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Temperature dependence of the effective interdimer exchange interaction in a weakly coupled antiferromagnetic dimer copper compound

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We report a variation with temperature T of the effective interdimeric interaction $J'_{\rm eff}$ in the antiferromagnetic (AFM) copper dimeric organic compound $\mathrm{Cu_2[TzTs]_4}$ (N-thiazol-2-yl-toluenesulfonamidate $\mathrm{Cu^{II}}$). This T dependence was obtained from measurements of the effects in the electron paramagnetic resonance (EPR) spectra of the proposed quantum phase transition associated with the exchange-narrowing processes. $\mathrm{Cu_2[TzTs]_4}$ contains exchange-coupled pairs of $\mathrm{Cu^{II}}$ spins $\boldsymbol{S}_{\mathbf{A}}$ and $\boldsymbol{S}_{\mathbf{B}}$ ($S = 1/2$), with intradimeric AFM exchange coupling $J_0 = (-115 \pm 1)\ \mathrm{cm}^{-1}$ ($\mathcal{H}_{\rm ex} = -J_0 \boldsymbol{S}_{\mathbf{A}} \cdot \boldsymbol{S}_{\mathbf{B}}$). The variation of the EPR linewidth of single crystals with field orientation around a "magic angle" where the transitions intersect and the integrated signal intensity of the so-called U peak of the powder spectrum were measured as a function of T. Modeling these data using arguments of exchange narrowing in the adiabatic regime considering the angular variation of the single-crystal spectra and a geometric description, we find that the effective interdimeric coupling $|J'_{\rm eff}|$ associated with the exchange frequency $\omega_{\rm ex}$ is negligible for $T \ll |J_0/k_{\rm B}|$ when the units are uncoupled and $|J'_{\rm eff}| = (0.080 \pm 0.005)\ \mathrm{cm}^{-1}$ ($|J'_{\rm eff}/J_0| = 7.0 \times 10^{-4}$) at 298 K. Within this T interval, two ranges of $|J'_{\rm eff}|$ with linear temperature variation but different slopes, with a kink at ~80 K, are observed and discussed. This T dependence arises from the growing population of the triplet state, and its relevance to the properties of various arrays of dimeric units is discussed. Our experimental procedures and results are compared with those of previous works in ion radical salts and dimeric metal compounds. The relation between the effective coupling $|J'_{\rm eff}|$ and the real interdimeric exchange coupling $|J'|$ related to the chemical paths connecting neighbor units is discussed.

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I. INTRODUCTION

The seminal ideas about dimeric units (DUs) [1–3] introduced ~65 years ago at the sunrise of magnetic resonance techniques have spread widely in interest and applications. A spin dimer ($\boldsymbol{S}_{i\mathbf{A}}, \boldsymbol{S}_{i\mathbf{B}}$) obeys the spin Hamiltonian [2–5]

$$\begin{aligned}\mathcal{H}_0(i) = \mu_{\rm B} \boldsymbol{B}_{\mathbf{0}} \cdot (\boldsymbol{g}_{\mathbf{A}} \cdot \boldsymbol{S}_{i\mathbf{A}} + \boldsymbol{g}_{\mathbf{B}} \cdot \boldsymbol{S}_{i\mathbf{B}}) - J_0 \boldsymbol{S}_{i\mathbf{A}} \cdot \boldsymbol{S}_{i\mathbf{B}} \\ + \boldsymbol{S}_{i\mathbf{A}} \cdot \mathcal{D} \cdot \boldsymbol{S}_{i\mathbf{B}},\end{aligned} \tag{1}$$

where $\boldsymbol{B}_{\mathbf{0}} = \mu_0 \boldsymbol{H}$ is the magnetic field, μ_0 is the vacuum permeability, $\boldsymbol{g}_{\mathbf{A}}$ and $\boldsymbol{g}_{\mathbf{B}}$ are the $\boldsymbol{g}$ matrices, and J_0 is the isotropic intradimeric exchange coupling that, for antiferromagnetic interaction ($J_0 < 0$), gives rise to a singlet ground state and an excited triplet state with energy $|J_0|$. $\mathcal{D}$ is the anisotropic spin-spin interaction matrix arising from dipole-dipole and anisotropic exchange, giving rise to the fine structure of the electron paramagnetic resonance (EPR) spectra, a very appropriate technique to study dimeric units [4–6]. Hyperfine couplings between the spins $\boldsymbol{S}_{i\alpha}$ and the nuclear spins and antisymmetric spin-spin couplings that may contribute to DUs without a center of symmetry [4] may be added to $\mathcal{H}_0(i)$ but are not needed for our present analysis. Isolated DUs described by Eq. (1) are zero-dimensional entities providing valuable model systems in physics [3,6–8], chemistry [9], and biochemistry [10,11]. The total Hamiltonian $\mathcal{H}$ for dimer arrays is a sum $\mathcal{H}_0 = \sum_i \mathcal{H}_0(i)$ of Eq. (1) over the dimeric units plus the contribution $\mathcal{H}'$ containing exchange couplings between spins in neighboring DUs,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' = \sum_i \mathcal{H}_0(i) - \sum_{i \neq j, \alpha, \beta} J'_{i\alpha, j\beta} \boldsymbol{S}_{i\alpha} \cdot \boldsymbol{S}_{j\beta}. \tag{2}$$

$\mathcal{H}'$ gives rise to triplet excitons [12,13] and a variety of quantum properties of higher-dimensional magnetic systems [14–17]. Arrays of interacting DUs have fascinating quantum and magnetic properties that have attracted great attention in recent years [6,14]. Molecular magnetism [3,6–8], spin ladders [18,19], and Bose-Einstein condensation in quantum magnets [14,17,20,21] are flowering upgrowths with $\mathcal{H}_0$ and $\mathcal{H}'$ of Eq. (2) having different characteristics, wide ranges of magnitudes, and multiple roles. Since ~1960 important lines of research about ion radical salts were followed in parallel to the work in metallic dimeric units, with many similar procedures and results [12,22,23].

Exchange-narrowing (EN) theory [24–27] states that an EPR spectrum split and broadened by intramolecular interactions as the dipole-dipole coupling may be narrowed by dynamical processes involving $\mathcal{H}'$, interchanging randomly the states of the perturbation. The classical papers on EN treated the changes in the EPR spectra of a paramagnet produced by weak exchange interactions transforming isolated spins in three-dimensional arrays. They use the adiabatic

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approximation, in which the perturbation averaged out by the exchange is essentially diagonal, a condition giving maximum transparency to the theory, and propose Gaussian fluctuations for the random local interactions [24–28]. Their results promoted progress in the understanding of spin diffusion and spin waves and played important roles in the progress of nonequilibrium statistical mechanics [29]. The basic processes of narrowing and merging the structures of the EPR spectra are described using a characteristic exchange frequency ω_{ex} and a distance $\delta\omega$ between the peaks of the structure. In paramagnetic compounds, ω_{ex} is related to the essentially T independent exchange couplings J' between neighboring spins that may be defined as $|J'| \approx \hbar\omega_{\mathrm{ex}}$, which depends on the chemical paths connecting the spins. In fact, there is not one interaction but a distribution over the neighbors. Since the short-range exchange couplings decrease exponentially with distance, average values of $|J'|$ are estimated from single-crystal EPR measurements [30–32]. Spectral changes are analyzed in three regimes [26,28]:

(a) For $\omega_{\mathrm{ex}} < \delta\omega$ the resonances broaden for increasing ω_{ex}, blurring their structures and changing shapes.

(b) For $\omega_{\mathrm{ex}} > \delta\omega$ the resonances narrow for increasing ω_{ex}, when the line structure merges to a single line.

(c) Between regimes (a) and (b), for $\omega_{\mathrm{ex}} \sim \delta\omega$ abrupt quantum transitions are observed.

The result [25] for the resonance width $\Delta\omega$ which has been applied to many situations is

$$\Delta\omega \approx \frac{(\delta\omega)^2}{\omega_{\mathrm{ex}}}. \tag{3}$$

The merging of the resonances and their widths in the slow and fast regimes [regimes (a) and (b), respectively] may be analyzed with a procedure proposed by Anderson [5,26,28] in which the resonance peaks are described by a complex line shape involving the unperturbed resonance frequencies and the exchange frequency. This method, equivalent to Bloch equations modified in the presence of exchange [5], has been used for chemical exchange processes in liquids [33], spin exchange in ion radical salts [23], and also small exchange couplings in solids [30,34–36]. EPR measurements in regime (c) have advantages in accuracy and quantum intuitiveness and are used here as described below.

If the material is composed of dimeric (or polymeric) antiferromagnetic (AFM) units instead of single spins, the EN phenomenon displays novel and interesting properties [37–39]. We show below that the exchange frequency ω_{ex} in coupled dimeric arrays is related to an effective $|J'_{\mathrm{eff}}|$ and not to $|J'|$ as in monomeric systems, a condition introducing severe changes in the exchange-narrowing processes. Since the magnetic moment of each unit varies with T approaching zero for $T \ll |J_0/k_{\mathrm{B}}|$, the effective coupling $|J'_{\mathrm{eff}}|$ should vary with the population of the excited triplet state, and the units may become magnetically isolated in the lattice at low T. This T dependence of the effective interaction between AFM DUs and its consequences for the spectra and properties of the dimer array are the goal of this investigation, in which we evaluate a T-dependent $|J'_{\mathrm{eff}}| = \hbar\omega_{\mathrm{ex}}$, measuring the effects of the quantum phase transition occurring in range (c). We study the merging and narrowing of the two allowed EPR absorptions within the excited triplet state around their intersection (crossing field B_{U}) arising from the anisotropic $\mathcal{D}$ term in Eq. (1) as a function of magnetic field orientation, moving through the quantum transitions occurring when the distance between these peaks equals the interaction $|J'_{\mathrm{eff}}|$.

We also consider the U peak, a unique feature of the powder spectra of weakly coupled DUs absent in single crystals, arising from the accumulation of EPR signal around B_{U}, from a range of field orientations where the resonances merge [37,39]. Our method replaces the study of the quantum transition occurring when the lowest Zeeman component of the triplet state crosses the singlet state as a function of the magnitude of the magnetic field, used by researchers studying Bose-Einstein condensation [14–17,20,21,40], with one where the two allowed EPR transitions intersect as a function of the orientation of $\boldsymbol{B_0}$. This replaces the method based on the Bloch equations used by other authors [23,30,34,35,41,42], avoiding less accurate fittings of line shapes.

We study the AFM compound $\mathrm{Cu_2[TzTs]_4}$ (N-thiazol-2-yl-toluenesulfonamidate $\mathrm{Cu^{II}}$), which has weakly coupled dimeric units [38,43] ($|J'/J_0| < 10^{-3}$), and EPR is best suited for our purpose. $|J'_{\mathrm{eff}}|$ is evaluated as a function of T with equal results from two independent sets of EPR data: linewidth as a function of field orientation in single crystals and intensity of the U peak in powder samples as a function of T. In order to achieve maximum transparency in the application of the EN theory to our data, we report measurements at ~34 GHz, where nondiagonal contributions of the $\mathcal{D}$ term are small compared with the dominant Zeeman interaction.

II. EXPERIMENTAL DETAILS AND RESULTS

The preparation, structure, and properties of dimeric $\mathrm{Cu_2[TzTs]_4}$ and the EPR techniques used were described elsewhere [37,38,43]. We collected EPR spectra of single crystals between 120 and 298 K at ~34.3 GHz with a Varian E110 EPR spectrometer equipped with a nitrogen gas-flux T controller and in powder samples between 4 and 298 K using a Bruker 500 spectrometer working at ~33.9 GHz with a helium-gas T controller. MATLAB [44] and EASYSPIN [45] (version 5.1.9) were used in the spectral calculations and fits. The parameters of the spin Hamiltonian $\mathcal{H}_0(i)$ for $\mathrm{Cu_2[TzTs]_4}$ reported previously [38] were verified, taking into account that the principal values D and E of the $\mathcal{D}$ matrix [5] for two interacting 1/2 spins of Eq. (1) are twice those for the spin $S = 1$ model used before [38]. In addition, the rhombic contribution $|E|$ is much smaller than the axial contribution $|D|$ and may be discarded, and the $\boldsymbol{g}$ matrices $\boldsymbol{g_A}$ and $\boldsymbol{g_B}$ are considered to be equal, with g_x and g_y differing within the experimental uncertainties. This allows us to assume axial symmetry for the problem with $g_{//} = 2.232$, $g_\perp = 2.045$, and $|D| = 0.390\ \mathrm{cm^{-1}}$ and produces an anisotropy $\delta\omega \propto |D|(3\cos^2\theta - 1)$ of the line distance, where θ is the angle between the magnetic field and the axial-symmetry direction. Figure 1 displays the angular variation of the positions of the two EPR transitions $M = \pm 1 \leftrightarrow 0$ of the excited $S = 1$ spin triplet at 34.34 GHz and 293 K in the ac^* and bc^* planes of a single-crystal sample of $\mathrm{Cu_2[TzTs]_4}$ and simulations obtained with these parameters. The distance $\delta\omega$ between these peaks varies due to the $\mathcal{D}$ term in Eq. (1), and their positions cross

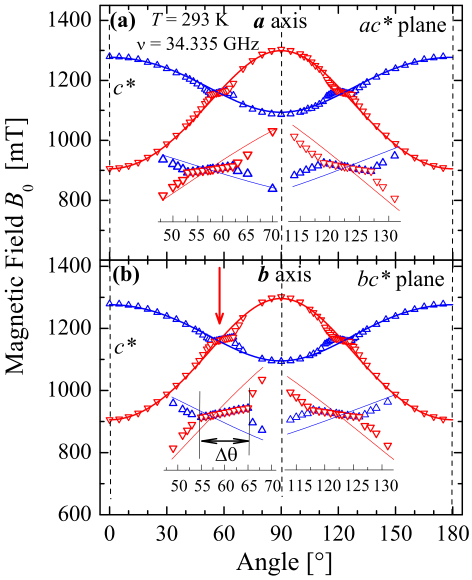

FIG. 1. Angular variation of the resonances $M = \pm 1 \leftrightarrow 0$ in the (a) ac^* and (b) bc^* crystal planes ($\boldsymbol{c^*} = \boldsymbol{a} \times \boldsymbol{b}$). Symbols are experimental results, and solid lines are obtained fitting the data outside of the merged ranges. Insets display the merging around the magic angles. Arrows in (b) indicate the magic angle and the angular range $\Delta\theta$ where the linewidth measurements as a function of T were performed.

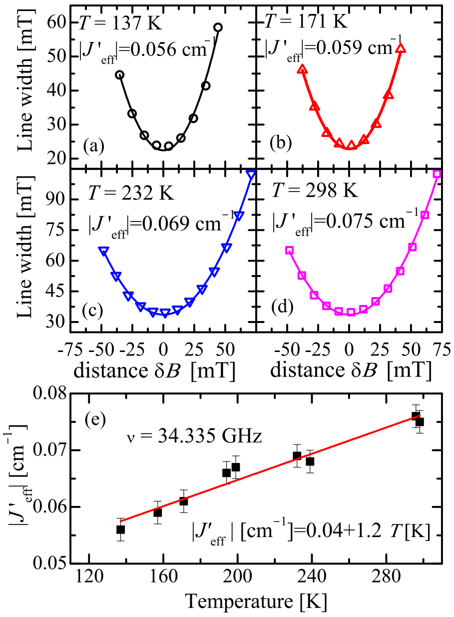

FIG. 2. (a)–(d) Linewidths of the merged signals around the magic angle in the bc^* plane [arrow in Fig. 1(b)] at selected T as a function of the distance between the fine-structure peaks without merging. $|J'_{\mathrm{eff}}|$ is obtained from fits of Eq. (3) to the data (solid lines). (e) Temperature variation of $|J'_{\mathrm{eff}}|$; symbols are experimental values with their estimated uncertainties. The line is a linear fit of the T dependence of $|J'_{\mathrm{eff}}|$.

($\delta\omega = 0$) at the so-called magic angles in cones at 54.7° and 125.3° around the z axis (where $3\cos^2\theta - 1 = 0$) [5]. Insets in Fig. 1 enhance the angular ranges where $\delta\omega \leqslant \omega_{\mathrm{ex}}$, where the two peaks merge due to the quantum entanglement produced by the interdimeric couplings. Associated with this collapse, the resonance displays a strong narrowing, which was used to calculate $|J'_{\mathrm{eff}}|$ at nine values of T in the range $120 < T < 298$ K in the merged region around the magic angle $\theta = 54.7°$ in the bc^* plane [red arrow in Fig. 1(b)] using Eq. (3). Figures 2(a)–2(d) display the widths of the merged resonances as a function of $\delta\omega$ between the resonances in the absence of merging calculated from the fit shown in Fig. 1, and the values of $|J'_{\mathrm{eff}}| = \hbar\omega_{\mathrm{ex}}$ are collected in Fig. 2(e), where a linear fit is included as a guide to the eyes. We also collected powder spectra at $\nu = 33.912$ GHz between 4 and 298 K. Simulated spectra at each T reproduce well the experimental result, with the exception of the central U peak [39] not predicted by $\mathcal{H}_0(i)$ of Eq. (1). Thus, we approximated this peak as arising from a single spin 1/2 that, when summed to the simulated dimeric spectrum, reproduces the full measured spectra. As an example of the analyses performed at each T, Figs. 3(a) and 3(b) display the spectra $d\chi''/dB_0$ and the integrated $\chi''(B_0)$, respectively, at $T = 120$ K. In Fig. 3(a), line 1 shows the observed spectrum, and lines 2 and 3 are the simulations obtained with Eq. (1) and that for the U peak; line 4, the sum of lines 2 and 3, is in good agreement with line 1. Equal results for $\chi''(B_0)$ are shown in Figs. 3(b), lines 1–4.

III. ANALYSIS OF THE DATA

The intensity $I_{\exp}(T)$ obtained by double integration of the powder spectra and the ratio R between the integrated intensity $I_{\mathrm{U}}(T)$ of the U peak and $I_{\exp}(T)$ are plotted in Figs. 4(a) and 4(b). The Bleaney and Bowers equation [1,3]

$$I_{\exp}(T) \propto \frac{1}{T[3 + \exp(-J_0/k_{\mathrm{B}}T)]}, \qquad (4)$$

normalized to a maximum value of 1, was fitted to the observed $I_{\exp}(T)$, leading to, for the intradimer exchange coupling $J_0 = (-115 \pm 1)$ cm^{-1}, a value similar to but more accurate than the value reported before [39] because of the wider T range of the data. The U peak becomes stronger at high T in nearly axially symmetric arrays of DUs because it collects in a narrow magnetic field range the response of all units with $\boldsymbol{B}_0$ oriented near the magic angle where the two peaks are collapsed. In addition, for these field orientations the signal is narrowest (Fig. 2) and, consequently, larger. Since ambiguities are found in the literature, we mention that the U peak behaves different from signals arising from paramagnetic monomeric copper contaminants whose EPR responses grow in intensity with decreasing T (see, e.g., Sartoris *et al.* [46] and Šimėnas *et al.* [47]), while the intensity of the U peak decreases with decreasing T and disappears at low T. The fraction R of DUs in an angular range $\pm\Delta\theta/2$ around the magic angle [Fig. 1(b)] is

$$R = \frac{\int_{\theta_{\mathrm{M}}-\Delta\theta/2}^{\theta_{\mathrm{M}}+\Delta\theta/2} \sin\theta\, d\theta}{\int_0^{\pi/2} \sin\theta\, d\theta} = 2\sin\theta_{\mathrm{M}} \sin(\Delta\theta/2). \qquad (5)$$

So $\Delta\theta = 2\sin^{-1}[R/(2\sin\theta_{\mathrm{M}})]$ ($\cong R/\sin\theta_{\mathrm{M}}$ for small R). We also calculated $\Delta\theta$ in terms of $|J'_{\mathrm{eff}}|$ from the angular variation of the positions of the EPR lines obtained fitting Eq. (1) to the data in Fig. 1, considering that the peaks $M = \pm 1 \leftrightarrow 0$ are

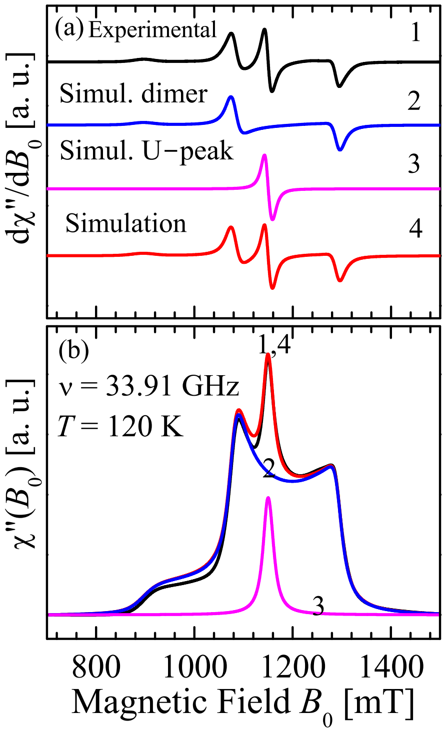

FIG. 3. (a) Line 1: EPR spectrum $d\chi''/dB_0$ at 120 K for a powder sample of $Cu_2[TzTs]_4$. Line 2: Simulation obtained fitting Eq. (1) to the experimental result (it does not reproduce the central U peak). Line 3: Simulation of the U peak. Line 4: Sum of lines 2 and 3. (b) Integrals $\chi''(B0)$ of lines 1–4 in (a).

merged when their distance $\delta\omega \leqslant \omega_{ex}$. With this condition we find that the effective exchange coupling $|J'_{\text{eff}}| = \hbar\omega_{ex}$ for $Cu_2[TzTs]_4$ is linearly related to R as $|J'_{\text{eff}}(T)|$ (cm^{-1}) $= 0.49R(T)$, and the measurement of R from the powder spectra allows evaluating $|J'_{\text{eff}}|$ in the T range 4–298 K, which is wider than the range of the linewidth measurements in Fig. 2. The linear relation between $|J'_{\text{eff}}|$ and R is maintained while $\Delta\theta$ is small and $\sin(\Delta\theta/2) \approx \Delta\theta/2$ in Eq. (5). The values of $|J'_{\text{eff}}|$ are shown in Fig. 4(c) together with those obtained from the linewidth measurements in a narrower T range (Fig. 2); the agreement of the two data sets is excellent considering the simplicity of the analysis. Our results for $Cu_2[TzTs]_4$ indicate that $J'_{\text{eff}} \sim 0$ below $\sim$25 K, and the dimeric units become uncoupled, and it increases linearly with T above 25 K up to a kink at 80 K, where the slope decreases to about half and stays constant up to 298 K, when $|J'_{\text{eff}}| \sim 0.08$ cm^1 and $|J'_{\text{eff}}/J_0| = 7.0 \times 10^{-4}$.

IV. DISCUSSION AND CONCLUSIONS

Using ideas of exchange narrowing [Eq. (3)], we calculated between 100 and 298 K a T dependence of the effective interdimeric exchange interaction $|J'_{\text{eff}}|$ for the antiferromagnetic compound $Cu_2[TzTs]_4$ from EPR linewidth measurements in single crystals with $\boldsymbol{B}_0$ oriented in the neighborhood of the magic angle. In a wider T range, 4–298 K, we obtained equal results from measurements of the relative intensity of the so-called U peak of the powder spectrum. In a previous

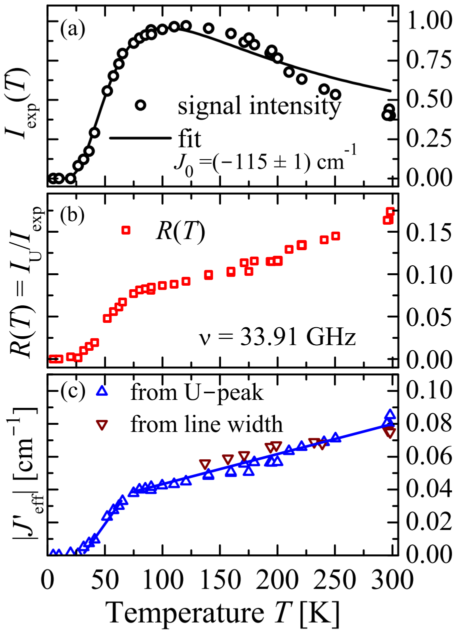

FIG. 4. (a) Integrated area of $d\chi''/dB_0$ in Fig. 3(a) (line 1) as a function of T. The line is a fit to Eq. (4) normalized to a maximum of 1, providing J_0. (b) Ratio $R(T)$ between the areas of the U peak and of the full spectrum. (c) Upward and downward triangles display $|J'_{\text{eff}}|$ calculated from the intensity of the U peak and from the linewidth, respectively. Solid lines emphasize the different behaviors of $|J'_{\text{eff}}|$ in the low- and high-T ranges.

work [39], we proposed that this peak is a consequence of the interdimer coupling $|J'_{\text{eff}}|$ [37,39]. Here we prove that its relative signal intensity R (the fraction of the sphere of field orientations in the powder sample where the condition $\delta\omega \leqslant \omega_{ex}$ holds) allows evaluating $|J'_{\text{eff}}|$ (exchange-narrowing phenomena do not depend on the sign of the interaction). The observed T dependence is a consequence of the depopulation with decreasing T of the excited triplet state, and the effective value of J'_{eff} becomes zero when the average magnetic moment of the AFM DUs cancels out. Our results explain why dimeric materials may not show the characteristic fine structure [5] of the dimeric EPR spectra for interacting DUs, even when the expected magnitude of the dipole-dipole interaction would suggest such a structure. They also explain changes with T of the fine and hyperfine structures of DUs, as in the results reported by Lancaster *et al.* [48], Sartoris *et al.* [46], and Khadir *et al.* [49] for organic dimeric Cu^{II} compounds, where no fine structure, at the T of the experiments, or U peaks in the powder spectra are observed because the collapse of the fine structure occurs for all orientations of $\boldsymbol{B}_0$ (because $|J'_{\text{eff}}| > |D|$) and not in restricted angular ranges. The usefulness of the U peak to determine interdimeric interactions is limited to cases where $|J'_{\text{eff}}|$ is significantly less than $|D|$. In other cases this peak would be wide and thus weak and barely observable. Our results for the variation with T of $|J'_{\text{eff}}|$ also explain the type of hyperfine structure observed in dimeric compounds. Sebastian *et al.* [50] reported that, at 4.5 K, the spectrum of dimeric $BaCuSi_2O_6$ displays hyperfine structure typical of monomeric Cu^{II} (present as an impurity trace) that merges and disappears at 9 K because the contribution of the spectrum of monomeric

$\mathrm{Cu^{II}}$ contaminant decreases with increasing T as $1/T$. Dimeric hyperfine structure was not observed in that work, where it should be wiped out by the interdimeric exchange, because $|J'_{\mathrm{eff}}|$ is greater than the hyperfine coupling parameter $|A|$. Instead, the dimeric $\mathrm{Cu^{II}}$ compound with a pyrophosphate tetra-anion and 2,2′-bipyridylamine [46] displays a rich EPR spectral variation with T that we now associate with the T dependence of $|J'_{\mathrm{eff}}|$. Hyperfine structure characteristic of dimeric units is observed at 12 K but disappears at higher T because of the increase in $|J'_{\mathrm{eff}}|$ and at lower T because the amplitude of the dimeric signal becomes negligible compared with that of paramagnetic $\mathrm{Cu^{II}}$ contaminants and displays monomeric hyperfine coupling at 4.5 K, as in the study of $\mathrm{BaCuSi_2O_6}$ [51]. Zvyagin *et al.* [52] reported the split of the EPR spectrum of $\mathrm{BaCuSi_2O_6}$ along a crystal axis below $T \sim 9$ K, showing a characteristic dimeric behavior with the two $M = \pm 1 \leftrightarrow 0$ transitions and the forbidden peak at half field. Considering our present results and their Figs. 3 and 4, we calculate $|J'_{\mathrm{eff}}| \sim 3|D|/2 \sim 0.15\ \mathrm{cm^{-1}}$ from the collapse of the two peaks at $T \sim 10$ K. We attribute this collapse to the increase in $|J'_{\mathrm{eff}}|$ with increasing T as a consequence of ω_{ex} becoming relevant compared to D and, consequently, to $\delta\omega$. This value of $|J'_{\mathrm{eff}}|$ for $\mathrm{BaCuSi_2O_6}$ is about one order of magnitude smaller than the value $J' = 2.2$ K estimated by Sasago *et al.* [53]. This is consistent with our results, considering that 10 K is one fifth of the singlet-triplet splitting [52,53] and the population of the triplet state is small.

Hoffmann *et al.* [42,54] studied structural dimeric copper compounds whose dimeric fine EPR structure (D term) is not resolved. The two peaks observed for most orientations of $\boldsymbol{B}_0$ arise from anisotropic $\boldsymbol{g}$ matrices of magnetically rotated $\mathrm{Cu^{II}}$ ions in the lattices. The value of $|J'|$ obtained in their works corresponds to the interaction between chemically identical but rotated $\mathrm{Cu^{II}}$ ions, whose g factors are averaged out. The strong decrease in $|J'|$ with increasing T (a result opposite to ours) was attributed to the lattice vibrations, a process different than that observed by us in $\mathrm{Cu_2[TzTs]_4}$.

Jones and Chesnut [41] studied the effect of interdimeric exchange in various ion radical salts fitting the EPR line shapes to the predictions of Bloch equations for exchange-coupled spin pairs [5]. Their results for the temperature dependence of the interaction indicated the existence of an activated process with activation energies which, according to them, depend on the assumptions made in the fitting processes. They attribute the observed increase in the interaction with increasing T to the varying population of the triplet state, like for the case of $\mathrm{Cu_2[TzTs]_4}$ studied here. In view of their results we tried without success to fit $|J'_{\mathrm{eff}}(T)|$ as an activated process $J'_{\mathrm{eff}}(T) = J'(0)\exp(-\Delta E/k_{\mathrm{B}}T)$, where $J'(0)$ is the limiting value for high T.

The observed T dependence of the interdimeric interactions $|J'_{\mathrm{eff}}|$ observed in $\mathrm{Cu_2[TzTs]_4}$ indicates that the environment of a DU acts as a single interaction like in effective-field theories suggesting similar behavior for weakly interacting AFM metal clusters. Naively, we may assume that $|J'_{\mathrm{eff}}| \approx |J'|$ times the relative population of the triplet state, where J' is the actual average interaction between spins in neighboring units [Eq. (2)]. However, this assumption does not explain the change in the slope of the temperature variation at $T \sim 75$ K. Possible explanations may require considering with more detail the dynamics of the spin excitations in $\mathrm{Cu_2[TzTs]_4}$ using complementary experimental techniques. In any case we propose that $|J'| \sim 0.08\ \mathrm{cm^{-1}}$, as it is $|J'_{\mathrm{eff}}|$ for the maximum population of the triplet state.

The value of J'_{eff} and its variation with T are important in various fields that have received much interest lately, such as molecular magnets [3,8], spin excitations in arrays of AFM clusters [6,14], quantum phase transitions [16,55], quantum spin ladders [18,56–58], and Bose-Einstein condensation in quantum magnets [14,16,17,21,59], and in the study of phase transitions and thermodynamic behavior studied earlier by Tachiki and Yamada [40,60] in dimeric $\mathrm{Cu(NO_3)\cdot 2.5H_2O}$ and more recently in other metal-organic materials [48,61,62].

Studies [14,20,21,63] of statistical properties of systems where the interactions $|J'_{\mathrm{eff}}|$ between dimeric units are larger than in $\mathrm{Cu_2[TzTs]_4}$ use inelastic neutron scattering [15,58] and thermodynamic measurements [62] providing information about the spin excitation bands arising from this interaction. These techniques are more complex than EPR for evaluating the T dependence of $|J'_{\mathrm{eff}}|$. The actual ratio $|J'_{\mathrm{eff}}/J_0|$ may favor using one technique or studying different phase transitions as the crossing of a Zeeman level of the excited spin triplet with the ground singlet as a function of the field intensity or the crossing of two EPR transitions within the excited triplet as a function of the field orientation, as exploited here. Even if some arguments are common to the two cases where quantum phase transitions are observed, much more theoretical work exists for the spin-wave analysis of the singlet-triplet transition as a function of the field intensity [14] than for the case of transitions within the spin triplet. In cases where $|J'_{\mathrm{eff}}/J_0|$ is small and the dimeric structure of the EPR spectrum is observed, like for $\mathrm{Cu_2[TzTs]_4}$, the temperature dependence of the intensity R of the U peak provides a simple and accurate way to evaluate $|J'_{\mathrm{eff}}(T)|$ that may be related to the spin excitations of the material.

In this work we considered that the exchange-narrowing process producing the collapse of the structure gives rise to quantum phase transitions [55] in the range $\omega_{\mathrm{ex}} \sim \delta\omega$ between the slow- and fast-fluctuating Anderson's [25,26] regimes when the exchange frequency equals the splitting $\delta\omega$ between the collapsing peaks. We swept through these transitions changing $|J'_{\mathrm{eff}}|$ with T or $\delta\omega$ with the orientation of the magnetic field. The entanglement of the triplet-state wave functions produced by small interdimeric interactions is responsible for important changes in the spectra. These interesting concepts [64] require further experimental and theoretical work.

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