Anomalous Magnetic Excitations of Cooperative Tetrahedral Spin Clusters

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An inelastic neutron scattering study of $Cu_2Te_2O_5X_2$ (X = Cl, Br) shows strong dispersive modes with large energy gaps persisting far above T_N, notably in $Cu_2Te_2O_5Br_2$. The anomalous features: a coexisting unusually weak Goldstone-like mode observed in $Cu_2Te_2O_5Cl_2$ and the size of the energy gaps cannot be explained by existing theories, such as our mean-field or random-phase approximation. We argue that our findings represent a new general type of behavior due to intercluster quantum fluctuations and call for development of a new theoretical approach.

An essential question in solid state physics is how local quantum states evolve into extended collective states. Contrary to the enormously complex spatially distributed electron problem, magnetic insulators offer an arena of clean, well defined spin models to pursue this evolution. An especially intriguing scenario occurs when the basic magnetic units consist themselves of several spins—clusters—which when isolated exhibit a nonmagnetic singlet ground state. Such systems oppose long-ranged magnetic order and, as we shall show, even when ordered retain features of their quantum ancestry.

Materials with isolated magnetic clusters have been studied intensively in the past because of their theoretical simplicity [1]—the magnetic ground state (GS) and excitations can usually be calculated analytically. The spectrum of an isolated $S = 1/2$ tetrahedron with antiferromagnetic (AFM) exchange interactions consists of 16 discrete states, the GS being a singlet $S_{tot} = 0$. When individual clusters, each with an internal level scheme and a singlet GS, are connected through intercluster interactions, the coupled system remains a singlet as long as interactions remain sufficiently weak. The discrete level scheme is expected to survive but the weak perturbative coupling gives rise to slight dispersion and possible lifting of degeneracies. In the opposite limit of comparable inter- and intracluster excitations the system may order where internal levels give way to regular dispersive collective excitations—spin waves.

The crystal structures of $Cu_2Te_2O_5Cl_2$ (CTC) and $Cu_2Te_2O_5Br_2$ (CTB) suggest Cu^{2+} tetrahedra as elementary magnetic units [2]. Susceptibility measurements yield intracluster interaction strengths of about 40 K in both

materials [3]. CTC and CTB order magnetically at the relatively low $T_N = 18$ and 11.4 K, respectively. These compounds display a similar, possibly the most complex incommensurate (ICM) magnetic order yet solved for spin-1/2 systems [4–6], thus providing a solid benchmark for both experimental and theoretical methods. As for the excitations, inelastic neutron scattering (INS) on powders indicates a dispersive mode and a flat mode around 5.5 meV for CTC and 6 meV for CTB [7]. A recent Raman study [8] shows more details of the magnetic spectrum.

CTC and CTB are isostructural with only 7% larger unit cell volume in CTB [2]. Yet, there are differences between the two materials. (i) The higher ordering temperature implies stronger intertetrahedral exchange interactions in CTC. (ii) In CTC the magnetic moment ($0.88\mu_B$) almost reaches the classical value of $1\mu_B$ while it is strongly reduced ($0.4\mu_B$) in CTB [6]. (iii) INS measurements on powders have revealed different temperature dependencies of the magnetic features, which seem to persist high above the ordering temperature in CTB [7]. Here we report comprehensive single-crystal INS investigations, providing access to the full momentum, **Q**, and energy, ω, dependent spectrum $S(\mathbf{Q}, \omega)$.

Single crystals with reported magnetization behavior were grown by vapor transport [3]. We employed one large crystal of CTC with mass 7 g, while for CTB five crystals of total mass 0.2 g were coaligned with an overall mosaicity of 2°. The samples were aligned in the $-k/3$, k, l and $(-k/2, k, l)$ scattering planes to allow access to the magnetic ordering vectors $\mathbf{k}' = (-0.150, 0.422, 1/2)$ and $\mathbf{k}'' = (-0.172, 0.356, 1/2)$ for CTC and CTB, respectively

[6]. The neutron scattering measurements were performed on the triple-axis spectrometers IN8 (thermal neutrons) and IN14 (cold neutrons) at ILL, Grenoble, France and TASP (cold neutrons) at SINQ, PSI, Switzerland.

Figure 1 shows intensity maps of the spectrum of CTC collected on IN8 at $T = 2$ K $\ll T_N$, (a)–(b), and at 20 K, (c)–(d), just above T_N. For all measured $\mathbf{Q}$, a mode is observed at 6 meV. This dispersionless mode contributes significant weight to the direction-averaged spectrum $S(Q, \omega)$ measured by powder INS [5,7]. However, the spectrum is dominated by a dispersive band, which exhibits a gap at the ordering wave vector $\mathbf{k}'$. The dispersive band approaches this energy near the $Q_l = 1$ zone boundary, roughly doubling the intensity there. Strong dispersion in all measured directions implies significant intercluster interactions. At 20 K, the gap has collapsed, but both modes are still visible, although heavily broadened and somewhat softened in energy.

High-resolution data from cold neutron spectrometers reveal several novel features, Figs. 2(a)–2(d). The intense dispersive band actually consists of four separate modes, all dispersing according to the overall envelope seen on the lower-resolution thermal instrument, Fig. 1(b). These four modes are sharp and resolution limited. The value of the energy gap at $\mathbf{k}'$ is $\Delta_{\text{Cl}}^{\text{min}} = 1.99 \pm 0.01$ meV. Careful searches below the gap revealed a very weak mode dispersing linearly away from the incommensurate Bragg peak, with no gap down to the experimentally accessible 0.5 meV. It is highly unusual that this Goldstone-like mode (GLM) [9] is much weaker than the gapped mode at 2 meV. In simple colinear systems, the neutron intensity can vanish if the fluctuations are along $\mathbf{Q}$. This cannot be the case for the ICM magnetic structure of CTC.
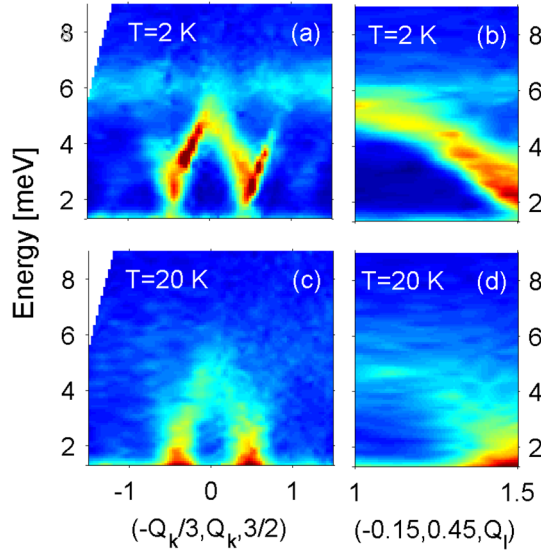
Our diffraction work [6] shows that two magnetic structures can exist in CTC, with propagation vectors $\mathbf{k}' = (-0.150, 0.422, 1/2)$ and $\mathbf{k} = (0.150, 0.422, 1/2)$. In our sample, only the $\mathbf{k}'$ propagation wave vector was present. Still, tetragonal symmetry implies two domains: $\mathbf{k}'$ and 90 degrees rotated $\mathbf{k}'_{90}$. It was therefore necessary to distinguish which of the four modes in Fig. 2(b) belong to which domain. We discovered that a moderate field of 2 T favors the ordering vector parallel to the field, thus producing a monodomain sample. This was exploited on the TASP spectrometer using vertical and horizontal field cryomagnets to select the $\mathbf{k}'$ and $\mathbf{k}'_{90}$ domains, respectively, Fig. 2(c). At $\mathbf{Q} = \mathbf{k}'$, two out of four peaks disappear upon application of the field, while the remaining two gain a factor of 2 in intensity. Hence, each domain contributes two modes to the dispersive band. Interestingly, the energy gap of 2.5 meV at the ordering vector $\mathbf{Q} = \mathbf{k}'$ is higher than the gap $\Delta_{\text{Cl}}^{\text{min}}$ at $\mathbf{k}'_{90}$. The magnetic order has lower symmetry than the tetragonal crystal lattice, so below T_N the crystallographically equivalent $\mathbf{k}'$ and $\mathbf{k}'_{90}$ points differ magnetically, and *a priori* need not have the same dispersion. The fact that for a $\mathbf{k}'$ single domain phase, the energy gap at the nonpopulated $\mathbf{Q} = \mathbf{k}'_{90}$ wave vector has a minimum probably signals the proximity of an instability towards a double-$\mathbf{k}$ magnetic structure. The gap increase at $\mathbf{k}'$ can be seen as repulsive hybridization with the GLM.

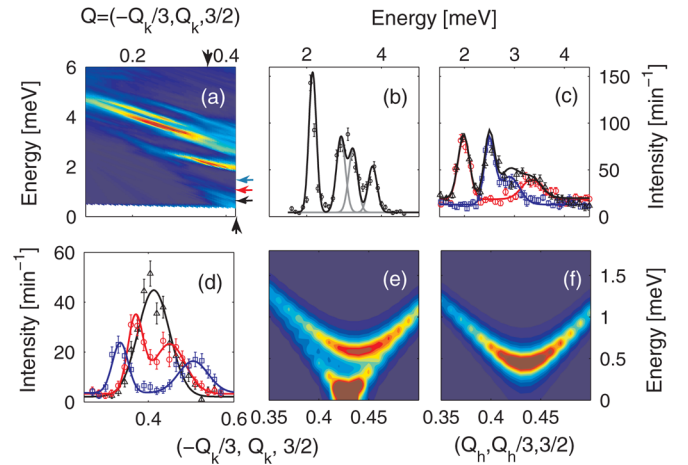Next, in Fig. 3 we present the excitation spectrum of CTB measured at IN8. A gapped band, dispersing in all

FIG. 2 (color online). High-resolution data on CTC at 1.5 K. (a) $S(\mathbf{Q}, \omega)$ map compiled from 12 energy scans on IN14. (b) Energy scan from IN14 at $\mathbf{Q} = (-0.12, 0.36, 3/2)$ showing 4 resolution limited modes. (c) Energy scans at $\mathbf{k}'$ from TASP in zero field (black triangles), 2 T parallel to $\mathbf{k}'$ (blue squares) and 2 T perpendicular to $\mathbf{k}'$ (red circles). Zero field intensities correspond to two half-populated domains and are multiplied by 2. Blue and red lines are Gaussian fits. Their sum (black line) reproduces accurately the zero field intensity. (d) $\mathbf{Q}$ scans from IN14 of the low-energy mode at 0.75, 1, and 1.75 meV (black triangles, red circles, blue squares). Lines are Gaussian fits. (e–f) RPA calculation of the spectrum of CTC around $\mathbf{k}'$ and $\mathbf{k}'_{90}$.

FIG. 1 (color online). Map of the excitation spectrum of CTC compiled from 96 individual energy scans on IN8 at 2 K (a)–(b) and at 20 K (c)–(d).
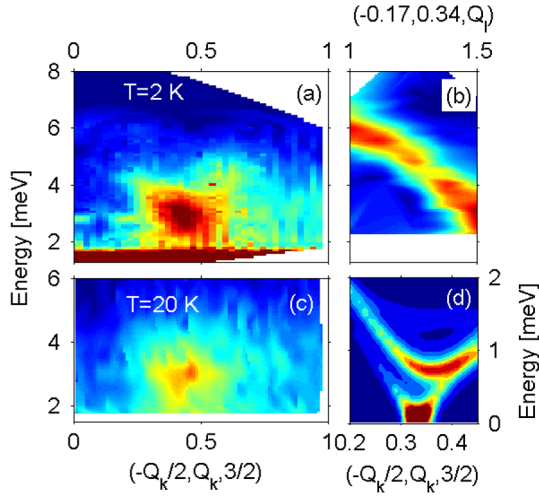
FIG. 3 (color online).   Excitation spectrum of CTB obtained at
IN8. (a)–(b) $S(\mathbf{Q}, \omega)$ maps at 2 K corresponding to Fig. 1(a) and
1(b). (c) Spectrum at 20 K. The gapped excitation remains.
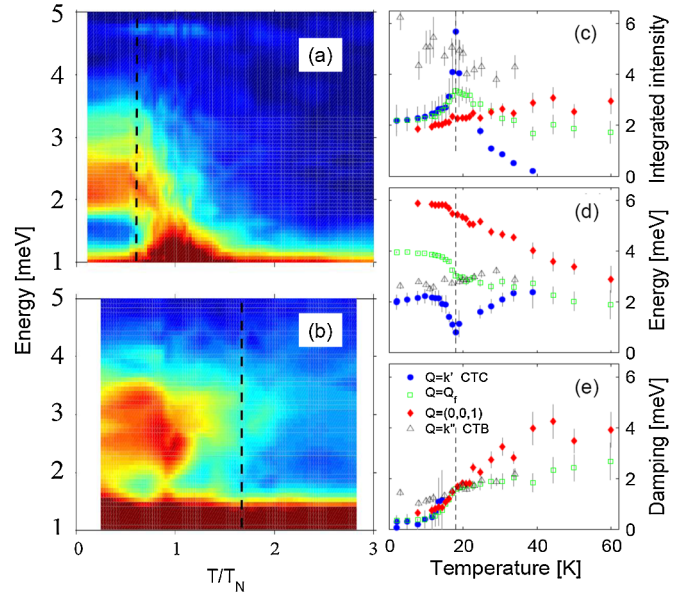(d) RPA-calculation of spectrum around $\mathbf{k}'$ at 2 K.

FIG. 4 (color online).   (a)–(b) Spectrum at $\mathbf{k}'$ and $\mathbf{k}''$ for CTC
and CTB, respectively, measured on IN8. Dashed vertical lines
indicate $k_B T = \Delta^{\min}/2$. (c)–(e) Temperature dependence of
integrated intensity, energy and damping (Lorentzian half-
width) extracted by fitting energy scans at $\mathbf{k}'$, $Q_f =
(-0.075, 0.225, 3/2)$ and $(0,0,1)$ in CTC and at $\mathbf{k}''$ in CTB. In
CTC both Q_f, chosen to achieve optimal resolution focusing,
and $(0,0,1)$ could be tracked to 60 K. At $\mathbf{k}'$ the most of intensity
softens at T_N. The low-T damping followed that of Q_f and was
fixed to the same T dependence above T_N. Just above T_N fits
were unstable and have been omitted. In CTB, the smaller
sample mass limited the analyzed range to 35 K, and sample
mosaicity prevented resolution focusing.

measured directions, similar to that of CTC, could be
observed at 2 K. The zone boundary energy (6 meV) is
similar to CTC, but the gap $\Delta^{\min}_{\mathrm{Br}} = 2.6 \pm 0.1$ meV is
higher. With the currently available sample size, high-
resolution measurements were not possible to confirm or
exclude the presence of a weak GLM.

Finally, we compare in Fig. 4 the temperature de-
pendence of the spectra at $\mathbf{k}'$ for CTC and $\mathbf{k}''$ for CTB.
In CTC, the gap at $\mathbf{k}'$ closes at T_N, above which there is
significant quasielastic scattering and only a weak inelastic
component. The fits at $Q_f = (-0.075, 0.225, 3/2)$ and at
$(0,0,1)$ show unusual temperature dependence. The inten-
sity is almost T independent with only a weak increase
around T_N. The band energy decreases and damping in-
creases as a function of temperature up to T_N, where both
display a pronounced kink to much slower T dependence.
It is unlikely that the low-T splitting in Fig. 2 would
increase with temperature; hence, the widths can be inter-
preted as damping, except maybe above 25 K for $(0,0,1)$,
where separation of optic and dispersive modes may con-
tribute. At $(0,0,1)$ intensity and energy have only faint
features at T_N. Together, this behavior is very unconven-
tional for a 3D-coupled system, where the spin waves
normally soften and dampen completely almost immedi-
ately above T_N. In lower-dimensional systems, damped
spin-waves can persist well above T_N due to a slowly
decreasing correlation length [10,11]. Our findings suggest
that significant correlations persist well above T_N up to
$k_B T \sim J$, or that the finite energy excitations above T_N can
be seen as heritage from the tetrahedral units. The situation
is even more dramatic in CTB, where most of the spectral
weight remains gapped beyond T_N, while only a weak
signature of gap closing is observed. The different behav-
iors above T_N in CTC and CTB derive from different ratios

of ordering temperature versus minimum gap. In CTC,
$k_B T_N \sim \Delta^{\min}$, meaning that once $T > T_N$, thermal fluctua-
tions smear out the gap. In CTB, $k_B T_N \sim \Delta^{\min}/3$, allowing
the gapped excitation to exist in a temperature range above
T_N before fluctuations smear the spectrum.

To understand the excitation spectrum, a model was
established, whose Hamiltonian includes Heisenberg,
Dzyaloshinskii-Moriya (DM) and dipole-dipole interac-
tions [12]. Parameters were self-consistently adjusted to
reproduce the ordering vector $\mathbf{k}'$, ordered moment, ther-
modynamic quantities and Raman spectra [13,14]. The
tetrahedral clusters were diagonalized and a mean-field
(MF) approximation was applied between clusters. The
excitation spectra calculated within a random-phase
approximation (RPA) and depicted in Figs. 2(e), 2(f),
and 3(d), reproduce several salient features of our data.
(i) At the ordering vector $\mathbf{k}'$ there is both a GLM and a
gapped mode. (ii) At $\mathbf{k}'_{90}$ there is only a gapped mode, with
lower energy than at $\mathbf{k}'$. (iii) CTB has a higher gap than
CTC. (iv) There is a correspondence between the observed
and calculated (not shown) high-temperature spectra for
both compounds. There are, however, also important dis-
crepancies between experiment and theory. The calculated

gaps are almost 4 times smaller than observed, and the intensity of the calculated GLM is stronger than the gapped mode, contrary to experiment. This is surprising because MF/RPA theory should work well in the limit of weakly coupled tetrahedra and in the limit of well connected tetrahedra, where classical 3D correlations normally would dominate. To our understanding, any other conventional semiclassical theory for excitations of an ordered state will yield a similarly strong GLM and therefore not explain our findings.

We discuss three possible origins of these discrepancies. (i) Sample imperfections could pin the ordered structure, potentially shifting excitation energies. However, careful bulk measurements show no indications of magnetic defects. Furthermore, only the $\mathbf{k}'$ domain is seen in our CTC sample, indicating good sample quality. It is further unlikely that imperfections could reduce the spectral weight of the GLM and raise the energy of the gapped mode without broadening Bragg peaks and excitations, all of which are resolution limited. (ii) It is possible to remedy the energy scale by introducing large DM interactions (or other anisotropic terms) in the Hamiltonian. However, this does not fix the relative intensities. (iii) The Hamiltonian-parameter fits prescribe coupling along the c axis and ab planes comparable to the intracluster interactions [12], which we conclude lead to intercluster quantum fluctuations not contained in the MF/RPA.

Quantum fluctuations may renormalize excitation energies and intensities [15] and angles between the spins in an ICM structure [16]. Since the MF-Hamiltonian was tuned to match the ICM structure, the true Hamiltonian might have slightly different parameters and could yield slightly different renormalized energies. However, this would still give an intense GLM within MF/RPA.

When localized magnetic singlet units are coupled increasingly strongly into a 3D lattice, there may be a quantum phase transition to an ordered state, where the fundamental excitations change from singlet-triplet excitations to spin waves. In the coupled-dimer material $TlCuCl_3$, the pressure-induced long-range order hosts Goldstone-like and gapped transverse spin-waves coexisting with a longitudinal mode [17], described in a theory coupling individual dimer states using a bond-operator formalism. However, in $TlCuCl_3$ the excitation spectrum behaves in the usual manner where the low-energy GLM is more intense than the gapped modes.

To conclude, we have in $Cu_2Te_2O_5X_2$ ($X = Cl$, Br) discovered a new situation where an ordered magnetic structure of coupled clusters is accompanied by a very weak GLM (in CTC) and an intense gapped excitation (in both CTC and CTB). In addition to this discovery, we provide a full experimental description of the excitation spectra, and report an MF/RPA theory that accounts qualitatively for several features except the unusual intensity ratio and absolute gap value. We argue that this behavior is not limited to the specific materials CTC and CTB, but represent a new general type of scenario caused by inter-cluster quantum effects. We therefore call for efforts to develop a new theoretical paradigm capable of bridging the gap between local quantized clusters and the semiclassical excitations accompanying conventional long-range order. The first step in this challenge is to identify a minimal model (dimensionality, type of magnetic order, etc.) that captures the scenario.

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