Magnetic excitations in the quantum spin system TlCuCl₃

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The $S = \frac{1}{2}$ quantum system TlCuCl₃ has a nonmagnetic singlet ground state and a finite-energy gap to triplet excited states. At $H_c \sim 6$ T it undergoes field-induced three-dimensional magnetic ordering. Its dynamical spin properties in zero field were studied by inelastic neutron scattering on single crystals. The elementary spectrum consists of well-defined triplet waves of dimer origin. From the observed energy dispersion, the underlying spin-exchange coupling scheme is rationalized. Appreciable three-dimensional correlations are reported, in accordance with the high-field phase. An antiferromagnetic Heisenberg model in the strong-coupling approximation satisfactorily accounts for the energy and intensity dependence of the triplet excitations in the whole reciprocal space. TlCuCl₃ is characterized as a strongly coupled spin system in the vicinity of a quantum critical point. A comparison with the parent compound KCuCl₃ is proposed.

In low dimensional antiferromagnets (AF), zero-point spin fluctuations and nonlinear interactions are responsible for unconventional magnetic properties. The classical picture of long-range staggered Néel order as the realization of a broken symmetry, and of well-defined spin waves as the resulting Goldstone modes completely fails in the description of $S = \frac{1}{2}$ dimer, chain, or ladder compounds. These isotropic spin systems are characterized by a nonmagnetic, quantum disordered singlet ground state. Their elementary spectrum is generally distributed in a broad (q, ω) dynamical range. However in the strong-coupling limit, i.e., when a valence bond dominates the spin interactions, the propagation of sharp triplet waves above an energy gap of dimer origin is supported.[1–3] The complete microscopic characterization of the triplet waves allows as to determine the underlying magnetic interactions, and to conclusively elucidate the mechanisms behind the unconventional properties. Among dynamical experimental techniques, inelastic neutron scattering (INS) directly yields momentum resolved information on the singlet and triplet states through the transition matrix elements of the spin operator $S(q)$. It thus provides on a quantitative basis the privileged testing ground of theoretical and numerical predictions. Currently, much interest is devoted to the occurrence of quantum phase transitions in strongly coupled spin systems.[4] Upon application of an external field H at "$T = 0$", the singlet-triplet excitation gap Δ is decreased and eventually overcome at $g\mu_B H_c \sim \Delta$. In the presence of weak three-dimensional (3D) exchange interactions, at $H > H_c$ field-induced magnetic order occurs.[5,6] The fundamental nature of the transition at the quantum critical point H_c, as well as the spin interactions at finite magnetization are the subject of recent theoretical studies.[7,8] Local dynamical probes were successfully applied to the investigation of the field and temperature dependence of Δ in a number of compounds.[9–11] Unfortunately, the lack of single crystals of suitable size for a neutron analysis has often prevented the generalization of such investigations to the complete recip-

rocal space. $S = \frac{1}{2}$ TlCuCl₃ constitutes a recent example where field-induced magnetic ordering has been observed by magnetization measurements.[12] A theoretical model based on Bose-Einstein condensation of the triplet states has been proposed to account for the experimental observations.[13] In the following we provide a comprehensive INS study of the elementary spectrum in zero field, and determine the corresponding dynamical spin-spin correlation function. As it will be shown, TlCuCl₃ not only represents an appealing starting point for quantum critical investigations on a microscopic level, it also directly relates to isostructural KCuCl₃. The latter is a well-characterized quantum disordered magnet near the strong-coupling limit, with weak 3D interdimer spin correlations in additional to a strong AF intradimer spin correlation.[14,15] The same effective coupling scheme is found to account for the observed elementary excitations in TlCuCl₃, albeit with markedly increased interdimer coupling strengths. The resulting dynamical characterization is put into the context of previous experiments performed by complementary techniques, whose main conclusions are for convenience summarized below. The issues raised in connection with a recent INS investigation are partly clarified.[16]

Monoclinic TlCuCl₃ crystallizes in the space group $P2_1/c$, with four formula units per unit cell.[17,18] Unconventional magnetic properties are determined by the $S = \frac{1}{2}$ exchange interactions between the Cu²⁺ ions, which are arranged in centrosymmetric dimer pairs. Static measurements reveal that the ground state is a nonmagnetic singlet and that the spectrum has a finite spin gap Δ to triplet excitations, which is estimated from high-field magnetization as $\Delta/k_B \sim 7.5$ K.[12,19] Spin interactions are almost isotropic, with coinciding static behavior when scaled by the gyromagnetic factor g.[12] The above issues qualitatively apply to the isostructural $S = \frac{1}{2}$ quantum system KCuCl₃ as well, whose magnetic properties are dominated by an AF valence bond between neighboring Cu²⁺ ions.[20] Comprehensive INS investigations in the latter were accurately reproduced by a

Heisenberg spin-exchange model $H = -\frac{1}{2}\Sigma_{ij} J_{ij} S_i \cdot S_j$ in the strong-coupling approximation (Ref. 21, and references therein). It is natural to adopt in the following the same microscopic approach in the description of TlCuCl$_3$.

High-quality single crystals of TlCuCl$_3$ were grown from a stoichiometric melt by the Bridgman method. Neutron diffraction from a powder sample obtained by the same procedure led to the determination of the cell parameters and atomic positions at $T = 1.5$ K adopted throughout this study. Two large crystals were aligned for neutron investigations in the scattering planes defined by the [1, 0, 0], [0, 0, 1] and [0, 1, 0], [1, 0, 4] directions, respectively. The experiments were performed on the IN22 and IN3 spectrometers installed at Institut Laue-Langevin (ILL), France, and on the DrüchaL and TASP spectrometers installed at the spallation neutron source SINQ, Paul Scherrer Institut (PSI), Switzerland. Instruments were operated at constant momentum transfer, with fixed final energy $E_f = 14.7$ meV (ILL) and $E_f = 4.7$ meV (SINQ PSI) and a pyrolitic graphite/berillium filter in front of the analyzer, respectively. The resulting neutron spectra are evaluated on the basis of the dynamical spin-spin correlation function adopted for isostructural KCuCl$_3$.[21] The underlying model predictions can be summarized as follows: The elementary spin excitations are well-defined triplet waves, whose energy dispersion in reciprocal space reflects the periodicity of the effective strong-coupling scheme. A three-dimensional dimer network supports the propagation of two triplet modes denoted by

$$\epsilon_{\pm}(q) = -\{J + J_{in}(q) \pm J_{out}(q)\}, \qquad (1)$$

where $J < 0$ is the strong AF intradimer bond, $J_{in}(q) = J_a \cos(2\pi q_h) + J_{a2c} \cos(4\pi q_h + 2\pi q_l)$ and $J_{out}(q) = 2J_{abc} \cos(\pi q_k)\cos(2\pi q_h + \pi q_l)$ the Fourier transforms of the weaker interdimer bonds. Eq. (1) describes the dynamical correlations within (J_{in}) and between (J_{out}) two sublattices, which are distincted by the different dimer orientation.[17] The transition matrix elements from the singlet ground state to the triplet excited states reflect to leading order the coherent sum of the two dimer structure factors[22]

$$I_{\pm}^{\alpha\beta}(\kappa) = \left[\frac{1}{2}\sin\left(\frac{\kappa \cdot R_1}{2}\right) \pm \frac{1}{2}\sin\left(\frac{\kappa \cdot R_2}{2}\right)\right]^2 \delta^{\alpha\beta}, \qquad (2)$$

with $\alpha, \beta = \{x, y, z\}$ the spin component, $\kappa = q + \tau$ the scattering wave vector, and $R_1 = 0.46a + 0.10b + 0.31c$, $R_2 = 0.46a - 0.10b + 0.31c$ the separation of the Cu^{2+} ions within the differently oriented dimers. The symmetry of the space group simplifies the expectations from Eq. (2) along particular directions of reciprocal space. This is the case for κ in the a^*c^* plane ($\kappa \cdot R_1 = \kappa \cdot R_2$, $I_- = 0$) and in the b^* direction ($\kappa \cdot R_1 = -\kappa \cdot R_2$, $I_+ = 0$). Higher-order corrections for the above expressions are readily obtained in a pertubative expansion.[21] Eqs. (1) and (2) directly enter the singlet-triplet neutron cross section, which is proportional to

$$\frac{d\sigma}{d\Omega d\omega} \sim |f(\kappa)|^2 n_0 \sum_{\alpha\beta}\left(\delta^{\alpha\beta} - \frac{\kappa^\alpha \kappa^\beta}{\kappa^2}\right) I_{\pm}^{\alpha\beta}(\kappa)$$

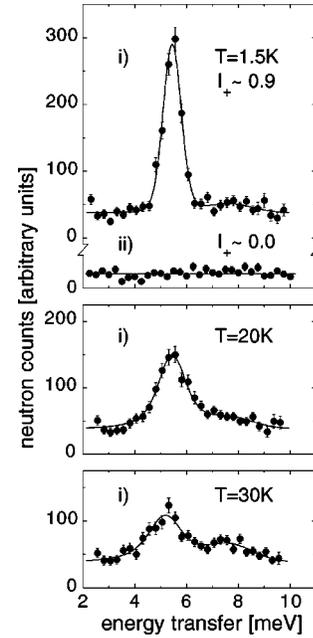$$\times \delta[\hbar\omega - \epsilon_{\pm}(q)], \qquad (3)$$

FIG. 1. Measured neutron profiles in the a^*c^* plane of TlCuCl$_3$ for $i = (1.35,0,0)$, $ii = (0,0,3.15)$ [r.l.u]. The spectrum at $T = 1.5$ K consists of the magnetic excitation mode ϵ_+ described by Eqs. (1) and (2) (upper panel). The observed temperature renormalization is indicative of its magnetic nature (lower panels). Background anomalies are addressed in the text.

where $f(\kappa)$ denotes the magnetic form factor of the Cu^{2+} ion, and n_0 is the thermal population of the singlet ground state. The present investigations were accordingly organized to cover the above issues.

The typical outcome of the neutron profiles in the a^*c^* scattering plane is shown in Fig. 1 under different experimental conditions (IN22, ILL). The spectrum is dominated by a well-defined excitation mode, whose magnetic nature is confirmed by the observed wave-vector dependence (upper panel) and temperature renormalization (lower panels). In accordance with the expectations from $I_+(\kappa)$ in Eq. (2) this mode corresponds to ϵ_+. Anomalies affecting the background will be discussed below. The $T = 1.5$ K energy dispersion of the magnetic excitations along the main directions of reciprocal space is summarized in Fig. 2 in a reduced scheme representation as indicated. Above a modest spin gap $\Delta \sim 0.8$ meV, triplet modes are observed to propagate in all directions of reciprocal space revealing appreciable 3D exchange interactions between the dimers, in accordance with the ordered high-field phase of TlCuCl$_3$.[12] Major dispersion is reported in the plane normal to [1, 0, -2], which is favored by the nearly planar Cu$_2$Cl$_6$ dimer arrangement. Data are well explained by the second-order expressions derived from Eq. (1) in Ref. 21, with the parameters reported in Table I. Microscopic considerations behind the adopted exchange scheme are found in Refs. 21 and 23. The least-squares fit relies on a large experimental body, comprising additional directions not shown in Fig. 2. A complete account thereof will be given elsewhere. Our analysis indicates that the same effective exchange-coupling scheme is realized both in KCuCl$_3$ and TlCuCl$_3$, but that the underlying cou-
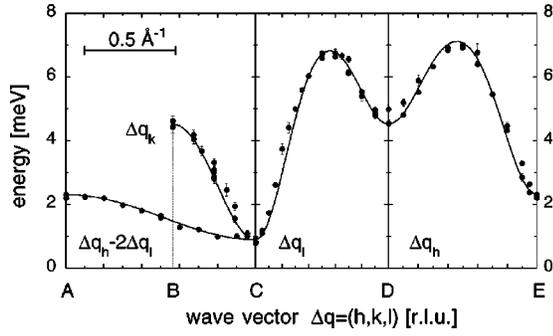
FIG. 2. Observed energy dispersion of the magnetic excitation modes in TlCuCl$_3$ at $T = 1.5$ K. Full circles from the relevant directions of reciprocal space are arranged in a reduced scheme representation, with $A = E = (1/2, 0, 0)$, $B = (0, 1, 0)$, $D(0, 0, 0)$ [r.l.u.]. Zone centering corresponds to $C = (0, 0, 1)$ for $\Delta q = (h, 0, l)$, $C = (0, 0, 0)$ for $\Delta q = (0, k, 0)$. Lines are fits to the model expectations explained in the text with the parameters reported in Table I.

pling strengths markedly differ. Whereas the intradimer spin correlation is comparable, the interdimer spin correlations in the title compound are much increased. The shortening of the a cell axis (which involves all couplings) in TlCuCl$_3$ with respect to KCuCl$_3$,[18] and the role of the covalent Tl$^+$ ion may represent notable qualitative support along these lines. Quantitatively, the strongest correlation increase concerns dimer sites separated by $\pm(2, 0, 1)$ lattice units (l.u.). The energy minimum calculated from Table I corresponds to $\Delta = 0.90(6)$ meV, which only slightly overestimates the experimental observations at $\Delta \sim 0.8$ meV (Fig. 2). From the curvature of the energy dispersion around the minimum, the effective mass of the diluted triplet gas can be inferred using the relation $\hbar^2/m = \partial^2 \epsilon / \partial^2 q$, as explained in Ref. 13. Our investigations clearly evidence the strongly anisotropic nature of such an effective-mass tensor $m = m(q)$, providing at the same time a complete experimental set for a quantitative approach (Fig. 2). A detailed analysis of the elementary triplet spectrum beyond second-order expansions is encouraged, along the lines presented in Ref. 24 for KCuCl$_3$.

The characteristic intensity modulation $I(\kappa)$ predicted from Eq. (2) is a powerful tool to selectively access the two excitation modes, and to confirm the assignments regarding the dominant valence bond. Figure 3 (IN3, ILL) shows the integrated intensity for the triplet excitations observed along $\kappa = \kappa_k + \kappa_\perp$, with constant $\kappa_\perp \cdot R_1 = \kappa_\perp \cdot R_2 = 0$ and $\kappa_\perp \cdot R_1$

TABLE I. Coupling parameters describing the observed magnetic excitations in KCuCl$_3$ and TlCuCl$_3$, evaluated by least-squares fits to the same second-order model expressions from Eq. (1) presented in Ref. 21.

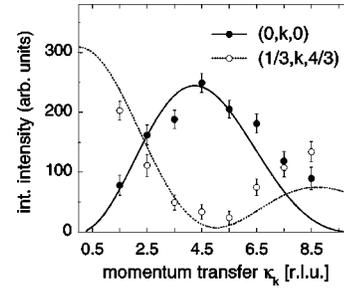| J_{ij} [meV]	R_{ij} [l.u.]	KCuCl$_3$	TlCuCl$_3$
J_a	$\pm(1, 0, 0)$	0.210(5)	0.472(11)
J_{a2c}	$\pm(2, 0, 1)$	0.340(5)	1.430(8)
J_{abc}	$\pm(1, +\frac{1}{2}, \frac{1}{2})$	$-0.372(4)$	$-0.619(5)$
	$\pm(1, -\frac{1}{2}, \frac{1}{2})$		
J	$(0, 0, 0)$	$-4.287(4)$	$-5.424(11)$

FIG. 3. Observed spectral weight of the magnetic excitation modes in TlCuCl$_3$ at $T = 1.5$ K. Data collected at $\kappa = (0, k, 0)$ (full circles) and $\kappa = (\frac{1}{3}, k, \frac{4}{3})$ (open circles) for $k = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots$ [r.l.u.] are compared to the model expectations from Eq. (3) as indicated.

$= \kappa_\perp \cdot R_2 \sim \pi$. The scattering geometry is chosen to reflect the exclusive $I_-(\kappa)$ and nearly exclusive $I_+(\kappa)$ intensity contribution to Eq. (3) respectively. Along each direction, reciprocal points occurring at the same energy are considered. This limits instrumental effects and allows us to fit the data on a common basis. Model expectations are corrected by the spherical spin-only Cu^{2+} form factor[25] and are allowed to scale by a prefactor valid for both data sets. Considering the absence of other free parameters, the overall intensity dependence as well as the extrema observed around $\kappa_k \sim 5$ reciprocal-lattice units (r.l.u.) are in satisfactory agreement with the model predictions. Corresponding behavior extends to the observations in the whole reciprocal space (see also Fig. 1), and can be described by the expressions based on Eq. (2) reported in Ref. 21. Although a strong-coupling approach apparently captures the relevant experimental observations in TlCuCl$_3$, we remark that the parameter range determined from Table I is at the limit of the model stability, expressed by the self-consistent condition $|\{J_{in}(q) \pm J_{out}(q)\}/J| < 1$.[26] Collective quantum correlations of higher order may not be negligible, possibly comprising the presence of multiple triplet states in the spectrum.[27,28] Though not directly addressed in the present study, expectations for the energy range and spectral weight of these higher excited states can be derived from Table I following Ref. 29.

A separate issue concerns the background, which was far from being smooth. At selected points of reciprocal space, unexpected features are reported. An example is shown in Fig. 1, where beside the expected ϵ_+ contribution to the neutron profile, an additional weak signal is detected, which increases as the temperature increases. Its energy does not compare with the expectations for the ϵ_- mode. In a recent INS experiment on TlCuCl$_3$ restricted to the a^*c^* scattering plane, the presence of three excitations was reported, one of which centered at $E \sim 12$ meV, and the two other showed dispersive behavior in the energy range considered in the present report.[16] The authors identified the lowest-lying excitations as magnetic, in agreement with our results. However, the limited instrumental resolution and κ range prevented a complete spectral analysis. Extending the above study to the whole reciprocal space, we fully characterize the nature of the elementary magnetic interactions. Our conclusions are based on a detailed study of the energy and intensity of the triplet excitation modes, which can be described by the parameters from Table I within a strong-coupling ap-

proximation. Regarding the observed anomalies, these are more pronounced around nuclear zone boundaries and for large scattering vectors. It is well known that under such circumstances phonon branches may enter the inelastic neutron cross section.[30] Moreover, the observed temperature dependence of their intensity is incompatible with the renormalization expected from direct excitations in strongly coupled quantum clusters.[2,3,27] In light of the above facts, our preliminary observations suggest a phonon contamination of the spectrum in the same energy range shared by the magnetic excited states. In this case, anharmonic magnetoelastic interactions may strongly affect the collective dynamical properties.[31] Future experimental efforts will hopefully address the above topics on a quantitative basis.

To sum up, a complete INS investigation of the dynamical magnetic properties in $S = \frac{1}{2}$ TlCuCl$_3$ is consistently explained assuming a 3D valence bond system. Relevant magnetic units are Cu dimers, supplemented by important interdimer correlations as quantitatively determined. The elementary spin excitations at $T = 1.5$ K are well-defined triplet modes, propagating above a modest energy gap $\Delta \sim 0.8$ meV in all directions of reciprocal space. The energy dispersion and the spectral weight of these excitations is satisfactorily explained by a Heisenberg model in the strong-coupling limit. However, the overall energy bandwidth is comparable to the leading term J in the model description. Subtleties in the observed neutron spectra indicate the presence of thermally activated excitations. A meaningful extension of the above characterization will be given by neutron investigations in a finite magnetic field. In this respect TlCuCl$_3$ deserves utmost attention, as it allows the microscopic study of a quantum phase transition in a strongly coupled spin system. The above determination of the elementary triplet excitations provides a useful paradigm to organize such future studies. At the same time, it will hopefully motivate additional efforts towards a deeper understanding of three-dimensional quantum magnets.

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