Quantum Spin Systems: From Spin Gaps to Pseudo Gaps

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Summary: Many low dimensional spin systems with a dimerized or ladder-like antiferromagnetic exchange coupling have a gapped excitation spectrum with magnetic bound states within the spin gap. For spin ladders with an even number of legs the existence of spin gaps and within the t-J model a tendency toward superconductivity with d-wave symmetry is predicted. In the following we will characterize the spin excitation spectra of different low dimensional spin systems taking into account strong spin phonon interaction (CuGeO\(_3\)), charge ordering (NaV\(_2\)O\(_5\)) and doping on chains and ladders (Sr\(_{14-x}\)Ca\(_x\)Cu\(_{24}\)O\(_{41}\)). The spectroscopic characterization of the model systems mentioned above has been performed using magnetic inelastic light scattering originating from a spin conserving exchange scattering mechanism. This is also bound to yield more insight into the interrelation between these spin gap excitations and the origin of the pseudo gap in high temperature superconductors.

1 Introduction

There is a general consensus that part of the unusual physics of doped two-dimensional spin systems, i.e. the observation of pseudo gaps and high temperature superconductivity, can be mapped onto one dimension. As the pseudo gaps are evident not only in transport and thermodynamic measurements but also in NMR spectroscopy they certainly involve spin degrees of freedom. It was predicted that the binding of mobile holes in spin ladders can lead either to a superconducting or a charge-ordered ground state. The observation of superconductivity in the spin ladder/chain compound Sr\(_{14-x}\)Ca\(_x\)Cu\(_{24}\)O\(_{41}\) and the discussion of a phase separation into 1D spin and charge stripes in high temperature superconductors (HTSC) and related compounds encouraged this assumption\(^3\). However, since for Sr\(_{14-x}\)Ca\(_x\)Cu\(_{24}\)O\(_{41}\) there is some evidence of a crossover toward a two-dimensional system\(^4\) and a possible vanishing of the spin gap under pressure\(^5\) it is not clear whether two-leg or the recently studied

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three-leg ladders provide useful analogs to HTSC. Therefore, an investigation of the excitation spectrum of low dimensional spin systems, in particular in compounds with a spin gap is important and may shed some light on the similarities and differences between both classes of materials.

2 Structural Elements of Low Dimensional Spin Systems

In the systems discussed here the low energy excitations are mainly due to the spin degrees of freedom. The magnetic properties may often be described by the Heisenberg exchange spin Hamiltonian. If, in addition, the exchange is restricted to low dimensions then chains, spin ladders, and further systems with a more complex exchange pattern are realized.

Two building principles are used to reduce the superexchange of a 3d ion-oxygen configuration to less than three dimensions. These are on the one hand an enlarged distance or missing bridging oxygen between two 3d ion-sites or on the other hand a superexchange path with an angle close to 90°. Due to the Kanamori-Goodenough rule (vanishing superexchange via perpendicular oxygen O2p-orbitals) a non collinear exchange path leads to a magnetic insulation of, e.g. neighboring CuO chains. In this way compounds representing chains, zigzag double chains or ladders with different numbers of legs are realized. Fig. 1 shows a comparison of several possible 3d ion-oxygen configurations. Compounds that incorporate these structural elements exhibit a number of unusual properties which are related to strong quantum fluctuations.
3 Excitation Spectrum and Phase Diagram

The excitation spectrum of a one-dimensional spin system (spin chain) with nearest neighbor exchange coupling is characterized by a degeneracy of the singlet ground state with triplet excitations in the thermodynamic limit. Assuming negligible spin anisotropies the ground state is not magnetically ordered even for $T=0$ and there are gapless excitations. The spin-spin correlations are algebraically decaying. The elementary excitations in such a system are therefore described as massless asymptotically free pairs of domain wall-like solitons or $s=1/2$ spinons. A quantum phase transition from this gapless critical state into a gapped spin liquid state may be induced by a dimerization, i.e. an alternation of the coupling constants between nearest neighbors, or by a sufficient frustration due to competing next nearest neighbor antiferromagnetic exchange. This gapped state is characterized by extremely short ranged spin-spin correlations and may be described as an arrangement of weakly interacting spin dimers.

A simple representative of the quantum disordered state is the two-leg spin ladder with a larger exchange coupling along the rungs than along the legs of the ladder. The singlet ground state is composed of spin dimers on the rungs. An excitation in the picture of strong dimerization corresponds to breaking one dimer leading to a singlet-triplet excitation $\Delta_{01}$. Studies on three-, four- or five-leg ladders led to the conjecture that ladders with an even number of legs have a spin gap while odd-leg ladders are gapless. A family of compounds that may represent these systems are the Sr cuprates, e.g. the two-leg ladder compound SrCu$_2$O$_3$ and the system Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ that is composed of a chain and a ladder subcell and moreover shows superconductivity under pressure.

In the limit of an infinite number of coupled chains a two-dimensional Heisenberg system is obtained and the spin gap vanishes. This limit has also been used to study the two-dimensional high temperature superconductors. Within this framework, also weakly doped two- and three-leg ladder were theoretically investigated.

4 Magnetic Bound States in CuGeO$_3$ and NaV$_2$O$_5$

A salient feature of low dimensional quantum spin systems with a gapped excitation spectrum is the existence of magnetic bound states, i.e. triplet excitations that are confined to bound singlet or triplet states. These states are characterized by a well-defined excitation with an energy reduced with respect to the energy of a two-particle continuum of "free" triplet excitations. In the case of a spin chain the binding energy originates from frustration and/or interchain interaction. In general, these states may therefore be used to study...
the triplet-triplet interaction, the coupling parameters and the phase diagram of the system.

Magnetic bound states of singlet character may be investigated using light scattering experiments. The light scattering process involved results from a spin-conserving exchange mechanism [20, 21]. For these investigations spin-Peierls compounds are very promising as they show a transition from a homogeneous to a dimerized phase for temperatures below the spin-Peierls temperature $T_{SP}$. Therefore, excitations of these systems may be characterized due to their behavior in dependence on temperature, i.e. as function of the dimerization of the spin system. Magnetic bound states have been identified in light scattering experiments on CuGeO$_3$ as a single [21] and on NaV$_2$O$_5$ as multiple singlet states [22].

Raman spectra of CuGeO$_3$ shown in Fig. 2 show for $T<T_{SP}=14$ K additional dimerization-induced modes which are zone-folded phonons with the exception of one mode at 30 cm$^{-1}$. The Fano-lineshape of these modes at 104 cm$^{-1}$ and 224 cm$^{-1}$ is caused by spin-phonon coupling. The excitation at 30 cm$^{-1}$ is identified as a singlet bound state. Its energy $\Delta_{00}=30$ cm$^{-1} \approx \sqrt{3}\Delta_{01}$, with $\Delta_{01}=16.8$ cm$^{-1}$ the singlet-triplet gap and the quasi-linear increase of its intensity with decreasing temperature support this interpretation [15, 21].

Corresponding experiments on the compound NaV$_2$O$_5$ with $T_{SP}=34$ K [23] given in Fig. 3 show more transition-induced modes. Using the criteria discussed above, three modes at 67, 107 and 134 cm$^{-1}$ are candidates for singlet bound
states. In addition there is a decrease of the background scattering intensity for frequencies $\Delta \omega < 120 \text{ cm}^{-1}$ which is indicative of $2\Delta_0$ in agreement with magnetic susceptibility data [24]. This compound differs from the spin chain system CuGeO$_3$ in the sense that it represents a quarter-filled spin ladder that only for $T > T_{\text{SP}}$ may be mapped on a spin chain [25]. Furthermore, there is strong evidence that the transition at $T_{\text{SP}}$ is not a spin-Peierls transition but an electronically driven dimerization connected with a charge ordering of the $s=1/2$ V$^{4+}$ and V$^{5+}$ on the rungs of the ladders [26, 27, 28].

5 The Doped Chain/Ladder System Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$

In the compound Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$, which incorporates both CuO$_2$ chains and Cu$_2$O$_3$ ladders, a substitution of Sr by the isovalent Ca together with applied pressure leads first to a transfer of holes from the chains to the ladders followed by a delocalization of the holes [29]. Superconductivity is observed for pressures around 3GPa with a maximum transition temperature of $T_c = 12$ K [13]. Ca-substitution and applying pressure reduces the b and c axis parameters leading to strong changes of the electronic properties, e.g., a reduction of the anisotropy in the resistivity. In samples with $x=11.5$ the anisotropy of the resistivity $\rho_a/\rho_c$ at $T=50$ K decreases from 80 ($P=0$) to 10 ($P=4.5$ GPa), i.e. it shifts towards a

Figure 3  Raman light scattering spectra of NaV$_2$O$_5$ at 100 and 5 K with incident and scattered light parallel to the (bb) ladder direction. The additional modes in the low temperature phase are marked by arrows.
Figure 4 Raman light scattering spectra of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ with x=0 in intraladder (cc) polarization (the curves have been given an offset for clarity). The doubled gaps of the chain and the ladder system as well as additional modes are marked by arrows. To emphasize the small redistribution of spectral weight the background of the scattering intensity at high frequencies is indicated by a dotted line [29].

Concerning the origin of the smaller gap in the chains a dimerization and charge ordering is discussed. Indeed, superstructure peaks that increase in intensity for temperatures below 50 K are observed in X-ray scattering on samples more two-dimensional behavior [5].

For x=0 a singlet-triplet gap in the chains, $\Delta_{01\text{ chain}}=140$ K or 125 K, has been determined using magnetic susceptibility [31] and NMR experiments [32], while a gap in the ladder of $\Delta_{01\text{ ladder}}=375$ K in neutron scattering experiments [33] or 550 K in NMR [34] has been observed. For x≠0 the gap in the chain system rapidly disappears. However, the effect on the gap in the ladder system is unclear. While in NMR experiments a strong decrease of the gap with substitution from $\Delta_{01\text{ ladder}}=550$ K (x=0) to 270 K (x=11.5) has been observed [34], the corresponding neutron experiments show no change at all [33]. In optical conductivity measurements inspired by similar results in HTSC the opening of a ”pseudo gap” is claimed [35]. Finally, with applied pressure NMR experiments indicate a change of the gap in the ladder to a ”pseudo spin gap” [6]. Although the coexistence of this gap with superconductivity would be a very important piece of evidence, these results could up to now neither be proved nor disproved by other methods.

Concerning the origin of the smaller gap in the chains a dimerization and charge ordering is discussed. Indeed, superstructure peaks that increase in intensity for temperatures below 50 K are observed in X-ray scattering on samples
with $x=0$. Surprisingly, the corresponding dimers are formed in the chains between the Cu spins that are separated by 2 times the distance between the nearest neighbor Cu ions. The distance between two neighboring dimers is 4 times the distance of nearest neighbor Cu ions. Therefore, the dimerization corresponds to ordered Zhang-Rice singlets on the chains. The importance of these singlet states is also discussed for the 2D HTSC. In NMR experiments on $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ the existence of both Cu$^{2+}$ and Cu$^{3+}$ in the chains has been verified.

In Raman scattering experiments with light polarization parallel to the ladder direction (bb) both gaps are identified as a renormalization of the scattering intensity to lower frequency at $2\Delta_{0_1 \text{ chain}}=280\text{ K}$ and $2\Delta_{0_1 \text{ ladder}}=700\text{ K}$. These values are close to the frequencies found in the above discussed neutron experiments (see Fig. 4 and phonon spectra in Ref. [37]), and differ substantially from the NMR results.

The signatures of both chain and ladder gaps weaken and broaden with increasing temperature till they disappear for temperatures above 100 and 350 K for the chain and ladder, respectively. Furthermore, additional modes are observed at low temperatures at 360 and 375 cm$^{-1}$. Although these modes may be phonons, it is interesting to note that their energies correspond to $1.48\Delta_{0_1 \text{ ladder}}$ and $1.54\Delta_{0_1 \text{ ladder}}$, respectively, making them candidates for singlet bound states.
of the ladder. In Fig. 5 Raman spectra of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ with different $x=0$, 2, 5 and 12 are compared. Strong changes of the phonon lines in the frequency range $120 \text{ cm}^{-1} < \Delta \omega < 350 \text{ cm}^{-1}$ are evident that may be related to a change of the commensurability of the chain and ladder subcells. In addition, the gap of the chain subsystem is suppressed with increasing Ca substitution. In contrast to these effects, the signature of the gap in the ladder subsystem is only broadened but not shifted in frequency. This supports the negligible substitution dependence of $\Delta_{01}^{\text{ladder}}$ observed in neutron scattering. The additional modes that are tentatively attributed to bound states are also not influenced by Ca substitution.

6 Conclusion

The low energy excitation spectrum of low dimensional spin systems has been under intense investigation during the last years. Both CuGeO$_3$ and NaV$_2$O$_5$ can be considered as model compounds as a spin gap opens below a phase transition temperature $T_{SP}$. In inelastic light scattering experiments this spin gap is evidenced by a renormalization of the background intensity below $2\Delta_{01}$. Furthermore, well defined singlet bound states consisting of two triplet excitations are found. As their multiplicity and binding energy crucially depend on system parameters their analysis gives a wealth of information on the principal magnetic interactions in the system. These bound states are the magnetic analog of exciton states in semiconductors.

It has been argued that the pseudo gap in HTSC can be understood in terms of a spin gap. In this context, the investigation of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ should be very useful, as this substance consists of both ladders and dimerized chains and becomes superconducting. It therefore can be understood as a link between the low dimensional spin gap systems and HTSC. Inelastic light scattering on $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ samples with $x=0$ shows, in close analogy to CuGeO$_3$ and NaV$_2$O$_5$, a drop in intensity for frequencies below $2\Delta_{01}$. Possibly, magnetic bound states for the ladder emerge as well. For $x \neq 0$ the gap in the chains vanishes in agreement with results of other methods. On the other hand, the gap of the ladder persists even for $x=12$, the doping concentration for which superconductivity occurs under applied pressure. It will be of particular interest to follow the evolution of the spin gap approaching the superconducting phase. Therefore, measurements under hydrostatic pressure are highly desirable and under preparation. A comparison of NMR, neutron and Raman scattering results shows that the first method does not sample the same physical quantity as the other two. This problem is not fully understood. The question how this spin gap and the pseudo gap as observed in HTSC are related could be addressed by these investigations. It is questionable whether the spin gap and the pseudo gap
can be directly identified in $\text{Sr}_{14-\delta}\text{Ca}_\delta\text{Cu}_{24}\text{O}_{41}$ as proposed in Ref. [35] as the energy scales of the superconducting gap and the spin gap are different by more than an order of magnitude. Nevertheless, the study of these low dimensional quantum spin systems is of fundamental importance for the understanding of collective quantum phenomena in strongly correlated electron systems, such as magnetism and superconductivity.

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