Pressure-Induced Quantum Phase Transition in the Spin-Liquid $TlCuCl_3$

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The condensation of magnetic quasiparticles into the nonmagnetic ground state has been used to explain novel magnetic ordering phenomena observed in quantum spin systems. We present neutron scattering results across the pressure-induced quantum phase transition and for the novel ordered phase of the magnetic insulator $TlCuCl_3$, which are consistent with the theoretically predicted two degenerate gapless Goldstone modes, similar to the low-energy spin excitations in the field-induced case. These novel experimental findings complete the field-induced Bose-Einstein condensate picture and support the recently proposed field-pressure phase diagram common for quantum spin systems with an energy gap of singlet-triplet nature.

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Classical magnets typically show long-range magnetic order below a characteristic temperature, where the amount of thermal fluctuations is reduced below a critical value and the magnetic moments align in a well-defined structure. On the other hand quantum fluctuations can prevent the formation of such an ordered ground state even down to the lowest temperature "$T = 0$ K". The spin system remains in a quantum-disordered (spin-liquid) state. The ordered state is then eventually recovered above the critical value, the quantum critical point [1], of an external parameter like pressure, magnetic field, or doping. Pressure-induced magnetic ordering could recently be observed in the highly frustrated compound $Tb_2Ti_2O_7$ with pyrochlore structure [2] and in the dimer spin system $TlCuCl_3$ [3,4]. We have investigated the spin dynamics across the pressure-induced quantum phase transition and in the novel ordered phase of the latter compound using inelastic neutron scattering (INS). The INS spectra show a softening of the triplet excitations at the critical pressure p_c and are consistent with two degenerate "gapless" Goldstone modes with a linear initial dispersion at $p > p_c$, similar to the spin wave excitations in an ordered classical magnet. This experimental finding can directly be compared to the excited states found in the field-induced ordered phase [5] and supports the description of the unconventional ground states, with induced magnetic order, in terms of condensates of magnetic quasiparticles [6–9]. Our results are further a motivation for corresponding studies of the related quantum spin systems with low-dimensional spin Hamiltonians like spin ladders [10] or Haldane spin chains [11] with residual three-dimensional interactions.

The magnetic insulator $TlCuCl_3$ is a model compound for a dimer spin system with a spin energy gap $\Delta \approx 0.7$ meV between the singlet ground state ($S = 0$) and the first excited triplet states ($S = 1$). The singlet results from a dominant antiferromagnetic interaction (J) connecting the two $S = 1/2$ moments in a pair (dimer) of Cu^{2+} ions. These dimers are part of a three-dimensional exchange network (J_1, J_2, J_3 following the notation in [7,8]) leading to considerable dispersion of the triplet waves along all directions in reciprocal space [12,13]. The relative strength of the exchange interactions defines the nature of the ground state, which is a quantum-disordered dimer spin liquid down to the lowest temperatures. However, several possibilities have recently been found to recover a magnetically ordered ground state. *First*, replacing partially the $S = 1/2$ Cu^{2+} ions by nonmagnetic Mg^{2+} ions (as impurities) introduces free magnetic moments, which show impurity-induced long-range order [14]. *Second*, the degeneracy of the triplet state is lifted by an external magnetic field, see Fig. 1(a)–1(c). The energy of the lowest Zeeman split triplet mode ($S = 1$; $S_z = +1$) can then be driven to zero at $H_c = \Delta/g\mu_B \approx 5.7$ T, where Bose-Einstein condensation of magnetic quasiparticles occurs [5–9,15,16]. *Third*, the application of external or internal (chemical) pressure can lead to a reduction of the spin gap or even its complete collapse [8,17], see Fig. 1(a), 1(d), and 1(e), since the bandwidth, average energy, and spin gap of the triplet waves are governed by the size and relative strength of the interdimer and intradimer interactions J_i and J, respectively. Especially an increase of J_i, a decrease of J, or a combination of both by pressure application enables long-range order, which has recently been confirmed by magnetization as well as neutron diffraction measurements [3,4]. The spin structures are basically identical in the pressure-induced, field-induced, and impurity-induced ordered phases [3,18–20].

The linear and Q-independent Zeeman splitting of the triplet waves reducing the spin energy gap has been observed by INS at $H < H_c$ [21], but at $H > H_c$ the nature of

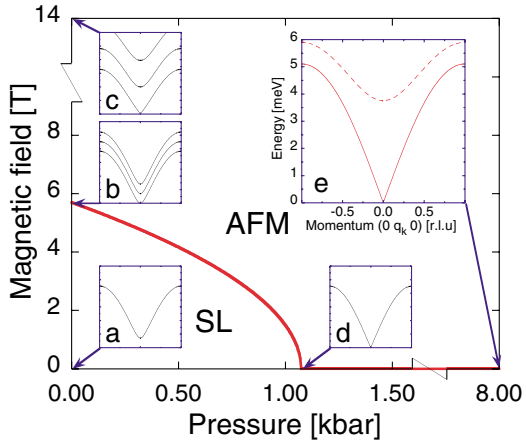

FIG. 1 (color). Magnetic field versus pressure phase diagram for the dimer compound $TlCuCl_3$ at $T = 0$ K. A square root phase boundary separates the spin-liquid (SL) phase from the AFM phase. Insets: Spin dynamics around the AFM zone center [7,8], $\boldsymbol{Q} = \boldsymbol{q} + \boldsymbol{\tau} = (0\ q_k\ 0) + (0\ 4\ 0)$ in reciprocal lattice units (r.l.u.). Common scale for (a)-(e), possible anisotropy gaps are not considered. (a) Degenerate triplet modes [12,13]. (b) Zeeman split triplet modes at H_c [21]. (c) Spin dynamics in the field-induced ordered phase [5]. (d) Degenerate and linear triplet modes close the spin energy gap at the critical pressure p_c (e) Spin dynamics in the pressure-induced ordered phase. Two degenerate transverse Goldstone modes (solid line) and a longitudinal amplitude mode (dashed line) are expected [8].

the excitation spectrum changes dramatically [5]. The spin dynamics in the field-induced ordered phase is characterized by the coexistence of a gapless, linear Goldstone mode with gapped and quadratic dimer excitations, see Fig. 1(c), which supports the interpretation of the ground state as a condensate consisting of triplet ($S = 1$; $S_z = +1$) and singlet states ($S = 0$; $S_z = 0$). This experimental finding especially contrasts the classical picture of an ordered antiferromagnet, where the dynamics is dominated by spin waves only. However, a recent low-frequency ESR study [22,23] gave evidence for a tiny and anisotropic spin gap with minimal value $\tilde{\Delta} \approx 0.09$ meV at $H = 14$ T, which was not observed in our previous INS experiments because of the limited instrumental resolution. The origin of this gap in terms of exchange anisotropy [23] or Dzyaloshinsky-Moriya interactions [24] is currently under discussion, whereas the spin gaps of the excitations at $H > H_c$ for the $S = 1$ Haldane spin system $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ and the $S = 3/2$ dimer compound $Cs_3Cr_2Br_9$ could recently be attributed to large single ion anisotropies [25,26].

We focus now on the pressure dependence of the spin dynamics at $H = 0$ T. The magnetic interactions between the spin moments in insulators strongly depend on the exchange pathways defined by the interatomic distances and bond angles. On the other hand the ground state of a spin system strongly depends on the dimensionality, the relative sign as well as the strength of the exchange interactions. The elementary excitations, the $S = 1$ triplet states, can delocalize by hopping to a neighboring dimer site, which leads to dispersion of these excitations with a bandwidth defined by the interdimer couplings J_i. Assuming an increase of the bandwidth by an increase of J_2 and J_3, which is motivated in Ref. [8], the spin energy gap can progressively be reduced or eventually be closed by application of pressure. Internal pressure, e.g., substitution of Tl^+ by K^+ or NH_4^+, unfortunately increases the spin gap [27] or produces a more complex behavior with magnetization plateaus caused by a superstructure of inequivalent dimer sites [28], respectively. However, external pressure offers the unique possibility to continuously tune $TlCuCl_3$ through the quantum phase transition separating the dimer spin liquid from the magnetically ordered phase. The three triplet components ($S = 1$; $S_z = +1, 0$, and -1) can condense into the singlet ground state at $p = p_c$. More specifically, a continuous evolution of the degenerate triplet waves in zero field from a gapped and quadratic dispersion at $p = 0$ kbar to a gapless and linear dispersion at $p \geq p_c$ is predicted theoretically [8]. This is in explicit contrast to the transition at $H = H_c$, where the degeneracy of the $S = 1$ triplet states is lifted and only the triplet component with $S_z = +1$ closes its individual spin gap [7,8]. At $p > p_c$ the "classical" dynamics of an ordered antiferromagnetic (AFM) should therefore be recovered. Two degenerate spin wave branches (transverse) and a longitudinal mode are expected, with strongly pressure-dependent stiffness and gap, respectively [8].

Elastic and inelastic neutron scattering experiments have been performed on the triple-axis spectrometer TASP installed at the Swiss spallation neutron source, SINQ, Paul Scherrer Institute. The measurements were performed at fixed final energy $E_f = 4.7$ meV with a cooled beryllium filter in front of the focusing analyzer. A standard instrumental setup with 80'-open-open horizontal collimation has been applied to gain intensity. $TlCuCl_3$ single crystals (sample masses 0.5 and 2.0 g)

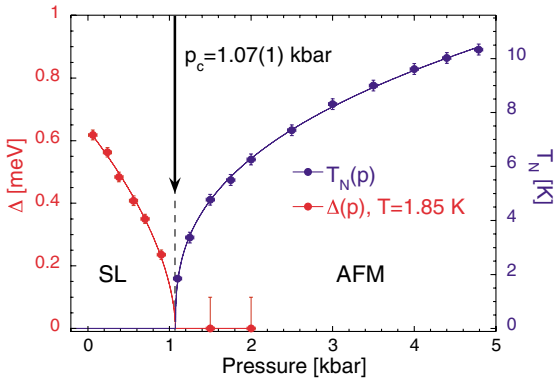

FIG. 2 (color). Pressure-induced quantum phase transition in $TlCuCl_3$ between SL and AFM phases. Singlet-triplet gap $\Delta(p)$ and Néel temperature $T_N(p)$ measured at $\boldsymbol{Q} = \boldsymbol{\tau} = (0\ 0\ 1)$ r.l.u.

were mounted in a clamp pressure cell (aluminum/TiZr) and a tunable ^{4}He-gas pressure cell ($p < 5$ kbar), respectively, and inserted in a standard ^{4}He cryostat to achieve temperatures $T \geq 1.5$ K. The clamp pressure cell contained additionally the pressure medium Fluorinert^{TM} FC-77 and NaCl powder for calibration. For this setup the pressure was determined by measuring the relative change of the lattice constants of NaCl using neutron powder diffraction. The refinements of the diffraction patterns yield a value $p = 7.3(5)$ kbar at $T = 4.2$ K with no significant deviations for the NaCl powder on top and below the sample position inside the clamp cell, which further indicates the quasihydrostatic conditions of our high-pressure setup.

The pressure dependence of the singlet-triplet spin energy gap $\Delta(p)$ has been measured up to $p = 2.0$ kbar. The results are summarized in Fig. 2 and typical energy scans are presented in Fig. 3(a). We observe a softening of the gap for increasing $0 < p < p_c$. The INS spectra at $p_c < p \leq 2$ kbar are consistent, within instrumental resolution, with a gapless excitation spectrum. Neutron diffraction experiments have been performed to observe long-range magnetic ordering above p_c. The Néel temperature as a function of pressure $T_N(p)$ is extracted from the characteristic temperature dependence of magnetic Bragg peaks and shown in Fig. 2. A combined fit to $\Delta \propto (p_c - p)^{\alpha}$ and $T_N \propto (p - p_c)^{\beta}$ yields $p_c = 1.07(1)$ kbar, $\alpha = 0.56(4)$ and $\beta = 0.37(2)$. Our high-pressure value $T_N(7.3\ \text{kbar}) \approx 14$ K and $T_N(14.8\ \text{kbar}) \approx 16.9$ K from Ref. [3] (not shown) satisfactorily agree with the fitted phase boundary for $p_c < p < 5$ kbar.

Additional INS experiments were performed at $p = 7.3$ kbar to study the spin excitations around the AFM zone center $\boldsymbol{Q} = \boldsymbol{q} + \boldsymbol{\tau} = (0\ q_k\ 0) + (0\ 4\ 0)$ r.l.u. Fig. 3(b) shows a representative scan at $E = 1.5$ meV and $T = 1.5\ \text{K} < T_N$, which exhibits a two-peak structure at $q_k \approx \pm 0.1$ r.l.u. The absence of the inelastic lines at $T = 30\ \text{K} > T_N$ as well as around the AFM zone boundary $\boldsymbol{\tau} = (0\ 3\ 0)$ at $T = 1.5\ \text{K} < T_N$ and $E = 1.5$ meV proves that the observed inelastic signals correspond to the spin dynamics in the pressure-induced ordered phase. The resulting dispersion of the spin waves is presented in Fig. 4 and compared to our results in the field-induced ordered phase at $H = 14\ \text{T} > H_c$ [5]. The striking observation is the considerable increase of the spin wave stiffness in the pressure-induced ordered phase, which further proves that the compression of the crystal structure leads to an increase of the effective exchange interactions. The expression $\hbar\omega(q_k) = a \sin(\pi q_k/2) \approx a(\pi/2)q_k$ yields $a = 8.67(4)$ meV/(r.l.u.) at $p = 7.3$ kbar compared to $a = 4.08(1)$ meV/(r.l.u.) observed at $H = 14$ T and $a = 4.51$ meV/(r.l.u.) calculated for $p = p_c$ [8]. The spin wave stiffness along the reciprocal b^* direction reads $a = (2J_3(J + J_1 + J_2 + 2J_3))^{1/2}$, i.e., it is sensitive to both the intradimer and the interdimer exchange interactions. It is not possible to determine the detailed changes of the interactions on the basis of the dispersion relation along only one direction. But following the discussion in Ref. [8],

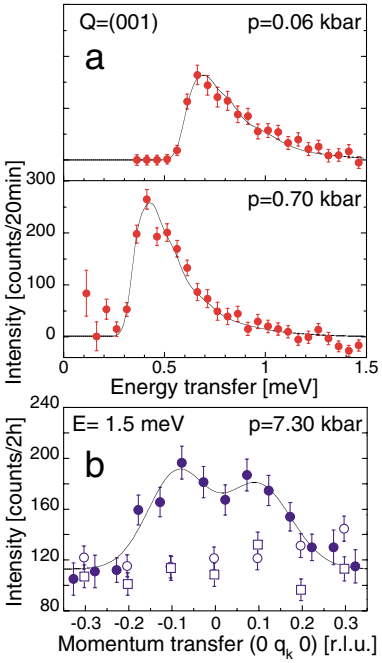

FIG. 3 (color). (a) Inelastic neutron scattering intensity in $TlCuCl_3$ at the AFM zone center $\boldsymbol{Q} = \boldsymbol{\tau} = (0\ 0\ 1)$ r.l.u., $p < p_c$ and $T = 1.85$ K. Elastic incoherent and inelastic background scattering measured away from the AFM zone center have been subtracted. (b) Constant-energy scan at $E = 1.5$ meV (solid circles), $\boldsymbol{Q} = \boldsymbol{q} + \boldsymbol{\tau} = (0\ q_k\ 0) + (0\ 4\ 0)$ r.l.u. and $T = 1.5$ K. To be compared with the corresponding scan at $T = 30\ \text{K} > T_N$ (open circles) and at the AFM zone boundary $\boldsymbol{\tau} = (0\ 3\ 0)$ r.l.u. (open squares). Solid lines in (a) and (b) represent least-square fits including convolution with the full 4D resolution ellipsoid.

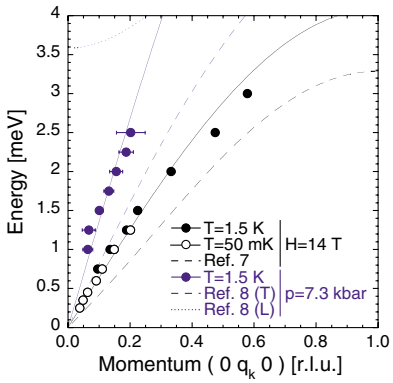

FIG. 4 (color). Spin dynamics in $TlCuCl_3$ measured at $p = 7.3\ \text{kbar} > p_c$ and $H = 0$ T compared with $p = 0$ kbar and $H = 14\ \text{T} > H_c$ [5], $\boldsymbol{Q} = \boldsymbol{q} + \boldsymbol{\tau} = (0\ q_k\ 0) + (0\ 4\ 0)$ r.l.u. The solid lines represent fits described in the text. Predictions from theory [7,8] are shown for the field-induced (dashed black line) and the pressure-induced ordered phase with transverse (T, dashed blue line) and longitudinal (L, dotted blue line) modes.

the dimer unit itself (J) as well as J_1 are expected to be stable towards small distortions in contrast to $J_2(p)$ and $J_3(p)$. Assuming mainly the pressure-induced change of these values, we derive approximately an increase by a factor of 2 at $p = 7.3$ kbar. The additional first-order type distortion of the lattice at the ordering transitions, as recently observed by NMR [29], and the uncertainty in the exact pressure dependence of the exchange interactions can easily explain the quantitative, but systematic deviations between theoretical predictions and experiment, see Fig. 4. The external pressure may further promote possible sources of anisotropy in $TlCuCl_3$. As a consequence a gap in the spin wave spectrum may equally be expected in the pressure-induced ordered phase, which is indicated by our data, but could not clearly be resolved under the present experimental conditions [Bragg and incoherent scattering dominate below $E \approx 0.8$ meV around $\tau = (0\ 4\ 0)$ r.l.u.]. The nature of the anisotropy has further to be known in order to improve our model and can therefore not be considered in the present analysis.

We have up to now no experimental evidence for the longitudinal mode predicted by theory. Its verification remains a formidable task, because a finite lifetime, caused by decay processes into pairs of spin waves, and a strongly reduced spectral weight, compared to the transverse modes, are expected, according to recent calculations [8]. Further experimental studies on high-flux instruments and in an extended energy range are planned to search for this unconventional mode.

To summarize, we have studied the spin dynamics across the pressure-induced quantum phase transition of a dimer spin liquid, see Fig. 1. The singlet-triplet spin energy gap $\Delta(p)$ softens at $p_c = 1.07(1)$ kbar, where AFM ordering occurs with a power-law dependence of $T_N(p)$. At $p = 7.3$ kbar, i.e., above the critical pressure p_c, linear spin waves are observed with a considerably increased stiffness compared to the low-energy mode in the field-induced ordered phase measured at $H = 14\ \mathrm{T} > H_c$ and zero pressure, which is consistent with recent theoretical predictions. These results clearly demonstrate that dimer quantum spin systems with a spin energy gap of singlet-triplet nature can be driven to an ordered phase by external pressure. The driving mechanism for the quantum phase transition is hereby the change in the exchange interactions closing the spin gap at p_c. The ordered phase might then be described by a condensation of triplet quasiparticles into the singlet ground state, which has also successfully been applied to the field-induced ordered phase [5–9]. However, only the lowest Zeeman split triplet mode ($S = 1$; $S_z = +1$) closes its individual spin gap at H_c, whereas three degenerate triplet modes ($S = 1$; $S_z = +1$, 0, and -1) soften at p_c. With the present work we hope to stimulate future experimental and theoretical studies of possible pressure-induced ordered phases in related spin systems with quantum-disordered ground states.

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