Persistence of singlet fluctuations in the coupled spin tetrahedra system Cu$_2$Te$_2$O$_5$Br$_2$ revealed by high-field magnetization and $^{79}$Br NQR - $^{125}$Te NMR

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We present high-field magnetization and $^{79}$Br nuclear quadrupole resonance (NQR) and $^{125}$Te nuclear magnetic resonance (NMR) studies in the weakly coupled Cu$^{2+}$ ($S=1/2$) tetrahedral system Cu$_2$Te$_2$O$_5$Br$_2$. The field-induced level crossing effects were observed by the magnetization measurements in a long-ranged magnetically ordered state which was confirmed by a strong divergence of the spin-lattice relaxation rate $T_1^{-1}$ at $T_0=13.5$ K. In the paramagnetic state, $T_1^{-1}$ reveals an effective singlet-triplet spin gap much larger than that observed by static bulk measurements. Our results imply that the inter- and the intra-tetrahedral interactions compete, but at the same time they cooperate strengthening effectively the local intratetrahedral exchange couplings. We discuss that the unusual feature originates from the frustrated intertetrahedral interactions.

Frustrated quantum spin systems have proven to be fertile ground for studying the rich variety of quantum phases, novel magnetic excitations, and quantum criticality. In particular, in quasi-zero dimensional systems where localized spin clusters (dimers or tetrahedra with a singlet ground state) are weakly coupled to each other, combined quantum effects of reduced dimensionality and frustration can lead to an intriguing ground state due to the proximity to a quantum critical point (QCP). In this case, the concomitant occurrence of localized singlet fluctuations and collective gapless excitations may allow Goldstone-like and gapped transverse modes and a longitudinal mode.

The oxohalide Cu$_2$Te$_2$O$_5$X$_2$ (X=Br,Cl) represents a weakly coupled spin tetrahedral system in which four Cu$^{2+}$ spins form a distorted tetrahedron with comparable nearest and next-nearest exchange constants, $J_1$ and $J_2$. It undergoes an incommensurate magnetic ordering at 11.4 K for Br and at 18.2 K for Cl, but the nature of the magnetic behaviors for the two systems differs from each other. The Cl system features an almost fully ordered magnetic moment of Cu$^{2+}$ ($0.88 \mu_B$) and a mean-field-like behavior of $T_N$ in fields. In this regard, the chloride can be approximated by a classical magnet, although the effect of residual quantum fluctuations seems to persist. For the Br system, by comparison, an unusual transition at 11.4 K (Ref. [9]) takes place in a singlet background with a strongly reduced magnetic moment of 0.4$\mu_B$. The anomalous field dependence of the transition temperature $T_0$ and the presence of a longitudinal magnon coexisting with a gapped singlet-like mode manifests the dominance of quantum fluctuations. Chemical and hydrostatic pressure measurements suggest the closeness of the Br system to a QCP.

Currently, there is a lack of understanding of the interplay between the inter- and the intratetrahedral interactions in Cu$_2$Te$_2$O$_5$Br$_2$, which is likely the cause for many discrepancies between experiment and theory in this system. Motivated by this, we carried out high-field magnetization measurements, as well as $^{79}$Br ($I=3/2$) nuclear quadrupole resonance (NQR) and $^{125}$Te ($I=1/2$) nuclear magnetic resonance (NMR) in a high-quality Cu$_2$Te$_2$O$_5$Br$_2$ single crystal. A remarkable finding is that a softening of the trilopon spectral weight in this system is negligible, in spite of the large intertetrahedral (IT) coupling which leads to a three-dimensional (3D) magnetic order at low temperatures, indicating the unconventional role of the IT coupling for the magnetic properties of Cu$_2$Te$_2$O$_5$Br$_2$.

Single crystals of Cu$_2$Te$_2$O$_5$Br$_2$ were prepared by the halogen vapor transport technique, using TeBr$_4$ and Br$_2$ as transport agents. High-field magnetization measurements were performed at the Dresden High Magnetic Field Laboratory using a pulse magnet with a 20 ms-duration pulsed field. The magnetic moment was detected by a standard inductive method with a pick-up coil device up to 60 T at 1.4 K. $^{79}$Br NQR and $^{125}$Te NMR measurements were performed in the temperature range 13 – 300 K. A single NQR line of $^{79}$Br was detected at 87.4 MHz at 15 K in zero field, as reported in Ref. [17]. $^{125}$Te NMR was measured in the fields of 8 T and 11.8 T along the $c$ axis. While the $^{125}$Te NMR spectrum consists of four lines from four inequivalent Te sites for an arbitrary orientation of the magnetic field, those lines collapse into a very narrow single line when the external field $H$ is parallel to the $c$ axis, allowing accurate determination of the Knight shift $K$ and complete saturation of the line for the measurements of $T_1^{-1}$.

Figure 1 shows the high-field magnetization curve $M(H)$ measured at 1.4 K in the ordered state. A strongly anisotropic magnetization behavior was observed. For $H$ perpendicular to the $c$ axis, $M(H)$ displays a linear field dependence at high fields while it shows a smaller slope at low fields. The change in the slope might be related to a spin-flop-like transition for helical magnetic ordering. In contrast, for $H$ parallel to the $c$ axis, $M(H)$ is much reduced with a concave curvature. Up to 60 T, we find two tiny magnetization jumps at $H_{c1}=21.2$ T...
and $H_{c2} = 42.4$ T, which are equally spaced as evident from the derivative $dM/dH$. We find that $g_B H_{c2} = 31$ K, where $g = 2.15$ agrees with the onset of the Raman scattering continuum, i.e., $43\text{ cm}^{-1} = 2\Delta = 62$ K, where $\Delta$ can be interpreted as the spin gap between the lowest excited triplet ($S_z = +1$) and a singlet ($S = 0$). Therefore, we conclude that the first level crossing occurs at $H_{c1}$. Then, $H_{c2}$ may be attributed to the level crossing between one of the quintet ($S_z = +2$) and a singlet. From the slope of $-2g_B H$, the quintet energy level at $H = 0$ is estimated to be $\sim 125$ K from the singlet which also turns out to be a reasonable value (i.e., $\sim 3J_1$ where $J_1 \sim 47$ K [Ref. 4] is the nearest neighbor exchange) [see the red (gray) solid line in Fig. 4]. The finite slope in $M(H)$ below $H_{c2}$ indicates the presence of magnetic moments due to an admixture of triplets to the otherwise singlet ground state. Dzyaloshinsky-Moriya (DM) interactions can admix triplet excitations into the singlet ground state and thus give rise to a weak linear field dependence for $H < H_{c1}$. However, they are not sufficient to explain the observed strong, nonlinear increase of the magnetization. Since the ground state is magnetically ordered, we invoke the substantial IT interactions as an origin. However, the observation of the magnetization steps is compatible neither with a half-magnetization plateau predicted for a chain of spin tetrahedra in a spin gap state nor with a mean-field theory of coupled tetrahedra which does not show such steps. This suggests an intriguing role of the IT interactions, which induce a long-range ordering while retaining the discrete energy levels of an isolated tetrahedron. This might be associated with a complex frustrated IT interactions.

Figure 2 shows the $^{125}\text{Te}$ Knight shift $\kappa$ measured at $8$ T and $11.8$ T parallel to the $c$ axis as a function of $T$. $\kappa(T)$ increases with decreasing $T$ reaching a maximum at $\sim 34$ K. The local maximum is followed by a rapid drop at low $T$, which is a typical behavior found in spin gap systems. In spin dimer and spin ladder systems, $T^\alpha \exp(-\Delta_K/T)$ is used to extract the singlet-triplet gap of $\Delta_K$. However, no analytic expression for the exponent $\alpha$ is known for a spin tetrahedral system. In addition, in our case the prefactor $T^\alpha$ is expected to be nullified due to strong IT and DM interactions. Thus, an activated Arrhenius form is employed to describe $\kappa(T)$ at low $T$. Note that the bulk static susceptibility $\chi(T)$ was unable to measure the spin gap directly since it is strongly affected by paramagnetic impurities at low $T$, whereas $\kappa(T)$, i.e., the local static susceptibility is insensitive to impurities. As shown in the inset of Fig. 2, $\kappa(T)$ depends on $H$ only at sufficiently low $T$, yielding $\Delta_K = 23$ K and $20$ K, at $8$ T and $11.8$ T respectively. The $H$-dependence of $\Delta_K$ is in satisfactory agreement with the Zeeman splitting estimated from $H_{c1}$ in $M(H)$ (see the open triangles of Fig. 4).

The spin-lattice relaxation rates $T_1^{-1}$ of $^{125}\text{Te}$ in fields parallel to the $c$ axis as well as $^{79}\text{Br}$ in zero field as a function of $T$ are presented in Fig. 3(a). While $T_1^{-1}$ is almost $T$-independent above $100$ K, it starts to decrease exponentially with decreasing $T$ below $\sim 70$ K. This indicates that most of spectral weights lie at the spin singlet state due to proximity to a QCP, despite the long-ranged magnetic ordering at $T_0$. (For the $^{79}\text{Br}$, $T_1^{-1}$ is not measurable above $50$ K due to the shortening of the spin-spin relaxation time $T_2$.) Near $15$ K, all the $T_1^{-1}$ data, regardless of the presence or the magnitude of $H$,
start to increase abruptly and diverge at a well-defined temperature $T_0 = 13.5$ K, confirming the magnetic origin of the transition. The extremely narrow transition width ($\ll T_0$) above $T_0$ corroborates the 3D character of the magnetic order suggested in previous studies. 

Surprisingly, $T_0$ identified in our study is considerably higher than 11.4 K in Ref. 8 and 10.5 K in Ref. 17. While a higher $T_0$ usually suggests a higher sample quality, the strongly sample-dependent variation of $T_0$ up to 30% is quite unusual. Rather, we interpret such a largely varying $T_0$ as a signature that the system lies in the vicinity of a QCP. Namely, $T_0$ is directly related to the quantum instability which is very sensitive to nonmagnetic impurities or “chemical doping”.

Another peculiar feature is that $T_0$ is robust against $H$ up to 11.8 T. This is in good agreement with the thermal conductivity measurements in which $T_0$ increases with increasing $H$ only for $H \perp c$ but does not change for $H \parallel c$ up to 6 T. Thus, our data indicate that the anisotropy of $T_0(H)$ persists at least up to 12 T, which may be related to the anisotropy of the magnetization.

In Fig. 3(b), $T_1^{-1}$ is plotted against $T^{-1}$ to examine a thermal activation behavior. Below ~30 K (0.033 K$^{-1}$), all the data are well fit by an Arrhenius form $T_1^{-1} \propto \exp(-\Delta T_1/T)$ giving rise to the $H$-dependent spin gap $\Delta T_1(H)$ (solid lines). The obtained values of the gap $\Delta T_1$ as a function of $H$ are drawn in Fig. 4. Clearly, $\Delta T_1(H)$ follows a Zeeman splitting expected for a singlet-triplet gap in an isolated tetrahedron, shown as a dashed line given by $\Delta T_1(0) = g\mu_B H$ with $\Delta T_1(0) = 56$ K. Thus, our results show that $H$ parallel to the $c$ axis has no influence on both $T_0$ and the spin gap itself, and does not cause any field-induced effect, suggesting that the singlet tetrahedron is almost intact in fields. This is in contrast to the theoretical prediction and thus suggests that the DM interaction, which should give a nontrivial $H$-dependence, is fairly small in this system, at least, for $H \parallel c$.

An unexpected finding is that the spin gap values of $\Delta T_1(H)$ are much bigger than those from both the magnetization and the Knight shift, implying that $T_1^{-1}$ sees a larger spin gap. In fact, a larger gap from $T_1^{-1}$ than from the spin susceptibility is often observed in low-dimensional spin gap systems. One plausible expla-
nation is because $T_{J}^{-1}$ samples the $q$-sum dynamical susceptibility, i.e., $T_{J}^{-1} \propto \sum_{q} \chi''(q, \omega_{j})$ where $A(q)$ is the hyperfine form factor and $\omega_{j}$ the nuclear Larmor frequency, so that $\sum_{q} \chi''(q, \omega_{j})$ may exhibit a larger gap if the gap formed in $\chi''(q, \omega_{j})$ is larger at $q = Q$ than at $q = 0$. That is, the contribution of the dominant spin fluctuations at $q = Q$ to $T_{J}^{-1}$ decreases more rapidly than that near $q = 0$ with decreasing $T$, resulting in a larger gap. However, such a strong $q$-dependence of the spin gap is somewhat unlikely in the present case because the singlet-triplet gap should correspond to band-like gapped excitations as detected in inelastic neutron scattering (INS) study. Instead, we note that $\Delta_{J_{1}}(H = 0) = 56$ K = 4.82 meV falls into the center of the gapped excitations in INS data. Therefore, it seems that both $T_{J}^{-1}$ and INS, which are commonly described by $\chi''(q, \omega)$, detect similarly a spin gap larger than those obtained from static bulk measurements. Also, since $\Delta_{J_{1}}$ clearly displays a Zeeman splitting for a singlet-triplet gap, one can rule out a possible contribution to $\Delta_{J_{1}}$ from the quintet state. Then, we conjecture that the discrepancy in the measured spin gap values is due to frustrated IT quantum fluctuations and anisotropic DM interactions. This may lead to a band-like broadening of triplet excitations. Indeed, the recent single crystal INS measurements show that most of the spectral weight of excitations remains gapped without a substantial softening to a lower energy. In this case, the spin gap determined by the Raman scattering, the magnetization, and the Knight shift corresponds to the lowest energy of the triplon band. On the other hand, $T_{J}^{-1}$, i.e., the $q$-sum dynamical susceptibility, may see the effective spin gap where most of the spectral weight remains gapped. Assuming that the singlet-triplet gap in a completely decoupled tetrahedron $\Delta_{ST} = J_{1} = 47$ K, $\Delta_{J_{1}}(0) = 56$ K indicates that $\Delta_{ST}$ is promoted, rather than suppressed, by $J_{IT}$. The shift of the spectral weight to higher than $\Delta_{ST}$ highlights an unconventional role of the IT interactions. In semiclassical theories, higher dimensional interactions lead to a softening of the spectral weight. Thus, the gap difference $\Delta_{J_{1}}(0) - g\mu_{B}H_{c1} = 25$ K is related to the magnitude of $J_{IT}$, which in turn determines the triplon bandwidth and the longitudinal magnon energy.

The large effective singlet-triplet spin gap detected by $T_{J}^{-1}$ in the paramagnetic state, and the quantized energy levels in the magnetically ordered state detected by the equally spaced magnetization jumps, imply that the average spectral weight of the triplon is shifted to higher energies while the $q = 0$ spectral weight remains intact through the magnetic transition. This is contrasted by a coupled spin dimer system and suggests the significance of the IT quantum fluctuations related to a zero dimensionality. As a possible origin we resort to peculiar spin networks. In the studied compound, the IT interactions are frustrated since they couple the four tetrahedra in the vertical, horizontal, and diagonal directions. In this unique spin network, the IT interactions can induce the helical magnetic ordering without accompanying a softening of the triplon spectral weight. Instead, an overall energy scale of the triplon can be shifted to higher energies because the frustrated IT interactions are added to the intratetrahedral ones. Here, frustration together with a zero dimensionality retains singlet fluctuations. Indeed, this accounts for the unconventional increase of the spin gap by applying pressure, leading to a quantum phase transition to a spin singlet state. That is, both the magnitude and the frustration degree of the IT interactions are enhanced by pressure.

In conclusion, a combined study of the magnetization and $^{125}$Te NMR-$^{79}$Br NQR in the weakly coupled quantum spin system Cu$_2$Te$_2$O$_5$Br$_2$ showed that a 3D magnetic order emerges from a singlet background which would be expected in a simple isolated spin 1/2 tetrahedral system. Remarkably, our data suggest that the IT coupling not simply induces a 3D magnetic order but also increases the effective spin gap by enhancing the intratetrahedral spin-exchange processes. This unusual feature is attributed to the frustrated IT interactions which may account for the discrepancy between experiment and theory, and thus our findings will forward the establishment of a theoretical model adequate for this unique quantum system.

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