Coexistence of localized and collective magnetism in the coupled-spin-tetrahedra system Cu$_4$Te$_5$O$_{12}$Cl$_4$

Kwang-Yong Choi,1,* Seunghwan Do,1 Peter Lemmens,2 Johan van Tol,3,4 Jiseon Shin,5 Gun Sang Jeon,5 Yurii Skourski,5 Jong-Soo Rhye,6 and Helmut Berger6

1Department of Physics, Chung-Ang University, Seoul 156-756, Republic of Korea
2Institute for Condensed Matter Physics, TU Braunschweig, D-38106 Braunschweig, Germany
3Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, USA
4National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA
5Department of Physics, Ewha Womans University, Seoul 120-750, Republic of Korea
6Dresden High Magnetic Field Laboratory, Forschungszentrum Dresden-Rossendorf, 01314 Dresden, Germany

We report high-field magnetization, electron spin resonance (ESR), and Raman scattering measurements of the coupled spin-tetrahedra system Cu$_4$Te$_5$O$_{12}$Cl$_4$ with magnetic ordering at $T_N = 13.6$ K. We find thermodynamic and spectroscopic signatures for the concomitant occurrence of localized and collective magnetism. Magnetization measurements up to 60 T exhibit a spin-flop transition at $H_{c1} = 16$ T only for $H || c$ as well as periodic magnetization steps at $H_{c2} = 24.8$, $33.8$, $42.3$, and $49.7$ T, which are independent of the crystallographic orientations. For $T > T_N$, the temperature dependence of ESR linewidth is described by a critical power law, $\Delta H_{1/2}(T) \propto (T - T_N)^{-0.56 \pm 0.02}$. For $T < T_N$, an antiferromagnetic resonance mode is observed for $H || c$, and its linewidth is given by $\Delta H_{1/2}(T) \propto T^{-1.13 \pm 0.04}$, being close to $T^4$ expected for a classical magnet. Raman spectra show three one-magnon-like excitations superimposed on a broad two-magnon continuum. While the two higher frequency modes show an intensity variation in accordance to a three-dimensional Heisenberg antiferromagnet, the lower frequency mode clearly deviates. These results suggest that Cu$_4$Te$_5$O$_{12}$Cl$_4$ is a unique material which shows a dual character of zero-dimensional, localized and three-dimensional, collective magnetic behaviors.

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I. INTRODUCTION

Coupled spin-tetrahedra systems have proven to be a versatile reservoir to explore the crossover from localized spin dynamics to a more collective behavior. When intra- and intertetrahedral interactions compete with each other, there emerge a variety of interesting phenomena [1–3]. This showed up in the low-energy excitations, which constitute transverse (Goldstone) and longitudinal magnon (Higgs) modes along with gapped singlet excitations [4].

To date, only a handful of materials Cu$_2$Te$_2$O$_x$X$_2$ ($X = \text{Br, Cl}$) [designated as Cu2252], Cu$_4$Te$_5$O$_{12}$Cl$_4$ (designated as Cu45124), K$_x$Cu$_y$OCl$_{10}$, and CuSeO$_3$ have been known to realize such coupled tetrahedra [5–8]. In the last decade, research on spin tetrahedra systems has predominantly focused on the oxohalide Cu2252 family, in which four Cu$^{2+}$ spins form a distorted tetrahedron aligned in chains along the $c$ axis and are separated by lone-pair ions within the $ab$ plane [5]. The Br and Cl compounds undergo an incommensurate magnetic ordering at $T_N = 11$ and 18 K, respectively [1]. Despite the fact that both compounds share the same magnetic structure, marked differences in magnetic excitations and spin dynamics were found between them [9–22]. The Cl compound was largely described by a classical magnet while the Br compound was considered to lie in close proximity to a quantum critical point. Even for the case of the Cl compound, showing an apparent classical behavior, a mean-field or random-phase approximation theory failed to account for inelastic neutron scattering spectra [4]. This has spurred a debate on the role of spatially anisotropic intertetrahedral exchange interactions in these materials, calling for further investigations of more isotropically coupled spin tetrahedra.

Cu45124 is regarded as an isotropic cousin of Cu2252 which has a noncentrosymmetric space group $P4$. Three-dimensional (3D) arrangements of spin tetrahedra in Cu45124 are due to the centrosymmetric tetragonal structure (space group $P4/n$) and allow for the examination of intrinsic features to the 3D coupled zero-dimensional (0D) spin clusters.

Cu2252 and Cu45124 have the [CuO$_3$Cl] distorted square as a common structural unit. A corner-sharing of four such squares leads to the formation of a Cu tetrahedron as sketched in Fig. 1(a). The major structural difference between the two compounds is the presence of a Te(1)O$_4$ complex for Cu45124, which connects Cu tetrahedra in the $ab$ plane [see Fig. 1(b)]. In comparison to Cu2252, this structural change leads to the reduction of intratetrahedral and in-plane diagonal intertetrahedral interactions while strengthening out-of-plane intertetrahedral couplings [23]. This indicates that a magnetic dimensionality is increased and anisotropic exchange contributions are diminished in Cu45124. Magnetic susceptibility and specific-heat data exhibit an antiferromagnetic long-range ordering at $T_N = 13.6$ K [6]. Consistently with first-principle calculations [23], the overall energy scale of magnetic Raman excitations is reduced as compared to Cu2252.

In this paper, we employ high-field magnetization, electron spin resonance (ESR), and Raman spectroscopy to investigate the magnetic properties of Cu45124, a more three-dimensional...
The samples were installed into a He-cooled closed cycle cryostat with a temperature range of $T = 3–300$ K. The spectra were collected via a Dilor-XY 500 triple spectrometer equipped with a nitrogen cooled charge-coupled device detector.

III. RESULTS AND DISCUSSION

A. Magnetic susceptibility and high field magnetization

Figure 2 presents the field dependence of the dc magnetic susceptibility $\chi(T) = M/B$ for $H \parallel a$, measured in a low-temperature range of $T = 2–25$ K. With decreasing temperature $\chi(T)$ shows a broad maximum around $T_{\text{max}} = 18$ K and, subsequently, a small kink at $T_N = 13.6$ K, as indicated by the arrow and, finally, drops to a finite residual value as $T \to 0$. The broad maximum is related to the onset of short-range antiferromagnetic ordering, typical for frustrated spin systems. The kink feature indicates a transition to the long-range ordered state for $T < T_N$.

Applying an external field, the maximum position of $\chi(T)$ shifts slightly to lower temperature but the transition temperature, identified by taking the derivative of $\chi(T)$, shows a nonmonotonic field dependence. As plotted in the inset of Fig. 2, $T_N$ slightly increases as the field is raised up to 5 T and then undergoes a slight decrease for $\mu_0 H > 5$ T. We recall that Cu2252-Cl showed a small decrease of $T_N$ with increasing $H$, which is consistent with a classical antiferromagnet [1,10]. This is contrasted by the increase of $T_N$ with an applied field, for Cu2252-Br, which was discussed in terms of dominant singlet fluctuations. Since single-ion anisotropies of Cu$^{2+}$ ions are negligible, the observed field dependence of $T_N$ for Cu45124 may result from the competition between 3D magnetic ordering and 0D singlet fluctuations.

Shown in Fig. 3 is the high-field magnetization curve $M(B)$ measured at $T = 1.5$ K for $H \parallel c$ and $H \parallel a$ using a pulsed field magnet. $M(B)$ exhibits a concave curvature with fine structures up to 60 T. $M(B)$ is anisotropic between $H \parallel c$ and $H \parallel a$ in lower fields while it becomes isotropic in higher fields. For
inset of Fig. 3). They are independent of the crystallographic levels of spin tetrahedra. With capture magnetization steps [12], reproduced well an overall shape of \( H \parallel c \) conditions by

\[
H = J_1 \sum_{i=1}^{4} S_i^a \cdot S_{i+1}^a + J_2 (S_1^a \cdot S_3^a + S_2^a \cdot S_4^a)
+ J_3 \sum_{i=1}^{4} S_i^b \cdot S_{i+1}^b + \sum_{\alpha} (S_i^\alpha \cdot S_{i+1}^\alpha + S_i^\bar{\alpha} \cdot S_{i+1}^\bar{\alpha})
+ 2J_6 \sum_{\alpha} (S_i^\alpha \cdot S_{i+1}^\alpha + S_i^\bar{\alpha} \cdot S_{i+1}^\bar{\alpha}) - g\mu_B H \cdot \sum_{\alpha} \sum_{i=1}^{4} S_i^\alpha,
\]

where \( S_i^\alpha \) denotes the spin at \( i \)th site in tetrahedron \( \alpha \), and \( \bar{\alpha} = A(B) \) for \( \alpha = B(A) \) (note that \( S_i^\alpha \equiv S_i^\bar{\alpha} \) in the first term).

The above Hamiltonian commutes with \( S_n = \sum_{i=1}^{4} S_i^\alpha \cdot \hat{n} \), where \( \hat{n} \) is the unit vector along the direction of magnetic field \( H \), and the \( \bar{\alpha} \) component of total spin is a good quantum number. It is obvious that the energy of the \( n \)th eigenstate with \( S_n \) changes linearly with \( H \),

\[
E_m(S_n;\mu_0 H) = E_m(S_n;\mu_0 H = 0) - g\mu_B H S_n.
\]

For \( \mu_0 H = 0 \), the ground state lies in the Hilbert space with \( S_n = 0 \); while the energy of the state with higher \( S_n \) decreases faster. Accordingly, we can expect that the system undergoes successive transitions to the states with higher values of \( S_n \).

The procedure of numerical calculations is as follows: For a set of coupling constants \( \{J_1, J_2, J_3, J_6\} \) we diagonalize the Hamiltonian in Eq. (1) numerically within the Hilbert space of \( S_n = -4, -3, \ldots, 4 \), respectively, yielding \( \{E_m(S_n, \mu_0 H = 0)\} \). Using Eq. (2), we can determine the ground state in the presence of magnetic field \( H \). We calculate the magnetic fields where quantum phase transitions occur between the states with different \( S_n \), which correspond to the magnetization jumps observed in experiments. We vary the values of coupling constants and obtain the optimal set, \( J_1 = 25.1 \) K, \( J_2 = 17.6 \) K, \( J_3 = 23.8 \) K, and \( J_6 = 26.4 \) K, which reproduces best the experimentally observed magnetization jumps.

Figure 4 shows the energy levels of the eigenstates as a function of \( H \) for the optimal set of exchange couplings. As is expected, four successive transitions from \( S_n = 0 \) to \( S_n = 4 \) occurs, resulting in four magnetic jumps.

The green line in Fig. 3 represents the numerical result for \( S_n \) with the variation of \( H \). The numerical results capture nicely the first four periodic magnetization jumps, corroborating a quantized nature of the observed magnetization steps. It is worthwhile to mention that the two-tetrahedron model can explain only the first four jumps because in the model the total spin \( S_n \) is limited to 4. It is expected that the cluster with more

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(Color online) Magnetization vs pulsed magnetic field for \( \text{Cu}_2\text{Te}_5\text{O}_{12}\text{Cl}_4 \) measured at \( T = 1.5 \) K for \( H \parallel c \) and \( H \parallel a \). The green solid line represents the magnetization calculated numerically from the coupled-tetrahedra spin model sketched in Fig. 1(c). See the text for parameters. Inset: Derivative \( dM/dB \) of the magnetization. Five peaks in \( dM/dB \) correspond to magnetization jumps.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{(Color online) Energy (per spin) of the eigenstates of a two-tetrahedron cluster as a function of magnetic field. The energy of the ground state is represented by a thick (red) solid line. As the magnetic field is increased, the total spin \( S_n \) of the ground state increases. Magnetization shows a jump at the magnetic field where a lower-spin state undergoes a transition to a higher-spin one.}
\end{figure}
tetrahedra can give the jumps at higher magnetic fields as well as can yield the smooth magnetization jumps as observed in the experiment.

The estimated $J_1$ in this work turns out to be a little smaller than that from the earlier study, 32.9 K, which is estimated from $\chi(T)$ based on the isolated tetrahedra model [6]. It is of interest to note that the intertetrahedral coupling constants, $J_2$ and $J_3$, are comparable to the intratetrahedral ones. Complementary to the mean-field theory, our cluster-based calculation allows for the identification of the magnetization steps. However, it is beyond the scope of the present study to account for the concomitant spin-flop and magnetization steps of $M(B)$.

### B. Electron spin resonance

To investigate the development of spin correlations we employed a high-frequency ESR technique at $\nu = 240$ GHz. In Fig. 5 we present the temperature dependence of ESR spectra for $H \parallel c$, i.e., an easy-axis direction. Each spectrum is scaled to unity. At room temperature we observe a broad signal described by a single Lorentzian absorption profile. This implies that the ESR linewidth is exchange-narrowed due to fast electronic fluctuations induced by an exchange interaction between the Cu$^{2+}$ ions. The $g$ factor is evaluated from the relation $g_\perp = h\nu/\mu_B B_{\text{res}} = 2.104 \pm 0.006$ where $\mu_B$ is the Bohr magneton and $B_{\text{res}} = 8.149 \pm 0.003$ T is the resonance field. The obtained $g$ value is typical for a copper ion with a quenched orbital moment.

As the temperature is lowered, the spectrum undergoes a broadening and a shift to lower field. In the vicinity of $T_N$, the ESR signal wipes out and reappears for temperatures below $T_N$. Upon cooling below 10 K, the spectrum narrows substantially and shifts strongly toward higher field. To analyze their evolution, we extracted the resonance field ($B_{\text{res}}$) and the peak-to-peak linewidth ($\Delta B_{pp}$) by fitting to a Lorentzian profile. The resulting $B_{\text{res}}(T)$ and $\Delta B_{pp}(T)$ are plotted in Fig. 6 as a function of temperature.

The linewidth is very broad even at room temperature and amounts to $\Delta B_{pp}(300 \text{ K}) = 1.635 \pm 0.004$ T. As the temperature approaches $T_N$, $\Delta B_{pp}(T)$ exhibits a critical broadening while $B_{\text{res}}(T)$ is $T$ independent for temperatures down to 20 K.

In the paramagnetic regime, the temperature dependence of the linewidth is given by $\Delta B_{pp}(\theta, T) = \alpha(\theta, T)\Delta B_{pp}(\theta, \infty)$ where $\Delta B_{pp}(\theta, \infty)$ is the linewidth in an uncorrelated high-temperature limit. For nonfrustrated classical magnets, $\Delta B_{pp}(T)$ is $T$ independent in the paramagnetic state. For the studied compound, however, $\Delta B_{pp}(T)$ shows a strong $T$ dependence in the whole measured temperature range. Such a behavior has been often reported in frustrated spin systems and is associated with the persistence of local spin correlations up to the Curie-Weiss temperature $\theta_{CW}$ [24–26]. Noticeably, for Cu45124 the spin correlations persist to 30 K below $T_N$, indicating that $\theta_{CW}$ does not provide a good energy scale for coupled zero-dimensional magnetism. We find that the broadening is well described by a critical power law, $\Delta B_{pp}(T) \propto (T - T_N)^{-p} + \Delta B_{pp}(\infty)$ with the exponent of $p = 0.56 \pm 0.02$ and $\Delta B_{pp}(\infty) = 1.062 \pm 0.006$ T (see the solid line in Fig. 6). The extracted critical exponent lies between $p \approx 0.3(9) - 0.4(8)$ of the distorted triangular antiferromagnet $\alpha - \text{CaCr}_2\text{O}_4$ and

![Fig. 6.](https://example.com/fig6.png)
\( p \approx 0.7(5) \) of the geometrically frustrated chain compound FeTe_2O_3Br [25,26].

Next, we will turn to the antiferromagnetic resonance (AFMR) mode observed for temperatures below \( T_N \). For an antiferromagnetically ordered magnet, the AFMR modes arise from spin-wave excitations by a microwave at \( Q = 0, \pm \vec{q}_{ICM} \). In the case of a two-sublattice antiferromagnet, two AFMR modes are allowed as sketched in the inset of Fig. 5. The lower resonance mode occurs when an external field is applied in an easy-axis direction, i.e., \( H \parallel c \). The easy-axis AFMR mode softens to zero as the applied field is increased to \( \mu_0 H_{SR} \). The observed AFMR mode is indicated by the full circle in a frequency-field diagram. Since the employed frequency is smaller than a zero-field gap, the higher resonance mode cannot be probed.

Upon cooling from \( T_N \), the AFMR signal significantly narrows as \( T \to 0 \) and its resonance field shifts towards higher fields. The AFMR linewidth is determined by the population of magnons and follows a power law \( \Delta B_{pp} \propto T^n \) with \( n = 4 \) for an antiferromagnet [27]. The linewidth of Cu45124 shows a power-law behavior \( \Delta B_{pp}(T) \propto T^n \) with \( n = 3.13 \pm 0.04 \). The obtained exponent is close to the classical value of \( n = 4 \). This is contrasted to other frustrated magnets, which show a much smaller exponent of \( n = 1.4–2.2 \) [24–26].

The weaker T dependence is normally taken as evidence for persisting singlet fluctuations into the ordered state. Based on this observation, we conclude that Cu45124 behaves almost like a classical magnet in the ordered state due to the 3D intertetrahedral interactions. On the other hand, the large \( \Delta B_{pp} \) and its T dependence persisting up to 30 \( \theta_{CW} \) in the paramagnetic phase signal the significance of 0D spin fluctuations. This coexisting feature is also reflected in \( M(B) \), which displays the spin-flop transition at lower field and the magnetization steps at higher field.

C. Phononic Raman spectra

Takagi et al. [6] have already reported Raman scattering measurements of Cu45124. In the previous study, however, the full spectrum of lattice and spin excitations could not have been elucidated due to the lack of sizable single crystals. Here we reinvestigated temperature dependence of lattice and magnetic excitations with a view of obtaining a better understanding of coupled tetrahedra.

Figure 7 compares the Raman spectra of Cu45124 measured at \( T = 3 \) K in \((aa),(cc), \) and \((ab)\) polarization. In these scattering configurations, we observe a total of 38 sharp modes in the frequency range 50–800 \( \text{cm}^{-1} \). For the tetragonal \( P4/n \) space group, the factor group analysis yields the total irreducible representation for Raman-active modes \( \Gamma_{\text{Raman}} = 18A_g(aa,bb,cc) + 18B_g(aa,bb,ab) + 17E_g(bc,ca) \). In the measured scattering geometry, we expect \( 18A_g + 18B_g \) modes, which match well with the observed number of phonons. The surplus two peaks might be due to a polarization leakage.

Assigning symmetries and eigenvectors to the specific phonon modes is almost impossible because of a dense distribution of the phonon spectrum. Instead, we group the phonon modes into four spectral regimes in accordance with the frequency separation: 40–190 (I), 200–330 (II), 340–550 (III), and 600–800 \( \text{cm}^{-1} \) (IV). The high-energy IV modes involve the vibrations of the [CuO_3Cl] blocks. The middle-energy III (II) modes contain the motions of Te, Cu, and O atoms where the lightest O (heaviest Te) atoms have the largest net atomic displacements. In the case of the group I, the Cl atoms, having a weak interaction with the other atoms, are mainly responsible for the lowest frequency modes.

Consistent with the previous study [6], the phonon modes do not show anomalously behavior and their temperature dependence is well described by weakly anharmonic displacements. Nonetheless, we find some indication of additional weak spin-phonon coupling.

In Fig. 8 we plot the frequency of the representative modes at 155 and 453 \( \text{cm}^{-1} \) as a function of temperature. The errors are within the symbol size. A tiny but discernible anomaly is observed for the 155-\( \text{cm}^{-1} \) mode in the vicinity of \( T_N \). To discriminate the small effect, the temperature dependence of the frequency is fitted to a model based on phonon-phonon
decay processes [28],
\[ \omega_{ph}(T) = \omega_0 + \frac{C}{1 + 2/(c^{\text{harm}/2k_B} T - 1)}, \]
where \( \omega_0 \) is the bare phonon frequency and \( C \) is the constant. This model provides a nice description to the experimental data over the whole temperature with \( \omega_0 = 156.65 \pm 0.07 \) (457.14 \( \pm 0.05 \) cm\(^{-1}\)) and \( C = -0.36 \pm 0.03 \) \((-2.27 \pm 0.06) \) cm\(^{-1}\) for the 155 (453)-cm\(^{-1}\) mode. The tiny drop of the 155-cm\(^{-1}\) mode below \( T_N \) is due to magnetoelastic couplings. Such a tiny effect can be understood if taking into account the long, high symmetry of Cu-O-Te-O-Cu exchange paths and the compensation of spin-phonon couplings due to the existence of an inversion center.

D. Magnetic Raman scattering

We turn now to the magnetic excitations which show a marked variation in intensity and energy with temperature. We observe sharp three modes at 35 (marked as \( M_1 \)), 40 (\( M_2 \)), and 57 cm\(^{-1}\) (\( M_3 \)) superimposed on a weak, broad continuum (2\( M \)) extending from 15 to 150 cm\(^{-1}\), as shown in Fig. 9(a). We note that the third magnetic mode \( M_3 \) was not resolved in the earlier study [6].

In the Fleury-Loudon-Elliott approach [29], the magnetic Raman scattering intensity is proportional to \( I_R \propto \langle |\langle j | \sum S_i \cdot \tilde{S}_j | j \rangle|^2 \rangle \). Inelastic scattering of an AFM ground state \( \langle S = 1/2, S_z = \pm 1/2 \rangle \) by light occurs via double spin-flip processes into a higher state \( \langle S = 1/2, S_z = \mp 1/2 \rangle \) since a Raman scattering process conserves the total spin of the \( z \) component \( \langle S_z^\text{tot} = 0 \rangle \). The spectral weight of this two-magnon scattering is given by the density of states of a two-magnon spectrum,
\[ \rho_2(\omega) = \sum \delta(\omega - \omega_0 k) \],
where \( \omega_0 \) is a one-magnon dispersion. Based on the broad line shape and temperature dependence, the continuum is assigned to two-magnon scattering. The sharp \( M_3 \) peaks disappear for \( T > T_N \). This behavior is characteristic of one-magnon-like excitations. These zone-center transverse and longitudinal magnon modes are Raman active by virtue of spin-orbit coupling and/or anisotrophic exchange interactions which manifest themselves in an exchange anisotropy [30]. Indeed, the spin-flop field of \( \mu_0 H_{sf} = 16 \) T is surprisingly large in view of the nearly quenched orbital moment of the Cu\(^{2+}\) ion. This is suggestive of the large magnitude of the anisotropic part relative to the exchange interaction.

In Figs. 9(b) and 9(c) we present the detailed temperature dependence of the magnetic Raman scattering spectra after subtracting phonon peaks. Upon warming through \( T_N \), the one-magnon \( M_1 \) modes dissolve into a continuum of excitations. At high temperatures, the one- and two-magnon excitations turn into an intense quasielastic peak due to overdamped spin excitations. For a quantitative analysis we fit them to Gaussian profiles by taking into account the broad continuum. The representative fit is shown in Fig. 9(a). The resulting parameters are summarized in Fig. 10.

The energy of the \( M_i \) modes is plotted in Fig. 10(a) as a function of temperature. The temperature dependence of the peak energies is found to be described by the relation \( E(T) = A(T - T_N)^\beta + E_0 \) with \( \alpha = 0.49 \pm 0.05, 0.54 \pm 0.07, \) and \( 0.57 \pm 0.05 \) for the respective \( M_i \) \( (i = 1–3) \). Since \( I_R \propto \langle S_z S_j S_k S_l \rangle \), the intensity of the magnetic

![FIG. 9. (Color online) (a) Representative fit of Cu\(_2\)Te\(_2\)O\(_2\)Cl\(_4\) at \( T = 3 \) K to Gaussian profiles. \( M_i (i = 1–3) \) are the three sharp magnetic signals. The shaded region denotes a total magnetic contribution consisting of two-magnon continuum and three one-magnon-like excitations. (b) and (c) Temperature dependence of the low-energy magnetic Raman scattering obtained after subtracting all phonon modes.](image)

![FIG. 10. (Color online) (a) Peak frequency of the magnetic signals, \( M_i (i = 1–3) \). See the text for the solid lines. (b) Scattering intensity of \( M_i \) on a log-log plot as a function of the reduced temperature, \( 1 - T/T_N \). (c) Temperature dependence of the scattering intensity of two magnon continuum, \( 2 M \) and quasielastic scattering, \( Q.E. \). (d) Temperature dependence of the magnetic specific heat derived from the intensity of \( Q.E \) normalized by \( T^2 \).](image)
Raman scattering yields the temperature dependence of the order parameter \( M_s \), \( I_\text{R} \propto M^4 \propto (1 - T/T_N)^d \). The critical exponent is evaluated to be \( \beta = 0.750 \pm 0.07, 0.387 \pm 0.04, \) and \( 0.363 \pm 0.09 \) for the respective \( M_s (i = 1-3) \). This is evident from a log-log plot of \( I_\text{R} \) in the reduced temperature, \( 1 - T/T_N \). The \( M_2 \) and \( M_3 \) mode is very close to \( \beta = 0.367 \) known for a 3D Heisenberg antiferromagnet. In contrast, the large value \( \beta = 0.750 \pm 0.07 \) of the \( M_1 \) mode, even bigger than a mean-field value \( \beta = 0.5 \), suggests that the \( M_1 \) mode is of different origin from the transverse magnons, \( M_2 \) and \( M_3 \). A candidate is the excited singlet pertaining to an isolated tetrahedron [20]. The other possibility is the longitudinal magnon whose energy should vanish as the temperature approaches \( T_N \) [10]. The \( M_1 \) mode undergoes a softening by 10 cm\(^{-1}\) but it has a finite energy at \( T_N \). This behavior indicates a weakly first-order transition. It is interesting to note that in Cu2252-Br, hydrostatic pressure can be used to induce a similar softening with aspects of weak first-order behavior [21].

In addition to the sharp excitations discussed above, we have also observed broader signals of magnetic origin, a 2M continuum and quasielastic scattering. With increasing temperature the 2M scattering intensity increases and even forms a maximum at 20 K, i.e., very close to the maximum in the magnetic susceptibility. The same behavior is observed in the related compound Cu2252. The 2M scattering persists to 160 K, implying the persistence of finite-energy short-range spin correlations up to \( \approx T_{2N} \). This is consistent with the critical-like broadening of the ESR linewidth in the same temperature range.

The quasielastic Raman scattering originates from either diffusive fluctuations of a four-spin time correlation function or fluctuations of the magnetic energy density [31,32]. Using a hydrodynamic description of the correlation function [33,34], the quasielastic Raman response is approximated by a Lorentzian profile \( I_{Q\text{E}}(\omega) \propto C_m T^2 D_T k^2/|\omega|^2 + (D_T k^2)^2 \), where \( k \) is the scattering wave vector, \( D_T \) is the thermal diffusion constant, and \( C_m \) is the magnetic specific heat. Since the scattering intensity of \( I_{Q\text{E}}(T) \) is proportional to \( C_m T^2 \), the magnetic specific heat is derived from the relation \( C_m \propto I_{Q\text{E}}(T)/T^2 \). In Fig. 10(d) the derived \( C_m \) is plotted as a function of temperature. We are able to identify a sharp peak at \( T_N \), which is similar to the thermodynamic specific-heat data [6].

![Fig. 11. (Color online) Comparison of the high-field magnetization between Cu45124 (upper panel) and Cu2252-Cl (lower panel) measured at \( T = 1.5 K \) for \( H \parallel c \) and \( H \parallel a \).](image)

**IV. DISCUSSION**

A direct comparison between Cu45124 and Cu2252 allows examining the influence of dimensionality and crystal symmetry on magnetism in coupled spin tetrahedra systems. The two compounds have similar magnetic parameters. This is nicely demonstrated by the ratio of \( T_N \) versus the temperature of susceptibility maximum: \( T_N/T_{\chi\text{max}} = 0.79 \) and 0.72 for Cu2252 and Cu45124, respectively. Here we summarize the key results of the magnetization, ESR, and magnetic Raman-scattering measurements.

**Magnetization.** In Fig. 11 we compare the \( M(H) \) between Cu45124 and Cu2252-Cl measured at the same temperature and orientation. For \( H \parallel c \) and \( H \parallel a \), \( M(H) \) of Cu45124 resembles each other except for the low-field spin-flip transition at \( \mu_0 H_{SF} = 16 \) T. The rather isotropic magnetization is consistent with the more 3D network of the spin tetrahedra in Cu45124. In contrast, Cu2252-Cl shows a very anisotropic magnetization curve between the two orientations: for \( H \parallel a \), \( M(B) \) increases almost linearly with \( H \) while for \( H \parallel c \), \( M(B) \) displays successive, sharp magnetization steps at \( \mu_0 H = 28.3, 31.5, \) and 34.3 T. If these are interpreted as successive spin-flip transitions, their energies are almost twice \( \mu_0 H_{SF} = 16 \) T of Cu45124. This suggests that Cu2252 has strong anisotropic intertetrahedral interactions.

**ESR.** As compared in Fig. 12(a), in the paramagnetic phase the ESR linewidth is \( \Delta_B(300 \text{K}) = 1.635 \pm 0.004 \text{ T} \) for Cu45124 and 1.823 \pm 0.009 T for Cu2252. The ESR spectrum becomes broader by 10% for Cu2252 than for Cu45124. This is related to the increase of the intratetrahedral interactions [23]. In the AFM phase the sharp AFMR mode is observed for Cu45124, which follows a classical behavior. In contrast, a well-defined AFMR mode cannot be probed for Cu2252 in the used frequency and field range [see the red line in Fig. 12(a)]. This might be due to a huge magnon gap as indicated by the large spin-flip field amounting to about 31 T.

**Magnetic Raman excitations.** As summarized in Fig. 12(b), Cu45124 has three sharp magnetic modes at 35 (\( M_1 \), 40 (\( M_2 \), and 57 cm\(^{-1}\) (\( M_3 \), while Cu2252 has four magnetic modes at 23 (\( M_1 \), 39 (\( M_2 \), 49 (\( M_3 \), and 67 cm\(^{-1}\) (\( M_4 \) [20]. In addition, there appears a broad two-magnon continuum extending from 20 to 130 cm\(^{-1}\). The center position of the continuum is \( E_m = 72 \text{ cm}^{-1} \) for Cu45124 and \( E_m = 81 \text{ cm}^{-1} \) for Cu2252. The magnetic energy and spectral weight shifts by 10% to higher energy for Cu2252. This scales with the strength of the intratetrahedra interactions and is consistent with the increase of the ESR linewidth by the same amount.

Taking the above results together, our thermodynamic and spectroscopic data demonstrate that Cu45124 behaves like a...
curves and the large spin-flop field advocate a more anisotropic magnetic structure with the increased quasi-one dimensionality. It is supported by the first-principle calculations [23], which showed pronounced in-plane diagonal intertetrahedral interactions relative to out-of-plane ones. Thus, we conclude that the difference of magnetism between Cu45124 and Cu2252 is mainly dictated by the nature of intertetrahedral exchange interactions: more 3D intertetrahedral interactions for Cu4512 vs more 1D (or 2D) intertetrahedral interactions for Cu2252. The lower connection of the spin tetrahedra in Cu2252 partly explains why a mean-field or random-phase approximation failed to reproduce the size and intensity of the gapped excitations probed by inelastic neutron scattering [4,18]. Given that Cu4512 lies proximate to a mean-field limit, we propose to test the validity of a mean-field theory to account for low-lying excitations using inelastic neutron-scattering experiments.

V. CONCLUSION

We have presented a combined high-field magnetization, high-frequency ESR, and Raman-scattering study of the coupled spin-tetrahedra system Cu₄Te₅O₁₂Cl₄. Our thermodynamic and spectroscopic data reveal the many-sided aspects of coupled spin-tetrahedra magnetism that cannot be fully disclosed in the related compound Cu₃Te₂O₁₂Cl₂ due to anisotropic spin-tetrahedra connections. In the case of Cu₃Te₂O₁₂Cl₂, the three-dimensionally isotropic network of spin tetrahedra with reduced in-plane intertetrahedral couplings places the studied system closer to a 3D coupled spin tetrahedra system, rendering the observation of both zero-dimensional quantized and three-dimensional collective magnetic behaviors. The observed coexistence is not well understood by current existing theories. While further studies are needed to obtain a unified picture of a crossover from zero- and three-dimensional physics, Cu₄Te₅O₁₂Cl₄ is an interesting class of 3D coupled zero-dimensional materials.

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FIG. 12. (Color online) Comparison of ESR between Cu45124 (blue line) and Cu2252 (red line) in a paramagnetic phase at $T = 300 \, \text{K}$ and in an antiferromagnetic phase at $T = 3 \, \text{K}$. (a) Comparison of magnetic Raman spectra between Cu45124 (upper panel) and Cu2252 (lower panel) at $T = 3 \, \text{K}$. (b) Three-dimensional antiferromagnet: (i) the spin-flop transition at $\mu_0H_{\text{SF}} = 16 \, \text{T}$ in the magnetization curve, (ii) the AFMR mode following the $T$ dependence $\Delta B_{pp}(T) \propto T^{3.13 \pm 0.04}$ expected for a classical magnet, and (iii) the transverse magnon $M_2$ and $M_3$ modes whose intensities display an order parameter of a 3D Heisenberg antiferromagnet. This is further supported by the first-principle calculations [23], which disclosed a three-dimensional arrangement of spin tetrahedra. However, detailed features cannot be captured within a conventional 3D antiferromagnet.

Significantly, there are experimental indications that an isolated tetrahedron related physics is not totally exhausted in spite of 3D interactions. The periodic magnetization jumps and the $T$ dependence of the $M_1$ mode are taken as a signature from the quantized energy bands and singlet fluctuations. Although the 3D interactions broaden the energy levels of the spin tetrahedra, each band does not fully overlap at least in the low-energy regime. The crossover to a 3D classical magnet is not yet completed and thus the remnant of 0D feature is still visible. Cu45124 exhibits both localized and collective magnetism in thermodynamic and spectroscopic measurements.

These observations are in stark contrast to Cu2252. Neither the periodic magnetization jumps nor the conventional AFMR mode are observed. Rather, the anisotropic magnetization