

Quantum behavior of multiple monomeric arrays of spin $\frac{1}{2}$

Vinicius T. Santana^{1,*}, Rosana P. Sartoris², and Rafael Calvo^{2,3,†}

¹CEITEC – Central European Institute of Technology, Brno University of Technology, Purkyňova 123, 61200 Brno, Czechia

²Departamento de Física, Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral (UNL), 3000 Santa Fe, Argentina

³Instituto de Física del Litoral, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and UNL, 3000 Santa Fe, Argentina



(Received 12 February 2025; revised 1 July 2025; accepted 8 July 2025; published 25 July 2025)

Spin arrays provide a framework for studying cooperative spin phenomena and correlated states. Advances in high-frequency electron paramagnetic resonance (HF-EPR) above 90 GHz offer new opportunities to investigate these systems, determine the effect of weak spin-spin interactions, and evaluate their magnitudes. Here, we investigate the cupric coordination compound $\text{Cu}(\text{L-met})_2$, where anisotropic $S = \frac{1}{2}$ spins occupy two rotated structural sites, forming weakly coupled spin arrays via supramolecular interactions. Previous EPR studies at 9.7 GHz and 33.6 GHz identified pseudo-one-dimensional magnetic behavior with a single, orientation-independent spectral peak, allowing estimates of exchange couplings. In this work, HF-EPR spectra up to 450 GHz and magnetic fields (B_0) up to 16 T display a more complex spectral landscape: the number of resonances switches between one and two as a function of the orientation of B_0 , revealing different dynamical regimes. This behavior indicates a crossover between a collective quantum-correlated phase and a regime where spins behave independently, allowing us to construct quantum dynamical phase diagrams across frequency and field space. These findings reinforce molecular compounds as promising platforms for exploring tunable spin dynamics, with implications for quantum information science. The observation of spin-spin interactions persisting at room temperature highlights their potential for robust quantum coherence in molecular systems.

DOI: [10.1103/71h7-vhj7](https://doi.org/10.1103/71h7-vhj7)

I. INTRODUCTION

Spin arrays with weakly coupled neighboring magnetic units are relevant for applications in molecular magnetism [1,2] and quantum information processing [3,4]. Each unit of the array may be a mononuclear molecule where the Zeeman interaction is dominant, or a polynuclear molecule containing two or more spins, where the intramolecular spin-spin couplings are greater than the Zeeman interactions [5]. We define these two cases as monomeric and polymeric arrays, respectively. In addition, when the crystal structures of the array obey space groups with two or more rotated anisotropic spin units per unit cell (asymmetric units), we call them multiple monomeric (or multiple polymeric) arrays. Weak intermolecular couplings within the arrays may induce collective behavior that cannot be adequately described without quantum statistical modeling [6,7].

Electron paramagnetic resonance (EPR) is traditionally known for studying metal ions diluted in nonmagnetic lattices, where spin-spin coupling is negligible [8,9]. However, the early exploration of infinite magnetic spin arrays, including phenomena such as exchange narrowing [10,11], marked a

significant milestone in EPR's history [12–20]. These studies inspired the foundational theories of magnetic resonance proposed by Anderson [6,21] and Kubo and Tomita [7], which mathematically formalize the roles of exchange and dipole-dipole interactions in coupled spin arrays. Subsequently, the behavior of multiple anisotropic monomeric arrays was analyzed using these theories by Yokota and Koide [22], and Sack [23]. In particular, spin anisotropy introduced by ligand fields [24,25], reflected in the g matrix for $S = \frac{1}{2}$ ions (or the D matrix for $S > \frac{1}{2}$), plays a crucial role in shaping the behavior and potential applications of such arrays.

Many materials comprising weakly coupled spin arrays, demonstrating phenomena such as spin diffusion [26,27] and other effects associated with spin-spin couplings, were extensively studied in subsequent years as advances in EPR instrumentation allowed more precise measurements [28–45]. EPR investigations also extended to materials with rotated spins within the unit cell, but employing a classic model with coupled Bloch equations to elucidate spin dynamics [43,46–51].

We distinguish two kinds of exchange-narrowing processes: the one described by Gorter and Van Vleck [10,11] and Anderson and Weiss [21] (see also Pake [52]) for arrays of equal spins coupled by exchange and dipole-dipole interactions, and that occurring in an exchange-coupled lattice with different rotated anisotropic spins [6,7,22,23], where EPR spectra collected in single-crystal samples display the abrupt merging and narrowing of the resonances predicted by Anderson, around field orientations where the peaks of rotated spin sites would intersect in the absence of coupling [53–58].

*Contact author: santana@vutbr.cz

†Contact author: calvo.rafael@gmail.com

The study of spin arrays has advanced significantly in recent decades, driven by developments in information processing and quantum materials [59–61]. Currently, the experimental capabilities of EPR have expanded, allowing access to higher microwave frequencies and producing digital spectra of superior quality and easier to analyze [62]. Extending EPR studies of spin arrays under these enhanced conditions is therefore of considerable relevance.

We recently reviewed previous measurements and used EPR to investigate single-crystal and powder samples of arrays of dimeric units of spins $\frac{1}{2}$, demonstrating the existence of entanglement arising from interdimer coupling [63–68], which can be detected by features of the powder sample spectra. From a different perspective, entanglement in exchange-coupled spin arrays similar to ours has been witnessed using thermodynamic (not spectroscopic) measurements [69–72]. This is important because dimeric spin arrays have been recognized as relevant in information processing [73,74] and quantum phase transitions [75–77]. Grimaudo *et al.* [78–80] reported analytical solutions to the problem of spin qubits and interacting two-spin qubits surrounded by weakly interacting neighbors and the implications for quantum transitions and the presence of quantum entanglement.

In this work, we study the quantum properties of multiple-monomeric spin arrays by collecting EPR spectra at high microwave frequencies (HFEPR) in single crystal and powder samples as a function of microwave frequency (ν), the corresponding magnitude of the magnetic field $B_0 = \mu_0 H$ (μ_0 is the permeability of the vacuum), and temperature (T). For single-crystal samples, spectra were also collected as a function of the orientation of B_0 . The spin dynamics arising from the spin-spin coupling and the quantum properties of the array modify the observed spectra. We investigate these properties for the cupric compound of the amino acid *L*-methionine, trans-bis(*L*-methioninato)copper^{II}, $[C_{10}H_{20}CuN_2O_4S_2]$, named Cu(*L*-met)₂, whose monoclinic crystal structure [81] features a layered array of anisotropic copper^{II} ions in rotated sites A and B related by a C_2 rotation around the monoclinic b axis.

Section II summarizes predictions of Anderson's [6] and Kubo's [7] theories for the EPR spectra of coupled multiple monomeric arrays of anisotropic spins in rotated sites. Section III describes the reported crystal structure [81] of Cu(*L*-met)₂ and the EPR results reported at low microwave frequencies [33,34,37]. The new HFEPR results in single-crystal and powder samples are described in Sec. IV and discussed in terms of the quantum correlations produced by the couplings in the monomeric spin array in Sec. V, where convenient phase diagrams in terms of the magnitude and orientation of B_0 are proposed. Section VI summarizes the results of our investigation and the proposed explanation for the spectra of multiple monomeric arrays. The experimental techniques used are described in Sec. VII.

II. EPR SPECTRA OF MULTIPLE MONOMERIC ARRAYS

In this section, we discuss the application of Anderson's mathematical model [6] to analyze the merging and narrowing of the EPR spectral lines of an exchange-coupled spin array as Cu(*L*-met)₂. The general theory [6,7] originally applied to

multiple monomeric arrays by Yokota and Koide [22], and Sack [23] is employed to analyze the new HFEPR results. For a more comprehensive description of the model, refer to Pastawski's work [82].

A nontrivial spin Hamiltonian $\mathcal{H}$ describing a multiple monomeric array of spin- $\frac{1}{2}$ sites with interacting, alternating rotated spins A and B, denoted as $S_{i,A}$ and $S_{j,B}$, in an applied field B_0 , consists of the sum of an anisotropic Zeeman term ($\mathcal{H}_Z$) and an isotropic exchange-type spin-spin interaction term ($\mathcal{H}_{ex}$) [29,83],

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{ex} = \sum_i \mu_B [B_0 \cdot (g_A \cdot S_{i,A} + g_B \cdot S_{j,B})] - \sum_{i,j} J S_{i,A} \cdot S_{j,B} \quad (1)$$

where μ_B is the Bohr magneton. Exchange is a short-range coupling and Eq. (1) considers a single value J for the magnitude of the AB-type spin-spin coupling of nearest-neighbor spin pairs. Next-nearest-neighbor couplings of AA- and BB-type pairs are not considered. Dipole-dipole (anisotropic) spin-spin interactions are discussed later. The anisotropic g matrices, g_A and g_B , are related by a rotation of 180° around the b axis. For $J = 0$, the spectrum of the array at a frequency ν displays two peaks at fields

$$B_A = h\nu(g_A\mu_B)^{-1} \text{ and } B_B = h\nu(g_B\mu_B)^{-1}, \quad (2)$$

determined by g factors defined as [29,83]

$$g_A = (\mathbf{h} \cdot \mathbf{g}_A \cdot \mathbf{g}_A \cdot \mathbf{h})^{1/2}, \quad g_B = (\mathbf{h} \cdot \mathbf{g}_B \cdot \mathbf{g}_B \cdot \mathbf{h})^{1/2} \quad (3)$$

where $\mathbf{h}$ is the orientation of B_0 in the sample, defined by polar and azimuthal angles (θ, φ) , in an orthogonal frame $\mathbf{xyz}$,

$$\mathbf{h} = B_0/B_0 = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta). \quad (4)$$

$\mathcal{H}_Z$ of Eq. (1) can be rewritten as

$$\begin{aligned} \mathcal{H}_Z &= \mu_B B_0 \cdot \mathbf{g} \cdot \sum_i S_i + \mu_B B_0 \cdot \mathbf{G} \cdot \sum_i s_i \\ &= \mathcal{H}_Z(1) + \mathcal{H}_Z(2) \end{aligned} \quad (5)$$

where

$$\mathbf{g} = \frac{1}{2}(\mathbf{g}_A + \mathbf{g}_B), \quad \mathbf{G} = \frac{1}{2}(\mathbf{g}_A - \mathbf{g}_B), \quad (6)$$

$$S_i = S_{i,A} + S_{i,B}, \quad S = \sum_i S_i, \quad (7)$$

$$s_i = S_{i,A} - S_{i,B}, \quad s = \sum_i s_i. \quad (8)$$

$\mathcal{H}_Z(1)$ of Eq. (5) is proportional to the total spin S , which commutes with and is not changed by $\mathcal{H}_{ex}$. $\mathcal{H}_Z(2)$ is proportional to s [defined in Eq. (8)], which does not commute with $\mathcal{H}_{ex}$ and is averaged out when J increases.

To explain the effect of the exchange interaction in the spectra of a spin array, we define the dimensionless parameter x ,

$$x = \frac{|J|}{g\mu_B\delta B}, \quad (9)$$

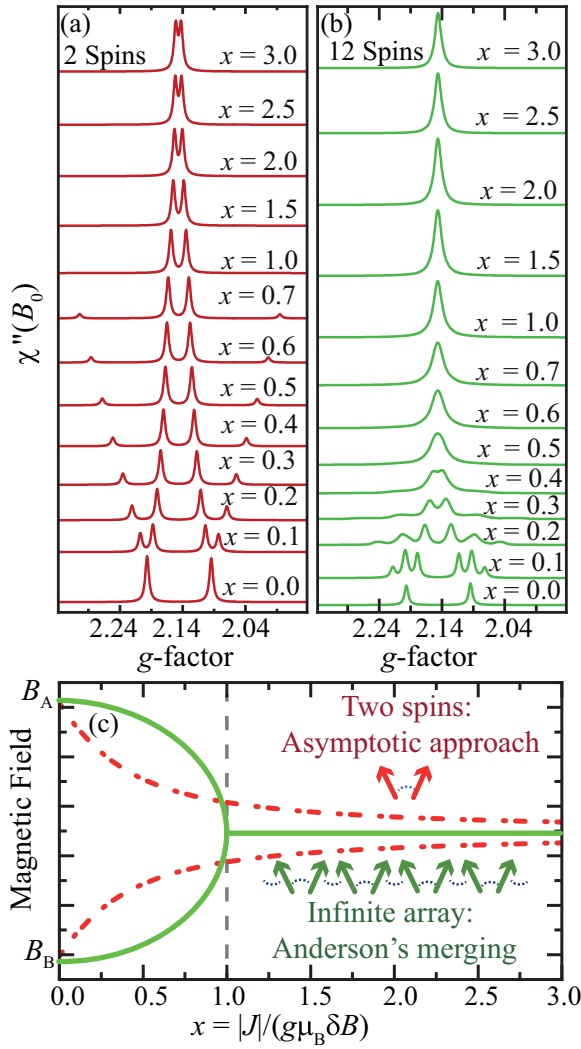


FIG. 1. (a) Response χ'' vs g of two spins $\frac{1}{2}$, S_A and S_B , with g_A and g_B (defined in Eqs. (2) and (3)) simulated for various values of x [Eq. (9)]. (b) Same as (a) when the two spins are replaced by a ring of 12 coupled alternating spins. (c) The red lines display the asymptotic approach shown in (a) of the positions of the EPR peaks of a pair of spins coupled by J . The green lines are the positions of the EPR peaks proposed by Anderson for an infinite alternating A-B lattice

where $\delta B = |B_A - B_B|$ is the magnetic field difference between the peaks defined in Eq. (2) in the absence of interaction and $g = \frac{1}{2}(g_A + g_B)$. The exchange coupling J between spin neighbors is a material's intrinsic property that depends on the chemical pathway supporting it. The parameter x can be tuned by changing δB , something achieved in the experiments by varying ν and also, in single crystals because of the spin anisotropy, the orientation $\mathbf{h}$. The evolution of the EPR absorption spectra $\chi''(B_0)$ of a single pair of interacting rotated spins A and B with the parameter x may be simulated with EasySpin [84] in finite arrays: the two peaks approach asymptotically to one peak at the central position as $x \rightarrow \infty$ [see spectra in Fig. 1(a)]. When the two spins are replaced by an array [85] of coupled alternating spins A and B, the simulated spectra display multiple peaks for $x < 1$; for larger x two of them merge to the center much faster than for the case of a

single pair of spins [see spectra in Fig. 1(b)]. According to Anderson's theory [6,23,83,86], for an infinite array of coupled alternating spins, the two peaks approach for $x < 1$ and merge suddenly at $x = 1$. This statistical solution of an infinite array replaces the asymptotic behavior of isolated pairs of spins, a result that transforms simple changes of behavior of spin arrays into abrupt phase transitions. The green full lines in Fig. 1(c) compare this sudden merging with the asymptotic approach of two coupled spins shown with red dashed-dotted lines. In an infinite spin array, the EPR peaks broaden linearly with x up to $x = 1$. For $x > 1$, one of the merged peaks continues to widen, weakens, and in infinity arrays rapidly disappears, while the other narrows according to the relation [83]

$$\Delta B = \frac{g\mu_B}{|J|}(\delta B/2)^2, \quad (10)$$

where ΔB is the linewidth of the collapsed EPR peak. In a single crystal with spin arrays, the simultaneous processes of peak merging and narrowing can be observed in the measured EPR spectra as the orientation of the magnetic field $\mathbf{B}_0$ is varied, allowing to evaluate $|J|$. In a first method, one measures the approach of the two EPR peaks and determines their merging at $x = 1$, where $|J| = g\mu_B\delta B$. A second method is to measure the linewidth in the region where the peaks have merged, near the crossing orientation, and apply Eq. (10). The merging and narrowing processes give rise to the exchange narrowing phenomenon for the alternating infinite lattice [6,7,10,21,86].

The behavior of the EPR signal of the infinite array is described in two ranges of x . For $x > 1$ ($|J| > g\mu_B\delta B$), the states of the array are mixed by the spin-spin interaction, and we observe a single merged EPR peak for the two dissimilar spins (in our case, copper in sites A and B). On the other hand, for $x < 1$, the spins are distinguishable, and two split peaks are observed. When $g_A = g_B$, $\delta B = 0$ at field orientations where the peaks intersect. Also, since δB increases linearly with ν , a larger coupling $|J|$ is required to merge the EPR peaks at a higher frequency. Equation (10) was used to evaluate $|J|$ from the spectra of single crystals of $\text{Cu}(\text{L-met})_2$ at 33.6 GHz (see Fig. S2 within the Supplemental Material [87]). At the microwave frequencies used by Levstein *et al.* [33], the merged phase occurs for any orientation of $\mathbf{B}_0$ ($x > 1$). Our HFEPR spectra of single-crystal samples support the existence of two phases with distinct dynamic regimes and the hypothesis of a dynamical phase transition.

In the following, we summarize the model of Bencini and Gatteschi [1] for the exchange narrowing to discuss these two dynamic regimes. The equation of motion of the magnetization is

$$\frac{dM_x}{dt} = i\omega(t)M_x, \quad (11)$$

where $\omega(t) = \omega_0 + \omega_1(t) = g\mu_B B(t)$ with $B(t) = B_0 + B_1(t)$ being the total external magnetic field acting on the spins. The time average of $\omega_1(t)$ is zero and its time dependence is characterized by a time correlation function $\langle \omega_1(t)\omega_1(t + \tau) \rangle$.

The expectation value of $M_x(t)$ is evaluated as

$$\begin{aligned} \langle M_x(t) \rangle &= M_x(0)e^{i\omega_0 t} \left\langle \exp \left\{ i \int_0^t \omega_1(t') dt' \right\} \right\rangle \\ &= M_x(0)e^{i\omega_0 t} \phi'(t), \end{aligned} \quad (12)$$

so

$$\langle M_x(t)M_x(0)^* \rangle = |M_x(0)|^2 e^{i\omega_0 t} \phi'(t). \quad (13)$$

Thus, the absorption spectrum, centered around ω_0 and modulated by $\omega_1(t)$, is given by the normalized Fourier transform

$$I(\omega - \omega_0) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i(\omega - \omega_0)t} \phi'(t) dt, \quad (14)$$

that is characterized by its second moment,

$$M_2 = \Delta^2 = \int_{-\infty}^{+\infty} (\omega - \omega_0)^2 I(\omega - \omega_0) d\omega, \quad (15)$$

and by the correlation time of ω_1

$$\tau_c = \frac{\int_0^\infty \psi(t) dt}{M_2}, \quad (16)$$

where $\psi(\tau) = \langle \omega_1(t)\omega_1(t + \tau) \rangle$.

The product $\Delta\tau_c$ describes the resonance regimes. It is slow if $\Delta\tau_c \gg 1$, corresponding to the region where $x < 1$ in Fig. 1(c), where the spin-spin coupling is ineffective and the spins behave independently. For $\Delta\tau_c \ll 1$, the spins are in the fast regime where $x > 1$ and their resonance peaks are merged. The relationship between the correlation time τ_c and the exchange coupling J is usually defined as $\tau_c \approx \hbar/|J|$. According to Anderson's theory [6], the transition from one regime to the other of Fig. 1(c) indicates the value of the correlation function of $\omega_1(t)$. The value of $|J|$ determines the correlation time τ_c , which in turn determines the shape of the spectrum.

As summarized by Bencini and Gatteschi [1], the stochastic theory of magnetic resonance [6,7] explains the phenomenon of exchange narrowing, but it is also especially convenient to discuss our results for the merging and narrowing of the resonances described in Fig. 1, which are the basis of this phenomenon.

III. CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF $\text{Cu}(\text{L-MET})_2$

The preparation and x-ray structure of the copper^{II} derivative of the amino acid *L*-methionine, $\text{Cu}(\text{L-met})_2$, was reported by Ou *et al.* [81] It crystallizes in the monoclinic space group $P2_1$ with two rotated molecules, A and B, and cupric ions Cu_A and Cu_B per unit cell ($Z = 2$), related by a rotation of 180° around the monoclinic b axis. Figure 2(a) shows a single molecule of $\text{Cu}(\text{L-met})_2$ plotted with Mercury [88] using the crystallographic information (CIF) file TBLMCU obtained from CCDC [81,89]. The Cu^{II} ions are in sites without inversion symmetry, equatorially bonded to the carboxylate oxygen O1 and the amino nitrogen N1 of one *L*-met molecule, and to the equivalent O2 and N2 of a structurally different *L*-met, in an approximate square planar coordination, at distances of about 2 Å. Weakly bonded oxygens O3 and O4 of carboxylate groups of neighbor $\text{Cu}(\text{L-met})_2$ molecules are in the apical positions of each copper at 2.751 Å and 2.675 Å. Ou *et al.* [81] also reported the EPR spectrum of a powder sample at X band, which displayed the inconclusive result of a single peak at the average g value of 2.139.

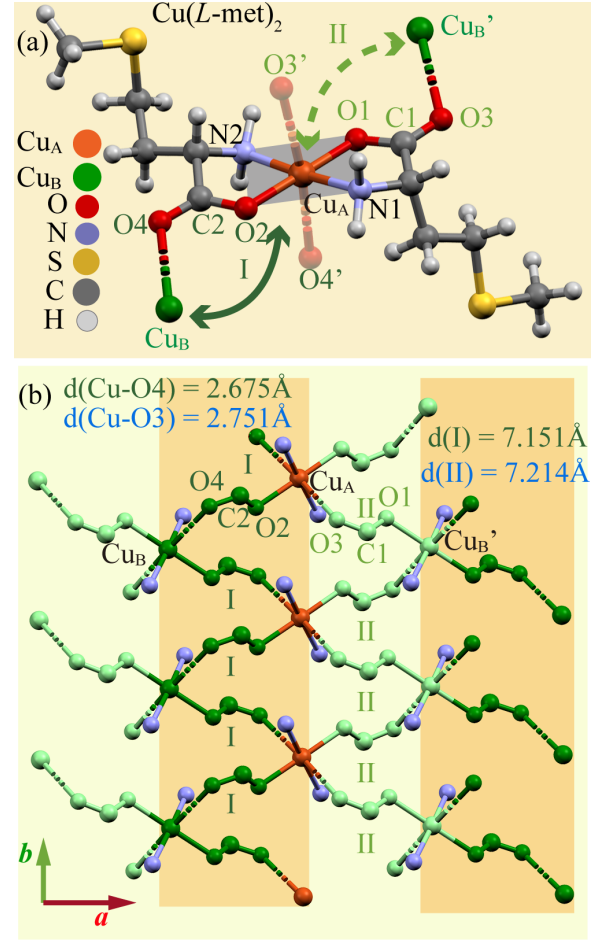


FIG. 2. Crystal structure of $\text{Cu}(\text{L-met})_2$ according to Ou *et al.* [81] (a) Single-molecule $[\text{C}_{10}\text{H}_{20}\text{CuN}_2\text{O}_4\text{S}_2]$ with Cu^{II} ions in elongated octahedral coordination, bonded to two slightly different *L*-methionine molecules. (b) The layered structure of the Cu^{II} ions in the ab plane and chemical paths I and II supporting the exchange coupling between nearest-neighbor spins. The color bands indicate couplings of different magnitude (see text.)

The single anisotropic EPR peak observed [33] in single crystals of $\text{Cu}(\text{L-met})_2$ at 9.7 GHz and 33.6 GHz for all orientations of $\mathbf{B}_0$ was assigned to the merged signals of copper spins in sites A and B produced by the spin-spin coupling (Sec. II). The green symbols in Fig. S1 within the Supplemental Material [87] display the g^2 factor measured in the planes of a single crystal at 33.6 GHz [33]. The matrix $\mathbf{g}^2$ that fits these results allowed calculating the green lines $g^2(\theta, \varphi)$ in this figure. Assuming that $g^2(\theta, \varphi)$ of the single peak is the average of $g_A^2(\theta, \varphi)$ and $g_B^2(\theta, \varphi)$, Levstein *et al.* [33] calculated the angular variations shown with red and blue lines (Fig. S1 within the Supplemental Material [87]) and the matrices $\mathbf{g}_A^2$ and $\mathbf{g}_B^2$. Table I contains the matrices $\mathbf{g}^2$, $\mathbf{g}_A^2$, and $\mathbf{g}_B^2$ obtained by them. They also reported the angular variation of the linewidth ΔB and evaluated from their data the coupling $|J|$ assuming that $\Delta B = \frac{1}{2} g\mu_B(\delta B)^2/|J|$ (see Sec. II). Since at this frequency the spins of the array are merged at all orientations, observing and measuring the merging was not possible.

As shown in Fig. 2(b), Cu atoms type A are connected to four rotated Cu neighbors type B in ab planes by the

TABLE I. Matrix elements of the symmetric matrices $\mathbf{g}^2$, $\mathbf{g}_A^2$, and $\mathbf{g}_B^2$ of $\text{Cu}(\text{L-met})_2$, constructed from the results at 33.6 GHz and 300 K [33] (see Fig. S1 within the Supplemental Material [87]).

	$\mathbf{g}^2$	$\mathbf{g}_A^2$	$\mathbf{g}_B^2$
$(\mathbf{g}^2)_{xx}$	4.490(1)	4.490(1)	4.490(1)
$(\mathbf{g}^2)_{yy}$	4.446(1)	4.446(1)	4.446(1)
$(\mathbf{g}^2)_{zz}$	4.633(1)	4.633(1)	4.633(1)
$(\mathbf{g}^2)_{xz}$	-0.320(1)	-0.320(1)	-0.320(1)
$(\mathbf{g}^2)_{xy}$	0	-0.228(1)	0.228(1)
$(\mathbf{g}^2)_{yz}$	0	0.292(1)	-0.292(1)

syn-anti equatorial-apical carboxylate bridges, O1–C–O3 or O2–C–O4 [see Fig. 2(b)]. Comparing the EPR and structural results for $\text{Cu}(\text{L-met})_2$ [33,81] with those for the copper-amino acid compounds with *L*-phenylalanine [32,90], and *L*-leucine [34,91], where rotated copper ions are connected by equatorial-apical carboxylate bridges similar to O1–C–O3 and O2–C–O4 in $\text{Cu}(\text{L-met})_2$, Levstein and Calvo [36] found that the magnitude of J is inversely proportional to the lengths of the apical segments of the bridge, and decreases linearly with increasing length of the apical $\text{Cu} \cdots \text{O}$ distances. Further support for this result was obtained for other compounds [92]. Thus [36], the magnitude of the exchange coupling supported by the path O1–C–O3 in $\text{Cu}(\text{L-met})_2$ is negligible compared to that supported by the path O2–C–O4. The color bands parallel to the $\mathbf{b}$ axis in Fig. 2(b) indicate different carboxylate groups and magnitudes of the exchange couplings. They break down the layered 2D crystallographic structure to a 1D magnetic behavior with zig-zag chains along the $\mathbf{b}$ axis [33,37], and the low-frequency EPR results indicate that the spin array

of the cupric ions in $\text{Cu}(\text{L-met})_2$ is quasi-one-dimensional multiple monomeric.

IV. HFEPR RESULTS

This section describes the experimental results collected during this work in single crystal and powder samples of $\text{Cu}(\text{L-met})_2$, as a function of frequency ν between 90 GHz and 450 GHz, at different T . The procedures used in these measurements are described in Sec. VII.

A. Single-crystal samples

1. Frequency dependence

Our HFEPR results in single crystal samples are described using the orthogonal system of axes $\mathbf{xyz} \equiv \mathbf{abc}^*$ as the reference frame, with $\mathbf{c}^* \equiv \mathbf{a} \times \mathbf{b}$. We collected $d\chi''/dB_0$ spectra vs B_0 in the ab plane ($\theta = 90^\circ$, with $\varphi = 0^\circ$ on the $\mathbf{a}$ axis, and $\varphi = 90^\circ$ on the $\mathbf{b}$ axis). At $\nu = 310$ GHz ($B_0 \sim 10.45$ T) and $T = 280$ K, the spectra exhibit a single peak near these axes, while in the rest of the plane, they exhibit two peaks that merge into one as the field orientation approaches the axes. Figure 3(a) displays the spectra in the ab plane. Figure 3(b) displays the spectra at $\varphi = 0^\circ$ and $\varphi = 43^\circ$. The peaks have Lorentzian line shapes and were fitted as such to obtain their central field (g -factor) and peak-to-peak widths; green triangles in Fig. 3(c) display the g^2 factor in the field orientations where the HFEPR spectra display one peak; red squares and blue circles display g_A^2 and g_B^2 in the angular range where two peaks are observed. The data clearly show that, rather than crossing at a well-defined angle, the peaks suddenly merge and remain merged over a range of angles φ . Because of these results, we define two phases of the material. One covers

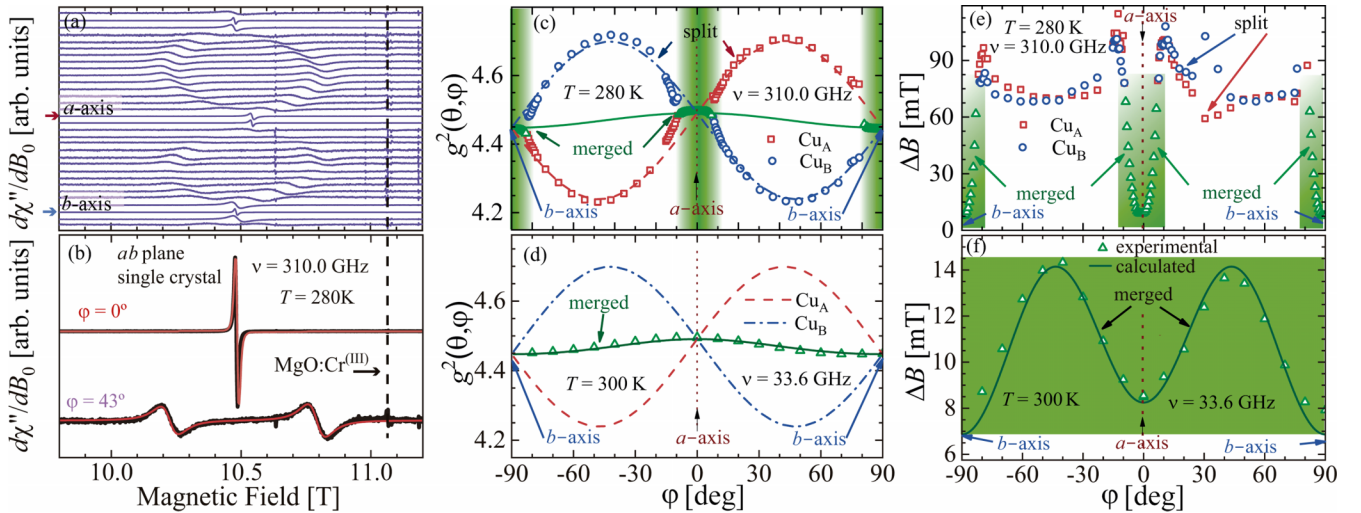


FIG. 3. HFEPR $d\chi''/dB_0$ single-crystal spectra vs B_0 in the ab plane, at $\nu = 310$ GHz and $T = 280$ K. (a) Spectra with B_0 in the ab plane normalized to the same height. (b) Spectra with B_0 at $\varphi = 0^\circ$ ($\mathbf{a}$ axis) displaying one narrow peak, and at $\varphi = 43^\circ$, displaying two wider peaks. Red lines are fittings to Lorentzian line shapes used to extract the central fields (g -factors) and linewidths ΔB . (c) Angular variation of the g^2 factor in the ab plane. Green triangles are used in the angular range with one merged peak (merged range), and red squares and blue circles when peaks from sites A and B are separately observed (split range). Green solid lines, red dashed lines, and blue dashed-dotted lines are simulations obtained using Eq. (3). (d) Same as (c), for the data reported at 33.6 GHz [33]. (e) HFEPR data at 310.0 GHz, and 280 K, of the widths of the peaks of the single crystal spectra as a function of the angle φ in the ab plane. (f) Same as (e) for the data [33] at $\nu = 33.6$ GHz and 300 K.

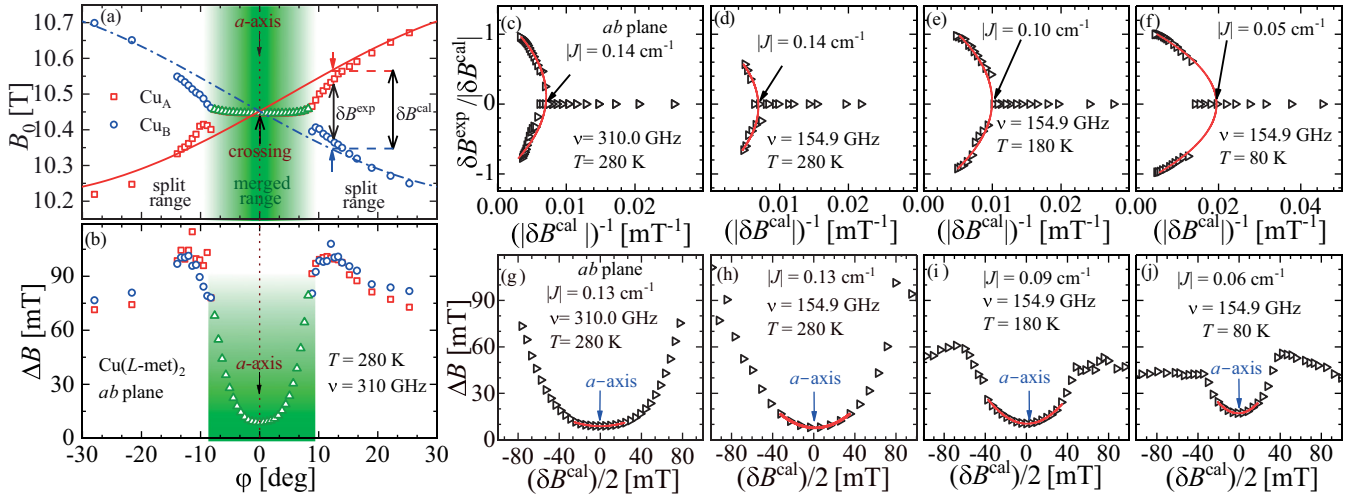


FIG. 4. Merging (a) and narrowing (b) of the EPR peaks at $\nu = 310.0$ GHz and $T = 280$ K, covering a reduced angular range of Figs. 3(c) and 3(e) around the a axis. The symbols show the positions B_0 (a) and the widths ΔB (b) of the signals (one or two peaks) observed in this angular range. Red squares and blue circles indicate information about Cu_A and Cu_B , respectively. δB^{exp} and δB^{cal} are defined and used later to calculate the exchange coupling $|J|$. The solid and dash-dotted lines display the positions calculated using the g^2 matrices in Table I. The light green band in (a) and (b) describe the merged angular range in the ab plane. (c)–(j) Merging and narrowing of the peaks A and B of a single crystal spectrum measured in the ab plane around the a axis, where they would cross as a function of the angle $|\varphi|$ in the absence of spin-spin coupling. (c)–(f) Ratio $\delta B^{\text{exp}}/\delta B^{\text{cal}}$ plotted as a function of $(\delta B^{\text{cal}})^{-1}$. (g)–(j) Width ΔB of the merged peak, plotted as a function of $\delta B^{\text{cal}}/2$. Within this range, the width increases as the square of $\delta B^{\text{cal}}/2$. The plots in (c)(d) and (g)(h) allow us to obtain independent values of $|J|$ that agree within uncertainties at $T = 280$ K for 310 GHz and 154.9 GHz. (d-f, h-j) show the data at $\nu = 154.9$ GHz at three T , 280 K, 180 K, and 80 K. The calculated J values are summarized in Table II.

the angular range displaying a single peak and is called the merged phase; the other covers the angular range exhibiting two peaks and is called the split phase. Besides merging, the linewidth of the single peak displays an impressive narrowing at the expected intersection, in the coupled phase.

Correspondingly, green full lines, red dashed lines, and blue dashed-dotted lines display the values of the functions $g^2(\theta, \varphi)$, $g_A^2(\theta, \varphi)$, and $g_B^2(\theta, \varphi)$ calculated using Eq. (3) and the matrices $\mathbf{g}^2$, $\mathbf{g}_A^2$, and $\mathbf{g}_B^2$ of Table I. Figure 3(d) is similar to Fig. 3(c), but displays the data and simulations at 33.6 GHz, where a single merged peak was observed for all field orientations in three orthogonal planes [33]. Thus, for the data at 310.0 GHz (average field $B_0 \sim 10.4$ T) the spin array is partially in the merged and split phases, depending on the field orientation, while it is in the merged phase for all field orientations at 33.6 GHz, with $B_0 \sim 1.13$ T [data in the plane ab displayed in Fig. 3(d)]. The matrices $\mathbf{g}^2$, $\mathbf{g}_A^2$, and $\mathbf{g}_B^2$ obtained from the measurements at 33.6 GHz and 300 K, given in Table I fit well the data at both frequencies. Figures 3(e) and 3(f) use the same color codes as Figs. 3(c) and 3(d) to display the widths of the peaks of the spectra at 310.0 GHz and 33.6 GHz in the ab plane as a function of φ . Within the ab plane, two regimes corresponding to the two phases contribute to the behavior of the linewidth. At 33.6 GHz, the spin array is in the merged phase for all orientations and only one dynamical regime with a narrow linewidth is observed. At high frequency, both regimes occur, and the linewidth in each of them differs by a factor of eight. Additionally, for B_0 within an angular range around the a and b axes where the peaks should cross, there is the narrowing predicted by Anderson's model [Eq. (10)], enabling the calculation of $|J|$.

2. Merging and narrowing processes

The positions and widths of the peaks at 310.0 GHz and 33.6 GHz displayed in Figs. 3(c)–3(f) differ from the expectations for the classical exchange narrowing process for arrays of identical spins described by the seminal papers of Anderson [6,21,52], in which the isotropic spin-spin interaction (exchange) averages out the dipolar coupling, thus narrowing the resonance. In the multiple monomeric spin array of $\text{Cu}(\text{L-met})_2$, the resonance properties of neighboring spins differ for most field orientations, becoming equal only around orientations where the EPR transitions cross. Within the angular range where the difference between the Zeeman terms of the sites, $\mathcal{H}_Z(2)$ in Eq. (5), does not exceed $|J|$, the influence of $\mathcal{H}_{\text{ex}}$ [defined in Eq. (1)] becomes dominant. This leads to significant modifications in the EPR spectra that we suggest as a signature of spin entanglement (see Sec. V). Figures 4(a) and 4(b) describe a typical measurement of the merging and narrowing of the peaks in the ab -plane of a single-crystal sample. The magnetic field difference δB^{exp} , measured experimentally between peaks A and B, and the calculated magnetic field difference δB^{cal} , expected in the absence of exchange, as defined in Fig. 4(a), are used to determine the magnitude of the exchange coupling at various frequencies ν and temperatures T .

The merging of the peaks observed at 310 GHz is illustrated in Fig. 4(c), where the ratio between the observed and calculated positions, $\delta B^{\text{exp}}/\delta B^{\text{cal}}$, are plotted as a function of $(\delta B^{\text{cal}})^{-1}$. This plot reveals a merging transition similar to the one shown in Fig. 1(c) at $x = 1$, where two peaks merge into a single peak with $\delta B^{\text{exp}}/\delta B^{\text{cal}} \rightarrow 0$ at $\delta B^{\text{cal}} = |J|/(g\mu_B)$. The data in Fig. 4(c) allow extraction of the coupling

TABLE II. Exchange coupling $|J|$ obtained as a function of T and ν (B_0) from single-crystal narrowing and merging data.

T [K]	ν [GHz]	$ J $ [cm^{-1}] from narrowing data	$ J $ [cm^{-1}] from merging data
300	33.6	0.14(1)	
280	310.0	0.13(1)	0.14(1)
280	154.9	0.13(1)	0.14(1)
180	154.9	0.09(1)	0.10(1)
80	154.9	0.06(1)	0.05(1)

$|J| = 0.14 \text{ cm}^{-1}$. Figure 4(g) displays the increase of the width of the peak observed around the a axis in the ab plane as a function of $\delta B^{\text{cal}}/2$. The data displayed in Fig. 4(g) allow for the calculation of a coupling constant $|J| = 0.13 \text{ cm}^{-1}$ from the narrowing at 280 K. The $|J|$ values obtained from both the merging and the narrowing of the peaks are in agreement within their accuracy. They also agree with the value $|J| = 0.14 \text{ cm}^{-1}$ recalculated from Levstein *et al.* [33] linewidth data at 33.6 GHz and 300 K, following a procedure identical to that described above [Figs. 4(a) and 4(b)] for the HFEPR data. This means that, within uncertainties, $|J|$ does not depend on the frequency of the measurement (or the magnitude of the applied B_0).

Measurements of the merging and narrowing of the peaks, similar to those in Figs. 4(c) and 4(g), were performed at $\nu = 154.9 \text{ GHz}$ ($B_0 \sim 5.22 \text{ T}$) at three temperatures, 280 K, 180 K, and 80 K, and are displayed in Figs. 4(d)–4(f) and

4(h)–4(j). The values of $|J|$ obtained at 280 K at 154.9 GHz and 310.0 GHz are equal within their uncertainties, further supporting the independence of $|J|$ with frequency ν . However, the data indicate that the exchange coupling $|J|$ decreases as T decreases. Table II collects the values of the exchange coupling obtained from the HFEPR results.

B. Powder samples

The EPR spectrum of a powder sample is the response of the material integrated over all magnetic field orientations. Even though we collected data in single crystals too, the spectra of a powder are easier to obtain and analyze, and they are related to a well-defined condition of the spin array, which provides useful information for our purpose.

1. Frequency dependence

Figure 5(a) shows spectra $d\chi''/dB_0$ for a powder sample of $\text{Cu}(\text{L-met})_2$, collected at selected ν between 90 GHz and 425 GHz, corresponding to B_0 of approximately 3.03 T and 14.32 T, respectively, at $T = 280 \text{ K}$. The horizontal axis represents the g factor, defined as $g = h\nu/\mu_B B_0$, which allows comparing spectra obtained at different frequencies. Six well-defined peaks are observed, with relative intensities that vary with ν , a result that deviates from usual powder EPR spectra in the classic literature dealing with isolated paramagnetic systems.

The previously presented HFEPR data from single crystals demonstrate that the merged and split phases of the sample contribute to the powder spectrum at distinct orientations of

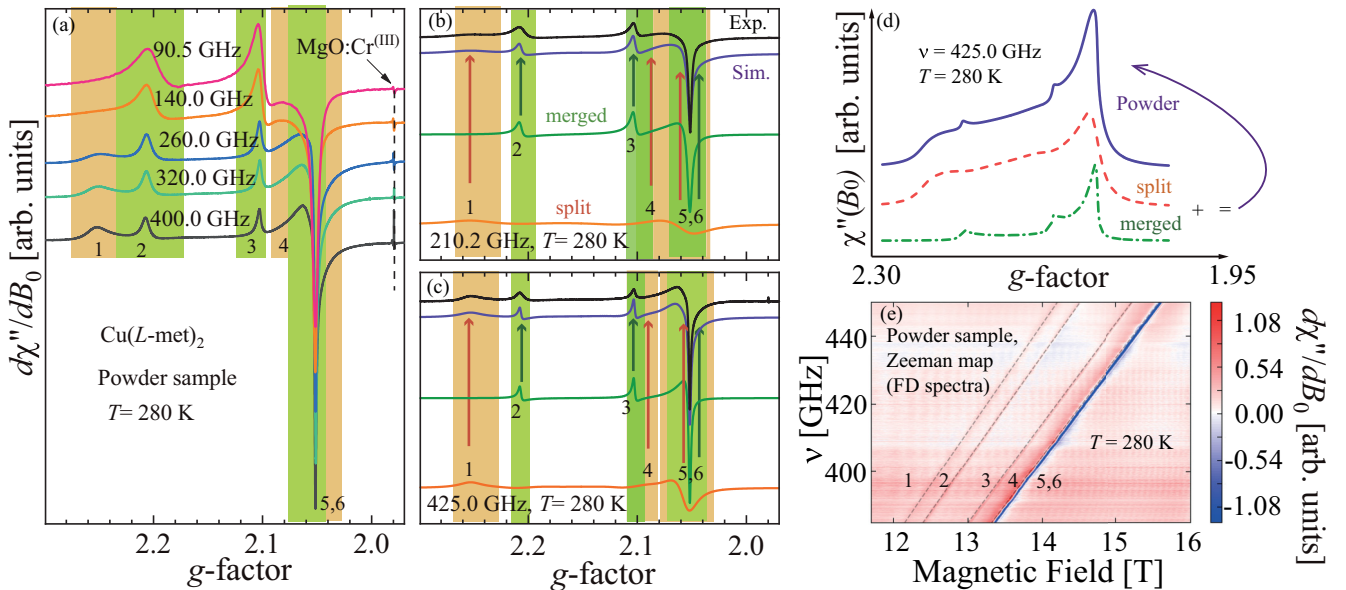


FIG. 5. HFEPR spectra $d\chi''/dB_0$ of powdered samples of $\text{Cu}(\text{L-met})_2$ at selected ν . (a) Spectra collected at five values of ν . Numbers 1–6 identify the peaks as described in the text. (b)(c) Spectra at 210 GHz and 425 GHz. The black spectrum is the experimental result. Green and orange spectra are simulations of merged and split phases calculated from the corresponding set of randomly distributed orientations in the solid angle of the sphere. Their sum (violet line), fits the data. (d) Absorption spectra χ'' displaying the individual contributions of each phase and their contribution at each magnetic field (g value). (e) Zeeman map obtained for a powder sample of $\text{Cu}(\text{L-met})_2$ using frequency-domain sweeps. The position, strength, and widths of the peaks of the spectra as a function of B_0 are described by a color scale of $d\chi''/dB_0$. The dashed lines are linear fits of $\nu = \nu(B_0)$ providing slopes proportional to g_p for each peak which reproduce the square root of the eigenvalues of the g^2 matrices of Table I.

TABLE III. Values of g_p obtained from the Zeeman map of a powder sample, compared with the square roots of the eigenvalues of the matrices $\mathbf{g}^2$ and $\mathbf{g}_A^2$ (or $\mathbf{g}_B^2$) of Table I (in parenthesis) and the values used for the powder simulation in square brackets.

	Merged phase	Split phase
g_1	2.057 (2.058) [2.052]	2.057 (2.057) [2.057]
g_2	2.107 (2.109) [2.103]	2.057 (2.058) [2.055]
g_3	2.208 (2.211) [2.207]	2.220 (2.258) [2.253]
$\langle g \rangle$	2.124 (2.126) [2.121]	2.111 (2.112) [2.123]

the magnetic field. In the case of a powder, all orientations are sampled simultaneously, with both phases contributing additively to the observed spectra. To simulate the powder spectrum, we used evenly distributed orientations over the solid angle (see Sec. VII) and determined selectively the contributing phase by comparing the exchange interaction $|J| = 0.14 \text{ cm}^{-1}$, obtained for single crystals at $T = 280 \text{ K}$, with the peak separation $|\delta B^{\text{cal}}|$ calculated at each frequency using the matrices $\mathbf{g}_A^2$ and $\mathbf{g}_B^2$ from Table I.

For orientations corresponding to the split phase, where $|\delta B^{\text{cal}}| > |J|/(g\mu_B)$, two peaks were simulated using $\mathbf{g}_A$ and $\mathbf{g}_B$, with a linewidth of 90 mT, comparable to the linewidths observed in single crystals at 310 GHz and 280 K [see Fig. 3(e)]. For orientations corresponding to the merged phase, where $|\delta B^{\text{cal}}| < |J|/(g\mu_B)$, only one peak was simulated using $\mathbf{g}$ (Table I), with the linewidth determined by the value of $|\delta B^{\text{cal}}|$, following the parabolic relation in Eq. (10), shown in Fig. 3(g).

The powder spectrum was obtained by summing the spectra from each phase, according to the conditions $|\delta B^{\text{cal}}| > |J|/(g\mu_B)$ for the split phase and $|\delta B^{\text{cal}}| < |J|/(g\mu_B)$ for the merged phase, and then comparing the result with the experimental data. An example of the selectively simulated powder spectra and their sum is illustrated with the absorption spectra $\chi''(B_0)$ in Fig. 5(d). Minor adjustments to the g values from Table I were necessary, but a consistent set of g values and linewidths was used to simulate spectra at 280 K across all frequencies and are shown in square brackets in Table III. It is important to emphasize that the g values of the merged phase are not related to a molecule but are the average over two rotated molecules and do not reflect any local symmetry. Examples for the simulation at $\nu = 210 \text{ GHz}$ and 425 GHz are provided in Figs. 5(b) and 5(c).

These simulations enabled us to assign all six peaks in the spectra: peaks 1, 4, and 6 correspond to the split phase, while peaks 2, 3, and 5 belong to the merged phase, as indicated by orange and green vertical bands. As the microwave frequency increases, the relative contribution of the merged phase decreases [see Figs. 5(a)–5(c)]. This is consistent with the results of Levstein *et al.* [33] at 33.6 GHz, where the signal arises entirely from the merged phase. The contribution of the split phase is small at 280 K for lower frequencies because of its broad linewidth and the small fraction of split orientations.

Figure 5(e) displays a Zeeman map of the evolution of the peaks of the powder spectrum $d\chi''/dB_0$ vs B_0 with the microwave frequency, collected as described in Sec. VII. The

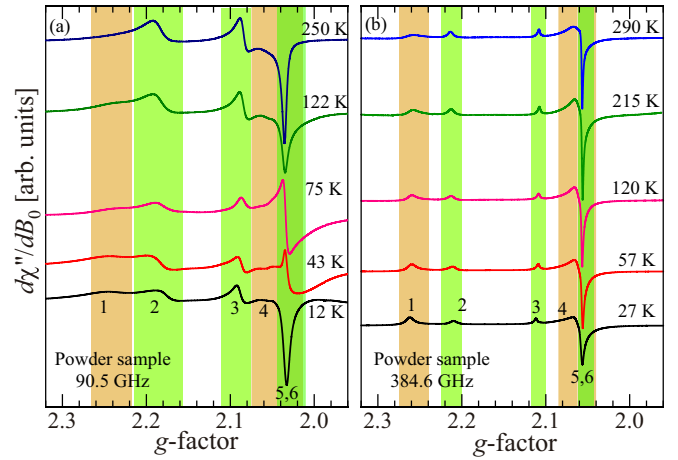


FIG. 6. HFEPR spectra $d\chi''/dB_0$ at 90.5 GHz and 384.6 GHz of a powder sample as a function of T . The vertical color shadings and the numbers identify the peaks corresponding to each phase.

position, width, and color intensity of the lines in Fig. 5(e) belong to the main peaks of the powder spectra identified in Figs. 5(a)–5(c). The resonance condition

$$\nu = (g_p \mu_B / h) B_0, \quad (17)$$

was used to perform linear regressions for calculating the slope g_p , representing the g value of the peaks in the map, for each line in Fig. 5(e). The resulting fits are the dashed lines shown in Fig. 5(e), and the four values of g_p of each peak are displayed in Table III for each phase. We include in parentheses in Table III the square root of the corresponding eigenvalues $(g^2)_i^{1/2}$ of the matrices $\mathbf{g}^2$ and $\mathbf{g}_A^2$ (or $\mathbf{g}_B^2$) of Table I, which, within uncertainties, are equal to the values of g_p of the merged and split phases, respectively, in agreement with the assumptions.

2. Temperature dependence

Figures 6(a) and 6(b) display the HFEPR spectra at five selected T between 90.5 GHz and 384.6 GHz, as a function of the decreasing g factor. These spectra display a whole change of the intensity arising from Curie paramagnetism, equal for the two phases, without a particular insight. They also display changes in the relative intensity of the peaks of each phase, the consequence of changes in the magnitude of the coupling $|J|$ with T . Since the whole change obscures observing relative changes, the spectra were normalized to the same area. The fractions of the two phases calculated from the simulation of powder spectra exhibit changes that follow the behavior observed in single-crystals supporting the decrease of $|J|$ with decreasing T .

V. DISCUSSION

When the rotated spins A and B of $\text{Cu}(\text{L-met})_2$ are uncoupled, their EPR spectra display two peaks obeying a Zeeman Hamiltonian with $\mathbf{g}$ matrices, $\mathbf{g}_A$ and $\mathbf{g}_B$ [Eq. (3)], related by rotation. EPR studies at 9.7 GHz and 33.6 GHz [33] of single crystals of $\text{Cu}(\text{L-met})_2$ displayed a single anisotropic peak for all orientations of the applied field, which was assigned

to the merging of the two peaks by the exchange coupling $\mathcal{H}_{\text{ex}}$ [Eq. (1)] between A and B neighbor spins. In this work we study the quantum properties of the compound, using high-frequency field measurements HFEPR facilities. Our results, described in Sec. IV, allow us to upgrade and discuss the quantum properties of $\text{Cu}(\text{L-met})_2$, and the role of spin anisotropy.

A. Merging and narrowing of the peaks of the spectra

The EPR spectra of single crystal samples of multiple monomeric anisotropic spin arrays display sudden merging and narrowing phenomena in the presence of the exchange coupling [21]. Our interest is oriented on learning about the transition of the material from one situation to the other. The new multifrequency HFEPR study of the merging and narrowing process reflects an appealing behavior strongly dependent on microwave frequency and temperature, allowing an updated quantum description of the material. Rather than crossing, the EPR peaks A and B of the single crystal spectra merge to a common field and display a strong narrowing along a line over the sphere of orientations $\mathbf{h}$ of $\mathbf{B}_0$ [Eq. (4)] where they intersect in the absence of coupling [i.e., when $g_A(\theta, \varphi) = g_B(\theta, \varphi)$, see Eq. (3)]. Merging and narrowing of the EPR peaks have been observed previously for other multiple monomeric arrays at low microwave frequencies [43,45,53–56,58]. Here, the multifrequency character and much higher frequencies in a quasi-continuous way of our HFEPR measurements allow us to explore a larger range of magnetic fields $\mathbf{B}_0$ applied to the sample, observe new features, and analyze the results with higher detail and from new points of view. Throughout this work, we develop procedures to utilize EPR spectra of powder samples as a source of magnetic information, which may be of interest to chemists studying the properties of other coordination compounds with multiple monomeric spin arrays.

In simple terms, the exchange coupling between neighbor dissimilar spins $\mathbf{S}_{i,A}$ and $\mathbf{S}_{j,B}$ occurring throughout the array, is the sum of terms as

$$-J\mathbf{S}_{i,A} \cdot \mathbf{S}_{j,B} = -J\left[\frac{1}{2}(S_{i,A}^+ S_{j,B}^- + S_{i,A}^- S_{j,B}^+) + S_{i,A}^z S_{j,B}^z\right]. \quad (18)$$

The z term creates an energy band with width $|J|$ around the Zeeman energies of the spins; the nondiagonal terms produce flip-flop transitions of neighbor spins along the lattice, creating a spin-dynamics of traveling excitations that shows up as the merging and narrowing of the peaks of the EPR spectra. These nondiagonal terms have been reported to be responsible for creating entanglement on EPR time scales in dimers of Mn_4 single-molecule magnets [93,94]. We analyze our HFEPR data under the hypothesis that, in an infinite lattice, this process is not continuous but there is a sudden transformation of the spin system when the magnitude of $|J|$ becomes larger than the energy difference between spins A and B. Using the g anisotropy of the spins, one can induce a reversible discontinuous transition from a phase of distinguishable (split) spin states to a phase of indistinguishable (merged) spin states by changing the orientation of the magnetic field $\mathbf{B}_0$. We associate these changes with quantum dynamical phase transitions [82] controlled by the orientation of the applied magnetic field.

B. Dependence on $\mathbf{B}_0$ and T of the HFEPR spectra. The spin-spin exchange coupling

Changing the microwave frequency requires varying the applied magnetic field to comply with the resonance condition [Eq. (17)]. The HFEPR spectra of $\text{Cu}(\text{L-met})_2$ change with $\mathbf{B}_0$ as it varies the magnetic field difference $\delta B(\theta, \varphi)$ between the resonance peaks of the copper sites. The changes are as shown in Figs. 4(c)–4(j) for a single crystal sample and in Figs. 5(a)–5(c) for a powder sample. The fact that our data from different measurements allow for calculating similar values of the physical properties and fitting complementary data indicates the solid grounds used in the interpretation.

The results in single crystals allow for obtaining good agreement between the values of the spin-spin coupling $|J|$ both from the merging of the two peaks of the spectra and from the narrowing of the merged peak. We find that $|J|$ does not change with ν (see Table II), i.e., with $\mathbf{B}_0$ increasing by a factor of $\sim$ ten, at constant T , from 33.6 GHz in Fig. S2 within the Supplemental Material [87] to 310 GHz in Figs. 4(c), 4(d), 4(g), and 4(h). On the other hand, data with the same frequency (and field) but different T [Figs. 4(d)–4(f) and 4(h)–4(j)], display important changes of $|J|$. Phonons can modulate interatomic distances or angles in the exchange pathway. For example, at higher T , the increased vibrational amplitudes can transiently improve the orbital overlap, enhancing $|J|$. On the other hand, specific phonon modes can disrupt exchange pathways at lower T , reducing $|J|$. Mechanisms in which lattice vibrations modulate J through dynamic lattice distortions or spin-lattice coupling are described in [95,96].

The main advantage of EPR measurements to characterize spin arrays is that data obtained at room temperature gives information about the magnitude $|J|$ of couplings smaller than 1 K. Besides, it has been shown for copper amino acid compounds such as $\text{Cu}(\text{L-but})_2$ and $\text{Cu}(\text{D,L-but})_2$ [35,97], and the copper-peptide compound CuTrpGly [98] that the values of $|J|$ obtained from the EPR spectra compare well with results obtained from thermodynamic measurements such as magnetic susceptibility or specific heat at very low T . This work allowed us to evaluate the coupling $|J|$ with higher accuracy and prove its independence from the microwave frequency or applied magnetic field within a large range, and its temperature dependence (see Table II). We explain these results proposing that the coupling between the two types of spins A and B in the lattice of $\text{Cu}(\text{L-met})_2$ admix their wave functions and for field orientations where $|J| > |\delta g \mu_B B_0|$, it creates a quantum merged phase, governed by the field orientation $\mathbf{h}$.

C. Quantum phase diagrams in $\text{Cu}(\text{L-met})_2$

Our HFEPR results show that the spin array of $\text{Cu}(\text{L-met})_2$ is in a collective merged phase for orientations (θ, φ) of $\mathbf{B}_0$ in which the magnitude $|J|$ of the spin-spin coupling and the difference between the Zeeman energies $Z_{AB} = |\delta g(\theta, \varphi) \mu_B B_0|$ of the rotated spins A and B, hold $|J| > Z_{AB}$. The differences between the g values $|\delta g(\theta, \varphi)|$, and those between the Zeeman energies of these sites, $|\delta g(\theta, \varphi) \mu_B B_0|$, can be calculated from the matrices $\mathbf{g}_A^2$ and $\mathbf{g}_B^2$ given in Table I, whose eigenvectors reproduce the orientation of the nearly octahedral molecules A and B [Fig. 2(a)] in the structure of the compound [25]. Merged and split phases in a single-crystal sample

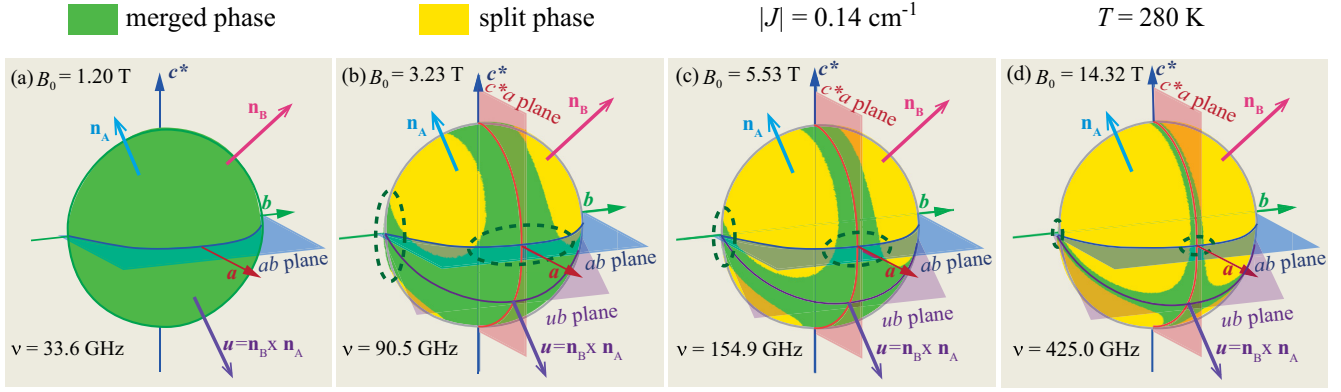


FIG. 7. (a)–(d) Phase diagrams for the merged-split transition as a function of the orientation $\mathbf{h}$ of $\mathbf{B}_0$ for four values of ν and B_0 . Crystal axes and planes are indicated as a guide. Green color indicates the merged orientation range; yellow is the split range.

display different EPR spectra and can be observed for different field orientations. Figures 7(a)–7(d) display phase diagrams for merged and split phases, as a function of the orientation $\mathbf{h}$ of the magnetic field [see Eq. (4)]. These diagrams depend on the microwave frequency, which sets the average magnitude of the applied magnetic field, and on T , which changes the coupling $|J|$. These transitions are produced when the orientation of $\mathbf{B}_0$ crosses the condition $|J| = Z_{AB}$ where there is a sudden reversible transition. These phases contribute additively to the spectra of powder samples following a well-defined selection rule. Phase diagrams were calculated at four microwave frequencies (magnetic-field) 33.6 GHz (1.20 T), 90.5 GHz (3.23 T), 154.9 GHz (5.53 T), and 425.0 GHz (14.32 T) in the sphere of orientations $\mathbf{h}$ of the applied $\mathbf{B}_0$, at room temperature, when $|J| = 0.14 \text{ cm}^{-1}$. The vectors $\mathbf{n}_A$ and $\mathbf{n}_B$ in the diagrams correspond to the axial directions of the copper sites. The green-colored surface of the sphere corresponds to the merged phase and was calculated for each microwave frequency, selecting from a set of 70 000 (see Sec. VII) randomly distributed orientations (θ, φ) of $\mathbf{B}_0$, those where the condition $|J| > Z_{AB}$ holds. The merged phase covers the full sphere at 33.6 GHz, and partially at higher frequencies, reflecting the observed spectra of powder samples where the fraction R of the spins in the merged phase decreases with increasing microwave frequency.

Figure 8 displays the fraction R of the spins of a powder sample in the merged phase vs the exchange coupling in cm^{-1} . It was calculated with the model described in Sec. II as the fraction of a set of randomly distributed directions in the solid angle of a sphere in which $|J| > g\mu_B\delta B$, at various selected frequencies between 33 GHz and 425 GHz. The vertical dashed line corresponds to the value $|J| = 0.14 \text{ cm}^{-1}$ obtained from the single-crystal data at $T = 280 \text{ K}$ and indicates that the highest ν at which all spins of a sample are in the merged phase at 280 K is $\sim 50 \text{ GHz}$. At 425 GHz and 280 K only 20% of the spins of a powder sample are in the merged phase, and the population of the merged phase would decrease asymptotically as the frequency increases.

D. Dipole-dipole interactions

The absence of a dipolar coupling term $\mathcal{H}_{dd}$ in Eq. (1), the anisotropic coupling between spins that gave rise to the

concept of exchange narrowing in solids [10,11,52], requires an explanation. We deal here with a kind of exchange-narrowing phenomenon that parallels dipole-dipole narrowing at its origin and occurs simultaneously with it. However, for the multiple monomeric anisotropic spin arrays we are dealing with, their contributions are much smaller, with consequences that are easily distinguished from the problem treated here. Also, the dipole-dipole coupling has been proven to produce field shifts of the peaks of the EPR spectra of low-dimensional lattices [99,100] (not observed here), with results that have not interfered with this work.

VI. CONCLUSIONS

Leveraging the experimental capabilities currently available, we build upon seminal EPR works presented in the references [12–20,22] to offer new insights into the statistical quantum behavior of molecular systems named here as multiple monomeric arrays of spin $\frac{1}{2}$. This work implements Pryce’s exceptional and advanced ideas [14] in his attempt to explain EPR results about CuSO_4 , including his prediction of two peaks when the applied frequency exceeds the exchange interaction in a system with rotated cupric ions in a lattice.

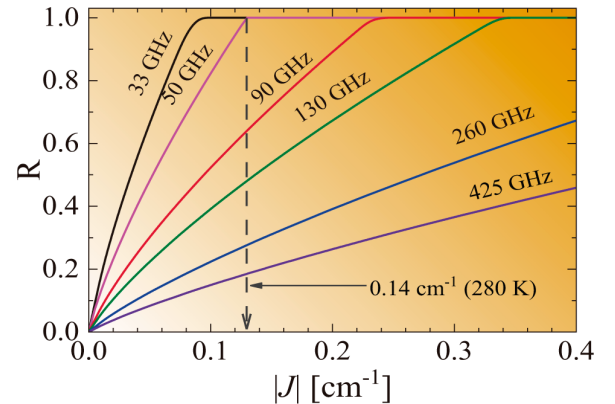


FIG. 8. Fraction R of spins of a powder sample in the merged phase calculated at various frequencies, as a function of the exchange coupling $|J|$. The dashed vertical line indicates the value $|J| = 0.14 \text{ cm}^{-1}$ measured at $T = 280 \text{ K}$ in single crystals and powder samples.

His ideas remained a theoretical proposal because of the lack of experimental capability at the time. Our new spectroscopic data provide information about the dynamic effect of the isotropic exchange coupling in spin chains using EPR peaks of anisotropic spins, allowing separation of the behavior in two phases according to the orientation and magnitude of an applied magnetic field.

We present a novel empirical view of the quantum behavior of a spin array by probing the system with a frequency one order of magnitude beyond previously reported experiments for $\text{Cu}(\text{L-met})_2$, reaching a critical value determined by the intermolecular exchange coupling J , and allowing observation of distinct quantum phases of the spin array. When the difference between the Zeeman energies of rotated AB spin pairs becomes larger than $|J|$, the spins suffer a collective transition from a quantum-merged regime with spectra displaying one peak, as at low frequency, to the split spin regime with EPR spectra displaying two peaks. This indicates the importance of using a wide range of microwave frequencies and the equivalent applied fields $\mathbf{B}_0$ to be able to observe changes in the quantum properties. The frequency and field ranges are determined by the spin anisotropy and the exchange coupling.

Our data in single crystals allow us to follow the phase transitions observing the merging and narrowing of the peaks of the spectra at these field orientation ranges. This transition involves the fundamental process of the exchange narrowing phenomenon, but cannot be observed in the classical case of the dipolar interaction, which does not offer a resolved structure but a statistical distribution of couplings. Spectra of powder samples collect selectively field orientations contributing to the spectra of each spin phase, allowing the simultaneous observation of both phases. Simulations of these spectra require methods that explicitly consider the angular selection suggested by the single-crystal data, allowing confirmation of the hypothesis of the proposed model. The powder spectra and the angular variation of the single crystal spectra allowed to evaluate $|J|$ following different procedures, with equal results. Also, we show that $|J|$ does not change with the frequency of the measurements that require fields B_0 one order of magnitude larger. Meanwhile, $|J|$ shows important changes with temperature that are attributed to lattice vibrations modulating the exchange pathway. The powder EPR results reinforce the advantage of using EPR to calculate exchange couplings in the mK range using data even at room temperature, reproducing values reported by magnetic susceptibility or specific heat at very low T .

Our results allow us to construct quantum phase diagrams where the driving parameter is the orientation $\mathbf{h}$ of the magnetic field $\mathbf{B}_0$. They vary with the microwave frequency and it is shown that at 33.6 GHz the merged phase covers all orientations of a sphere, while at the higher frequencies, it covers a small portion, and the spin array is split for most orientations.

We propose that the merging and narrowing are produced by flip-flop transitions [Eq. (18)]. In this case, it involves transitions between spin $\frac{1}{2}$ with the Zeeman energy; that is different from what was proposed for dimeric arrays [68], where flip-flop transitions were shown to correspond to transitions between spin 1 states (singlet-triplet transitions) with much larger energy corresponding to the intradimeric exchange $|J_0|$.

As a perspective to continue this work, it would be interesting to apply other techniques, such as pulsed EPR, for probing the relaxation times and their behavior in the phase transition and at the narrowest width of the peaks. We imagine that the observed enhancements in the relaxation times at the merged phase could be a very valuable characterization for systems of this kind for future applications in quantum information processing.

Moreover, our experimental results provide solid ground for developing new theoretical studies on the quantum behavior of weakly coupled multiple monomeric arrays. As a perspective for future experimental works, arrays with more than two symmetry-related sites and different exchange paths can be studied using solely powder samples to evaluate the exchange couplings.

VII. METHOD

Single crystals of $\text{Cu}(\text{L-met})_2$ were prepared as described before [33,81]. Powder samples were ground from single crystals, as finely as required for the EPR experiments at high frequency. The HFEPR spectrometer used in this work has been described previously [62,101,102]. About 15 mg of the ground powder was diluted with 5 mg of ground Eicosane 99% (Sigma Aldrich, CAS 112-95-8, an inert material that is EPR silent) and pressed under 5 ton/cm² to form a pellet with 5 mm diameter and 1 mm height, suitable to be loaded in the simple sample holder for HFEPR, on the top of a mirror [101]. Eicosane is used to make the pellet less brittle and to avoid unwanted rotation of microcrystals in a powder sample under high magnetic field. A small but still detectable amount of MgO doped with 0.5% of Cr^{III} impurities ($g = 1.9797$) was added to the mixture to serve as a standard for line intensity and g factor calibration.

The powder sample was measured at room temperature and various frequencies between 90 GHz and 450 GHz. Above 450 GHz, the EPR spectra are incomplete under the highest available $\mathbf{B}_0$ of 16 T. Several spectra were obtained at varying temperatures at 90 GHz and 385 GHz, as indicated in Fig. 6. A sweep rate of $\mathbf{B}_0$ between 1 mT/s and 1.5 mT/s and a modulation field of 1.5 mT at 15 kHz were used in all measurements. We used a low-pass digital filter with a time constant of 300 ms for the acquisition. The range of $\mathbf{B}_0$ was chosen according to the microwave frequency.

The powder sample was also measured at room temperature using frequency-domain (FD) sweeps of 5 s from 385 GHz to 450 GHz saving spectra with 36 621 points for each sweep. Each frequency sweep was taken while simultaneously sweeping $\mathbf{B}_0$ from 11.6 T to 16 T with a rate of 0.318 mT/s, resulting in a collection of FD spectra at 2520 different values of $\mathbf{B}_0$. A modulation amplitude of 1.5 mT at 15 kHz was used. The described FD experiment is better visualized in a frequency-field map (Zeeman map) with a resolution of 36621×2520 as shown in Fig. 5(e). Horizontal sections of this map provide equivalent CW field-swept spectra that are comparable to the ones obtained at fixed frequencies like the ones in Figs. 5(a)–5(c); however, there are some advantages in the FD approach. For example, the time to sweep the magnetic field in the range 11.6–16 T at the used rate in the FD experiment is 3.8 hours, which

is approximately the time necessary to obtain the displayed map in Fig. 5(e). Getting a similar result with field sweeps, even with a resolution of 1 GHz, would take many days. Moreover, the determination of the g factor using the map prevents errors related to the calibration of B_0 , as it is extracted from the slope of the resonance peak positions according to the EPR resonance condition. A challenging aspect of this extraction is associated with the determination of the peak positions.

Single-crystal samples were measured in a sample holder equipped with a piezo-rotator capable of providing reproducible steps of $\sim 0.1^\circ$. The data were taken every 5° away from the expected calculated intersection of the peaks for Cu^{A} and Cu^{B} and every 1° closer to the intersection, where the peaks display a narrowing.

To simulate and fit single-crystal spectra to a given spin Hamiltonian, we used EasySpin [84], a set of programs working in Matlab. For powder spectra, we used sets of up to 70 000 directions equally spaced in a sphere obtained with the iterative procedure Repulsion proposed by Bak and Nielsen [103] and a Fortran program that minimizes the average

angular distance between one and the surrounding directions. The 70 000 orientations were needed to provide sufficient quality for the final simulated spectra, avoiding artifacts in the final result. The spectrum corresponding to each direction was obtained with EasySpin, and a selective sum of them gives the spectra of the powder. This method has the advantage of summing specific directions that hold a given condition, i.e., preferred ranges of field orientations.

Crystal structure drawings were made using Mercury [88].

ACKNOWLEDGMENTS

All authors contributed equally to this work. V.T.S acknowledges the support to this work from the Grant Agency of the Czech Republic (GAČR) under contract No. 24-11928M. R.C. is an Emeritus member of CONICET.

DATA AVAILABILITY

The data that support the findings of this article are openly available [104].

- [1] A. Bencini and D. Gatteschi, *Electron Paramagnetic Resonance of Exchange Coupled Systems* (Springer, Berlin, 1990).
- [2] O. Kahn, *Molecular Magnetism* (Wiley VCH, New York, 1993).
- [3] A. Gaita-Ariño, F. Luis, S. Hill, and E. Coronado, Molecular spins for quantum computation, *Nat. Chem.* **11**, 301 (2019).
- [4] A. Chiesa, P. Santini, E. Garlatti, F. Luis, and S. Carretta, Molecular nanomagnets: A viable path toward quantum information processing? *Rep. Prog. Phys.* **87**, 034501 (2024).
- [5] D. Gatteschi, A. L. Barra, A. Caneschi, A. Cornia, R. Sessoli, and L. Sorace, EPR of molecular nanomagnets, *Coord. Chem. Rev.* **250**, 1514 (2006).
- [6] P. W. Anderson, A mathematical model for the narrowing of spectral lines by exchange or motion, *J. Phys. Soc. Jpn.* **9**, 316 (1954).
- [7] M. Kubo and K. Tomita, A general theory of magnetic resonance absorption, *J. Phys. Soc. Jpn.* **9**, 888 (1954).
- [8] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970), p. 911.
- [9] J. A. Weil and J. R. Bolton, *Electron Paramagnetic Resonance. Elementary Theory and Practical Applications*, 2nd ed. (Wiley-Interscience, Hoboken, NJ, 2007), p. 664.
- [10] C. J. Gorter and J. H. Van Vleck, The role of exchange interaction in paramagnetic absorption, *Phys. Rev.* **72**, 1128 (1947).
- [11] J. H. Van Vleck, The dipolar broadening of magnetic resonance lines in crystals, *Phys. Rev.* **74**, 1168 (1948).
- [12] D. M. S. Bagguley and J. H. E. Griffiths, Paramagnetic resonance and magnetic energy levels in chrome alum, *Nature (London)* **160**, 532 (1947).
- [13] D. M. S. Bagguley and J. H. E. Griffiths, Paramagnetic resonance in copper sulphate, *Nature (London)* **162**, 538 (1948).
- [14] M. H. L. Pryce, Theory, *Nature (London)* **162**, 539 (1948).
- [15] D. Halliday and J. Wheatley, Paramagnetic resonance absorption in chrome Alum, *Phys. Rev.* **74**, 1712 (1948).
- [16] R. D. Arnold and A. F. Kip, Paramagnetic resonance absorption in two sulfates of copper, *Phys. Rev.* **75**, 1199 (1949).
- [17] J. Wheatley and D. Halliday, Paramagnetic absorption in single crystals of copper sulfate pentahydrate, *Phys. Rev.* **75**, 1412 (1949).
- [18] D. M. S. Bagguley and J. H. E. Griffiths, Paramagnetic resonance in copper sulphate, *Proc. R. Soc. London A* **201**, 366 (1950).
- [19] H. Abe and K. Ôno, Paramagnetic resonance spectra of some cupric salts (I), *J. Phys. Soc. Jpn.* **11**, 947 (1956).
- [20] D. M. S. Bagguley and J. Owen, Microwave properties of solids, *Rep. Prog. Phys.* **20**, 304 (1957).
- [21] P. W. Anderson and P. R. Weiss, Exchange narrowing in paramagnetic resonance, *Rev. Mod. Phys.* **25**, 269 (1953).
- [22] M. Yokota and S. Koide, The exchange effects on the absorption spectrum by the paramagnetic crystal with anisotropic g -factors, *J. Phys. Soc. Jpn.* **9**, 953 (1954).
- [23] R. A. Sack, A contribution to the theory of the exchange narrowing of spectral lines, *Mol. Phys.* **1**, 163 (1958).
- [24] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962), pp. 268.
- [25] B. N. Figgis and M. A. Hitchman, *Ligand Field Theory and its Applications* (Wiley-VCH, New York, 2000), Chap. 10.
- [26] R. E. Dietz, F. R. Merritt, R. Dingle, D. Hone, B. G. Silbernagel, and P. M. Richards, Exchange narrowing in one-dimensional systems, *Phys. Rev. Lett.* **26**, 1186 (1971).
- [27] P. M. Richards and M. B. Salamon, Exchange narrowing of electron spin resonance in a two-dimensional system, *Phys. Rev. B* **9**, 32 (1974).
- [28] Y. Servant, J.-C. Bissey, and M. Maini, An X-band and Q-band single crystal electron paramagnetic resonance study of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, *Phys. B: Condens. Matter* **106**, 343 (1981).
- [29] R. Calvo and M. A. Mesa, EPR study of electronic and magnetic properties of bis(*DL*- α -amino-*n*-butyrate)copper(II). A layered magnetic system, *Phys. Rev. B* **28**, 1244 (1983).

- [30] R. Calvo, M. A. Mesa, G. Oliva, J. Zukerman-Schpector, O. R. Nascimento, M. Tovar, and R. Arce, Structural and magnetic properties of a copper amino acid salt. Copper(II)bis(α -amino-isobutyrate), *J. Chem. Phys.* **81**, 4584 (1984).
- [31] R. Calvo, H. Isern, and M. A. Mesa, EPR study of Cu(*L*-ILE)₂, a copper amino acid salt, *Chem. Phys.* **100**, 89 (1985).
- [32] A. M. Gennaro, P. R. Levstein, C. A. Steren, and R. Calvo, EPR of layered magnetic metal—amino acid salts. I. Cu(*L*-phe)₂, *Chem. Phys.* **111**, 431 (1987).
- [33] P. R. Levstein, C. A. Steren, A. M. Gennaro, and R. Calvo, EPR of layered magnetic metal-amino acid salts. II. Cu(*L*-Met)₂, *Chem. Phys.* **120**, 449 (1988).
- [34] C. A. Steren, A. M. Gennaro, P. R. Levstein, and R. Calvo, Exchange interactions in bis(*L*-leucinato)copper(II), *J. Phys.: Condens. Matter* **1**, 637 (1989).
- [35] P. R. Levstein, R. Calvo, E. E. Castellano, O. E. Piro, and B. E. Rivero, Molecular structure and exchange interactions in *trans*-bis(*L*-2-aminobutyrate)copper(II) and *trans*-bis(*DL*-2-aminobutyrate)copper(II), *Inorg. Chem.* **29**, 3918 (1990).
- [36] P. R. Levstein and R. Calvo, Superexchange coupling mediated by carboxylate and hydrogen bridges in copper amino acid complexes, *Inorg. Chem.* **29**, 1581 (1990).
- [37] P. R. Levstein, H. M. Pastawski, and R. Calvo, Spin diffusion in low-dimensional copper-amino-acid complexes, *J. Phys.: Condens. Matter* **3**, 1877 (1991).
- [38] R. Calvo, M. C. G. Passeggi, M. A. Novak, O. G. Symko, S. B. Oseroff, O. R. Nascimento, and M. C. Terrile, Exchange interactions and magnetic dimension in Cu(*L*-alanine)₂, *Phys. Rev. B* **43**, 1074 (1991).
- [39] R. Calvo, P. R. Levstein, E. E. Castellano, S. M. Fabiane, O. E. Piro, and S. B. Oseroff, Crystal structure and magnetic interactions in bis(*D,L*-alaninato)copper(II)hydrate, *Inorg. Chem.* **30**, 216 (1991).
- [40] C. D. Brondino, N. M. C. Casado, M. C. G. Passeggi, and R. Calvo, Exchange interaction between copper(II) ions through glutamic acid molecules, *Inorg. Chem.* **32**, 2078 (1993).
- [41] R. Calvo, C. A. Steren, O. E. Piro, T. Rojo, F. J. Zuniga, and E. E. Castellano, Crystal structure and magnetic properties of diaqua(*L*-aspartato)copper(II), *Inorg. Chem.* **32**, 6016 (1993).
- [42] M. C. G. Passeggi and R. Calvo, Evaluation by EPR of the exchange interactions coupling anisotropic spins at symmetry-related sites in paramagnetic crystals, *J. Magn. Reson. Ser. A* **114**, 1 (1995).
- [43] D. M. Martino, M. C. G. Passeggi, and R. Calvo, Magnetic interactions in Cu(*L*-isoleucine)₂ · H₂O: An EPR measurement, *Phys. Rev. B* **52**, 9466 (1995).
- [44] R. P. Sartoris, L. Ortigoza, N. M. C. Casado, R. Calvo, E. E. Castellano, and O. E. Piro, Structure, single crystal EPR spectra, and exchange interactions in [Cu(*L*-proline)₂]₂ · 5H₂O and Cu(*D,L*-proline)₂ · 2H₂O, *Inorg. Chem.* **38**, 3598 (1999).
- [45] A. J. Costa-Filho, C. E. Munte, C. Barberato, E. E. Castellano, M. P. D. Mattioli, R. Calvo, and O. R. Nascimento, Crystal structures and magnetic properties of CuX₂(pdmp)₂ complexes (X = Br, Cl), *Inorg. Chem.* **38**, 4413 (1999).
- [46] S. K. Hoffmann and L. S. Szczepaniak, Dynamical averaging of two symmetry-related magnetic resonance tensors in single crystals, *J. Magn. Reson.* **52**, 182 (1983).
- [47] S. K. Hoffmann, Temperature dependence of a superexchange interaction determined from merging effect of copper(II) EPR lines, *Chem. Phys. Lett.* **98**, 329 (1983).
- [48] S. K. Hoffmann, J. Goslar, and L. S. Szczepaniak, Weak exchange interaction in cis-Cu(NH₂CH₂COO)₂ · H₂O single crystal: EPR studies, *Phys. Rev. B* **37**, 7331 (1988).
- [49] J. Goslar, W. Hilczner, S. K. Hoffmann, and M. Krupski, Temperature and pressure EPR studies of superexchange coupling in Cu(1-phenylpyrazole)₂Cl₂ crystals, *Phys. Status Solidi (b)* **167**, 291 (1991).
- [50] J. Goslar, W. Hilczner, and S. K. Hoffmann, Weak exchange effects in EPR anisotropy of dichlorobis(1-phenyl-3,5-dimethylpyrazole) Copper(II) Single Crystals, *Phys. Status Solidi (b)* **175**, 465 (1993).
- [51] S. K. Hoffmann, W. Hilczner, and J. Goslar, Weak long-distance superexchange interaction and its temperature variations in copper(II) compounds studied by single crystal EPR, *Appl. Magn. Reson.* **7**, 289 (1994).
- [52] G. E. Pake, *Paramagnetic Resonance. An Introductory Monograph*, 1st ed. (Benjamin, Inc., New York, 1962).
- [53] D. M. Martino, M. C. G. Passeggi, R. Calvo, and O. R. Nascimento, EPR spectroscopy and exchange interaction parameters in Cu(glycine)₂H₂O, *Phys. B: Condens. Matter* **225**, 63 (1996).
- [54] R. Calvo, M. C. G. Passeggi, N. O. Moreno, G. E. Barberis, A. B. Chaves, B. C. M. Torres, L. Lezama, and T. Rojo, Magnetic properties of Cu(*L*-aspartato)(H₂O): A linear chain antiferromagnet, *Phys. Rev. B* **60**, 1197 (1999).
- [55] E. D. Vieira, N. M. C. Casado, G. Facchin, M. H. Torre, A. J. Costa-Filho, and R. Calvo, Weak exchange interaction supported by a biologically relevant long chemical bridge in a Cu-peptide model compound, *Inorg. Chem.* **45**, 2942 (2006).
- [56] D. Venegas-Yazigi, K. A. Brown, A. Vega, R. Calvo, C. Aliaga, R. C. Santana, R. Cardoso-Gil, R. Kniep, W. Schnelle, and E. Spodine, Exchange interactions through π - π stacking in the lamellar compound [{Cu(bipy)(en)}{Cu(bipy)(H₂O)}{VO₃}]_n, *Inorg. Chem.* **50**, 11461 (2011).
- [57] V. Paredes-García, R. C. Santana, R. Madrid, B. Baldo, A. Vega, and M. Spohn, Single crystal electron paramagnetic resonance spectra of Cu(II) ions in Cu(tyrosine)₂. A study of weak exchange interactions mediated by resonance assisted hydrogen bonds (RAHB), *J. Inorg. Biochem.* **114**, 75 (2012).
- [58] V. T. Santana, B. N. Cunha, A. M. Plutín, R. G. Silveira, E. E. Castellano, A. A. Batista, R. Calvo, and O. R. Nascimento, Magnetic-field-tuned phase transition of a molecular material from the isolated-spin to the coupled-spin regime, *Phys. Chem. Chem. Phys.* **21**, 4394 (2019).
- [59] F. Troiani, V. Bellini, A. Candini, G. Lorusso, and M. Affronte, Spin entanglement in supramolecular structures, *Nanotechnology* **21**, 274009 (2010).
- [60] M. R. Wasielewski, M. D. E. Forbes, N. L. Frank, K. Kowalski, G. D. Scholes, J. Yuen-Zhou, M. A. Baldo, D. E. Freedman, R. H. Goldsmith, T. Goodson III *et al.*, Exploiting chemistry and molecular systems for quantum information science, *Nat. Rev. Chem.* **4**, 490 (2020).
- [61] Y. Chen, Y. Bae, and A. J. Heinrich, Harnessing the quantum behavior of spins on surfaces, *Adv. Mater.* **35**, 2107534 (2023).
- [62] A. Sojka, M. Šedivý, O. Laguta, A. Marko, V. T. Santana, and P. Neugebauer, High-frequency EPR: current state and perspectives, in *Electron Paramagnetic Resonance: Volume 27*, edited by V. Chechik, D. M. Murphy, and B. E. Bode (Royal Society of Chemistry, 2020), pp. 214–252.

- [63] L. M. B. Napolitano, O. R. Nascimento, S. Cabaleiro, J. Castro, and R. Calvo, Isotropic and anisotropic spin-spin interactions and a quantum phase transition in a dinuclear Cu(II) compound, *Phys. Rev. B* **77**, 214423 (2008).
- [64] M. Pereg, R. Baggio, R. P. Sartoris, R. C. Santana, O. Peña, and R. Calvo, Magnetism and structure in chains of copper dinuclear paddlewheel units, *Inorg. Chem.* **49**, 695 (2010).
- [65] R. Calvo, J. E. Abud, R. P. Sartoris, and R. C. Santana, Collapse of the EPR fine structure of a one-dimensional array of weakly interacting binuclear units: A dimensional quantum phase transition, *Phys. Rev. B* **84**, 104433 (2011).
- [66] R. Calvo, V. T. Santana, and O. R. Nascimento, Temperature dependence of the effective interdimer exchange interaction in a weakly coupled antiferromagnetic dimer copper compound, *Phys. Rev. B* **96**, 064424 (2017).
- [67] R. P. Sartoris, V. T. Santana, E. Freire, R. F. Baggio, O. R. Nascimento, and R. Calvo, Exchange couplings and quantum phases in two dissimilar arrays of similar copper dinuclear units, *Dalton Trans.* **49**, 5228 (2020).
- [68] R. Calvo, R. P. Sartoris, O. R. Nascimento, M. Šedivý, A. Sojka, P. Neugebauer, and V. T. Santana, Quantum phase transitions probed by EPR spectra in dimeric spin arrays with supramolecular couplings, *Coord. Chem. Rev.* **480**, 215007 (2023).
- [69] Č. Brukner, V. Vedral, and A. Zeilinger, Crucial role of quantum entanglement in bulk properties of solids, *Phys. Rev. A* **73**, 012110 (2006).
- [70] T. Chakraborty, H. Singh, D. Das, T. K. Sen, and C. Mitra, Quantification of entanglement from magnetic susceptibility for a Heisenberg spin 1/2 system, *Phys. Lett. A* **376**, 2967 (2012).
- [71] S. Sahling, G. Remenyi, C. Paulsen, P. Monceau, V. Saligrama, C. Marin, A. Revcolevschi, L. P. Regnault, S. Raymond, and J. E. Lorenzo, Experimental realization of long-distance entanglement between spins in antiferromagnetic quantum spin chains, *Nat. Phys.* **11**, 255 (2015).
- [72] P. Laurell, A. Scheie, E. Dagotto, and D. A. Tennant, Witnessing entanglement and quantum correlations in condensed matter: A review, *Adv. Quantum Technol.* **8**, 2400196 (2025).
- [73] J. R. Petta, A. C. Johnson, J. M. Taylor, E. A. Laird, A. Yacoby, M. D. Lukin, C. M. Marcus, M. P. Hanson, and A. C. Gossard, Coherent manipulation of coupled electron spins in semiconductor quantum dots, *Science* **309**, 2180 (2005).
- [74] G. Burkard, T. D. Ladd, A. Pan, J. M. Nichol, and J. R. Petta, Semiconductor spin qubits, *Rev. Mod. Phys.* **95**, 025003 (2023).
- [75] S. Sachdev, *Quantum Phase Transitions*, 2nd ed. (Cambridge University Press, Cambridge, 2011), p. 501.
- [76] V. Zapf, M. Jaime, and C. D. Batista, Bose-Einstein condensation in quantum magnets, *Rev. Mod. Phys.* **86**, 563 (2014).
- [77] E. Fogh, M. Nayak, O. Prokhnenko, M. Bartkowiak, K. Munakata, J.-R. Soh, A. A. Turrini, M. E. Zayed, E. Pomjakushina, H. Kageyama *et al.*, Field-induced bound-state condensation and spin-nematic phase in $\text{SrCu}_2(\text{BO}_3)_2$ revealed by neutron scattering up to 25.9 T, *Nat. Commun.* **15**, 442 (2024).
- [78] R. Grimaudo, A. Messina, A. Sergi, N. Vitanov, and S. Filippov, Two-qubit entanglement generation through non-Hermitian Hamiltonians induced by repeated measurements on an ancilla, *Entropy* **22**, 1184 (2020).
- [79] R. Grimaudo, A. S. Magalhães de Castro, A. Messina, and D. Valenti, Spin-chain-star systems: Entangling multiple chains of spin qubits, *Fortschr. Phys.* **70**, 2200042 (2022).
- [80] R. Grimaudo, SU(2)-Symmetric exactly solvable models of two interacting qubits, *Physics* **6**, 1111 (2024).
- [81] C.-C. Ou, D. A. Powers, J. A. Thich, T. R. Felthouse, D. N. Hendrickson, J. A. Potenza, and H. J. Schugar, Molecular structure and magnetic properties of *trans*-bis(*L*-methioninato)copper(II), $\text{Cu}(\text{C}_5\text{H}_{10}\text{NO}_2\text{S})_2$, *Inorg. Chem.* **17**, 34 (1978).
- [82] H. M. Pastawski, Revisiting the Fermi golden rule: Quantum dynamical phase transition as a paradigm shift, *Phys. B: Condens. Matter* **398**, 278 (2007).
- [83] R. Calvo, EPR measurements of weak exchange interactions coupling unpaired spins in model compounds, *Appl. Magn. Reson.* **31**, 271 (2007).
- [84] S. Stoll and A. Schweiger, EasySpin, a comprehensive software package for spectral simulation and analysis in EPR, *J. Magn. Reson.* **178**, 42 (2006).
- [85] Note that a closed ring of $N_S = 12$ was used as a representation of an infinite array since this was the highest number of spins we could add in order to have a successful simulation given our available computational resources. In any case, it was enough to demonstrate the expected merging of peaks expected for an infinite array.
- [86] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).
- [87] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/71h7-vhj7> for additional details on low-frequency EPR data used to calculate the g^2 matrix given in Table I and the value of J for the same set of data.
- [88] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, F. Mazzi, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. Van de Streek, and P. A. Wood, Mercury CSD 2.0 – New features for the visualization and investigation of crystal structures, *J. Appl. Crystallogr.* **41**, 466 (2008).
- [89] Crystal structure of TBLMCU, Available from The Cambridge Crystallographic Data Centre. CCDC: 1267555 (1978).
- [90] D. Van der Helm, M. B. Lawson, and E. L. Enwall, The crystal structure of bis(*L*-phenylalaninato)copper(II), *Acta Crystallogr. B* **27**, 2411 (1971).
- [91] T. G. Fawcett, M. Ushay, J. P. Rose, R. A. Lalancette, J. A. Potenza, and H. J. Schugar, Molecular structures of the copper-amino acid complexes Bis(*L*-leucinato)copper(II) and Bis(*D,L*-2-aminobutyrate)copper(II), *Inorg. Chem.* **18**, 327 (1979).
- [92] J. M. Schweigkardt, A. C. Rizzi, O. E. Piro, E. E. Castellano, R. C. Santana, R. Calvo, and C. D. Brondino, Structural and single crystal EPR studies of the complex copper *L*-glutamine: A weakly exchange-coupled system with syn-anti carboxylate bridges, *Eur. J. Inorg. Chem.* **2002**, 2913 (2002).
- [93] S. Hill, R. S. Edwards, N. Aliaga-Alcalde, and G. Christou, Quantum coherence in an exchange-coupled dimer of single-molecule magnets, *Science* **302**, 1015 (2003).
- [94] S. Hill and A. Wilson, Calculation of the EPR spectrum for an entangled dimer of $S = 9/2$ Mn4 single-molecule magnets, *J. Low Temp Phys* **142**, 271 (2007).
- [95] P. M. Richards, Correlations in magnetic exchange-lattice relaxation, *Phys. Rev.* **137**, A1327 (1965).

- [96] S. Mankovsky, S. Polesya, and H. Ebert, Exchange coupling constants at finite temperature, *Phys. Rev. B* **102**, 134434 (2020).
- [97] M. L. Siqueira, R. E. Rapp, and R. Calvo, Specific heat and exchange interactions of two isomer and isostructural copper–amino-acid complexes, *Phys. Rev. B* **48**, 3257 (1993).
- [98] A. J. Costa-Filho, O. R. Nascimento, L. Ghivelder, and R. Calvo, Magnetic properties of carboxylate-bridged ferromagnetic copper(II) chains coupled by cation- π interactions, *J. Phys. Chem. B* **105**, 5039 (2001).
- [99] R. Calvo and M. C. G. Passeggi, Shifts with temperature of the EPR signal in Cu(*L*-alanine)₂: A low-dimensional paramagnet, *Phys. Rev. B* **44**, 5111 (1991).
- [100] A. Fainstein, Dipolar fields in a low-dimensional paramagnet: Cu(*L*-leucine)₂, *J. Phys.: Condens. Matter* **4**, 4989 (1992).
- [101] A. Sojka, M. Šedivý, A. Lagiň, A. Gabriš, T. Lázníčka, V. T. Santana, O. Laguta, and P. Neugebauer, Sample holders for sub-THz electron spin resonance spectroscopy, *IEEE Trans. Instrum. Meas.* **71**, 1 (2022).
- [102] M. Šedivý, V. Santana, A. Sojka, O. Laguta, and P. Neugebauer, MEPROS – Modular electron paramagnetic resonance operating software for multifunctional high-frequency EPR spectrometer, *J. Magn. Reson.* **355**, 107556 (2023).
- [103] M. Bak and N. C. Nielsen, Repulsion, A novel approach to efficient powder averaging in solid-state NMR, *J. Magn. Reson.* **125**, 132 (1997).
- [104] V. T. Santana, R. P. Sartoris, and R. Calvo, Quantum behavior of multiple monomeric arrays of spins 1/2, Zenodo (2024), doi: 10.5281/zenodo.13869324.