Quantum Statistics of Interacting Dimer Spin Systems

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The compound $TlCuCl_3$ represents a model system of dimerized quantum spins with strong interdimer interactions. We investigate the triplet dispersion as a function of temperature by inelastic neutron scattering experiments on single crystals. By comparison with a number of theoretical approaches we demonstrate that the description of Troyer, Tsunetsugu, and Würtz [Phys. Rev. B **50**, 13 515 (1994)] provides an appropriate quantum statistical model for dimer spin systems at finite temperatures, where many-body correlations become particularly important.

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The temperature is without doubt the key control parameter in solid-state physics, for both historical and technical reasons. Historically, the study of thermal fluctuations created the discipline of statistical mechanics. As one technical example, the liquefaction of helium in 1908 enabled the discovery of superconductivity in 1911 [1]. While control parameters such as the magnetic field or applied pressure may seem rather abstract by comparison, in certain classes of system they have a profound effect on the quantum mechanical fluctuations of the dominant degrees of freedom. In this respect, dimer spin systems such as $BaCuSi_2O_6$ [2–4], $TlCuCl_3$ [5–9], and $Cs_3Cr_2Br_9$ [10] have recently attracted considerable attention as they exhibit both field- and (in $TlCuCl_3$) pressure-induced magnetic quantum phase transitions. The ordered phases have also been described as a novel state resulting from Bose-Einstein condensation of magnons [11,12].

To date, the primary experimental and theoretical studies of these systems have focused on elucidating the parameter dependence of the ground and excited states at "$T = 0$ K" [3,4,6–10]. However, the temperature dependence of the spin-spin correlation function $S(\boldsymbol{Q}, \omega)$ in such dimer-based compounds is also of fundamental interest. At finite temperatures, thermal fluctuations populating the excited triplet states above the energy gap, $\Delta \approx 7.5$ K, in the spin excitation spectrum of $TlCuCl_3$ become significant and compete with the intrinsic quantum fluctuations. The absence of a classical ordering transition in zero field and at ambient pressure, and the strong interdimer interactions, make $TlCuCl_3$ an ideal candidate for an experimental investigation of the quantum statistical description for such a spin system.

In $TlCuCl_3$, the antiferromagnetic (AF) dimer unit is formed by the two $S = 1/2$ magnetic moments in a pair of Cu^{2+} ions, and has a singlet ground state (total spin $S = 0$) with triplet ($S = 1$) excited states which may be considered as bosonic quasiparticles. Only in the high-temperature limit, relative to the intradimer exchange constant $J \approx 56$ K [5,13], is the system better described in terms of $S = 1/2$ fermions whose interactions are weak compared to the thermal fluctuations, and AF dimer correlations are strongly suppressed. In the intermediate regime, $\Delta < T < J$, a singlet-triplet description remains valid but the number of excited triplets becomes significant. Here the effect of interparticle interactions, particularly the intrinsic hard-core repulsion on each dimer bond, defines a challenging experimental and theoretical scenario. Temperature-dependent properties of dimer spin systems have, to date, been measured only in compounds of weakly interacting dimers with a spin gap large compared to the triplet bandwidth, including $BaCuSi_2O_6$ [2], $KCuCl_3$ [14], and $Cu(NO_3)_2 \cdot 2.5D_2O$ [15], where many-body correlation effects are less pronounced. The description of these data was restricted to RPA theory or phenomenological modeling.

In this Letter we present the results of a recent inelastic neutron scattering (INS) study of the spin dynamics in $TlCuCl_3$. The primary results include a comprehensive experimental survey of the triplet excitations up to temperatures approaching the intradimer interaction strength, $\Delta \ll T_{\max} \approx 0.7J$, and their theoretical modeling by quantum statistical considerations applied to the known zero-temperature states (i.e., with no additional fitting parameters). We characterize the evolution of the spin gap, $\Delta(T)$, which is of particular relevance to the quantum critical behavior of the compound, and shows a pronounced increase with temperature. We demonstrate that the data support strongly the Troyer-Tsunetsugu-Würtz (TTW) an-

satz for the quantum statistics of general dimer spin systems [16]. Our results may further be compared with those obtained for weakly interacting dimer compounds (above) and are closely related to extensive investigations of another class of gapped quantum magnets, $S = 1$ Haldane chains, which have been studied in model compounds such as $CsNiCl_3$ [17].

Thermal renormalization of the dispersion, spectral weight, and damping of the triplet modes in $KCuCl_3$, which shares the crystal structure and exchange coupling scheme of $TlCuCl_3$, are adequately described within a self-consistent RPA theory including higher-order corrections [14]. The considerably stronger interdimer interactions make this approach less successful for $TlCuCl_3$. We have therefore applied an extension of the bond-operator description of the compound [13] to finite temperatures, a procedure requiring [18] the inclusion of thermal population factors $n(E_\alpha(\boldsymbol{q}), \beta)$ in the mean-field (MF) equations defining the singlet density $\bar{s}$ and the triplet chemical potential μ; here E denotes the magnon energy, $\boldsymbol{q}$ its wave vector, $\beta = (k_B T)^{-1}$, and $\alpha = -1, 0, +1$ represents the $S_z = -1, 0, +1$ triplet modes. We assume explicitly that there are no additional factors which may change with temperature, such as renormalization of the intra- and interdimer interaction parameters due to phonons [19].

The singlet state and each of the triplets on a single dimer obey an exclusion constraint and are described appropriately as hard-core bosons. Their statistical properties have no straightforward extension to reciprocal space and no exact expression exists for a triplet thermal occupation function. However, the effects of the constraint were introduced by Troyer and co-workers [16] in the form of a statistical reweighting of the number of free-boson states of the N-dimer system to account for their complete local exclusion. The reweighting constitutes a suppression of state availability in all magnon occupation sectors M, being most significant at large M, and returns the effective single-dimer free energy

$$\tilde{f} = -\frac{1}{\beta} \ln\left[1 + \sum_\alpha z_\alpha(\beta)\right] \qquad (1)$$

with $z_\alpha(\beta) = \frac{1}{N}\sum_{\boldsymbol{q}} e^{-\beta E_\alpha(\boldsymbol{q})}$ the partition function for triplet mode α. The effective occupation function for this statistical ansatz (denoted TTW-MF) is then

$$n(E_\alpha(\boldsymbol{q}), \beta) = \frac{e^{-\beta E_\alpha(\boldsymbol{q})}}{1 + \sum_\alpha z_\alpha(\beta)}. \qquad (2)$$

Equation (2) reproduces both the low- and high-temperature limits expected for the constrained boson system [16], namely $n \sim e^{-\beta E_\alpha(\boldsymbol{q})}$ at low T (bosonic, M small) and $n \sim 1/4$ at high T (equipartition, M large), and we will test below the accuracy of exclusion implementation by statistical reweighting for the regime between these limits. For comparison we will show also the results (denoted Bose-MF) obtained by enforcing the constraint at the Holstein-Primakoff level [13] and considering a conventional bosonic magnon occupation factor. Figure 1(a) shows theoretical predictions for the thermal renormalization of the triplet dispersion: both approaches display a narrowing of the magnon band which arises because interdimer triplet hopping is obstructed by the exclusion condition when the concentration (M/N) of thermally excited triplets becomes significant.

The gap Δ at the dispersion minimum, which becomes the AF zone center in the magnetically ordered high-field and -pressure phases, deserves special attention. Figure 1(b) shows its thermal evolution as obtained from the above models, and from the RPA treatment applied to $KCuCl_3$ in Ref. [14]. The Bose-MF approach shows a very strong renormalization at higher temperatures due to the possibility of unlimited boson occupation. This effect is considerably weaker in the TTW-MF calculations, where it is limited by the exclusion encoded in the statistics. These approaches coincide at low temperatures, where the triplet occupation is too dilute for their hard-core nature to be relevant. By contrast, in the RPA treatment the onset of a perceptible bandwidth narrowing requires much higher temperatures.

These theoretical results clearly motivate INS measurements of the triplet dispersion relation as a function of temperature at zero and finite field. We have conducted INS experiments on single crystals of $TlCuCl_3$ at $H = 0$ T.

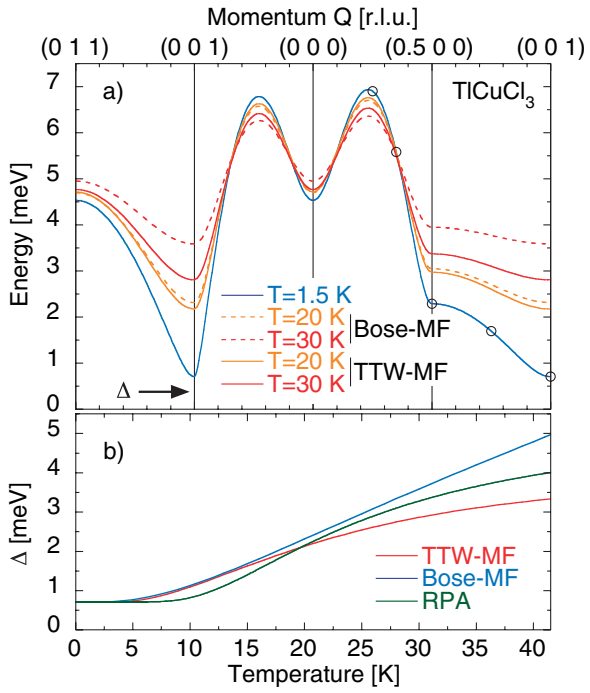

FIG. 1 (color). (a) Finite-T triplet dispersion for $TlCuCl_3$ from statistical models described in the text. Δ denotes the minimum singlet-triplet gap, $\boldsymbol{Q} = \boldsymbol{q} + \boldsymbol{\tau}$ the momentum, where $\boldsymbol{\tau}$ is a reciprocal-lattice vector, and open circles the $\boldsymbol{Q}$ values presented in Fig. 3. (b) Temperature dependence of $\Delta(T)$ from TTW-MF, Bose-MF, and RPA approaches.

These were performed on the triple-axis spectrometers TASP (SINQ), IN14 (ILL), and 2T (LLB), working in constant-k_f mode with a focusing pyrolytic graphite (PG) analyzer and monochromator. While 2T is operated with thermal neutrons of $k_f = 2.662$ Å^{-1} (14.7 meV) and 1.970 Å^{-1} (8.0 meV), TASP and IN14 use moderated (cold) neutrons with a characteristic spectrum shifted to lower energies, $k_f = 1.506$ Å^{-1} (4.7 meV). A cooled beryllium or PG filter is positioned between the analyzer and the sample, contained in a standard cryostat providing $T \geq 1.5$ K. The (horizontal) collimation adopted on the cold instruments was 60′-open-open and 40′-open-open, yielding an energy resolution of 0.2 meV (full width at half maximum height) in both cases. Corresponding values for the thermal instrument without additional collimation were 1.2 meV and 0.5 meV.

Typical INS spectra for the triplet modes in $TlCuCl_3$ measured for a number of temperatures at the band minimum ($\boldsymbol{Q} = (0\ 4\ 0)$ r.l.u.) are presented in Fig. 2(a). Upward renormalization of the excitation energy, the onset of damping, and reduction in the integrated intensity are observed. Figures 2(b) and 2(c) contrast the INS intensities measured at 1.6 and 39.8 K along $(Q_h 0\,0)$. The complete experimental survey, including representative $\boldsymbol{Q}$ values spanning the entire bandwidth, is presented in Fig. 3 and compared with the model calculations. For instrumental reasons the spin gap Δ must be measured in several experimental configurations to cover the full temperature range. The point $\boldsymbol{Q} = (1.35\ 0\ 0)$ r.l.u. is of particular interest: here the excitation energy corresponds approximately to J, and indeed it is nearly temperature independent. The downward renormalization of the dispersion maximum is evident. The continuity between data sets from different instruments and $\boldsymbol{Q}$ values underlines the accuracy of the experimental procedure, including the data analysis (below).

With regard to the calculated fits, the TTW-MF model is clearly favored by the experimental observations in the range 20 K $\leq T \leq$ 40 K [Figs. 2(c) and 3] where the thermal renormalization changes less rapidly due to the constrained magnon population. The Bose-MF approach fails markedly in this respect. For clarity, the RPA predictions are not shown in Fig. 3, and we state only that these fail, in particular, to reproduce the low-temperature behavior [cf. Fig. 1(b)]. The agreement between the TTW-MF result and the experimental data is excellent over the full temperature range of the investigation. We stress that no free parameters are introduced with respect to the low-temperature dispersion [5,13].

We turn to a discussion of the excitation linewidth. For modes of infinite lifetime, $S(\boldsymbol{Q}, \omega)$ is a δ function in energy ($E = \hbar\omega$), which within instrumental resolution is the case for the triplet modes measured in $TlCuCl_3$ at $T = 1.6$ K. However, at elevated temperatures a finite intrinsic linewidth (damping) is observed, and data analysis requires knowledge of the spectral function. Different $O(n)$ rotor models give a Lorentzian line shape in one dimension (1D) and at $T < \Delta$ [20], but neither limit is appropriate here. By contrast, the damped harmonic oscillator (DHO) line shape used frequently for phonons [21] is identical to a double Lorentzian if the real excitation energy is defined as $E_{\mathrm{DHO}}(\boldsymbol{q})^2 = E(\boldsymbol{q})^2 + \Gamma^2$, and thus depends on the damping

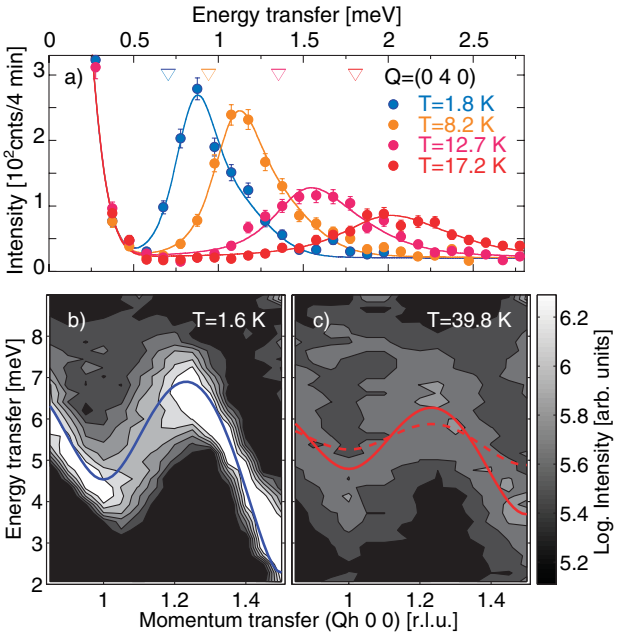

FIG. 2 (color). (a) INS spectra for $TlCuCl_3$ measured on IN14 at $\boldsymbol{Q} = (0\ 4\ 0)$ r.l.u.. Solid lines are Lorentzian-based least-squares fits including full 4D-resolution convolution (peak asymmetry) and triangles indicate the physical excitation energy. (b) and (c) INS intensity contour plots measured at 1.6 K and 39.8 K, compared with theoretical curves by the Bose-MF (dashed line) and TTW-MF (solid line) descriptions.

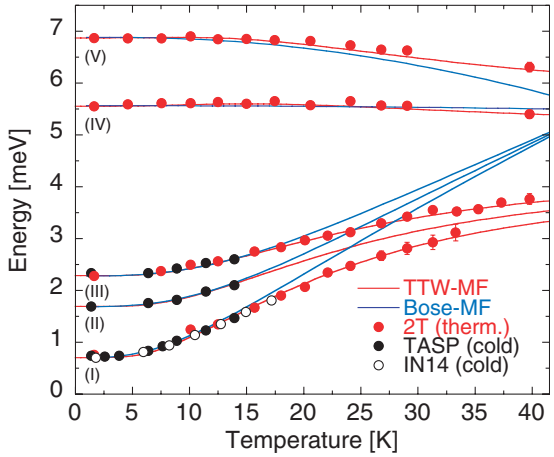

FIG. 3 (color). Temperature dependence of the excitation energies at (I) $\boldsymbol{Q} = (0\ 0\ 1)$ (closed black circles and closed red circles) and $\boldsymbol{Q} = (0\,4\,0)$ (open black circles), (II) $\boldsymbol{Q} = (0.25\,0 - 1.5)$, (III) $\boldsymbol{Q} = (0.5\,0 - 2)$, (IV) $\boldsymbol{Q} = (1.35\,0\,0)$, and (V) $\boldsymbol{Q} = (1.25\,0\,0)$ (all in r.l.u.). Data from different instruments as indicated. Solid lines are obtained from TTW-MF and Bose-MF calculations.

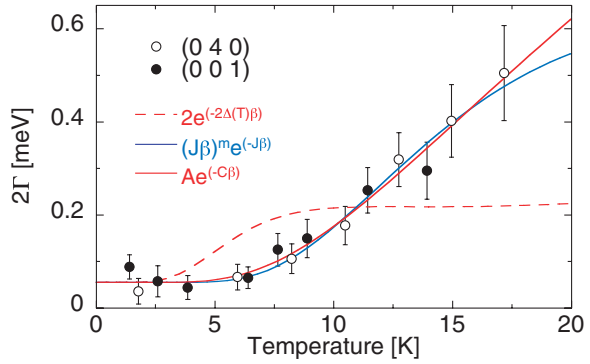

FIG. 4 (color). Temperature dependence of linewidth 2Γ for selected reciprocal-lattice points. Solid lines denote fits to the data as shown in the legend [$A = 3(1)$, $C = 2.7(5)$, and $m = 2.04(7)$]. The low-T offset of 0.05 meV is attributed to uncertainty in the resolution deconvolution.

Γ (half Lorentzian width at half maximum height). The DHO definition has been used to fit the finite-T triplet excitations in Haldane chains [17], and also for spin waves [22].

In the Bose-MF and TTW-MF approaches the energy is not renormalized by line-shape effects, consistent with the Lorentzian assumption. While a linewidth Γ may be computed from the phase space available for magnon decay and scattering, these considerations provide no proof of either a Lorentzian or a DHO form for triplet excitations in 3D, and nor is one available in the literature. We proceed on the basis of experiment: the INS measurements show that a Lorentzian yields an accurate description of the data. The spectra [Fig. 2(a)] were fitted with this line shape and the real excitation energy defined as $E(\boldsymbol{q})$. We suggest that this definition provides the correct description of the spectral function at finite temperatures in dimer spin systems. This conclusion is reinforced by the temperature dependence of the dispersion maxima, which show a downward renormalization with increasing T. This behavior is consistent with the Lorentzian model, whereas $E_{\mathrm{DHO}}(\boldsymbol{q})$ describes the maxima rising due to the strong increase of Γ with temperature. Qualitatively, this result may be traced once again to the hard-core nature of the magnon excitations.

Figure 4 shows the damping of the triplet modes, which is clearly activated. This behavior is expected from any model based on enhanced triplet-triplet scattering as the origin of a finite quasiparticle lifetime. We are unable to distinguish between fits using a variable activation energy or a variable power-law prefactor to an exponential with a constant activation energy of J [15] (Fig. 4). However, the data are definitely incompatible with an activation energy of $2\Delta(T)$, as would be expected from magnon decay terms present at third order in the triplet hopping Hamiltonian, and these processes may be excluded.

With the present investigation we would hope to initiate further studies. Detailed theoretical predictions for the finite-temperature spectral function of gapped excitations in 3D dimer spin systems are required. Experimental studies at magnetic fields around the critical field H_c and at finite temperatures, i.e., in the quantum critical regime, are further expected to reveal new physics.

In summary, we have investigated the thermal renormalization of triplet excitations in the strongly interacting dimer spin system $TlCuCl_3$ by means of INS. We find excellent agreement between the TTW-MF ansatz and the complete data set, which was taken up to $T \approx 0.7J$. The Bose-MF approach is in comparable agreement for $T < 20$ K and may therefore be considered as a suitable low-T approximation. However, at higher temperatures, where many dimer triplets are excited, their hard-core nature becomes manifest and an accurate quantum statistical description requires the TTW ansatz.

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