon integrated intensity and the pronounced two-phonon features only along the xx -polarization. In turn, a coupling of the magnetic excitations to dynamic phonons results in a change of the dimerization, $\delta(g(T))$, as well as the spin gap, $\Delta(g(T))$, depending on the strength of the spin-phonon coupling [139]. Our spectra exhibit a decrease of the spin gap and a strengthening of the dimerization with decreasing temperature. This is because an increase of $g(T)$ leads to a strong renormalization of $\Delta(g(T))$ and an enhancement of $\delta(g(T))$. All these effects are reminiscent of the spin-Peierls system CuGeO_3 in which dynamic phonons play an important role in the spin-Peierls transition. In CuGeO_3 two weakly dispersive optical phonons with frequencies $\omega \approx J$ and $\approx 2J$ are involved in the spin-Peierls transition [140]. A dynamic phonon coupling to 1D spin dynamics turns out to renormalize physical properties at *zero* temperature and to be necessary for a consistent description of the magnitude of the triplet gap and the strength of the dimerization. In TlCuCl_3 the increased phase volume due to strong interdimer interaction prevents additional spin-lattice instabilities. Instead, dynamic spin-phonon interactions induce a moderate renormalization of the spin gap and the peak energy at *finite* temperatures accompanying tiny lattice distortions (see Fig. 6.4(a)). In this respect, also the missing of anomalies in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ can be understood in terms of the absence of appreciable spin-phonon coupling [132].

In addition to the dynamic spin-phonon mechanism the influence of thermally activated triplets on the magnetic spectrum should also be taken into account. In contrast to narrow-bandwidth spin gap systems the spin gap of $\Delta \approx 7.5$ K in TlCuCl_3 is smaller than the bandwidth of the triplet branch which is comparable to the intradimer coupling constant $J \approx 61$ K [120, 129]. Firstly, with increasing temperature the resonant scattering of triplets near the Brillouin zone center will be damped because of a shortening of lifetime $\Gamma \approx \exp(-\Delta/k_B T)$. Secondly, interactions between thermally activated triplets lead to a weakening of the interdimer coupling as a function of temperature. This results in a weakening of the low dimensional character. These effects will contribute to a shift of spectral weight to higher energies with raising temperature.

6.6 Phononic Raman scattering of KCuCl_3

In the following we will address the weakly coupled spin dimer system KCuCl_3 . Raman spectra are displayed in Fig. 6.6 at low and room temperatures in

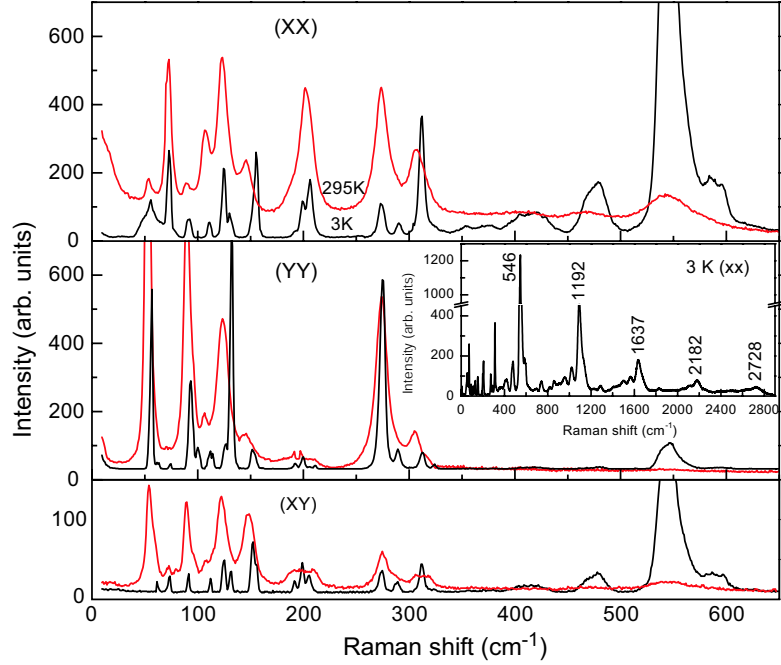


Figure 6.6: Raman spectra of KCuCl_3 in three different polarizations and at $T=3$ K and $T=295$ K, respectively. The inset displays a multiphonon scattering up to the fifth order in the (xx) polarization at 3 K.

xx , yy and xy polarizations, respectively. At room temperature we are able to detect 14 modes as first-order scattering. The observed modes are less than the expected 30 Raman-active modes of $\Gamma = 15A_g + 15B_g$ from the factor group analysis. The missing modes are attributed to a probable weakness of some phonon modes. With decreasing temperature nearly all modes become sharp and undergo a substantial hardening. Furthermore, the intensity of phonon modes with energies lower than 330 cm^{-1} becomes suppressed while that of phonon modes with energies higher than 330 cm^{-1} is strongly enhanced. In particular, we observe higher order scattering up to fifth order as displayed in the inset of Fig. 6.6. Here note that the higher-order signal appears as simple multiples of frequency between 330 - 600 cm^{-1} . Usually, in transition metal oxides anharmonic lattice potential shifts the peak energy of higher-order phonon mode to lower energy. Noticeably, this behavior is expected in molecules with local vibrations. Therefore, local ionic displacements are responsible for this. TiCuCl_3 shows also pronounced two-phonon scattering

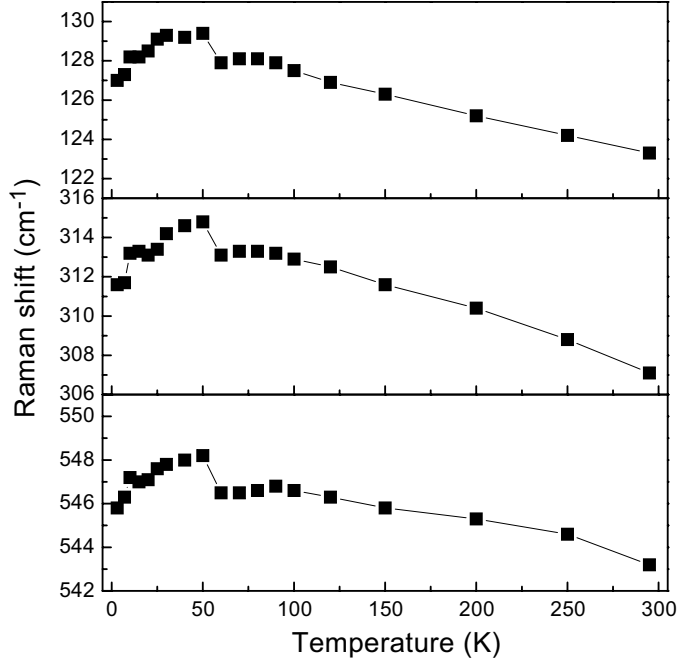


Figure 6.7: An evolution of the peak position at 123-cm^{-1} , 307-cm^{-1} and 543-cm^{-1} modes. Noticeably, complicated phonon anomalies are seen below 90 K. For the detailed description see the text.

(see the section 6.4). This might be related to dynamic spin-phonon couplings and will influence on properties of Bose-Einstein condensation of triplets.

In Fig. 6.7 the frequency of the 123-cm^{-1} , 307-cm^{-1} and 543-cm^{-1} modes is plotted as a function of temperature. All these modes exhibit commonly an anomalous behavior. Upon cooling from room temperature up to 90 K the phonon modes undergo an appreciable hardening by $5\text{-}6\text{ cm}^{-1}$ and then become more or less flat between 60 K and 90 K. Upon further cooling a weak jump by $1\text{-}2\text{ cm}^{-1}$ is observed around 55 K. After that, the phonon modes soften by $3\text{-}4\text{ cm}^{-1}$ while showing a weak drop around 10 K. Such an anomalous behavior cannot be understood within a thermal contraction caused by anharmonic interactions of the lattice. Rather, it should be attributed to appreciable ionic displacements caused by a coupling of phonons to spin degrees of freedom. The observed strong change of integrated phonon intensity as well as the broadening of the phonon mode (see Fig. 6.6) supports the strong coupling of phonon to spin. Noticeably enough, similar phonon anomalies have been observed in

TlCuCl₃. Compared to TlCuCl₃, KCuCl₃ displays a more drastic shift of phonon frequency. This is related to the fact that spin dynamics in KCuCl₃ has a more pronounced low-dimensionality which enhances lattice instabilities via magnetoelastic interactions.

6.7 Magnetic Raman scattering in KCuCl₃

We will now focus on the feature found at low energies in (xx) scattering configuration. As Fig. 6.8 displays, a weak and broad maximum extending from 25 cm⁻¹ to 50 cm⁻¹ starts to appear for temperatures below 150 K. With decreasing temperature down to 30 K the lower-energy maximum evolves into a more well-defined spectrum while its intensity becomes pronounced. Upon cooling further the signal becomes weak and is finally unobservable at about 3 K. At the same time, another broad maximum extending from 50 cm⁻¹ to 83 cm⁻¹ starts to develop below 100 K. This spectrum gains intensity and shifts to lower energy upon cooling. Furthermore, the lineshape becomes more asymmetric. It should be noted that the maxima are observed only in (xx) scattering geometry, i.e. the incident and scattered electric fields are parallel to the x -axis. The interdimer interaction along this direction is largest due to a strong overlap of Cu orbitals between dimers in neighboring double chains. Fig. 6.9 displays the temperature dependence of the onset energy and peak intensity of the maxima. Upon cooling the onset of the higher-energy maximum decreases from 51 cm⁻¹ ($\approx$ 73 K) to 39 cm⁻¹ ($\approx$ 56 K) with a change in slope around 30 K. Its corresponding intensity increases rapidly without any saturation. The onset of the lower-energy maximum amounts to roughly half of the higher-energy continuum. Its onset energy decreases in a similar manner as the higher-energy maximum does. However, the peak intensity shows an anomalous behavior; upon heating it increases rapidly and then shows a maximum around the spin gap $\Delta = 31$ K and finally decreases in the same manner as the higher-energy continuum. In the following we will discuss an origin of the maxima.

Firstly, we will concentrate on the higher-energy maximum. At 3 K the spectrum extends from 39 cm⁻¹ to 82 cm⁻¹. The onset corresponds to nearly twice the spin gap of $2\Delta \approx 42$ cm⁻¹. The higher cutoff energy of spectral weight lies in the range of twice the maxima of the triplet branch which amount to roughly 83 cm⁻¹ from INS data [122, 123]. Thus, we assign the observed broad maximum to a two-magnon continuum which corresponds to a double spin-flip process of two singlets into a higher singlet state consisting of two

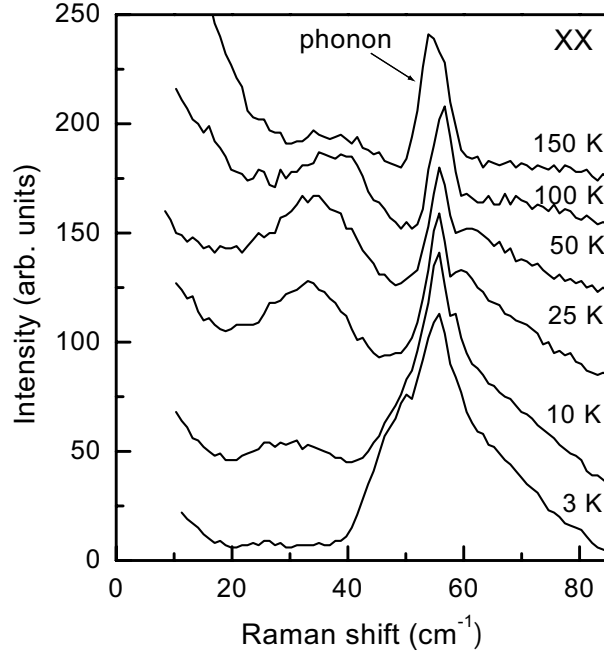


Figure 6.8: Raman spectra in the (xx) polarization at different temperatures. For clarity of the presentation the spectra are shifted. The sharp peak on top of the high-energy continuum is a phonon mode.

bound triplets. In contrast to usual spin gapped systems, the spectral weights undergo anomalous temperature dependence. Note that phonon anomalies are observed in the comparable temperature regime as seen in Fig. 6.7. Thus, we will attribute the anomalies in both spin and lattice degrees of freedom to magnetoelastic interactions. Up to now, two different mechanisms leading to phonon frequency shifts via spin-phonon couplings have been suggested. The first mechanism originates from a coupling of magnetic energy with ionic displacements in first order in a nonadiabatic regime [139]. The second mechanism arises from a coupling of magnetic energy with ionic displacements in second order [141]. The first mechanism in a dimerized spin system accompanies a change of dimerization, $\delta(g)$, as well as spin gap, $\Delta(g)$, depending on the strength of spin-phonon coupling g . Thus, in our case dynamic spin-phonon interactions are responsible for the observed anomalies. This is further supported by the fact that the exchange constant of $J \approx 48$ K in KCuCl_3 is comparable to the optical phonon energy seen at 58 cm^{-1} and 70 cm^{-1} (see

Fig. 6.6). Thus, a strong spin-phonon coupling is expected due to a large magnon density of states in the low energy region. Noticeably, the spin dynamics of TlCuCl_3 which is isostructural to KCuCl_3 can be well explained within dynamic spin-phonon couplings.

The consequence of *dynamic* spin-phonon couplings is the renormalization of spin gap as well as a change of dimerization. Actually, the spin gap decreases from 26 cm^{-1} ($\approx 37 \text{ K}$) at 90 K to 20 cm^{-1} (≈ 28) at 3 K as displayed in Fig. 6.9(a). In addition, the strengthening of dimerization is reflected in the change of the lineshape. Upon cooling a rather symmetric lineshape evolves into a more asymmetric form with a large spectral weight at the lower boundary. Such an asymmetric Raman spectrum with a tail towards higher energy is typical for a two-magnon continuum in low-dimensional spin gapped systems like the spin-Peierls system GuGeO_3 and the weakly coupled dimer system CaV_2O_5 [142]. This is due to a strong resonance of two neighboring magnons near the Brillouin zone center caused by the attraction between magnons [133, 134]. Therefore, we interpret the enforcement of asymmetry in lineshape in terms of a strengthening of dimerization due to increased spin-phonon couplings. Upon heating the decrease of spin-phonon coupling is related to a reduction of the lattice strain and a weakening of interdimer interactions induced by thermally excited triplets. The intrinsic dimerized system KCuCl_3 mimics spin-Peierls-like instabilities by changing the degree of dimerization and accompanying lattice instabilities.

Nextly, we will discuss the origin of the lower-energy continuum. Neutron scattering measurements and structural consideration rule out the existence of another singlet state. Furthermore, due to the unusual temperature dependence of the peak intensity and enhanced kinetic energy one triplet excitations and bound states should be excluded as a possible origin. Rather, it indicates that the scattering process arises from transitions between excited states. At finite temperature triplets are already excited. This can lead to a three-magnon scattering process [131]. That is, light scattering promotes one triplet into two adjacent triplets. To describe this process, let us consider four spins S_1, S_2, S_3 and S_4 forming one triplet and singlet denoted as $|t_0, s\rangle$. Here $t_{0,\pm 1}$ represents the triplet state with the corresponding S^z component. To catch insight into possible scattering processes, we will consider the simplified Raman operator $R=S_2 \cdot S_3$ in the limit of strong dimerization. Applying R on $|t_0, s\rangle$, one obtains

$$S_2 \cdot S_3 |t_0, s\rangle = (1/4)(-|s, t_0\rangle + |t_1, t_{-1}\rangle - |t_{-1}, t_1\rangle). \quad (6.1)$$

Here the first term conserves the number of magnons. The other terms cor-

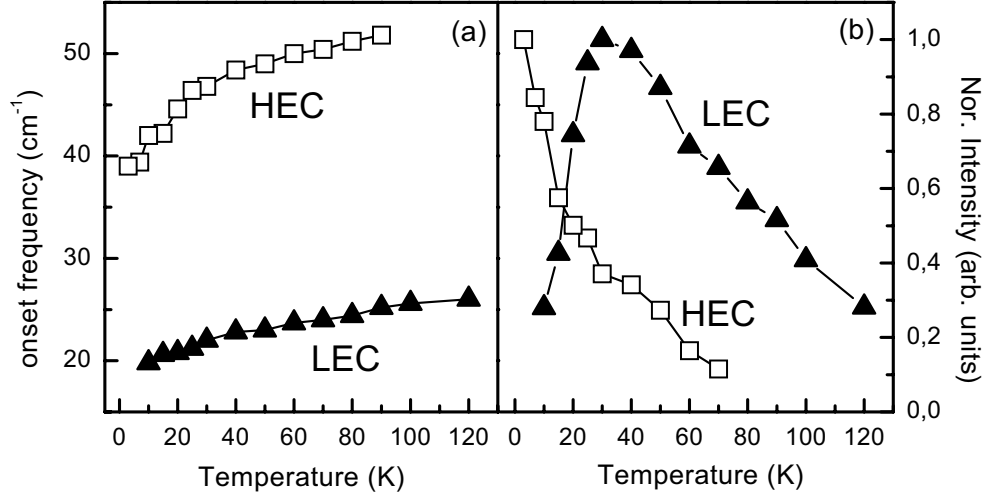


Figure 6.9: (a) Temperature dependence of the onset of the continuum. The onset of the continuum is determined by the lower cut-off frequency of the continuum. The LEC (HEC) stands for the lower (higher) energy continuum. (b) Temperature dependence of integrated intensity of the continuum. The line is a guide to the eyes.

responding to a three-magnon process induce a transition from one to two magnons resulting in the change of the number of magnons by one. The three-magnon process is given by transitions from the lowest magnon branch to the two-magnon continuum of $S=1$ excitations. The onset of the observed three-magnon continuum is thus roughly estimated by the energy difference between the onset of the two-magnon continuum at 40 cm^{-1} and the spin gap $\Delta = 21 \text{ cm}^{-1}$. The resulting value of 19 cm^{-1} lies in good agreement with the data shown in Fig. 6.9(a). The estimate of the higher cut-off energy is rather difficult due to substantial dispersion of triplets. If we start from the magnon with $\omega_i = \Delta = 21 \text{ cm}^{-1}$, we can induce a momentum conserving transition to the magnons with maximum energy $\omega_{f1} = \omega_{f2} = 40 \text{ cm}^{-1}$ with $\vec{q}_{f1} = -\vec{q}_{f2}$. This leads to the upper boundary of the three-magnon continuum at $(2 \times 40 - 21) = 59 \text{ cm}^{-1}$. This value is larger than the observed value of 37 cm^{-1} . The difference should be attributed to negligible spectral weight in higher energy regime.

Finally, we will look on the temperature dependence of the peak intensity in Fig. 6.9 (b). The strong increase from 0 K to 31 K is due to the increase of number of excited magnons. Above 31 K the peak intensity of the three-

magnon process decreases in the similar way as the two-magnon process does. This is related to a weakening of the dimerized state due to a thermally induced triplet-triplet interaction. Consistently, the temperature dependence of the spin gap (half of the onset energy in Fig. 6.9 (a)) shows a strong change around 30 K. This suggests that excited triplets play a decisive role in determining spin-phonon coupling.

6.8 Conclusions

To summarize, we have presented Raman scattering data of the coupled spin dimer system $ACuCl_3$ with $A=Ti$ and K . These compounds are the realization of a broad-bandwidth spin dimer system. In $TiCuCl_3$ we observed an anomalous temperature dependence of the two-magnon continuum along the xx -polarization parallel to the direction with the strongest interdimer interactions: upon cooling the spin gap decreases while spectral weight and peak energy shift to lower energy. These effects are attributed to (i) a phonon-modulated spin gap and exchange constant via dynamic spin-phonon coupling suggesting the significance of low-dimensionality together with low lattice symmetry in spin dynamics and (ii) interactions between thermally activated triplets due to a large bandwidth compared with the spin gap. Furthermore, the Fano lines on top of the magnetic continuum, a strong temperature dependence of integrated phonon intensity and pronounced two-phonon scattering are consistent with the coupled dynamics of spin and phonon degrees of freedom.

In $KCuCl_3$ we observe a two-magnon continuum which develops for temperatures below 100 K. In a similar way to $TiCuCl_3$, the temperature-dependent spin gap and lineshape accompany lattice anomalies. This indicates the significance of dynamic spin-phonon coupling. Compared to $TiCuCl_3$ phonon and spin anomalies are more pronounced. This can be ascribed to stronger low-dimensional character of spin dynamics in $KCuCl_3$. Moreover, for temperatures below 150 K an additional continuum appears. This is identified as a novel three-magnon continuum between excited triplet states.

Our study suggests that for both systems a reduced spin dimensionality is still crucial for the spin dynamics despite substantial three-dimensional interdimer interactions. Dynamic spin-phonon coupling in large-bandwidth spin dimer systems can result in a drastic change of spin dynamics reflected in the evolution of phononic and magnetic excitations. Furthermore, even in the dimerized system strong spin-phonon couplings can lead to instabilities in both lattice and spin degrees of freedom.

Here let us discuss some prerequisites for the observation of BEC of triplets in a gapped spin system. Excited triplets should be dominated by a kinetic energy against a short-range interaction as ACuCl_3 does. Taking into account of this fact, 3D Bose gas of triplets will be easily realized in 3D network of spin dimers. In contrast, when phase space is reduced as in quasi 1D spin dimer system and frustrated arrangement of spin dimers, excited triplets become localized. As a result, enhanced interaction energy leads to a crystallization of triplets with a large magnetic superlattice and the formation of magnetization plateaus. Furthermore, the system should not be plagued by the presence of a staggered g -tensor, Dzyaloshinskii-Moriya interaction or single-ion anisotropy which leads to the reopening of spin gap above the critical magnetic field. However, as our study shows, strong spin-phonon coupling does not essentially hamper the appearance of BEC even though it modifies the physical quantities in field-induced phase.

Chapter 7

Orthogonal dimer Heisenberg spin system $\text{SrCu}_2(\text{BO}_3)_2$

In this chapter we report Raman scattering measurements of the quasi-two-dimensional quantum antiferromagnet $\text{SrCu}_2(\text{BO}_3)_2$ and $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Cu}_2(\text{BO}_3)_2$. This compound has received considerable attention due to its relevance for the two-dimensional Shastry-Sutherland model [143, 144] which is given by the Hamiltonian $H = J \sum_{nn} S_i \cdot S_j + J' \sum_{nnn} S_i \cdot S_j$ where nn (nnn) stands for nearest (next nearest) neighbor spins. The ground state of the Shastry-Sutherland model is given by a direct product of dimer singlet states when the ratio $x = J'/J$ of the next nearest inter-dimer coupling J' to the nearest neighbor intra-dimer coupling J is smaller than a critical value near 0.7 [145]. Various experiments have confirmed that the orthogonally coupled spin dimers in the crystallographic ab -layer form a dimer singlet ground state with a spin gap of $\Delta_{01} = 34$ K and dispersionless elementary triplets [146, 147]. In addition, $\text{SrCu}_2(\text{BO}_3)_2$ ($x \approx 0.63 - 0.68$) is close to a quantum critical point ($x_c = 0.691$) which separates a short range dimer phase from a long range ordered Néel phase [148, 149]. Furthermore, the existence of intermediate phases such as helical order, plaquette-singlet order, or weak columnar-dimer order has been discussed for larger x [150]. Experiments using magnetic susceptibility under hydrostatic pressure have found evidence for a decrease of the spin gap under pressure, i.e. the dimer ground state can at least be weakened experimentally [151].

Despite the success of the 2D Shastry-Sutherland model in understanding the ground state and spin gap of $\text{SrCu}_2(\text{BO}_3)_2$, a lot of severe deviations show up [75]. At finite temperatures the significance of interlayer interactions is evident from the temperature dependence of the magnetic susceptibil-

ity [152, 153]. Interlayer coupling destabilizes the frustration-induced singlet dimer phase while enhancing long-range antiferromagnetic correlations [154]. A recent crystal structure study has revealed a displacive, second order structural phase transition at $T_s=395$ K [155]. The main structural distortion was observed as a continuous corrugation of the Cu-BO₃-layer in a wide temperature range below T_s . This corrugation induces a change of the interlayer interaction most clearly seen as a step-like jump in the magnetic susceptibility at T_s [156]. Furthermore, the importance of spin-phonon interactions is indicated by a substantial softening of the sound velocity both as a function of temperature and magnetic field [157]. This implies a sensitivity of the dimer system to specific ionic displacements. The observation of a magnetic superstructure by high field NMR measurements at the 1/8-magnetization plateau [158] further supports this. Finally, neutron scattering experiments and electron spin resonance (ESR) show multiparticle triplet bound states with an anomalous k-dependence of the structure factor [159, 160] and zero-field splitting [161] that is not in accordance with a pure 2D Shastry-Sutherland model [162]. The splitting of the triplets may be understood by taking into account a Dzyaloshinskii-Moriya (DM) interaction which partially lifts the magnetic frustration and suppresses the spin gap [160].

The above-mentioned results suggest that in order to develop a closer understanding of SrCu₂(BO₃)₂ the minimal model should be extended to a quasi-2D $J - J'$ model including spin-phonon coupling, lattice distortions and DM interaction.

7.1 Crystal structure and magnetic properties

At room temperature the crystal structure of SrCu₂(BO₃)₂ forms a tetragonal structure of $I\bar{4}2m$ with the lattice constants $a=8.995$ Å and $c=6.649$ Å [163]. A projection of this structure on the ab plane is shown in Fig. 7.1(a). In the ab -layer Cu²⁺ ions form dimers of planar, edge sharing CuO₄-groups. The spin dimers are connected through the triangular BO₃-groups. The copper dimer is coordinated from both sides by two equivalent oxygens belonging to the same BO₃-group in the form of a chelate. The bridging oxygens between the coppers are formed by the remaining third oxygen atom of the BO₃-group. The coordination of copper by the rigid BO₃-groups with threefold symmetry leads to a pronounced angular distortion of the CuO₄ square. Each Cu²⁺ ion has one nearest-neighbor Cu²⁺ ion and four next-nearest-neighbor Cu²⁺ ions in the plane. The distance between nearest-neighbor and next-nearest-neighbor

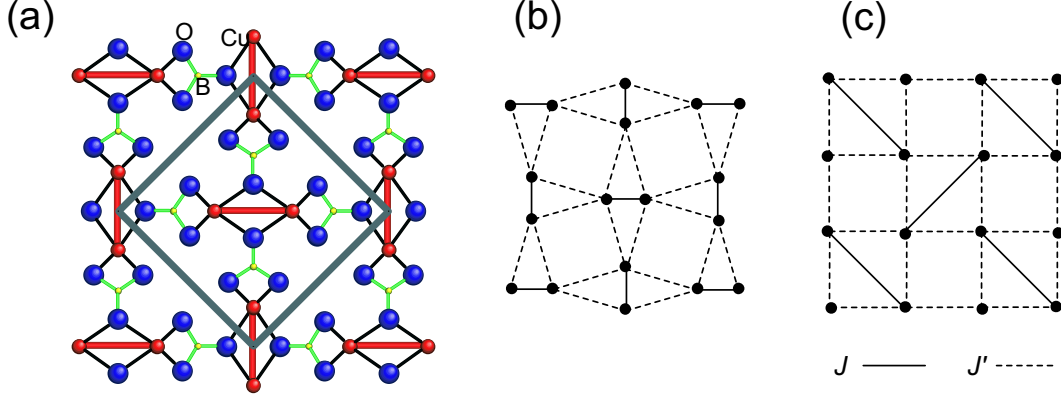


Figure 7.1: (a) Schematic view of the crystal structure of a CuBO₃ layer. (b) Two-dimensional orthogonal model. (c) The Shastry-Sutherland model which is topologically equivalent to (b).

Cu²⁺ ions is 2.905 Å and 5.132 Å, respectively. The bonding angle Cu-O-Cu is 102.42°, suggesting antiferromagnetic intradimer exchange interactions. The two-dimensional spin topology is schematically depicted in Figs. 7.1(b) and (c). Note that below 395 K the CuBO₃ plane is buckled.

At $T_s=395$ K a second order phase transition from the space group $I\bar{4}2m$ to $I4/mcm$ takes place [155]. The low-temperature phase is a maximal non-isomorphic subgroup of the space group of the high-temperature phase. Without any change of the crystal system, the symmetry reduction occurs through the continuous internal structural change; with increasing temperature the corrugation of the Cu-BO₃ layers is reduced and finally disappears above T_s . Therefore, the CuBO₃ plane is a mirror plane. The existence of a mirror plane is important for Dzyaloshinsky-Moriya interactions as will be discussed later.

As displayed in Fig. 7.2(a), the magnetic susceptibility of SrCu₂(BO₃)₂ shows a maximum at around 20 K and a rapid drop toward lower temperatures. This suggests the formation of a spin gap $\Delta_{01} \approx 34$ K [164]. The isolated dimer model with the intradimer exchange constant of ~ 35 K cannot reproduce the experimental data as seen in the inset of Fig. 7.2(a). The large difference between the Curie-Weiss constant $\theta = 102.5$ K and the spin gap indicates the existence of a frustrated antiferromagnetic next-nearest-neighbor coupling constant J' . In addition, the isolated dimer model can also not explain the presence of magnetization plateaux at $1/3, 1/4$ and $1/8$ (see Fig. 7.2(b)). The

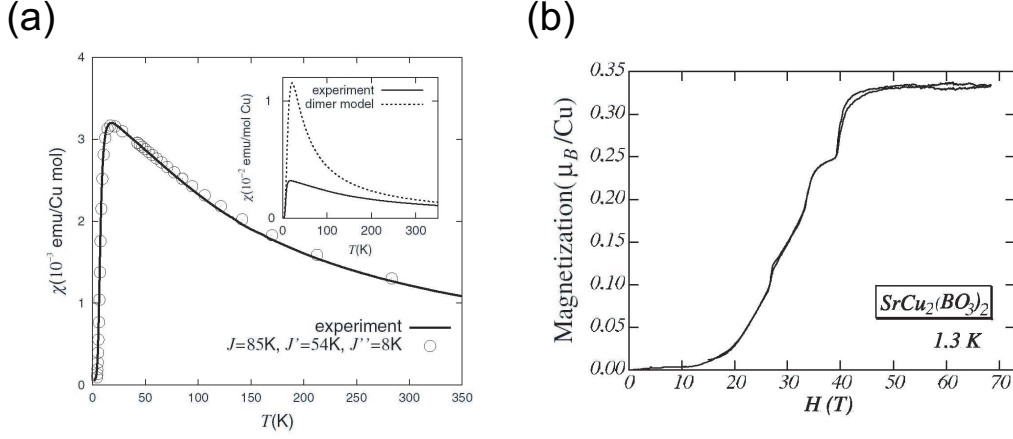


Figure 7.2: (a) Temperature dependence of the magnetic susceptibility (solid curve) and numerical calculation with the optimal parameters (open circle). The inset is the result of fitting by an isolated dimer model [144]. (b) The magnetization curve for $\text{SrCu}_2(\text{BO}_3)_2$ at 1.3 K [167]. Two-dimensional orthogonal model.

observed plateaux satisfy the condition of $n(S - m) = \text{integer}$ where n is the period of the ground state in the field, S is the magnitude of the spin and m is the magnetization per site in unit of $g\mu_B$ [165]. When n is different from the period of the lattice, symmetry breaking occurs at the magnetization plateau. Several nonequivalent spin sites at the $1/8$ plateau observed by NMR measurements confirm the symmetry breaking of the ground state. In addition, the realistic model should also take into account an interlayer interaction J'' , as a buckling in the CuBO_3 plane indicates its significance. Numerical calculation of three-dimensional orthogonal model leads to the optimal parameter set as $J = 85$ K, $J' = 54$ K and $J'' = 8$ K [144] (see the panel of Fig. 7.2(a)).

Next, we will briefly mention magnetic excited states of $\text{SrCu}_2(\text{BO}_3)_2$. The most distinctive feature of a triplet excitation is its almost localized nature. This originates from the frustration between J and J' which prevents a hopping of a triplet state from one dimer to another, resulting in flat triplet branch [148]. Strong interactions between the well-localized triplet excitations lead to the formation of multiparticle bound states in both the singlet and triplet sectors as well as the appearance of plateaus at $1/8$, $1/4$, and $1/3$ of the saturation magnetization [75, 146, 147]. On the other hand, higher-energy excitations

have a dispersive character. This implies that the bound states of two triplet excitations can move more easily than an isolated triplet. For very low temperatures ($T < \Delta_{01}$) Raman scattering measurements [132] show four well-defined modes with energies $\Delta_{00} = 30, 46, 56$ and 70 cm^{-1} in the (a'b') scattering configuration. This scattering geometry allows exchange Raman scattering on the Shastry-Sutherland lattice since the Raman operator has an odd parity to the reflection of the lattice. The observed modes are assigned to magnetic bound states with $S=0$. On the other hand, for (ab) polarization the singlet bound states become weak. Instead, a broad two-magnon-like continuum develops at elevated temperatures. This originates from thermally induced and strongly localized triplet states of the Shastry-Sutherland lattice.

7.2 Experimental details

High quality single crystals of $\text{SrCu}_2(\text{BO}_3)_2$ and $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Cu}_2(\text{BO}_3)_2$ were grown using a vertical travelling solvent floating zone method from a LiBO_3 -flux [166]. Samples with typical dimension $5 \times 5 \times 3 \text{ mm}^3$ were used for Raman scattering measurements. The measurements were done in a continuous helium flow optical cryostat by varying temperature from 5 K to room temperature. The high temperature measurements from 300 K to 450 K were carried out using a heating stage under vacuum. All spectra were taken in a quasi-backscattering geometry with the excitation line $\lambda = 514.5 \text{ nm}$ of an Ar^+ laser and analyzed by a DILOR-XY spectrometer and a nitrogen cooled CCD detector. The laser power of 5 mW was focused to a 0.1 mm diameter spot on the interlayer surface.

7.3 Symmetry analysis of phonon modes

Before discussing Raman spectra we will present a group theoretical analysis as a first step to understand the nature of the soft mode and its possible effect on the magnetic properties of $\text{SrCu}_2(\text{BO}_3)_2$. Our analysis is based on the result of a recent X-ray study [155] which provides a detailed information about the temperature dependence of the atomic parameters and crystal symmetry.

In the high temperature (HT) phase $\text{SrCu}_2(\text{BO}_3)_2$ has space group $I4/mcm$ where Sr atoms have D_4 (2a) site symmetry, Cu, B, and O1 atoms have C'_{2v} (4h) site symmetry, and O2 atoms possess C_s^h (8k) site symmetry (see Fig. 7.3(a)). A factor group analysis gives the experimentally observed infrared and Raman

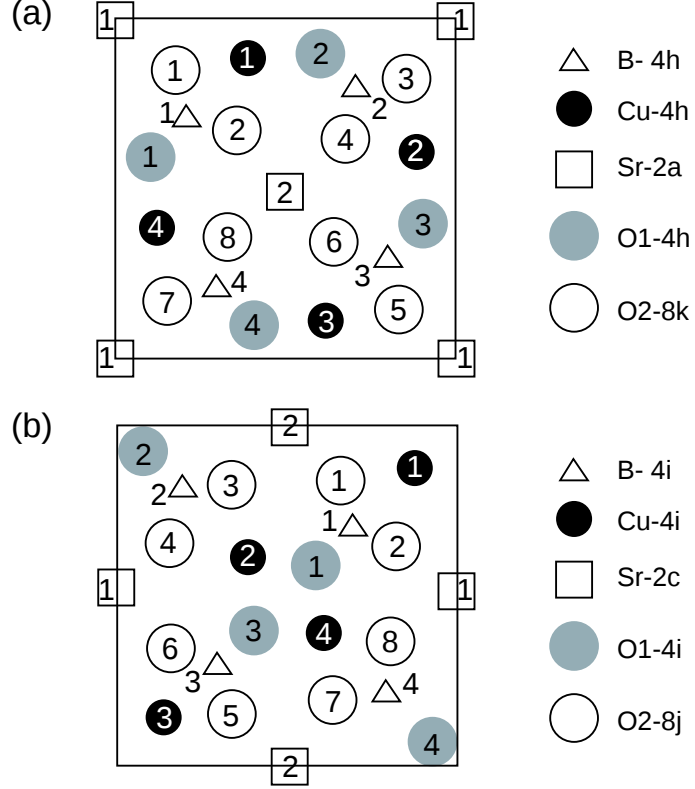


Figure 7.3: (a) Primitive unit cell and site symmetry of the atoms in the high temperature phase (space group $I4/mcm$) (b) Primitive unit cell and site symmetry of the atoms in the low temperature phase (space group $I\bar{4}2m$) of $\text{SrCu}_2(\text{BO}_3)_2$.

active modes as follows:

$$\begin{aligned} \Gamma_{HT} = & 5A_{1g} + A_{1u} + 6A_{2g} + 5A_{2u} + 5B_{1g} + 4B_{1u} \\ & + 5B_{2g} + B_{2u} + 6E_g + 11E_u. \end{aligned} \quad (7.1)$$

According to this representation one expects 27 Raman-active modes. The space group of the low-temperature (LT) phase is a maximal non-isomorphic subgroup of the space group of high-temperature phase. This group-subgroup relation is one of the prerequisites for the application of the Landau-theory for second order phase transitions. The LT phase has space group $I\bar{4}2m$ where Sr atoms occupy D_2 (2c) site symmetry, Cu, B, and O1 atoms have C_s (4i) site

symmetry, and O2 atoms belong to C_1 (8j) site symmetry (see Fig. 7.3(b)). The factor group analysis predicts

$$\Gamma_{LT} = 9A_1 + 7A_2 + 6B_1 + 10B_2 + 17E. \quad (7.2)$$

Subtracting the acoustic modes ($B_2 + E$) one obtains 56 Raman-active modes. With decreasing temperature through the structural phase transition at $T_s = 395$ K the expected evolution of phonon modes follows a subgroup connection of the space groups between HT and LT phases. In particular, in a second-order phase transition the new structure is a subgroup of the old structure. Thus, there will always be a zone-center A_1 component of the soft mode below T_s regardless of the symmetry of the soft mode in the higher symmetry phase. Furthermore, the HT phase loses m_z and m_x mirror planes, which are generators of the $I4/mcm$ space group. The translation symmetry remains the same. The 9 A_1 modes of the LT phase are correlated with ($5 A_{1g} + 4 B_{1u}$) modes of the HT phase. Thus, one of the four B_{1u} buckling modes at the Γ - point of the Brillouin zone is a soft mode in the HT phase approaching T_s . Normal coordinates of these modes are given by $Q_h^{B_{1u}} = \frac{1}{2}(U_{1z} - U_{2z} + U_{3z} - U_{4z})$ and $Q_k^{B_{1u}} = \frac{1}{2\sqrt{2}}(U_{1z} + U_{2z} - U_{3z} - U_{4z} + U_{5z} + U_{6z} - U_{7z} - U_{8z})$ for the h and k sites, respectively. It should be noted that these modes are silent and include only the displacements of the h and k c-site-ions along the z -direction. Such distortions violate the m_z , m_x and m_y symmetry planes and preserve the D_{2d} symmetry. According to the X-ray analysis in the LT phase, some in-phase superposition of $Q_{Cu}^{B_{1u}}$, $Q_B^{B_{1u}}$, $Q_{O1}^{B_{1u}}$, and $Q_{O2}^{B_{1u}}$ normal coordinates becomes frozen-in for temperatures below T_s (see Fig.9b in Ref. [155]). Precisely, this superposition represents an order parameter of the structural phase transition. Note that Sr ions with a site symmetry do not participate in this order parameter. In the LT phase four B_{1u} silent modes of the HT phase become Raman-active A_1 modes. The $Q_i^{IIA_1}$ and $Q_j^{IIA_1}$ normal coordinates of the A_1 mode correspond to $Q_h^{B_{1u}}$ and $Q_k^{B_{1u}}$, respectively (see the Appendix). As it was previously mentioned this soft mode involves an in-phase motion of almost all ions in the primitive cell (except Sr-ions) along the z -direction. The soft mode consists of a motion of atoms with heavy mass leading to a large effective mass. Thus, the energy of the soft mode is expected to be small even at low temperatures. In addition, the A_1 normal coordinates of $Q_i^{IA_1}$, $Q_j^{IA_1}$, and $Q_j^{IIA_1}$ contain xy -components of a motion of the ions in the LT phase. Thus, we can expect a mixing of the xy - and z -components of the normal coordinates. However, the X-ray analysis [155] did not show substantial shifts of Cu, B, and O-ions along the x - and y -direction in the LT phase, if compared to the HT phase. This implies that the A_1 modes hold the properties of the B_{1u} modes of the HT phase which

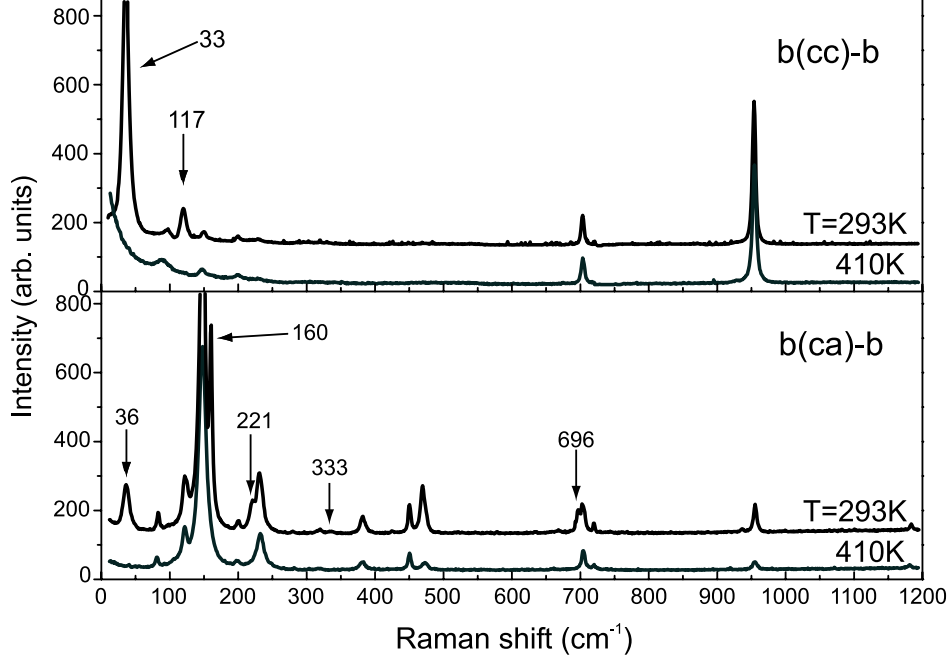


Figure 7.4: Raman spectra of $\text{SrCu}_2(\text{BO}_3)_2$ for two interlayer polarizations at 293 K and 410 K, respectively. The arrows indicate additional modes which appear for temperatures $T < T_s = 395$ K. Note that the intensity of these modes in b(ca)-b polarization is partly very weak.

consist of motions predominantly along the z -direction. Therefore, we expect a strong anisotropic Raman scattering of the A_1 modes: the dominant scattering intensity should be seen in zz polarization.

At last, we will mention that the 7 A_2 modes of the LT phase are correlated with the $(6A_{2g} + B_{2u})$ of the HT phase, the 6 B_1 modes with the $(5B_{1g} + A_{1u})$ modes, the 10 B_2 mode with the $(5B_{2g} + 5A_{2u})$ modes, and the 17 E mode with the $(6E_g + 11E_u)$, respectively. Therefore, one expects transition-induced scattering intensity of the $(4A_1 + B_1 + 4B_2 + 10E)$ modes in the LT phase which are infrared-active in the HT phase. The actual observability of these modes in interlayer polarizations depends on the evolution of the Raman tensor for each mode through the structural phase transition.

7.4 Interlayer soft mode

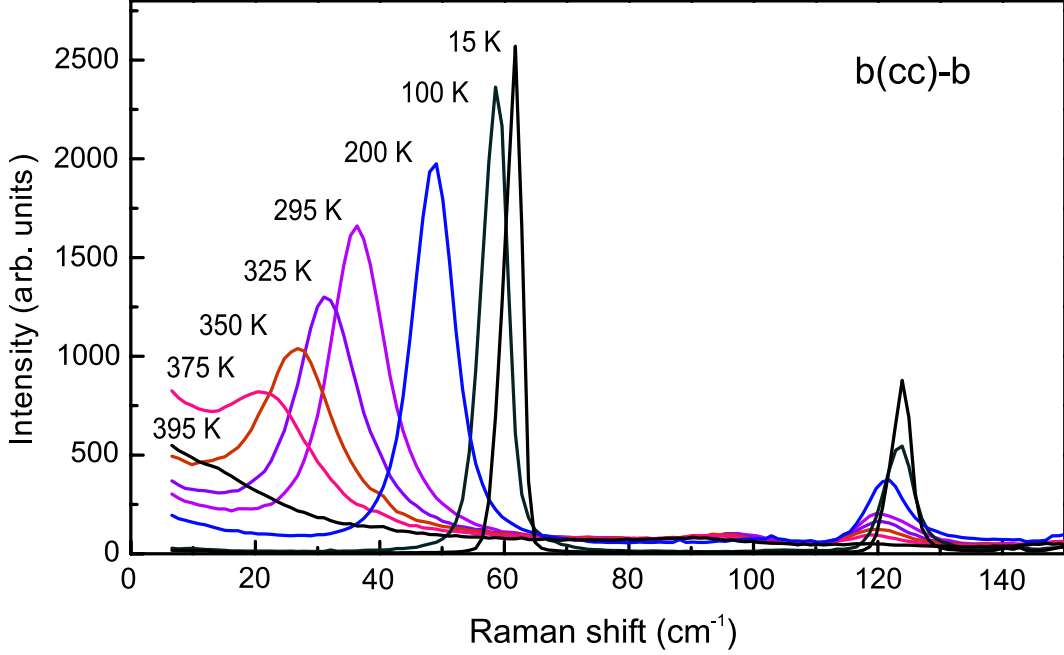


Figure 7.5: Softening of a phonon mode in (cc) polarization as a function of temperature. Note that an overtone of the 62 cm^{-1} -mode is present at 124 cm^{-1} .

Fig. 7.4 displays Raman spectra of $\text{SrCu}_2(\text{BO}_3)_2$ in (cc)- and (ca)-polarizations at 293 K and 410 K which lie below and above $T_s=395 \text{ K}$, respectively. The corresponding data of $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Cu}_2(\text{BO}_3)_2$ (not shown here) show only tiny frequency shifts of some phonon modes with respect to the undoped sample. Note here that the c axis is perpendicular to the layer. Thus, these data provide mainly information about interlayer lattice dynamics. For Raman spectra in intra-layer scattering geometries we refer to Refs.[75, 155]. At room temperature two additional modes at 33 and 117 cm^{-1} appear in the (cc)-polarization while five additional modes (see the arrows in Fig. 7.4) can be seen in the (ca)-polarization. Noticeably enough, four modes at 160 , 221 , 333 , and 696 cm^{-1} in the (ca) configuration turn up as a shoulder of high-temperature phonon modes. The appearance of additional modes in (ca) polarization can be ascribed to a mixing of weak ab plane motions with a strong modulation of

susceptibility tensor by a displacement along the c direction. A strong displacement along the c direction will cause infrared-active modes of the HT phase consisting of an ab plane motion to become Raman-active in the LT phase. As listed in the Appendix, the normal coordinate of the doubly degenerate E_u mode includes a xy plane motion of the h -site ions while that of the E_g mode contains a motion of the h -site ions along the z direction. Therefore, the observed modes in the (ca) polarization can be ascribed to an enhancement of Raman tensors of the E_u modes in the LT phase. Interestingly enough, the observed E_u mode in the LT phase is energetically very close to the frequency of the E_g mode in the HT phase. The shoulder structure of the additional modes with weak intensity indicates that the symmetry breaking is rather weak and that the crystal symmetries of the HT and LT phases are closely interrelated. In contrast, the 33- and 117-cm⁻¹-modes in the (cc) configuration and the 36-cm⁻¹-mode in the (ca) polarization are no longer observable in the HT phase. Thus, these modes are attributed to a soft mode which results from the structural phase transition. This is due to the fact that in a second order structural phase transition an optic soft mode is always Raman-active in the lower symmetry phase but it is not always Raman-active in the higher symmetry phase. The 33- and 36-cm⁻¹-modes in two different polarizations have close peak energies, indicating the same origin of them. The intensity of the 36 cm⁻¹-mode in (ca) polarization amounts to 10% of that of the 33 cm⁻¹-mode in (cc) polarization. The corresponding mode observed in (aa) polarization has negligible intensity compared to the mode with interlayer polarization [155]. This indicates an extreme anisotropy of the Raman tensor of the soft mode and is consistent with the symmetry analysis showing that the soft mode involves an in-phase motion of almost all ions in a primitive cell preferably along the c -axis (interlayer direction). A X-ray scattering structure analysis of SrCu₂(BO₃)₂ shows for $T > T_c$ an inversion center and completely flat CuBO₃ planes. For temperatures below $T < T_c$ atomic displacements are directed perpendicular to the ab plane leading to a buckling of the planes [155]. The in-phase motion also explains why the observed energy of the soft mode in our Raman experiments is so small. In addition, we observe a slight increase in integrated intensity of almost all phonon modes upon cooling. This can be ascribed to a change of both dipole matrix elements and band energies with the structural transition. The origin of the 117-cm⁻¹-mode will be discussed below.

The evolution of the low frequency modes in (cc) polarization is displayed in Fig. 7.5. Upon approaching the phase transition the 60 cm⁻¹-mode at $T=5$ K increases slightly up to 62 cm⁻¹ at $T=15$ K and finally disappears into the

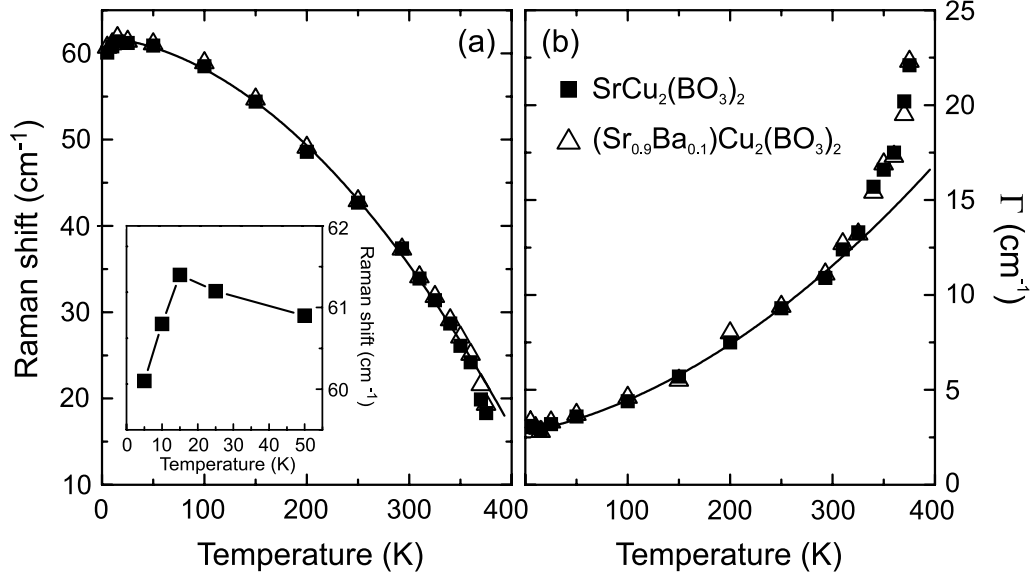


Figure 7.6: a) Temperature dependence of the soft mode. The inset shows a softening of the soft mode for temperatures $T < 15$ K. (b) Temperature dependence of the damping constant defined as the full width at half maximum of a Lorentzian profile. The solid lines give a fit using Eq. 7.3. The full square (open triangle) denotes the undoped (10%-Ba doped) sample.

tail of quasielastic scattering around T_s while softening roughly by 44 cm^{-1} . At the same time, its linewidth broadens strongly. Interestingly enough, an overtone of the 62 cm^{-1} -mode is observed at 124 cm^{-1} . This implies a strong anharmonicity of the soft mode. The second-order mode undergoes a small softening by 5 cm^{-1} suggesting that the original soft mode has a nearly flat dispersion with a large density of states. This can be explained as follows. The frequency of the soft mode around the Brillouin center will rapidly fall to zero as the transition is approached. In contrast, phonons at the vicinity of the zone boundary will remain robust. For first order scattering Raman spectroscopy is sensitive to the softening of phonons near the zone center. However, the whole Brillouin zone contributes to higher order Raman scattering. The spectral weight is proportional to the density of states if there are no interactions. Therefore, the resulting scattering intensity will be dominated by Brillouin zone boundary phonons with large spectral weights.

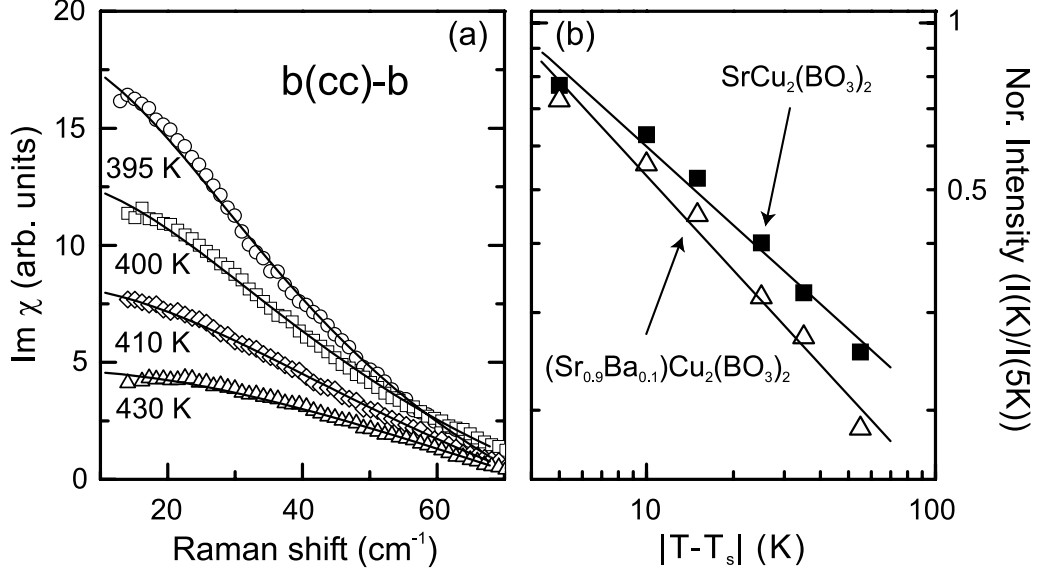


Figure 7.7: (a) Low energy Raman spectra for $T > T_s$ after correcting with the Bose-Einstein thermal factor. The solid line is a fit with a Lorentzian line. (b) The log-log plot of the normalized intensity as a function of $|T - T_s|$.

The temperature dependence of the frequency shift and the damping constant of the soft mode is plotted in Fig. 7.6. Within the experimental resolution we did not detect a difference between the undoped and the 10% Ba-doped samples. This observation strongly confirms that the soft mode does not include a motion of the Sr-ions, consistent with the symmetry analysis. Both the peak position and the linewidth change strongly over a large temperature range between 5 K and 370 K. Such a temperature dependence can be ascribed to anharmonic terms in the vibrational potential energy. Taking into account cubic and quartic anharmonic contributions, the temperature dependence of the peak position is given by [168]

$$\begin{aligned} \omega(T) = & \omega(0) + A\left(1 + \frac{2}{e^x - 1}\right) \\ & + B\left(1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2}\right), \end{aligned} \quad (7.3)$$

where $x = \hbar\omega(0)/2k_B T$ and $y = \hbar\omega(0)/3k_B T$ with $\omega(0)$, A , and B constants. The first term represents the frequency of soft modes at zero temperature. The

second and third terms originate from the decay of an optic phonon into three- and four-phonons due to anharmonicity, respectively. In the high temperature limit, the second and third terms vary as T and T^2 , respectively. The fit of the experimental data to equation 7.3 gives $\omega(0) = 62 \text{ cm}^{-1}$, $A = -0.48 \text{ cm}^{-1}$, and $B = -0.07 \text{ cm}^{-1}$. The smallness of the ratio $B/A = 0.15$, related to a small contribution of the four-phonon process to the softening, guarantees the validity of the fitting. Despite a reasonable agreement between the fitted curve and the experimental data in the overall temperature range one can see a deviation for temperatures above 350 K as well as at very low temperature. The temperature dependence of the linewidth can also be described using a similar relation as equation 7.3. The fitting values of the linewidth at zero temperature $\Gamma(0)$ and the coefficients A and B are found to be 2.7, 0.24 and 0.02 cm^{-1} , respectively. This leads to a ratio $B/A = 0.08$, also suggesting a small contribution of the four-phonon process. The origin of the discrepancy in the ratios with respect to the behavior of frequency and linewidth is not clear. It is certainly related to the strong anharmonicity. As shown in Fig. 7.6(b), significant deviations from the semi-phenomenological model can be seen for temperatures above 310 K. The pronounced discrepancy in the high temperature limit arises from a stronger broadening of the linewidth than a T^2 -dependence. This points to the necessity of higher order terms than the four-phonon processes in the model. The observation of pronounced harmonics (two-phonon scattering) already demands a more elaborate modelling.

Fig. 7.7 displays low energy Raman spectra for temperatures above T_s . Within the accessible low frequency resolution we have not observed a sharp central peak around T_s . Instead, a relatively broad elastic scattering maximum is observed which is fitted well by a Lorentzian profile. The intensity is reasonably described by $|T-T_s|^p$ with the power $p = 0.47$ and 0.56 for the undoped and the 10% Ba-doped samples, respectively (see Fig. 7.7(b) plotted on a logarithmic scale of $|T-T_s|$). As a possible origin of the central peak the decay of a soft mode into acoustic modes or phonon density fluctuations should be discussed. We notice that the observed behavior is in reasonable agreement to $|T-T_s|^{1/2}$ which is expected within the Landau theory for structural phase transitions which are not proper ferroelastic ones [169]. In this case a quadratic coupling of the order parameter η to a permeability tensor leads to only an η^4 contribution to the order parameter fluctuations in the intensity of the central peak. Thus, this suggests that the observed central peak is related to a fluctuation of the order parameter.

7.5 Buckling distortions in $\text{SrCu}_2(\text{BO}_3)_2$

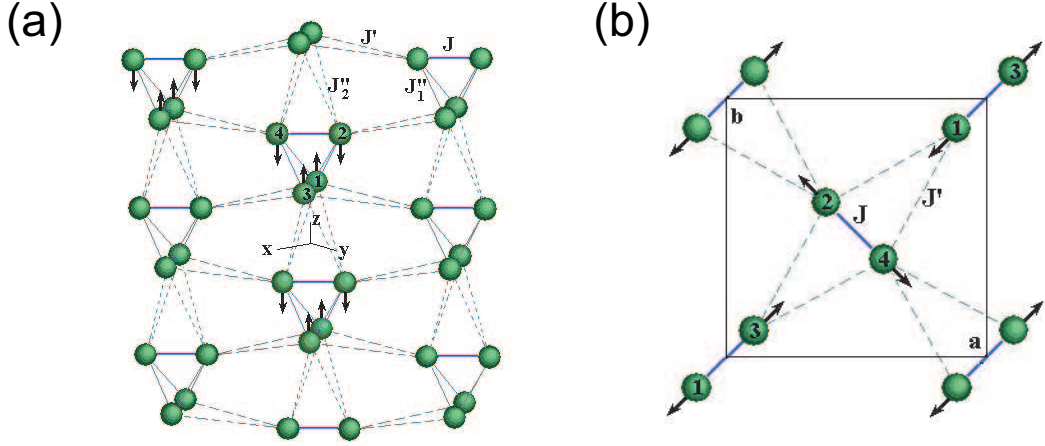


Figure 7.8: (a) Displacements of copper ions with Q^{IIA_1} - symmetry on the background of the already existing buckling distortions. (b) Displacements of copper ions with Q^{IA_1} -symmetry.

In dimerized spin systems spin-phonon interactions play an important role in determining the magnitude of spin gap and the strength of dimerization [75]. Optic and/or acoustic phonon anomalies can accompany the onset of a dimerized state as reported in CuGeO_3 [170] and $\text{SrCu}_2(\text{BO}_3)_2$ [171]. In $\text{SrCu}_2(\text{BO}_3)_2$ the in-plane elastic constant c_{66} shows a pronounced softening of 4.5% for temperature below 25 K [157, 171] which is attributed to an exchange striction coupling. Furthermore, under a magnetic field applied along the [100] direction an enormous softening of the in-plane c_{11} and c_{66} elastic constants takes place in the vicinity of the magnetization plateaus where excited triplets become highly mobile [157]. This highlights a close relation between spin-phonon coupling and DM interaction which promotes the hopping of triplets [160, 172]. One can also expect optic phonon anomalies around the magnetization plateaus [172]. This is because the alteration of intra-dimer bond lengths for each site results in the alternating magnetization.

The main aspect of the structural phase transition in $\text{SrCu}_2(\text{BO}_3)_2$ is buckling distortions due to strong anharmonicity. These lead to the alternation of distance between copper ions along the z -direction. As Fig. 7.8(a) displays, in the LT phase there are two different interlayer coupling constants J''_2 of longer

bonding length and J_1'' of shorter bonding length. At 100 K the relative distance between nearest neighboring Cu-ions along the upward and downward direction of the c -axis amounts to $\delta_z = 1.02 \text{ \AA}$, that is, 15% of the lattice constant c [155] (as sketched in Fig. 7.8(a)). Thus, we can safely neglect J_2'' . This buckling distortion, changing the bonding angle and distance via spin-lattice interaction, can modify anisotropic magnetic properties as a function of temperature.

With the special structural topology in mind we will turn to the anomalous decrease of the optic phonon frequency observed in the low temperature limit ($T < \Delta_{01} = 34 \text{ K}$). As displayed in the inset of Fig. 7.6(a), the peak energy of the soft mode reaches a maximum around 15 K and then softens by 3% with further lowering temperature. The energy of the soft mode $62 \text{ cm}^{-1} = 89 \text{ K}$ is comparable to the nearest neighbor intra-dimer coupling constant $J = 85 \text{ K}$ [156]. Furthermore, the softening is observed for temperature below the spin gap of 34 K. Thus, the observed softening should be attributed to a renormalization of phonon energy due to strong spin-phonon coupling. Further evidence for strong spin-phonon coupling can be provided by strong quasielastic light scattering induced by fluctuations of the energy density of the spin system [75]. As already shown in the symmetry analysis, the soft mode corresponds to motions of almost all ions along the interlayer direction. Consequently, the soft mode mediates all possible type of exchange interactions including the interlayer and the intralayer interactions. Since the soft mode has A_1 symmetry, it suffices to consider spin-phonon coupling in the Q^{IIA_1} - and Q^{IA_1} -symmetry displacements of Cu-ions (see the Appendix). Following Miyahara *et al.* [172] one can derive spin-phonon coupling of the soft mode in an exchange approximation.

First, we focus on the case of the Q^{IIA_1} normal mode which includes motions of Cu, B and O1 ions along the z -axis (see Fig. 7.8(a)). Spin-phonon interaction of the Q^{IIA_1} -symmetry reads as follows:

$$-Q^{IIA_1} \left(\beta \frac{\delta_z}{l_{\parallel}^2} J' \sum_{nnn} \mathbf{S}_i \cdot \mathbf{S}_j + \gamma \frac{l_{\perp}^z}{l_{\perp}^2} J_1'' \sum_{nnnz} \mathbf{S}_i \cdot \mathbf{S}_j \right) \quad (7.4)$$

where nnn ($nnnz$) stands for next-nearest neighboring Cu-ions in the ab -plane (along the z -direction). $\mathbf{l}_{\perp}$ ($\mathbf{l}_{\parallel}$) is the vector connecting them in the ab -plane (along the z -direction). β and γ denote the exponents of the distance dependence of $J'(\mathbf{r})$ and $J_1''(\mathbf{r})$, respectively. It is worth mentioning that the soft mode of the Q^{IIA_1} -symmetry does not mediate the intra-dimer interactions.

Moreover, in the HT phase the Q^{IIA_1} -type of spin-lattice interaction completely disappears because of the absence of buckling distortions as well as the cancellation of the inter-layer contribution by each other ($J'_1 = J'_2$). Assuming that $\beta \simeq \gamma$ one sees that the contribution of the inter-layer and the intra-layer interactions to spin-phonon coupling in the LT phase is comparable to each other with $l_\perp = 3.48\text{\AA}$, $l_\perp^z = 2.81\text{\AA}$ and $l_\parallel = 5.14\text{\AA}$ [155] and $J' = 0.635J$ and $J'' = 0.09J$ [144].

Another contribution to spin-phonon coupling comes from the Q^{IA_1} -symmetry uniform displacements of Cu-ions which consist of motions of Cu, B and O1 ions in the xy -axis (see Fig. 7.8(b)):

$$-Q^{IA_1} \left(\frac{\alpha}{l} J \sum_{nn} \mathbf{S}_i \cdot \mathbf{S}_j - \beta \frac{\sqrt{l_\parallel^2 - \frac{l_\perp^2}{4}} - \frac{l}{2}}{l_\parallel^2} J' \sum_{nnn} \mathbf{S}_i \cdot \mathbf{S}_j \right) \quad (7.5)$$

where nn stands for nearest neighboring Cu-ions. $\mathbf{l}$ is the vector connecting the intra-dimer Cu-ions. α denotes the exponent of the distance dependence of $J(\mathbf{r})$. Here note that this mode participates in the soft mode motion by an admixture of the Q^{IIA_1} normal mode due to strong anharmonicity. Furthermore, the Q^{IA_1} -type displacements can modulate the intra-dimer and the intra-layer exchange interactions. This implies that they can shift the quantum critical point $x = J'/J$ while increasing J' and decreasing J and vice versa. Because of the orthogonal and frustrated exchange topology and the predominant motions of the soft mode along the z -direction, however, the spin gap and the quantum critical point will undergo only a small change. Rather, the inter-layer interactions will be strongly modulated. However, the absolute strength of the interlayer interactions is small. All of these considerations explain why the observed softening of optic phonon modes is weak despite the possible contributions of the intra-dimer and the intra-layer interactions to spin-phonon couplings. Before leaving this discussion we will point out similar phonon anomalies reported in the alternating chain system $(\text{VO})_2\text{P}_2\text{O}_7$. A strong anharmonic phonon at 123 cm^{-1} softens in this compound by 10% [173]. Most probably, this mode mediates the exchange along the alternating chain and its energy amounts to the zone-boundary energy of a singlet-triplet excitation gap $E_{ZB}=125\text{ cm}^{-1}$ [174]. Strong spin-phonon coupling as well as the existence of a high symmetry phase under high pressure has been ascribed to be the origin for the anharmonicity of optical phonons [175, 176]. The similarity of $(\text{VO})_2\text{P}_2\text{O}_7$ and $\text{SrCu}_2(\text{BO}_3)_2$ suggests that the existence of a high symmetry phase at elevated pressure and/or temperature may play a decisive role in inducing anharmonicity and spin-phonon coupling in a dimerized system.

Finally, we will discuss another aspect of the structural phase transition related to the magnetic behavior and the relevance of antisymmetric interaction. Pronounced buckling distortions for temperature below $T < T_c$ can lead to a modification of anisotropic magnetic properties via spin-lattice interactions. The experimental observation of forbidden ESR transitions [161], a splitting of the first triplet excitation into three branches [159] and the unusual field dependence of magnetization plateaus [177] are not in accordance with a Shastry-Sutherland model based on isotropic superexchange. To explain the anomalous behaviors C  pas *et. al.* [160] derived the DM interactions from a simplified 2D spin model (corresponding to the HT phase) which lift partially the magnetic frustration as well as the degeneracy of the localized triplets.

However, we point out that the presence of the buckling distortions in the LT phase results in a complicated form of the DM interactions. In contrast to the assumption of C  pas *et. al.* [160], the LT phase loses m_z , m_y and m_x mirror planes (see the section 7.3). Thus, for the purpose of a more complete description of anisotropic interactions we have done a symmetry analysis using the exact symmetry of the LT phase. The exchange tensor of the intra-dimer interaction between copper ions 1 and 3 yields

$$J_{13}^{ij} = \begin{pmatrix} J_{13}^{xx} & d_{13}^z & D_{13}^y \\ d_{13}^z & J_{13}^{yy} & D_{13}^x \\ -D_{13}^y & -D_{13}^x & J_{13}^{zz} \end{pmatrix} \quad (7.6)$$

where d_{ij} and D_{ij} denote the component of symmetric and antisymmetric anisotropic (Dzyaloshinsky-Moriya) interactions, respectively. Here note that in the HT phase only the symmetric anisotropic interaction of d_{13}^z is present. An upper conventional estimate [178] is given by $d_{13}^z = (\Delta g/g)^2 J_{13} = 1.3$ K with the deviation of the g -factor from 2 $\Delta g = 0.28$ [161] and $J_{13} = J = 85$ K [144]. The appearance of the x - and y -component of DM interactions should be ascribed to a corrugation of the ab -plane which includes $Cu(1) - O_i(2) - Cu(3)$ and $Cu(1) - O_i(4) - Cu(3)$ exchange interaction paths. At 100 K the angle between the ab -plane and the plane including exchange paths amounts to $\varphi = 3.5^\circ$ [155]. This allows an estimate of the strength of the DM interactions [178]: $D_{13}^{y,x} = \sin \varphi (\Delta g/g) J_{13} = 0.63$ K. Because of the symmetricity of $D_{13}^y = D_{13}^x$ the orientation of the DM vector lies along the intra-dimer bond. The magnitude of the DM vector has a strong dependence on in-phase motions of $O_i(2)$ - and $O_i(4)$ -ions along the z -direction. In addition, under a continuous corrugation of the Cu-BO₃-layer the inter-dimer interactions will also undergo an appreciable modulation. From the symmetry analysis one obtains the exchange tensor of

inter-dimer interactions between copper ions 1 and 2:

$$J_{12}^{ij} = \begin{pmatrix} J_{12}^{xx} & D_{12}^z & D_{12}^y \\ -D_{12}^z & J_{12}^{yy} & d_{12}^x \\ -D_{12}^y & d_{12}^x & J_{12}^{zz} \end{pmatrix}. \quad (7.7)$$

It is worth noting that only the antisymmetric component D_{12}^z is present in the HT phase. In contrast, in the LT phase D_{12}^y - and d_{12}^x - components appear. The estimate of their magnitude was not done due to complicated exchange paths of the inter-dimer interactions. The analysis of the interlayer exchange tensors has been not pursued because of their weak strength.

Our symmetry analysis shows the presence of the symmetric anisotropic z -component of the intra-dimer interaction as well as the antisymmetric anisotropic z -component of the interdimer interaction in the HT phase. The latter is suggested by the analysis of the 2D spin model by C  pas *et. al.* [160]. To our best knowledge, until now the former has not been considered in the theoretical work despite the fact that it can remove partially the frustration because its orientation is directed antiparallel to the nearest neighboring dimers. In the LT phase the buckling distortions induce additionally the antisymmetric anisotropic x - and y -components of the intra-dimer interaction as well as the symmetric anisotropic x -component of the inter-dimer interaction. The estimated value of $D_{x,y} \sim 0.6$ K at 100 K is not negligible compared to $D_z \simeq 2$ K [160]. Therefore, we can conclude that a modulation of anisotropic interactions via spin-lattice couplings leads to an enhanced hopping of localized triplets and a mixing of triplet and singlet states. Thus, $\text{SrCu}_2(\text{BO}_3)_2$ lies closer to the quantum critical point than predicted based on pure 2D spin models.

7.6 Conclusions

We have presented a Raman scattering study of $\text{Sr}_{1-x}\text{Ba}_x\text{Cu}_2(\text{BO}_3)_2$ ($x = 0$ and 0.1) in interlayer polarization. With decreasing temperatures through the structural transition, a pronounced interlayer soft mode is observed. A symmetry analysis shows that this soft mode has an A_1 symmetry corresponding to in-phase motions of almost all ions along the interlayer direction. This explains the extreme anisotropy of the Raman tensor of the soft mode as well as its low energy. The doping dependence further confirms this. In addition, a displacement of atomic motions along the z -direction (buckling) leads to a small modulation of the intra-layer and the inter-layer interactions as well as the appearance of additional symmetric and antisymmetric anisotropic interactions.

For temperatures below the spin gap such a modulation results in the softening of the soft mode by 3%, indicating strong spin-phonon coupling. In particular, the buckling distortions and the special topology of $\text{SrCu}_2(\text{BO}_3)_2$ lead to the coupling of spin to the soft optical phonon by exchange modulation. Our results show that in a realistic model for $\text{SrCu}_2(\text{BO}_3)_2$ spin-phonon interactions, DM interactions and interlayer lattice dynamics should be taken into account to understand a variety of physical properties like the spin gap, the proximity to a quantum critical point and anomalous behavior of the spectroscopic data.

Chapter 8

The spin tetrahedra system $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ (X=Br,Cl)

In this chapter we present Raman scattering measurements of the spin tetrahedra system $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ (X=Br,Cl). In first approximation these compounds can be viewed as zero-dimensional system consisting of isolated spin-tetrahedra. Tetrahedral spin cluster shows a singlet ground state and a variety of singlet states inside a singlet-triplet gap [179]. Depending on the strength of inter-tetrahedral couplings, quantum phase transitions from nonmagnetic phases with a spin gap into magnetically ordered states can take place. Quantum fluctuations will be more pronounced in quasi-zero-dimensional systems near quantum critical point compared to higher-dimensional system. In this case, magnetic excitations will be dominated by spin singlet dynamics even in the regime of a long-range ordered state. Thus, longitudinal magnons arising from the oscillation of the magnitude of the local order parameter would live long enough to be detected as a well-defined mode. In addition, near a quantum critical point it is of great concern how the Néel temperature and the magnetization are scaled as a function of inter-tetrahedral couplings. One advantage of studying the tetrahedra spin cluster is that the eigenfunctions are exactly known. Thus, one can calculate analytically the physical quantities, guaranteeing a fruitful collaboration between theory and experiment.

8.1 Crystal and electronic band structure

The isostructural compounds of general formula $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ (X=Br,Cl) crystallize in the noncentrosymmetric tetragonal system, space group $P\bar{4}$ with two formula units per unit cell. The lattice parameters for the chloride are $a =$

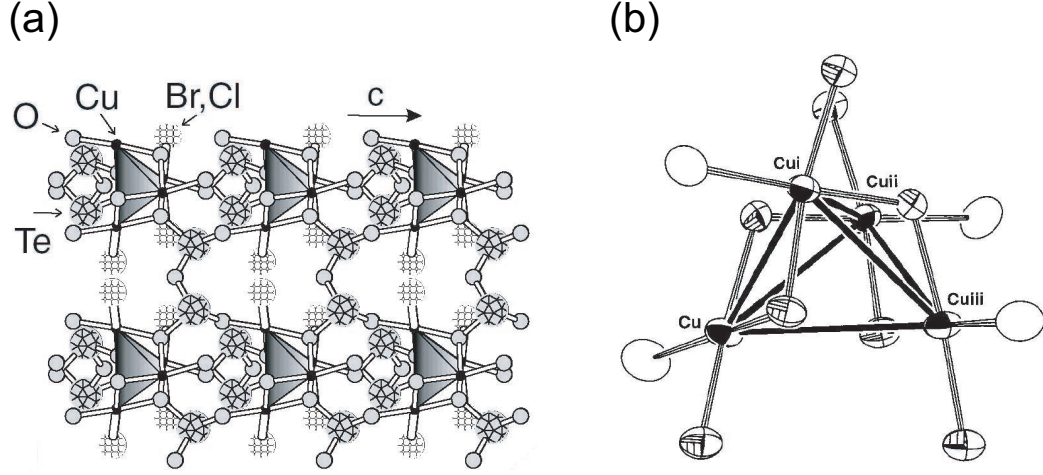


Figure 8.1: (a) Crystal structure of $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ [132]. The Cu tetrahedra are shaded. (b) Ortep drawings of an isolated cluster of four $[\text{CuO}_3\text{X}]$ square planes which show the tetrahedral arrangement of copper ions [179].

7.6209(3) Å and $c = 6.3200(4)$ Å while those for the bromide are $a = 7.8355(2)$ Å and $c = 6.3785(2)$ Å [179]. Thus, the bromide has a larger unit cell and slightly larger inter-tetrahedra (larger Cu-Cu intra-tetrahedra) distances than the chloride. On the other hand, bond angles show no essential change between them.

As Fig. 8.1(a) displays, the crystal structure of $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ consists of distorted tetrahedra which are formed by the four equivalent Cu^{2+} -ions located on a tetrahedral lattice. The copper atom is coordinated by three inequivalent oxygen atoms and one halogen atom $[\text{CuO}_3\text{X}]$ (see Fig. 8.1(b)). A somewhat distorted square is formed by the connection X-O1-O1-O2 where O1 (O2) is the intra-tetrahedral (inter-tetrahedral) oxygen. The tellurium atoms are coordinated by three oxygen atoms with Te-O distances ranging between 1.87 and 1.94 Å, and the $5s^2$ lone pairs (E), denoted by $[\text{TeO}_3\text{E}]$. Two $[\text{TeO}_3\text{E}]$ tetrahedra are linked via oxygen atom O3 to form $[\text{Te}_2\text{O}_5\text{E}_2]$ groups. The three-dimensional network is built up isolating the copper clusters in the $[100]$ and $[010]$ directions. In the $[001]$ direction clusters are linked together via only one $[\text{TeO}_3\text{E}]$ tetrahedron. This leads to the formation of spin tubes along the $[001]$ direction surrounded by large tunnels where $5s^2$ tellurium lone pairs and

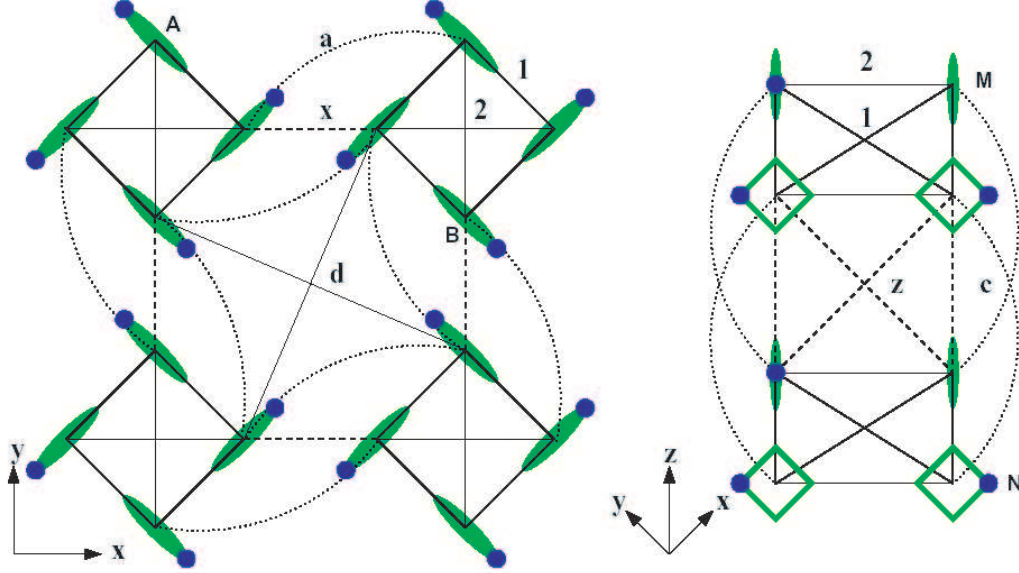


Figure 8.2: Schematic diagram of the hopping matrix elements in between the Cu^{2+} ions [180]. The ovals and the squares denote CuO_3X units linked by intra-tetrahedra hopping matrix elements t_α ($\alpha = 1, 2$). The in-plane (in-chain) hopping matrix elements are $\alpha = x, a$, and d ($\alpha = c, z$).

halogen atoms interact with each other.

The band structure is characterized by four narrow bands of width ~ 0.7 eV near the Fermi-level [180]. They are well separated from the occupied low-lying valence band by a gap of ~ 0.25 eV and the high-lying unoccupied Te- p bands by a gap of ~ 2 eV. The bands are dominated by Cu- $3d_{x^2-y^2}$ character with substantial admixture of Br (Cl) p , O1 and O2 p states. The band dispersion is substantial along all three crystallographic directions indicating that the inter-tetrahedral couplings are non-negligible in all three directions. The relevant hopping matrix elements t_α between Cu^{2+} ions are schematically illustrated in Fig. 8.2. The nearest intra-tetrahedral Cu-Cu transfer matrix element t_1 is mediated by O1-ions located in between two Cu-ions. The angle Cu-O1-Cu is 107° (109°) for X=Br (Cl). According to the Goodenough-Kanamori-Anderson rules the nearest neighbor intra-tetrahedra interactions should be weak antiferromagnetic with $t_1(\text{X}=\text{Cl}) > t_1(\text{X}=\text{Br})$. The next-nearest-neighbor intra-tetrahedral hopping matrix element t_2 comes from Cu-Cu overlap as well

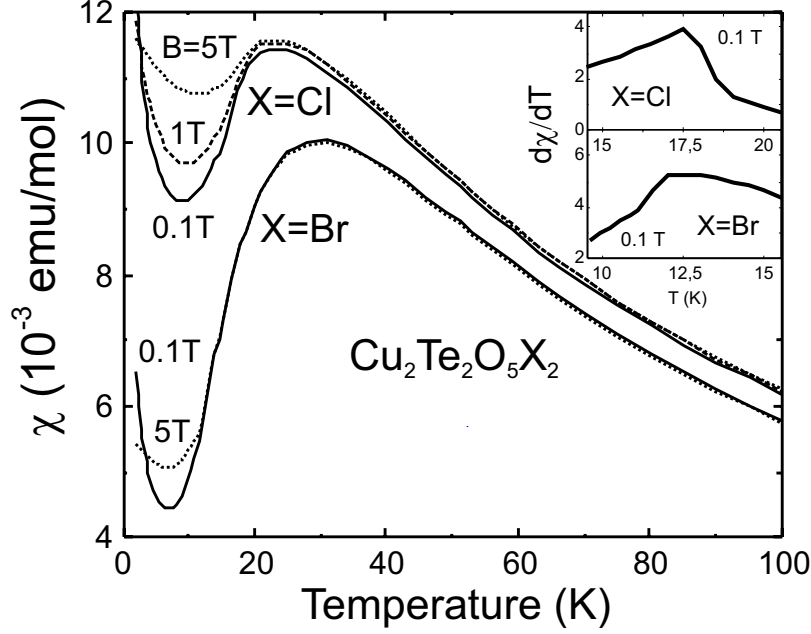


Figure 8.3: Magnetic susceptibility $\chi(T)$ of $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$, $\text{X}=\text{Cl}$ and Br , as a function of applied magnetic fields. The inset shows its derivative $\partial\chi(T)/\partial T$ at $B=0.1$ T [132].

as Cu-X-X-Cu pathes. *Ab-initio* calculations [180] show that the halogen-ions play a decisive role for unusual large inter-tetrahedra coupling. Four halogen orbitals give rise to X_4 -rings via $(\text{X-}p)-(\text{X-}p)$ covalent bonding. These X_4 -rings are covalently coupled to the respective Cu_4 -tetrahedrons. The chlorine compound has stronger copper-halogen coupling because the $\text{Cl-}3p$ orbital at the Fermi-level is more strongly distorted towards the $\text{Cu-}3d$ orbital compared to the $\text{Br-}4p$ orbital. The chloride (the bromide) is characterized as strongly (relatively strongly) coupled spin tetrahedra system.

8.2 Thermodynamic properties

Fig. 8.3 displays the magnetic susceptibility $\chi(T)$ as a function of temperature. Both systems show a well-pronounced maximum at 30 K and 23 K for the bromine and chlorine compounds, respectively. At low temperatures a rapid decrease of $\chi(T)$ is seen for the bromide, typical for spin gap systems. To catch

some insight $\chi(T)$ was first fitted by an isolated tetrahedra model with nearest-neighbor exchange constant J_1 and next-nearest-neighbor exchange constant J_2 [179]. In both cases, a reasonable fit which reproduces both the high-temperature regime and the maximum is found at $J_1=J_2 \approx 43$ K for the bromide and $J_1=J_2 \approx 38.5$ K for the chloride. Note that this result is rather artificial because an inter-tetrahedra coupling will shift the ratio of J_2/J_1 to lower values as will be discussed later.

A detailed investigation of $\chi(T)$ indicates the presence of long-range magnetic ordering as shown in the inset of Fig. 8.3. In the chloride a pronounced step-like increase of the slope in $\partial\chi(T)/\partial T$ with decreasing temperature is evident at $T_N = 18.2$ K. This implies that the susceptibility in the ordered state is smaller than it would be in the disordered state. In contrast, the low temperature behavior of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ is quite different and rather unusual. For temperatures below $T_{\chi_{\max}}$, $\chi(T)$ decreases considerably, by more than 50 %. This indicates the freezing out of a large part of the magnetic triplet excitations as expected in a system with a spin gap. The derivative $\partial\chi(T)/\partial T$ reveals a small but well discernible step at $T_o = 11.5$ K. This step has the opposite sign compared to $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$, i.e. the slope for $T < T_o$ is smaller than for $T > T_o$. This means that the magnetization in the ordered state is larger than it would be in the disordered state. This is opposite to the expected result for antiferromagnetic ordering.

The specific heat $C_p(T)$ of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ (see Fig. 8.4, upper curves with upper temperature scale) shows a mean field like transition with a sizeable anomaly at T_N . A magnetic field of 13.5 T leaves this anomaly almost unchanged, only a slight decrease of T_N from 18.2 K to 18.0 K is discernible. All these features: the reduction of the susceptibility for $T < T_N$, the mean field type of transition, the reduction of the anomaly in $\chi(T)$ in an applied field whereas no reduction is observed in $C_p(T)$ and the very weak decrease of T_N with increasing B , point to a 3D-antiferromagnetic ordering in a system with only weak spin-anisotropies. Since this transition occurs below the well-defined maximum in $\chi(T)$, with $T_N/T_{\chi_{\max}} = 0.78$, these results indicate the presence of significant inter-tetrahedra couplings in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$. The specific heat of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ at $B = 0$ (see Fig. 8.4, lower curves with lower temperature scale) shows a small but well-defined anomaly at $T = T_o$. Applying a magnetic field leads to a very strong increase of the size of the anomaly, by more than a factor of 3 at $B = 13$ T, and to a pronounced shift of T_o to higher temperatures, from $T_o(0) = 11.4$ K to $T_o(B=13\text{T}) = 12.4$ K. In thermodynamic terms, this shift corresponds to the larger magnetization of the ordered state compared to the disordered state. Noticeably enough, this reminds us of a field-induced mag-

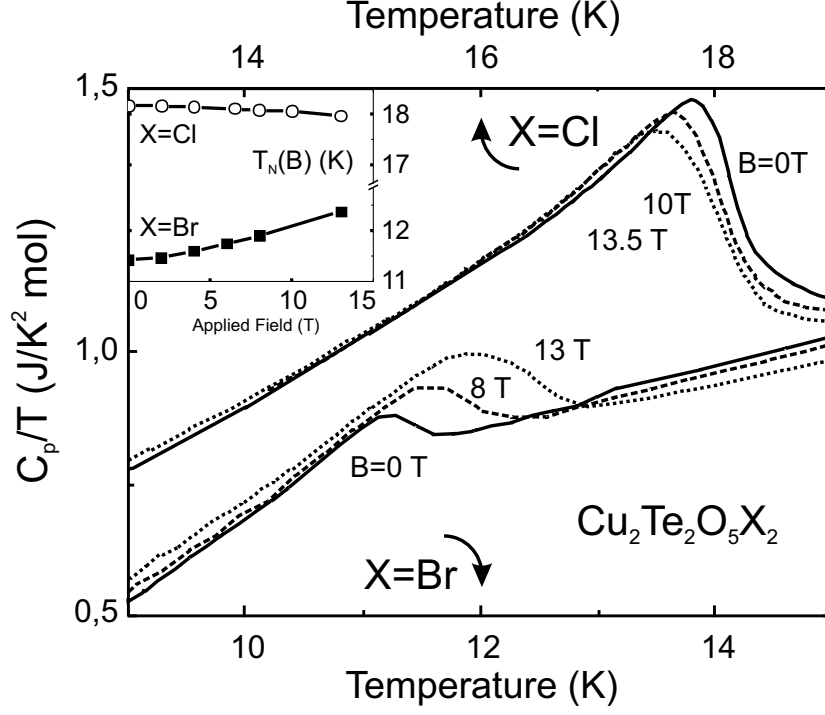


Figure 8.4: Specific heat $C_p(T)$ of $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ with $X=\text{Cl}$ (upper temperature axis) and $X=\text{Br}$ (lower temperature axis). The inset shows a low temperature phase diagram.

netization in spin gapped systems. This suggests that even in the long-range ordered state the spin singlet dynamics plays an important role in determining thermodynamic quantities. Fitting a power law to the field dependence of T_o as determined from $C_p(T)$, $T_o = a \cdot B^n$, we obtain $n = 1.41 \pm 0.05$. Using the low temperature parts ($T \ll T_o, T_N$) and the high temperature parts ($T > T_o, T_N$) of the specific heat results, we made a rough estimate of the magnetic specific heat and of the magnetic entropy $S_m(T)$. For $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$, the magnetic entropy at T_o is only a quite small portion of the total spin entropy expected at high temperatures $S_m(T_o) \simeq 1.3 \text{ J/Kmol} = 0.11 \cdot R \ln 2 / \text{spin}$, whereas for $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$, the entropy at T_N is much larger, $S_m(T_N) \simeq 4.1 \text{ J/Kmol} = 0.36 \cdot R \ln 2 / \text{spin}$. This indicates that in the Br-based compound, a large part of the magnetic degrees of freedom are freezing out at higher temperatures.

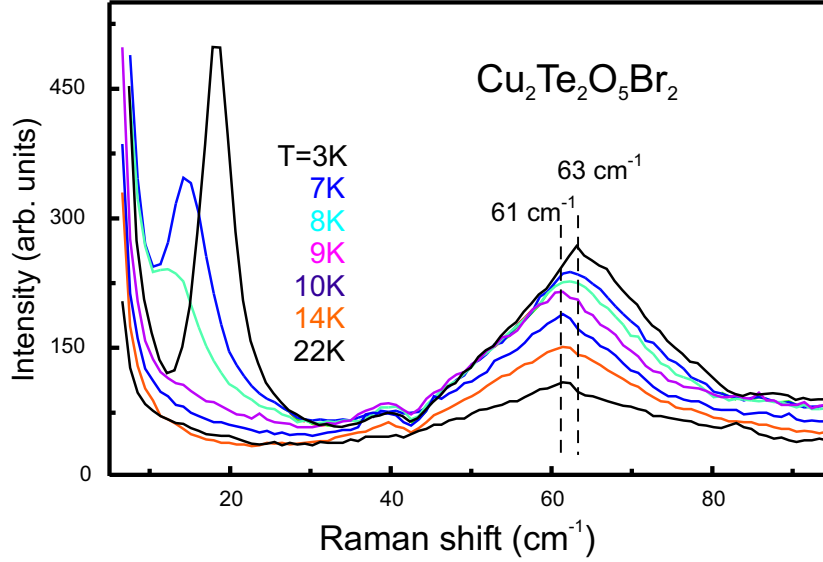


Figure 8.5: Raman scattering spectrum of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ in (cc) polarization parallel to the crystallographic c-axis [132].

8.3 Inelastic light scattering measurements

Fig. 8.5 displays Raman spectra of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ in c-axis polarization as a function of temperature. Phonon modes provide not so much information about spin dynamics. Thus, in the following we will concentrate solely on magnetic excitations observed in the low energy and temperature range. The high-temperature spectra are dominated by a pyramidal-shaped scattering continuum centered at $61\text{ cm}^{-1} = 88\text{ K}$, corresponding to $2J = 86\text{ K}$ previously determined from the magnetic susceptibility [179]. The continuum is attributed to a two-magnon-like scattering process. Its total linewidth and the low energy onset at 40 cm^{-1} both point to an appreciable inter-tetrahedra coupling. For reduced temperatures, $T < 9\text{ K}$, a second maximum with smaller linewidth develops. It shows a soft mode-like behavior and reaches its maximum energy of 18 cm^{-1} at lowest temperatures. This intensity is undoubtedly related to the instability observed in our thermodynamic experiments. In Fig. 8.6 Raman spectra in (xx) and (xy) polarizations are displayed. Here note that the x -axis is perpendicular to the c-axis. In contrast to (cc) polarization only the low-energy sharp signal is observed. It is seen below 9 K . This sharp maximum

has the same intensity in parallel and crossed polarizations despite a strong reduction of phonon modes in crossed polarization. The intensive signal at 40 cm^{-1} should be attributed to phonon mode. Strong temperature dependence of its intensity may be due to the coupling of this mode to the spin degree of freedom. In an antiferromagnetic ordered state one-magnon and two-magnon scattering are possible. However, the observed peculiar lineshape of the continuum as well as its evolution cannot be understood in terms of the conventional Néel ordered state (for comparison see section 3.2). The peak energy of the high-energy continuum softens from 63 to 61 cm^{-1} between 3 K and 9 K . At the same time, the spectral weight of the continuum undergoes a slight shift only in the high frequency side. Above 9 K there is no shift and damping of spectral weight. Rather, the total scattering intensity is simply suppressed, typical for a spin singlet state. Usually, in a long-range ordered state low-energy magnetic excitations are given by a Goldstone mode. However, thermodynamic and light scattering measurements provide evidence for the significance of spin singlet dynamics even for temperatures below T_c . The persistence of spin singlet dynamics into long-range ordered state is typical for magnetic excitations near a quantum critical point as discussed in the section 2.1. Then, a triangle-shaped continuum should be interpreted as the combined results of two-magnon scatterings from both spin singlet and long-range ordered states. In this light, the small shift of the continuum only in the high-energy side suggests that the two-magnon scattering arising from long-range ordering has a large spectral weight around 63 cm^{-1} . Furthermore, the low-energy sharp mode should be attributed to a new mode existing near the quantum critical point. To gain insight into this issue we have done measurements under a magnetic field.

In Fig. 8.7 Raman data for $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ in magnetic fields up to 6 T are displayed. The magnetic field has been applied perpendicular to the light scattering polarization. We observe a shift of the low-energy magnetic mode at $\nu_{long} = 16.3 \text{ cm}^{-1} = 23.4 \text{ K}$ (for $B = 0$) to higher energies as a function of B and the appearance of an additional, magnetic field-induced mode at $\nu_{sing} = 23.2 \text{ cm}^{-1} = 33.2 \text{ K}$ ($B \neq 0$). In the inset of Fig. 8.7 the energies of the respective modes are shown as a function of the magnetic field. While the higher energy mode does not show an appreciable magnetic field dependence (upper open symbols), the lower energy mode shows a nonlinear dependence on the magnetic field (lower full and open symbols). The full line is a fit to the data proportional to the square of the magnetic field. The dashed curve describing the higher energy mode is proportional to the weaker, positive field dependence of the transition temperature as determined by specific heat and magnetic susceptibility measurements [181]. This unusual field dependence rules out

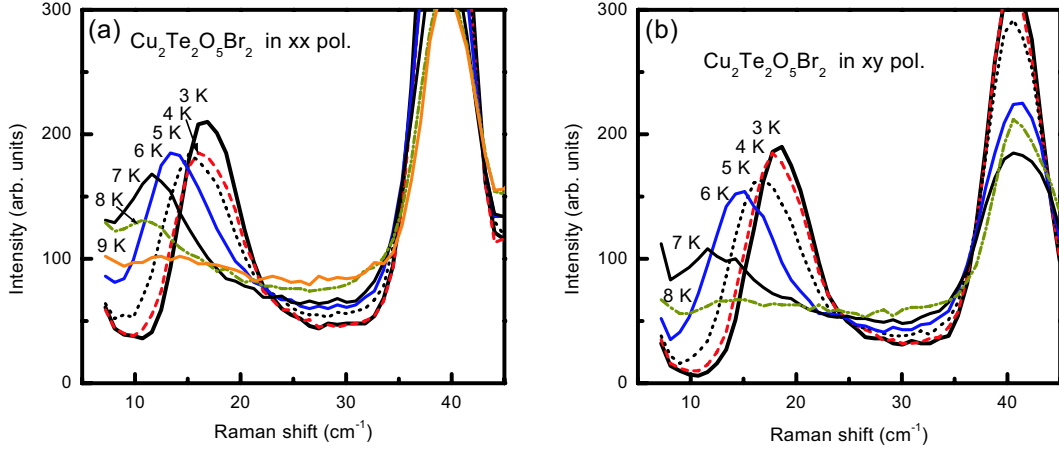


Figure 8.6: Raman scattering spectra of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ in (xx) and (xy) polarizations where the x-axis is perpendicular to the crystallographic c-axis.

one-magnon scattering as a possible origin. No change of the high-energy continuum under external field confirms its origin as two-magnon continuum.

We will now look on the magnetic excitations of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ at $B=0$. Fig. 8.8 shows the representative spectra in (xx) and (xy) polarizations. Here the x and y axis are parallel to one of the crystallographic axis. We observe four signals at 22, 40, 46, and 67 cm^{-1} which do not fit to phonon scattering. In other polarizations (not shown here) more or less the same feature shows up. This selection rule indicates that the spin tetrahedra of the chloride are strongly coupled in all three-dimensional directions. With raising temperature all four signals disappear around 15 K ($< T_N$) and are substituted by a broad two-magnon-like continuum centered around 46 cm^{-1} while quasielastic scattering becomes pronounced, as clearly seen in (xy) polarization. In the bromide the two-magnon-like continuum is already present for temperatures below T_o in contrast to the chloride. This suggests that for the chloride spin singlet dynamics is strongly suppressed in the long-range ordered state compared to the bromide. This is consistent with the mean-field-type of transition observed in the thermodynamic measurements. However, it is not totally frozen-in as indicated by the appearance of quasielastic scattering well below T_N . Spin singlet fluctuations can give rise to fluctuations of the magnetic energy of the system. Possibly, the magnetic structure of long-range ordered state is noncollinear. Next, we will think about an origin of the four signals.

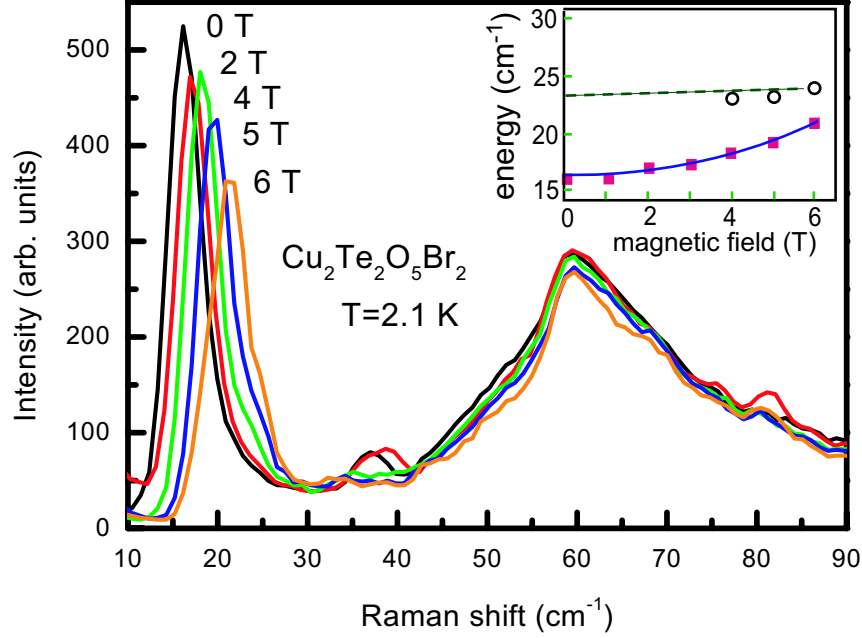


Figure 8.7: Raman spectra of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ in a magnetic field. The insets show a) spectra with higher resolution and b) the shift of the $\nu_{\text{sing}} = 23.2 \text{ cm}^{-1}$ mode (upper open symbols) and the $\nu_{\text{long}} = 16.3 \text{ cm}^{-1}$ mode (lower full and open symbols) as a function of the magnetic field. The dashed line shows the field dependence of the transition temperature [181] and the full line is a fit to the data proportional to the square of the magnetic field. The open (full) symbols show data with high resolution (normal resolution).

The peak position of the high-energy maximum at 67 cm^{-1} softens by 2 cm^{-1} . Its spectral weight shifts to lower energy. This behavior is comparable to the evolution of the continuum in the high frequency side for the bromide. In both systems, the exchange constant has a comparable energy so that the peak position of two-magnon scattering arising from antiferromagnetic ordering should lie in a close energy.¹ This suggests that the high-energy maximum originates

¹In a quasi-one-dimensional system the peak position is given roughly by $2J$. From the peak position of 63 cm^{-1} one obtains $J=45 \text{ K}$ in the bromide. This lies in a good agreement with the value of $J=47 \text{ K}$ estimated by mean field theory [181]. However, for the chloride, the situation is more complicated due to stronger inter-tetrahedra couplings which shift the peak energy to higher energy. Thus, despite a slightly higher peak energy of 67 cm^{-1} the exchange coupling constant is expected to be slightly smaller than that of the bromide.

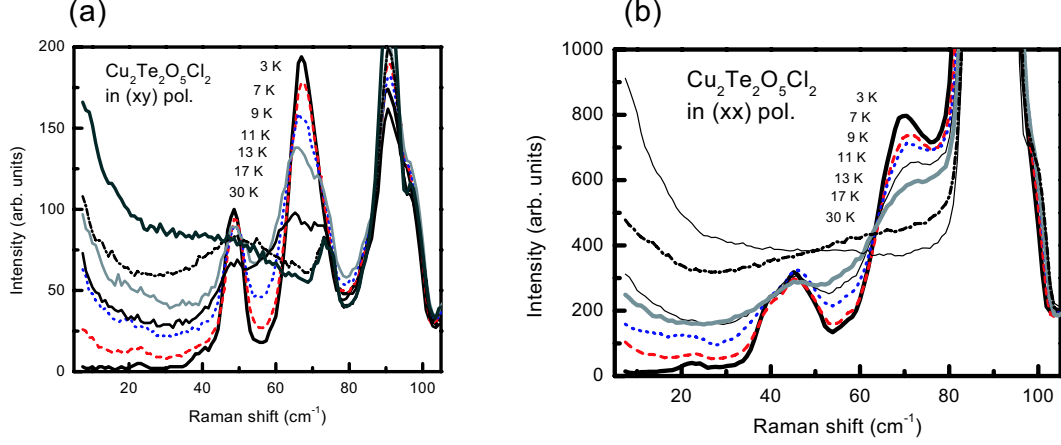


Figure 8.8: Raman scattering spectrum of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ in (xx) and (xy) polarizations. Here note that the x- axis is one of the crystallographic axes.

from the two-magnon scattering in antiferromagnetically ordered states. The other three maxima correspond to the 18 cm^{-1} -mode observed in the bromide. The increased number of this mode may be related to a change of magnetic structure. Later, this issue will be further pursued.

8.4 Mean-field approach to the spin-tetrahedra system

In order to shed light on the understanding of the observed unusual magnetic excitations we will start from isolated spin tetrahedra and then consider the inter-tetrahedra couplings in view of a mean-field approach [181]. This approach is justified because the thermodynamic and light scattering results evidence the significance of spin singlet dynamics even in the long-range ordered state. *A priori* there are two different exchange integrals, J_1 between nearest neighbors and J_2 between next-nearest neighbors. The Hamiltonian for isolated tetrahedra is given by

$$H_t = J_1[(\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_3 + \mathbf{S}_4)] + J_2(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_3 \cdot \mathbf{S}_4). \quad (8.1)$$

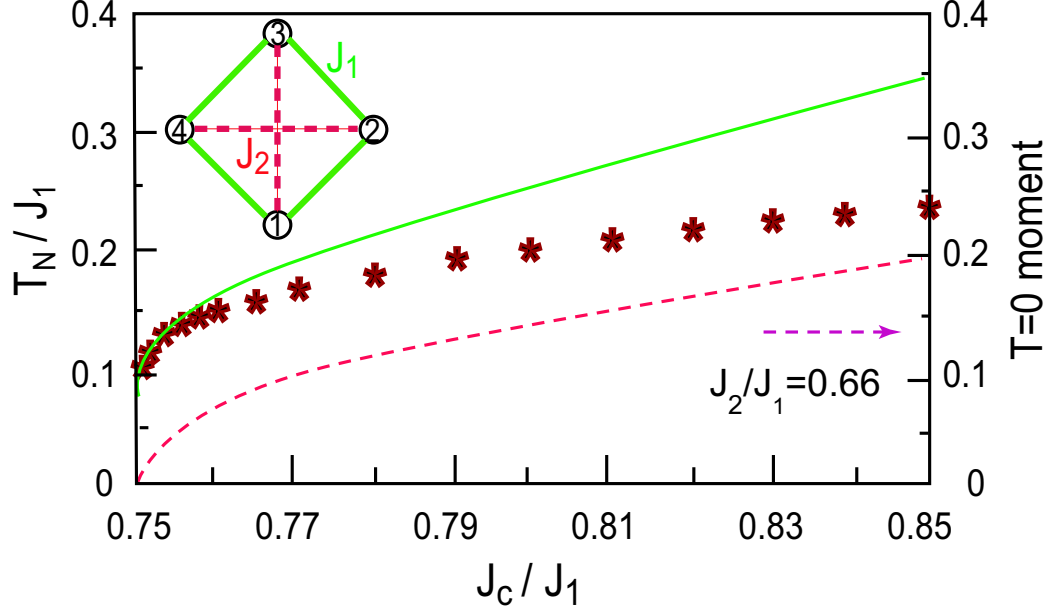


Figure 8.9: Néel-temperature (left scale) and spin tetrahedra mean-field moment (right scale) for $J_2/J_1 = 0.66$. Shown is the analytic approximation to leading order by Eq. (8.9) (solid line) and the numerical solution of the self-consistency equation (8.8) (stars). The dashed line (right scale) is the magnetic moment at zero-temperature Eq. (8.10). Note the logarithmic singularity in T_N for $J_c \rightarrow 0.75J_1$. Inset: Cu tetrahedron with exchange couplings J_1 and J_2 (solid/dashed lines) [181].

This Hamiltonian can be rewritten in terms of $\mathbf{S}_{13(24)} \equiv \mathbf{S}_{1(2)} + \mathbf{S}_{3(4)}$ and $\mathbf{S}_{tot} \equiv \mathbf{S}_{13} + \mathbf{S}_{24}$ as

$$H_t = \frac{J_1}{2}[\mathbf{S}_{tot}^2 - \mathbf{S}_{13}^2 - \mathbf{S}_{24}^2] + \frac{J_2}{2}[\mathbf{S}_{13}^2 - \mathbf{S}_{24}^2 - 3]. \quad (8.2)$$

The eigenstates of the isolated tetrahedra consist of two singlets, three triplets and one quintuplet. We denote with s_{kl} the spin-singlet state of two intra-tetrahedral sites k and l and with t_{kl}^α the respective triplet states, with $\alpha = \pm 1, 0$. For $J_2 < J_1$ the ground state singlet ψ_{s1} and the excited singlet ψ_{s2} are

$$\psi_{s1} = \frac{-1}{\sqrt{3}} \left[t_{12}^0 t_{34}^0 - t_{12}^+ t_{34}^- - t_{12}^- t_{34}^+ \right], \quad \psi_{s2} = s_{12} s_{34} \quad (8.3)$$

with eigenenergies $E_{s1} = -2J_1 + J_2/2$ and $E_{s2} = -3J_2/2 = E_{s1} + \Delta E_{s2}$, with $\Delta E_{s2} = 2J_1 - 2J_2$. The three triplets ψ_{t1}^α , ψ_{t2}^α and ψ_{t3}^α have the (excitation) energies $\Delta E_{t1} = J_1$, $\Delta E_{t2} = \Delta E_{t3} = 2J_1 - J_2$ with respective eigenstates

$$\begin{aligned}\psi_{t1}^0 &= \frac{1}{\sqrt{2}}(t_{12}^+ t_{34}^- - t_{12}^- t_{34}^+), \\ \psi_{t1}^- &= \frac{1}{\sqrt{2}}(t_{12}^0 t_{34}^- - t_{12}^- t_{34}^0), \\ \psi_{t1}^+ &= \frac{1}{\sqrt{2}}(t_{12}^+ t_{34}^0 - t_{12}^0 t_{34}^+), \\ \psi_{t2}^\alpha &= s_{12} t_{34}^\alpha, \quad \psi_{t3}^\alpha = t_{12}^\alpha s_{34}\end{aligned}\tag{8.4}$$

The quintuplet has the energy $\Delta E_q = 3J_1$. To explain long-range magnetic ordering let us introduce the inter-tetrahedra couplings which can be described in a mean-field approach² by :

$$H_{MF} = -J_c M (S_1^z + S_2^z - S_3^z - S_4^z), \quad \text{and} \quad M = \frac{1}{4} \langle S_1^z + S_2^z - S_3^z - S_4^z \rangle \tag{8.5}$$

with M being the staggered magnetization order parameter. J_c is here the sum over all inter-tetrahedra couplings.

The mean-field Hamiltonian H_{MF} couples ψ_{s1} and ψ_{t1}^0 leading to new eigenstates for $H = H_t + H_{MF}$:

$$\begin{aligned}|\varphi\rangle &= \cos \varphi |\psi_{s1}\rangle + \sin \varphi |\psi_{t1}^0\rangle, \\ |\tilde{\varphi}\rangle &= \sin \varphi |\psi_{s1}\rangle - \cos \varphi |\psi_{t1}^0\rangle\end{aligned}\tag{8.6}$$

with $\langle \tilde{\varphi} | \varphi \rangle = 0$ and new energies

$$\Delta E_{\varphi, \tilde{\varphi}} = \frac{J_1}{2} \left[1 \mp \sqrt{1 + 32M^2 J_c^2 / (3J_1^2)} \right] \tag{8.7}$$

with $\tan \varphi = -\Delta E_\varphi \sqrt{6} / (4J_c M)$. $|\varphi\rangle$ is the new ground-state and $|\tilde{\varphi}\rangle$ is the new excited state. When $J_c=0$ we have isolated tetrahedra and $|\tilde{\varphi}\rangle$ would correspond to the excited intra-tetrahedral triplet state $|\psi_{t1}^0\rangle$. For this excitation we should pay a magnetic energy corresponding to the spin gap Δ . For $J_c \neq 0$, $|\tilde{\varphi}\rangle$ evolves continuously from ψ_{t1} as a function of the inter-tetrahedral coupling J_c and becomes soft at the transition-point to the ordered state. In this case, the excitation from the new ground state singlet φ to excited triplet $\tilde{\varphi}$ leads to

²Despite the studied system lies close to quantum critical point the mean field approach will work reasonably because we develop theory from a short-range ordered singlet state.

a finite magnetization, $M \neq 0$. Thus, we identify this to a longitudinal magnon excitation. Here note that in contrast to a longitudinal magnetization, a transverse magnon is massless according to the Goldstone theorem. The molecular field couples also ψ_{t1} with the quintuplet ψ_q , though we neglect this coupling here since we are interested in phases with low transition temperatures T_N for which the high-energy quintuplet does not contribute significantly.

The calculation of the staggered magnetization $M = \text{Tr}[(S_1^z + S_2^z - S_3^z - S_4^z)e^{-\beta H}]/(4Z)$ (Eq. 8.5) leads to the following self-consistency equation,

$$M = \frac{e^{-\beta E_\varphi} - e^{-\beta E_{\tilde{\varphi}}}}{Z} \sqrt{\frac{2}{3}} \frac{\tan \varphi}{1 + \tan^2 \varphi}, \quad (8.8)$$

where $\beta = 1/T$ and Z is the partition function for the coupled tetrahedra system, i.e. $Z = e^{-\beta E_{s1}} + e^{-\beta E_{s2}} + \dots$. For $J_c = J_c^{(qc)} = 3J_1/4$ the magnetization M goes to zero and the system shows a second-order phase transition at T_N .

The transition-temperature T_N can be obtained from Eq. (8.8) by imposing $M = 0$. Assuming that (i) s_2 is the lowest excited state of a tetrahedron and (ii) at small temperatures only the leading order in a $1/T$ expansion is contributing in Eq. (8.8), T_N can be analytically derived:

$$T_N \simeq \Delta E_{s2} \log^{-1} \left(J_c^{(qc)} / (J_c - J_c^{(qc)}) \right). \quad (8.9)$$

T_N shows an inverse-log singularity close to the quantum critical point at $J_c = J_c^{(qc)}$. The critical $J_c^{(qc)} = 3J_1/4$ is independent of J_2 . In Fig. (8.9) we plot T_N as a function of J_c both as obtained in the analytic solution Eq. (8.9) and by solving numerically the self-consistent equation Eq. (8.8). Note that for the region $J_c \sim J_c^{(qc)}$, Eq. (8.9) provides a good approximation for T_N .

The inverse-log dependence of the Néel-temperature implies that T_N is substantial even near the quantum critical point, as illustrated in Fig. (8.9), in contrast to the magnitude of the zero-temperature magnetic moment,

$$M(T=0) = \frac{1}{\sqrt{6}} \sqrt{1 - \left(J_c^{(qc)} / J_c \right)^2}, \quad (8.10)$$

which has a standard mean-field form. For $J_c/J_1 \rightarrow \infty$ the coupling to the quintuplet ψ_q neglected in Eq. (8.10) would contribute and the zero- T moment would take the mean-field value of $1/2$. (compare Fig. 8.9). For $J_2 > J_1$ the tetrahedral ground-state changes to ψ_{s2} and the non-magnetic singlet ψ_{s2} sets therefore the scale for T_N .

An external longitudinal magnetic field does not induce additional couplings in between the different eigenstates but it leads to shifts in the respective

eigenenergies. A transversal magnetic field B_x induces, on the other hand, a coupling in between ψ_{t1}^0 and $\psi_{t1}^\pm$ (see Eq. (8.4)). The mean-field ground state, which breaks rotational invariance, can be written, in lowest order in B_x , as

$$|\varphi, B_x\rangle = \cos \alpha |\varphi\rangle + \frac{\sin \alpha}{\sqrt{2}} [|\psi_{t1}^+\rangle + |\psi_{t1}^-\rangle], \quad (8.11)$$

with $\tan \alpha = B_x \sin \varphi / (J_1 - \Delta E_\varphi)$. In lowest order in B_x , the ground-state energy, $\Delta E_{\varphi, B_x} = E_{\varphi, B_x} - E_\varphi$,

$$\Delta E_{\varphi, B_x} = -B_x^2 \sin^2 \varphi / (J_1 - \Delta E_\varphi), \quad (8.12)$$

decreases quadratically with B_x .

This result has an interesting consequence for the transition temperature. The energy of the excited singlet E_{s2} is not affected by B_x , its relative energy to the ground state ΔE_{s2} increases consequently with B_x (compare Eq. (8.7)). Eq. (8.9) tells us then that the Néel temperature also increases with B_x . Note that there is a smaller decreasing contribution in B_x to the Néel temperature coming from the log-term in Eq. (8.9) due to an enhancement of the effective J_1 . An order of magnitude estimate of the effect for $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ and $B_x = 13 \text{ T}$ yields $\Delta T_N \approx 0.8 \text{ K} = 0.56 \text{ cm}^{-1}$ which agrees well with the experimentally observed raise of $\sim 1 \text{ K}$ reported already in Ref. [132].

8.5 Longitudinal magnon and excited singlet in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$

In the following we shall address the origin of the sharp maximum near 18 cm^{-1} observed in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$. Under an external field this signal is splitted into two modes at $\nu_{long} = 16.3 \text{ cm}^{-1}$ and at $\nu_{sing} = 23.2 \text{ cm}^{-1}$. We interpret the field-induced higher energy mode at $\nu_{sing} = 23.2 \text{ cm}^{-1}$ as a transition to the second singlet $\psi_{s2} = s_{12}s_{34}$. Since this system is noncentrosymmetric, there is a nonzero Dzyaloshinski-Moriya (DM) interaction. Assuming a DM contribution to the Raman operator, i.e. $H_R^{(DM)} \sim \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ we find a non-zero Raman matrix-element

$$\langle \psi_{s2} | H_R^{(DM)} | \varphi, B^x \rangle \sim \sin \alpha \sim B^x M.$$

The 23.2 cm^{-1} -mode would therefore be observable only in the ordered phase and in an external magnetic field, consistent with experiment. Having identified this mode with the transition to ψ_{s2} we have then that

$$\Delta E_{s2} = 2J_1 - 2J_2 = \nu_{sing} \sim 33 \text{ K}. \quad (8.13)$$

Considering Eq.(8.13) and the magnetic susceptibility [179, 132] for $T > T_N$ we find a good fit with $J_1 \sim 47$ K and $J_2 \sim 31$ K which yields $J_2/J_1 \sim 0.66$. The experimental transition temperature [132] of $T_N^{(\text{Br})} = 11.4$ K for $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ implies via the self-consistency condition (8.8) that $J_c \sim 0.85J_1$.

Moreover, recalling Eqs. (8.9) and (8.12), for $B_x = 6$ T the energy ΔE_{s_2} of the excited singlet shifts by about 0.12 cm^{-1} . This increase is too small to be resolved by Raman spectroscopy.

Next, we turn to the sharp mode at $\nu_{\text{long}} = 16.3 \text{ cm}^{-1}$. The mean-field Hamiltonian (8.5) leads to a $\mathbf{Q} = \mathbf{0}$ ordering for $J_c > 0$ and the soft longitudinal magnon $|\tilde{\varphi}\rangle$ should be directly observable with Raman scattering measurements. For $J_c < 0$ ordering with $\mathbf{Q} = \pi$ would occur and additional backfolding to the zone-center via residual lattice distortions would be necessary. The matrix-element $\langle \tilde{\varphi} | H_R | \varphi \rangle$ of the Raman-operator $H_R \sim \mathbf{S}_i \cdot \mathbf{S}_j$ ($i, j = 1, \dots, 4$) is $\sim \cos \varphi \sin \varphi$. It vanishes in the decoupled-tetrahedra limit $J_c = 0$, $\varphi = 0$ and the transition should be observable only in the ordered phase. As Fig. 8.5 shows the sharp mode at $\nu_{\text{long}} = 16.3 \text{ cm}^{-1} = 23.4$ K becomes soft at the ordering temperature. In addition, it is observable only in the condensed phase and its energy increases quadratically (compare Eq. (8.15)) with the field. Therefore, we interpret it in terms of a longitudinal magnon.

The energy of this mode is strongly suppressed below its mean-field energy $E_{\tilde{\varphi}} - E_{\varphi} = 54$ K by dispersion. We can estimate the magnitude of this suppression by comparison with the results of a bond-operator-theory for a coupled dimer system [182, 183] (alternatively one may use a generalized RPA-approach [184]). The effective dimer-states are $(\psi_{s1}, \psi_{t1}^{\alpha})$. The gap of the longitudinal magnon has the form [182]

$$\Delta_{\text{long}} = \Delta_{\text{max}} \sqrt{1 - \left(J_c^{(qc)} / J_c \right)^2}. \quad (8.14)$$

For $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ we have $J_c = 0.85J_1$ ($(J_c^{(qc)} / J_c)^2 = 0.78$) and $\Delta_{\text{long}} \approx 0.47\Delta_{\text{max}}$. The energy scale Δ_{max} occurring in Eq. (8.14) is set by the longitudinal magnon-gap in the classical Néel ordered state, i.e. in the limit of strong inter-dimer (tetrahedra) couplings, where it has the value $\Delta_{\text{max}} \rightarrow J_c$. With $J_c \approx 0.85J_1$ and $J_1 \approx 47$ K we then find for $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ that $\Delta_{\text{long}} \approx 19$ K, which is qualitatively in agreement with the experimental value $\Delta_{\text{long}}^{(\text{exp})} = \nu_{\text{long}} = 23.4$ K.

For the longitudinal magnon, a calculation analogous to Eq. (8.12) leads to

$$\Delta E_{\tilde{\varphi}, B_x} = -B_x^2 \cos^2 \varphi / (J_1 - \Delta E_{\tilde{\varphi}}). \quad (8.15)$$

The resulting change $\Delta E_{\tilde{\varphi}, B_x} = E_{\tilde{\varphi}, B_x} - E_{\tilde{\varphi}}$ in the longitudinal-magnon energy is positive, as $J_1 - \Delta E_{\tilde{\varphi}} < 0$, and substantially larger than the shift for the ground-state $\Delta E_{\varphi, B_x}$ (and correspondingly for E_{s2}) since $\cos^2 \varphi \gg \sin^2 \varphi$. This trend is qualitatively in agreement with the Raman data presented in Fig. 8.7.

8.6 Longitudinal magnon in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$

Motivated by the success of interpreting the mode at 16.3 cm^{-1} in terms of a longitudinal magnon, we assign the three modes at 22, 40, and 46 cm^{-1} observed in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ to longitudinal magnons. According to Eq. (8.14), longitudinal magnon will harden in the chloride due to a larger inter-dimer coupling. This is consistent with experimental observations. Furthermore, the presence of the three longitudinal magnons can be explained by assuming other ordering patterns, $\langle S_1^z + S_2^z + S_3^z + S_4^z \rangle$ [185]. To substantiate this scenario, a neutron diffraction study should be performed. In addition, to determine quantitatively the coupling parameters for $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$, we need information about the energy of the second singlet as in $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$. Raman scattering measurements under an external field will be very helpful in resolving this problem. Finally, let us briefly mention why the longitudinal magnon in the studied system is sharp in contrast to weakly coupled chain system discussed in the section 2.1. One thinkable reason is that in $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ spin singlet dynamics is pronounced due to zero-dimensional tetrahedra spin topology compared to weakly coupled chain system.

8.7 Conclusion

We have presented a comprehensive set of theory and experimental data indicating that the isostructural spin-tetrahedral compounds $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ lie quite close to a quantum critical point approaching from the antiferromagnetic ordered phase. Whereas thermodynamic data provide evidence for a conventional 3D magnetic ordering in the chloride, light scattering measurements show exotic low-energy excitations as well as spin singlet dynamics at elevated temperatures. In contrast, both thermodynamic and light scattering data evidence strong spin singlet fluctuations even below the magnetic ordering temperature, leading to a very unusual transition. Our study suggests that this feature is generic near a quantum critical point and uncovers that the excited tetrahedral-singlet determines an inverse-log dependence of the ordering temperature T_N on the coupling parameters. Most importantly, a low-energy

longitudinal magnon has been observed. This new mode, missing in a conventional magnet, is a generic feature of a low-dimensional spin liquid system which undergoes a quantum phase transition into long-range ordering state.

Chapter 9

Conclusions

In this work diverse results obtained from a number of low-dimensional quantum spin systems using Raman spectroscopy have been presented. The main motivation of this thesis is to *hunt for* new types of elementary excitations which may be present in low-dimensional spin systems with exotic spin topology. Thus, instead of focusing on a few compounds with various experimental methods, a dozen of possible candidates are investigated using only one method. The studied systems are the double spin chain system LiCu_2O_2 , the three-dimensional coupled spin dimer systems ACuCl_3 ($A=\text{Tl}, \text{K}$), the two-dimensional Heisenberg antiferromagnetic system $\text{K}_2\text{V}_3\text{O}_8$, the quasi two-dimensional orthogonal dimer system $\text{SrCu}(\text{BO}_3)_2$ and the spin tetrahedra system $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ ($\text{X}=\text{Br}, \text{Cl}$).

Low-dimensional spin systems can be characterized by their spin liquid ground state, exotic magnetic excitations, and substantial spin-phonon coupling. The high sensitivity to spin and lattice dynamics as well as to their interplay with an unprecedented frequency resolution makes Raman spectroscopy an experimental choice in studying such systems. Complementary to neutron scattering, magnetic light scattering can probe the singlet sector of magnetic excitations as a spin conserving exchange process. In a Raman scattering process, higher-magnon scatterings have comparably strong scattering intensity. Thus, within a short accumulation time (*less than one hour*), high-resolution spectra are obtainable so that a detailed study of magnetic excitations is possible as a function of temperature.

In the following we will summarize the main results which lead to a deeper understanding of low-dimensional spin systems.

Observation of the coexistence of long-range order and dimerized state in the double spin chain system LiCu_2O_2

LiCu_2O_2 is a spin-dimer system which can be described as either frustrated spin chain or asymmetric zigzag spin ladder. The LiCu_2O_2 phase is intrinsically contaminated by nonmagnetic LiCuO -impurity phase in addition to magnetic one. Raman spectra show the broad two-magnon (2M) continuum with a peak at 100 cm^{-1} and the narrow and weak continuum with a peak at 110 cm^{-1} below $T_N \sim 9 \text{ K}$ and 200 K , respectively. The former is ascribed to 2M scattering from the Néel ordered state while the latter arises from 2M scattering from the dimerized state with spin gap $\Delta \sim 73 \text{ K}$. They are superimposed by each other, indicating that a *coherent* coexistence of long-range and short-range ordered state appears to be a generic feature of low-dimensional spin-gapped system with magnetic/nonmagnetic impurities.

Observation of three-magnon scattering and dynamic spin-phonon coupling in the three-dimensional coupled spin dimer systems ACuCl_3 ($\text{A}=\text{Tl}, \text{K}$)

The copper halides TlCuCl_3 and KCuCl_3 are the three-dimensional coupled spin-dimer systems showing a field-induced Bose-Einstein condensation of excited triplets. Strong interdimer couplings lead to a large-bandwidth of triplet excitations compared to a reduced spin gap. For both compounds we observed an anomalous temperature dependence of the two-magnon continuum: upon cooling the spin gap decreases while spectral weight and peak energy shift to lower energy. These effects are interpreted in terms of dynamic spin-phonon coupling. This leads to a phonon-modulated spin gap and exchange constant. In addition, interactions between thermally activated triplets should be also taken into account. Most significantly, three-magnon scattering has been observed in KCuCl_3 arising from light scattering from a thermally activated triplet branch to a higher lying two-magnon continuum. Our result suggests that this process is a generic feature of low-dimensional spin gap systems.

Two-magnon scattering in the two-dimensional Heisenberg anti-ferromagnetic system $\text{K}_2\text{V}_3\text{O}_8$

$\text{K}_2\text{V}_3\text{O}_8$ is a further example of two-dimensional Heisenberg spin systems in inorganic oxides. Separation of magnetic ($S=1/2$) $\text{V}^{4+}\text{-O}_5$ pyramids by

nonmagnetic ($S=0$) V^{5+} - O_4 tetrahedra leads to a small exchange constant of $J=12.8$ K. Thus, the nature of magnetic excitations and the role of quantum fluctuations can be studied over temperatures comparable to the exchange coupling constant in contrast to the undoped cuprates with $J \sim 1500$ K. Light scattering results show that zone boundary magnons persist up to $\sim 5J$ ($15T_N$). The damping and softening starts around J . This observation provides experimental evidence that in the $S=1/2$ 2D HAF system an appropriate energy scale for the magnetic excitations is the exchange constant. Anomalies seen in the lineshape and selection rule suggest the presence of other types of excitations possibly arising from the electronic or/and orbital sector. This may be related to a local symmetry breaking of the lattice.

Observation of inter-plane soft mode and a coupling of spin to soft mode in the quasi two-dimensional orthogonal dimer system $SrCu(BO_3)_2$

$SrCu_2(BO_3)_2$ is close to a realization of the two-dimensional Shastry-Sutherland model. In first approximation, its ground state and spin gap are reasonably understood within the pure Shastry-Sutherland model. The detailed thermodynamic, X-ray diffraction, neutron scattering, and high field NMR measurements show up a deviation, indicating the significance of interlayer lattice distortions. Light scattering measurements show the presence of a pronounced interlayer soft mode corresponding to in-phase motions of almost all ions along the interlayer direction. A displacement of atomic motions along the z -direction leads to a small modulation of the intra-layer and the inter-layer interactions as well as the appearance of additional symmetric and antisymmetric anisotropic interactions. For temperatures below the spin gap such a modulation results in the softening of the soft mode by 3%, indicating the strong coupling of spin to the soft optic phonon by exchange modulation. Our results show that in a realistic model for $SrCu_2(BO_3)_2$ spin-phonon interactions, DM interactions and interlayer lattice dynamics should be taken into account to understand a variety of physical properties like the spin gap, the proximity to a quantum critical point and anomalous behavior of the spectroscopic data.

Observation of longitudinal magnons in the spin tetrahedra system $Cu_2Te_2O_5X_2$ ($X=Br, Cl$)

The spin system $Cu_2Te_2O_5X_2$ ($X=Br, Cl$) which contains tetrahedral clus-

ters of Cu^{2+} with $S=1/2$ is a realization of three-dimensional coupled spin tetrahedra system. Thermodynamic data give evidence for 3D magnetic ordering at $T_N=18.2$ K in the chloride while unconventional transition at $T_o=11.3$ K in the bromide. Anomalous behaviors of the latter system indicate the dominance of spin singlet dynamics. Consistently, light scattering results show a dominant contribution to two-magnon-like continuum from spin singlet correlations even for temperatures below T_o . In contrast, such a contribution in the chloride is suppressed for temperatures below T_N . Noticeably enough, for both systems low-energy excitations are observed only below the ordering temperature. Based on a mean field theory, we identify low-energy excitations as longitudinal magnons corresponding to the oscillation of a local magnetic moment. The observability of longitudinal magnons is related to enhanced singlet dynamics in zero-dimensional spin tetrahedra near quantum criticality.

Appendix A

Normal modes in $\text{SrCu}_2(\text{BO}_3)_2$

Here we list some normal coordinates which are relevant for the analysis of the structural and magnetic properties of $\text{SrCu}_2(\text{BO}_3)_2$.

- low temperature phase

4i - positions (Cu, B and O1 ions)

A_1 - irreducible representation

$$Q_i^{IA_1} = \frac{1}{2\sqrt{2}}(-U_{1xy} + U_{2\bar{x}y} + U_{3xy} - U_{4\bar{x}y})$$

$$Q_i^{IIA_1} = \frac{1}{2}(U_{1z} - U_{2z} + U_{3z} - U_{4z})$$

A_2 - irreducible representation

$$Q_i^{A_2} = \frac{1}{2\sqrt{2}}(-U_{1\bar{x}y} - U_{2xy} + U_{3\bar{x}y} + U_{4xy})$$

B_1 - irreducible representation

$$Q_i^{B_1} = \frac{1}{2\sqrt{2}}(-U_{1\bar{x}y} + U_{2xy} + U_{3\bar{x}y} - U_{4xy})$$

B_2 - irreducible representation.

$$Q_i^{IB_2} = \frac{1}{2\sqrt{2}}(-U_{1xy} - U_{2\bar{x}y} + U_{3xy} + U_{4\bar{x}y});$$

$$Q_i^{IIB_2} = \frac{1}{2}(U_{1z} + U_{2z} + U_{3z} + U_{4z}).$$

E - irreducible representation;

$$Q_{1,i}^{IE} = \frac{1}{2}(U_{1x} + U_{2x} + U_{3x} + U_{4x});$$

$$Q_{2,i}^{IE} = -\frac{1}{2}(U_{1y} + U_{2y} + U_{3y} + U_{4y})$$

$$Q_{1,i}^{IIE} = \frac{1}{2}(U_{1y} - U_{2y} + U_{3y} - U_{4y})$$

$$Q_{2,i}^{IIE} = \frac{1}{2}(-U_{1x} + U_{2x} - U_{3x} + U_{4x})$$

$$Q_{1,i}^{IIIE} = \frac{1}{2}(U_{1z} - U_{2z} - U_{3z} + U_{4z})$$

$$Q_{2,i}^{IIIE} = \frac{1}{2}(-U_{1z} - U_{2z} + U_{3z} + U_{4z})$$

A_1 - irreducible representation for 8j - positions ;

$$Q_j^{IA_1} = \frac{1}{4}(U_{1xy} + U_{2xy} - U_{3\bar{x}y} - U_{4\bar{x}y} - U_{5xy} + U_{6xy} + U_{7\bar{x}y} + U_{8\bar{x}y})$$

$$Q_j^{IIA_1} = \frac{1}{4}(-U_{1\bar{x}y} + U_{2\bar{x}y} - U_{3xy} + U_{4xy} + U_{5\bar{x}y} - U_{6\bar{x}y} + U_{7xy} - U_{8xy})$$

$$Q_j^{IIIA_1} = \frac{1}{2\sqrt{2}}(U_{1z} + U_{2z} - U_{3z} - U_{4z} + U_{5z} + U_{6z} - U_{7z} - U_{8z})$$

• high temperature phase

B_{1u} - irreducible representation for 4h - positions ;

$$Q_h^{B_{1u}} = \frac{1}{2}(U_{1z} - U_{2z} + U_{3z} - U_{4z}) = Q_i^{IIA_1}$$

E_g - irreducible representation for 4h- positions ;

$$Q_{1,h}^{E_g} = \frac{1}{2}(U_{1z} - U_{2z} - U_{3z} + U_{4z}) = Q_{1,i}^{IIIE}$$

$$Q_{2,h}^{E_g} = \frac{1}{2}(-U_{1z} - U_{2z} + U_{3z} + U_{4z}) = Q_{2,i}^{IIIE}$$

E_u -irreducible representation for 4h- positions ;

$$Q_{1,h}^{IE_u} = \frac{1}{2}(U_{1x} + U_{2x} + U_{3x} + U_{4x}) = Q_{1,i}^{IE}$$

$$Q_{2,h}^{IE_u} = -\frac{1}{2}(U_{1y} + U_{2y} + U_{3y} + U_{4y}) = Q_{2,i}^{IE}$$

$$Q_{1,h}^{IIIE_u} = \frac{1}{2}(U_{1y} - U_{2y} + U_{3y} - U_{4y}) = Q_{1,i}^{IIIE}$$

$$Q_{2,h}^{IIIE_u} = \frac{1}{2}(-U_{1x} + U_{2x} - U_{3x} + U_{4x}) = Q_{2,i}^{IIIE}$$

B_{1u} - irreducible representation for 8k - positions ;

$$Q_k^{B_{1u}} = \frac{1}{2\sqrt{2}}(U_{1z} + U_{2z} - U_{3z} - U_{4z} + U_{5z} + U_{6z} - U_{7z} - U_{8z})$$

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Zusammenfassung

Im Rahmen der vorliegenden Arbeit wurden Raman-Spektroskopie-Untersuchungen an verschiedenen niedrigdimensionalen Quanten-Spin-Systemen durchgeführt. Hauptmotivation für diese Untersuchungen ist dabei die Suche nach ganz neuen Elementaranregungen, die in niedrigdimensionalen Spinsystemen mit exotischer Spintopologie auftreten.

Die dabei untersuchten Systeme sind zum einen durch die Ausbildung von Spin-Dimeren gekennzeichnet, die wie in ACuCl_3 ($A=\text{Tl}, \text{K}$), $\text{SrCu}(\text{BO}_3)_2$ oder LiCu_2O_2 durch spezielle Topologien hervorgerufen werden. Zum anderen wurden die Verbindungen $\text{K}_2\text{V}_3\text{O}_8$ und $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ ($X=\text{Br}, \text{Cl}$) erforscht, in denen ein langreichweitig geordneter Zustand auftritt, der durch starke Quantenfluktuationen charakterisiert ist. Für die Untersuchungen solcher Systeme eignet sich die Raman-Spektroskopie als experimentelle Methode in ganz besonderer Weise, da sie nicht nur Phononen sondern zudem magnetische Anregungen durch den Austausch-Streumechanismus zu detektieren vermag. Insbesondere magnetische Ramanstreuung liefert wesentliche Informationen über die Austausch-Kopplungskonstante, die Spinlücke, und Triplett-Triplett Wechselwirkungen.

Im Folgenden sollen die wesentlichen Resultate zusammengefasst werden, die zu einem eingehenderen Verständnis niedrigdimensionaler Spinsysteme führen.

Bei LiCu_2O_2 handelt es sich um eine frustrierte Spin-Kette. Dabei liegt neben der LiCu_2O_2 -Phase intrinsisch eine LiCuO -Fremdphase vor. Die Raman-spektren zeigen ein breites Zwei-Magnonen-Kontinuum mit einem Peak bei 100 cm^{-1} und ein weiteres schwaches Kontinuum mit einem Peak bei 110 cm^{-1} unterhalb $T_N \sim 9\text{ K}$, bzw. 200 K . Hier wird der erste Peak der Zwei-Magnon-Streuung in der dreidimensional geordneten Phase zugeschrieben, wohingegen der zweite auf zwei-Magnon-Streuung dem dimerisierten Zustand zurückgeführt werden kann, der durch ein Spingap von $\Delta \sim 73\text{ K}$ gekennzeichnet ist. Die Überlagerung beider Kontinua deutet darauf hin, dass eine *kohärente* Koexistenz von langreichweitiger Ordnung und Dimerisation ein generisches Merkmal niedrigdimensionaler Systeme mit nicht-magnetischen Verunreini-

gungen und Spin-Anregungslücke ist.

Die Kupfer-Halogenide TiCuCl_3 und KCuCl_3 sind dreidimensional gekoppelte Spin-Dimer-Systeme, die eine feldinduzierte Bose-Einstein-Kondensation der angeregten Triplet-Zustände aufweist. Die starke Kopplung zwischen einzelnen Dimeren äussert sich in einer grossen Bandbreite der Triplet-Anregungen im Vergleich zum reduzierten Spingap. In beiden Verbindungen zeigen die Raman-Spektren eine anomale Temperaturabhängigkeit des Zwei-Magnon Kontinuums: Beim Abkühlen verkleinert sich das Spingap, während das spektrale Gewicht und die Peakenergie zu niedrigeren Energien verschoben werden. Diese Effekte lassen sich durch *dynamische* Spin-Phonon-Kopplung interpretieren, die sowohl zu einem phononenmodulierten Spingap sowie einer phononenmodulierten Austauschkonstante führt. Darüber hinaus konnte in KCuCl_3 Drei-Magnonen-Streuung nachgewiesen werden. Dabei handelt es sich um Lichtstreuung aus dem thermisch angeregten Triplet-Zweig in das energetisch höher liegende Zwei-Magnon-Kontinuum. Dieses Resultat legt nahe, dass ein solcher Prozess ein generisches Merkmal niedrigdimensionaler Spinsysteme ist.

Mit $\text{SrCu}(\text{BO}_3)_2$ steht ein Kristallsystem zur experimentellen Untersuchung des Shastry-Sutherland-Modells zur Verfügung: Sein Grundzustand sowie sein Spingap kann in recht guter Übereinstimmung des reinen Shastry-Sutherland-Modells verstanden werden. Allerdings zeigen detaillierte thermodynamische Studien, Neutronen- und Röntgenstreuexperimente, sowie NMR-Studien kleine Abweichungen vom Modelverhalten, die die Bedeutung von Zwischenebenen-Gitterverzerrungen unterstreichen. Mit Raman-Lichtstreuung wurde eine ausgeprägte weiche Phononenmode gefunden, die zu einer Schwingung in Phase beinahe sämtlicher Ionen senkrecht zu den Ebenen korrespondiert. Die Auslenkung der atomaren Positionen längs der z-Achse resultiert in einer Modulation der Intra- sowie Zwischenebenkopplung sowie im Auftreten zusätzlicher symmetrischer und asymmetrischer anisotroper Wechselwirkungen. Für Temperaturen unterhalb des Spingaps führt eine solche Modulation zu einem Aufweichen der Phononenmoden um 3% und belegt eine Kopplung der Spins an weiche optische Phononen durch Austauschmodulation. Die Raman-Experimente zeigen, dass in einem realistischeren Modell, das $\text{SrCu}(\text{BO}_3)_2$ beschreiben soll, die Spin-Phonon-Kopplung, die Dzyaloshinsky-Moriya-Wechselwirkung und die Zwischenebenen-Gitterdynamik berücksichtigt werden müssen.

$\text{K}_2\text{V}_3\text{O}_8$ stellt ein Beispiel für ein zweidimensionales Heisenberg-Spinsystem mit einer antiferromagnetischen Austauschkonstanten $J = 12.8 \text{ K}$ dar. Durch die nur schwache magnetische Wechselwirkung können die Eigenschaften magnetischer Anregungen und der Einfluss von Quantenfluktuationen auf einer

leicht zugänglichen Temperaturskala untersucht werden. Die Lichtstreuung offenbart hier, dass Magnonen am Rand der Brillouin-Zone bis zu sehr hohen Temperaturen $\sim 5J$ ($\sim 15T_N$) existent sind. Sowohl die Dämpfung wie auch das Weichwerden beginnt in etwa bei J . Diese Beobachtung liefert die experimentelle Evidenz, dass in zweidimensionalen $S = 1/2$ -Heisenberg-Antiferromagneten durch die Austausch-Konstante J eine passende Energieskala für magnetische Anregungen gegeben ist. Darüber hinaus deuten Anomalien, die in der Linienform und den Auswahlregeln beobachtet werden, das Auftreten anderer Anregungstypen hin. Diese müssen vermutlich elektronischen oder orbitalen Freiheitsgraden zugeschrieben werden und könnten mit einer lokalen Symmetrie-Brechung verbunden sein.

Mit $\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2$ ($\text{X} = \text{Br}, \text{Cl}$) ist ein System dreidimensional gekoppelter Spin-Tetraeder realisiert, dessen thermodynamische Eigenschaften einem geordneten Antiferromagneten unterhalb $T_N = 18.2 \text{ K}$ für $\text{X} = \text{Cl}$, bzw. $T_o = 11.3 \text{ K}$ für $\text{X} = \text{Br}$ entsprechen. Anomalien des Letzteren zeigen die dominante Rolle der Spin-Singulett-Dynamik. In Übereinstimmung damit zeigen die Raman-Spektren einen dominanten Beitrag zum Zwei-Magnonen-Kontinuum, der durch Singulett-Korrelationen sogar unterhalb T_o ausgeprägt ist. Im Gegensatz dazu wird ein solcher Beitrag im Falle des Chlorids für Temperaturen unterhalb T_N unterdrückt. Es ist bemerkenswert, dass in beiden Verbindungen niederenergetische Anregungen ausschliesslich unterhalb der Ordnungstemperatur auftreten. Diese können ausgehend von einem Mean-Feld-Modell als longitudinale Magnonen identifiziert werden, das heisst Oszillationen des lokalen magnetischen Momentes. Die Beobachtung dieser longitudinalen Magnonen wird durch eine verstärkte Singulett-Dynamik der nulldimensionalen Spintetraeder nahe einem quantenkritischen Punkt ermöglicht.

List of Publications

- chapter 4

1. "Evidence for the coexistence of dimerization and long-range magnetic ordering in the double chain spin system LiCu_2O_2 : an inelastic light scattering study", **K.-Y. Choi**, S. Zvyagin, G. Cao, and P. Lemmens, Phys. Rev. B **69**, 104421 (2004).

- chapter 6

1. "Spin dynamics of the spin dimer system TlCuCl_3 probed by Raman spectroscopy", **K.-Y. Choi**, G. Güntherodt, A. Oosawa, H. Tanaka, and P. Lemmens, Phys. Rev. B **68**, 174412 (2003).

2. "Three-magnon light scattering observed in the coupled spin dimer system KCuCl_3 ", **K.-Y. Choi**, A. Oosawa, H. Tanaka, and P. Lemmens, submitted to Phys. Rev. B (2004).

- chapter 7

1. "Strong anharmonicity and spin-phonon coupling in the quasi-two-dimensional quantum spin system $\text{Sr}_{1-x}\text{Ba}_x\text{Cu}_2(\text{BO}_3)_2$ ", **K.-Y. Choi**, Yu. G. Pashkevich, K. V. Lamonova, H. Kageyama, Y. Ueda, and P. Lemmens, Phys. Rev. B **68**, 104418 (2003).

- chapter 8

1. "Low-energy Singlets in the Excitation Spectrum of the Spin Tetrahedra System $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ ", P. Lemmens, **K.-Y. Choi**, E. E. Kaul, C. Geibel, K. Becker, W. Brenig, R. Valenti, C. Gros, M. Johnsson, P. Millet, and F. Mila,

Phys. Rev. Lett. **87** 227201 (2001).

2. "Low-energy Singlets in the Excitation Spectrum of the Spin Tetrahedra System $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$ ", P. Lemmens, **K.-Y. Choi**, A. Ionescu, J. Pommer, G. Güntherodt, R. Valenti, C. Gros, W. Brenig, M. Johnsson, P. Millet, and F. Mila, Journ. Phys. Chem. Solids 63/6-8, 1115-1117 (2002).

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• Other activities

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