

Multi-step approach to microscopic models for frustrated quantum magnets – the case of the natural mineral azurite

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The natural mineral azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ is a frustrated magnet displaying unusual and controversially discussed magnetic behavior. Motivated by the lack of a unified description for this system, we perform a theoretical study based on density functional theory as well as state-of-the-art numerical many-body calculations. We propose an effective generalized spin-1/2 diamond chain model which provides a consistent description of experiments: low-temperature magnetization, inelastic neutron scattering, nuclear magnetic resonance measurements, magnetic susceptibility as well as new specific heat measurements. With this study we demonstrate that the balanced combination of first principles with powerful many-body methods successfully describes the behavior of this frustrated material.

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The natural mineral azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ has been used as a blue pigment since the time of the ancient Egyptians; the beautiful intense blue color (see Fig. 1 (a)) is due to the crystal field splitting of Cu $3d$ orbitals in square planar coordination. More recently, the discovery of a plateau at 1/3 of the saturation value in the low-temperature magnetization curve [1, 2] has triggered intensive interest in the magnetic properties of azurite. From the point of view of magnetism, the most important structural motives [3] are diamond-like chains which are formed by the spin-1/2 copper atoms (Fig. 1 (b)). If all exchange constants were antiferromagnetic, azurite would fall into the class of geometrically frustrated magnets. These systems are fascinating since the competition of the magnetic interactions suppresses classically ordered states and may give rise to new states of matter with exotic excitations (see Ref. [4] for a recent review). In particular, for a certain class of frustrated magnets including diamond chains, one expects localized (dispersionless) many-body states at high magnetic fields [5]; indeed inelastic neutron scattering (INS) on azurite exhibits an almost dispersionless branch of excitations [6].

There have been a number of attempts [1, 6–10] to derive a microscopic model for the complex magnetic properties of azurite. The results are, however, contradictory and up to now none of these models was able to yield a fully consistent picture of the experimentally observed behavior. Some authors favor a diamond chain model with all exchanges antiferromagnetic [1, 9, 11] while other

authors proposed one of the dominant exchange constants to be ferromagnetic [6–8]. Even more, Ref. [10] has argued that interchain coupling is important in azurite. The latter may be in agreement with the observation of a magnetic ordering transition at about 2 K [1, 12–14], but raises the question why no dispersion perpendicular to the chain direction is observed by INS [6].

In the present work, we combine first principles density functional theory (DFT) calculations with model computations based on different variants of the density-matrix renormalization group (DMRG) method [15–17] (see also Section S2) and resolve the underlying model for azurite. We find that an effective generalized spin-1/2 diamond chain model with a dominant next-nearest-neighbor antiferromagnetic Cu dimer coupling J_2 , two antiferromagnetic nearest- and third-nearest-neighbor Cu dimer-monomer exchanges J_1 and J_3 , and a significant direct Cu monomer-monomer exchange J_m (see Figs. 1 (b) and 3 (a)) explains a broad range of experiments on azurite [1, 2, 6, 18] and resolves the existing controversies.

Since the experimentally determined positions of the lighter atoms in a structure usually carry larger error bars than those of more heavy elements, we first performed a Car-Parrinello molecular dynamics calculation [19, 20] in order to optimize the positions of the C, O, and H atoms in azurite. With the optimized structure with a total of 30 atoms in the unit cell we determined the electronic properties of azurite [21]. The band structure shows six narrow Cu $3d_{x^2-y^2}$ bands at the Fermi level – correspond-

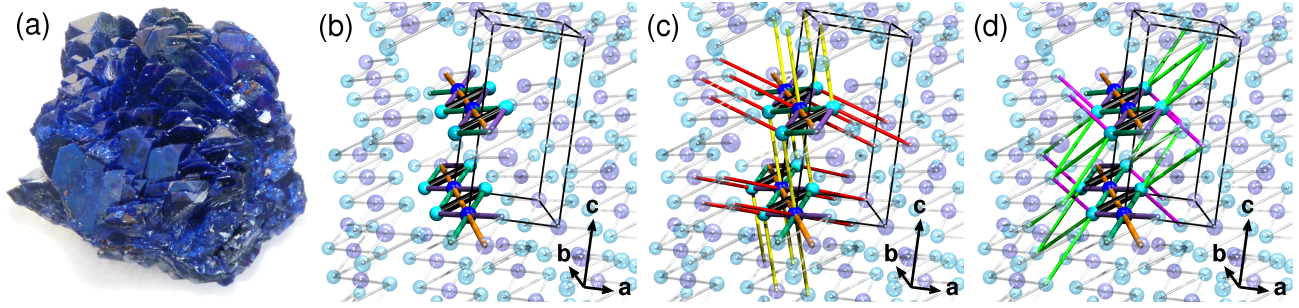


FIG. 1. (a) Example of an azurite crystal aggregate. (b)-(d) Arrangement of Cu^{2+} ions in the structure of azurite. The two inequivalent Cu^{2+} ions form dimers (cyan) and monomers (blue). (b) Most important exchange paths within the diamond chain running along the b -axis: Dimer coupling J_2 (black), dimer-monomer couplings J_1 and J_3 (magenta and green), and monomer-monomer coupling J_m (orange). (c)-(d) Three-dimensional couplings between diamond chains, connecting (c) monomer and dimer ions: J_5 (yellow) and J_6 (red) and (d) dimer ions only: J_4 (pink) and J_7 (light green).

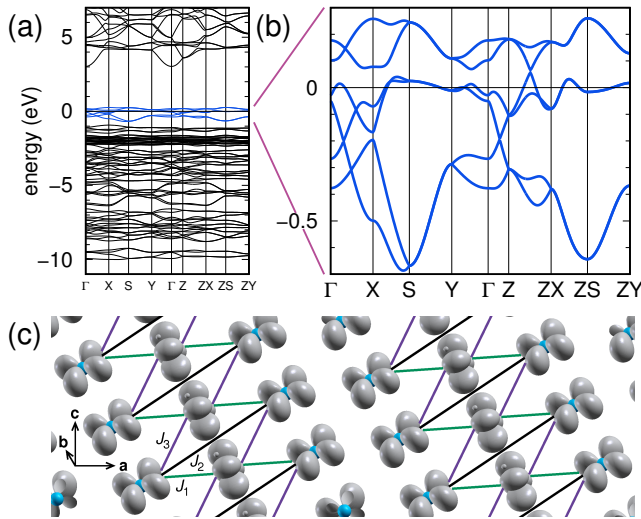


FIG. 2. Electronic structure of azurite, calculated with FPLAPW. (a) Band structure in a wide energy window. At the Fermi level the bands are dominantly of $\text{Cu } 3d_{x^2-y^2}$ character (blue bands). (b) Blow-up of the six bands at the Fermi level. (c) Electron density above $E = -0.75$ eV for an isovalue of 0.1 e/a.u.³. All density is centered at the Cu sites and it has $3d_{x^2-y^2}$ symmetry.

ing to the six Cu atoms per unit cell – separated by an energy of 0.9 eV from the occupied $\text{Cu } 3d_{z^2}$ bands and by a gap of $E_g \simeq 3$ eV from the higher unoccupied bands (Fig. 2 (a) and (b)). Fig. 2 (c) shows a charge density isosurface where a $d_{x^2-y^2}$ symmetry of the Cu d orbitals is evident without contribution of d_{z^2} character, contrary to previous suggestions [22, 23].

While the GGA calculation describes this system as metallic, the insulating behavior is correctly given within the GGA+U approach (see below). Here we first analyze the interaction paths based on the GGA bandstructure. We perform N -th order muffin tin orbital (NMTO) downfolding [24, 25] to obtain the tight-binding Hamiltonian parameters t_i describing the six $\text{Cu } 3d_{x^2-y^2}$ bands (see

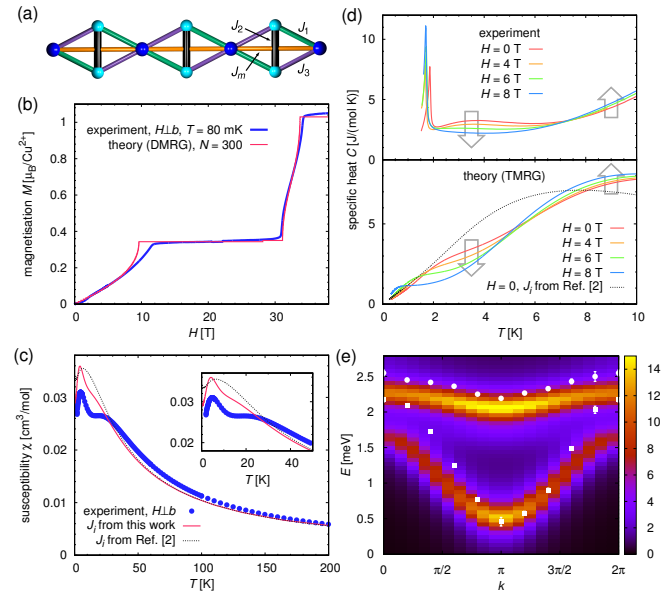


FIG. 3. (a) Generalized diamond chain model. (b) Comparison of computations for the magnetization curve for $T = 0$ and $N = 300$ spins with experimental data at $T = 80$ mK for $H \perp b$ [2]. (c) Experimental and theoretical zero-field magnetic susceptibility. (d) Experimental (upper panel) and theoretical (lower panel) specific heat results for various H fields. Arrows indicate the response to increasing magnetic field. (e) Theoretical transverse dynamic structure factor on the $1/3$ plateau ($H \approx 14$ T) and peak positions of INS spectra from Ref. [6] (white symbols). Color-coding represents the intensity in arbitrary units.

Fig. 2 (b)). Under the assumption that the exchange couplings are antiferromagnetic, we can estimate the magnitude of the exchange couplings via second-order perturbation theory: $J_i^{\text{AFM}} = 4t_i^2/U$ where U is the Cu $3d$ onsite Coulomb interaction strength. From this analysis we identify six further relevant couplings in addition to J_1 , J_2 and J_3 : the monomer-monomer exchange J_m also considered by Rule *et al.* [6] and the nearest-neighbor

	J_1	J_2	J_3	J_4	J_5	J_6	J_7	J_m	J_d
1 full model	13.5	42.8	12.5	2.7	0.6	4.4	-1.7	2.6	-0.4
2 minimal model	17.9	43.9	12.0	-	-	-	-	2.4	-
3 refined model	15.51	33	6.93	-	-	-	-	4.62	-
4 Ref. [1] model	19	24	8.6	-	-	-	-	-	-

TABLE I. Exchange constants in Kelvin (K) derived from FPLO GGA+U calculations with $U = 8$ eV and $J_H = 1$ eV for the various model steps considered in the present work (see text for explanation). The error margin for each J_i in the third line is estimated to be of the order 1 to 2 K.

Cu dimer interaction J_d along the chain. In addition, J_4 and J_7 provide couplings between Cu dimer atoms in neighboring chains, whereas J_5 and J_6 correspond to Cu monomer-dimer interchain-interactions. The interaction paths between chains are visualized in Fig. 1 (c) and (d).

Next, we obtain the correct sign (ferro- or antiferromagnetic) and magnitude of the J_i from total energy calculations for different Cu spin configurations in supercells with up to 60 atoms. We employ the full potential local orbital (FPLO) method [26] with the GGA+U functional for $U = 4, 6,$ and 8 eV. We map the energy differences of the frozen collinear spin configurations onto a spin-1/2 Heisenberg model and evaluate the exchange constants J in a dimer approximation [27]. The nine relevant Cu-Cu interaction paths obtained from the downfolding calculations have been probed with 10 different antiferromagnetic spin configurations together with the ferromagnetic configuration. The result for a choice of $U = 8$ eV and $J_H = 1$ eV is shown in the first line of Table I. As expected from experimental observations, J_2 dominates and exhibits a $1/U$ dependence (see Section S1). The two couplings J_1 and J_3 are very similar in magnitude, suggesting an almost symmetric diamond chain. We observe that except for $J_1, J_2,$ and $J_3,$ the coupling strengths are of the order of a few Kelvin. Comparing our set of parameters in Table I, line **1** to that obtained in Ref. [10], the main differences are that we determined the additional 3D couplings $J_4, J_5,$ and $J_7,$ and our value for $J_m,$ double-checked with two full potential methods [21, 26], is clearly nonzero.

At first sight, the fact that interchain coupling turns out to be appreciable is surprising because INS did not observe any dispersion perpendicular to the chain direction [6]. However, since the dimer exchange J_2 dominates, one can use perturbative arguments along the lines of Ref. [28] to show that there are no low-energy excitations dispersing perpendicular to the chains. The essential ingredients of the argument are that (i) the interchain exchange constants J_4 to J_7 are small compared to J_2 and (ii) they connect only to dimers of the neighboring chains (compare Figs. 1 (c) and (d)), *i.e.*, they contribute only in second or third order in perturbation theory (see Section S4); this would suggest using an ef-

fective one-dimensional model with the values of $J_1, J_2, J_3,$ and J_m adjusted to incorporate the effect of the three-dimensional couplings. Table I line **2** shows the results obtained by solving the 10 spin configurations only for the diamond chain couplings. This corresponds to an averaging over the 3D couplings and translates into a significant asymmetry of the diamond chain $J_1 > J_3.$ The effective one-dimensional model has the additional advantage that it is amenable to detailed quantum mechanical model calculations, thus allowing a quantitative comparison with experimental data for azurite.

From these results salient experimental features of azurite can already be understood at a qualitative level: two thirds of the Cu^{2+} spins are strongly bound by J_2 into dimer singlets while another third consists of monomer spins which interact weakly by J_m and additional effective monomer-monomer interactions which are generated by integrating out the dimers. In an applied magnetic field, the monomer spins are therefore polarized first while the dimer spins remain in the singlet state, giving rise to the $1/3$ plateau [1, 2, 18]. Furthermore, the two energy scales, *i.e.*, the low-energy scale given by the monomer-monomer interactions and the high-energy scale associated to the dimers give rise to the double-peak structures observed in the magnetic susceptibility [1] and the specific heat [1, 6]. Finally, we expect a band of low-energy monomer excitations dispersing along the chain direction and a band of dimer excitations at higher energies whose dispersion is additionally suppressed by the competition of J_1 and $J_3,$ as indeed observed by INS [6].

We will now show that we can also describe these experimental results quantitatively. The DFT results leave some freedom concerning the overall energy scale, however the ratios of the J_i are expected to be subject only to small errors [29]. We therefore first slightly refined the parameter ratios using the magnetization and INS experiments, leading to $J_1/J_2 = 0.47, J_3/J_2 = 0.21,$ and $J_m/J_2 = 0.14.$ The global energy scale is finally adjusted to the magnetization curve (see below) and we obtain the exchange coupling constants J_i in Table I, line **3**.

In order to fully account for the quantum nature of the spins residing on the Cu^{2+} ions, we use a spin 1/2 Heisenberg model $\mathcal{H} = \sum_{\langle i,j \rangle} J_{i,j} \vec{S}_i \cdot \vec{S}_j - g \mu_B H \sum_i S_i^z,$ where \vec{S}_i are spin 1/2 operators, $J_{i,j}$ is the exchange constant connecting sites i and j (see Fig. 3 (a)), H an external magnetic field and μ_B the Bohr magneton. The gyromagnetic ratio g is set to 2.06 [30].

Fig. 3 (b) shows a comparison for the experimental and computed magnetization curves. The overall energy scale is $J_2 = 33$ K, leading to our final parameter set in Table I, line **3**. The agreement of the theoretical magnetization curve in Fig. 3 (b) with the experimental result for $H \perp b$ [2] is excellent. Note that the experimental curve for $H \perp b$ exhibits a nice plateau as expected for a Heisenberg model whereas for $H \parallel b$ the

plateau is washed out [1], indicative of non-commuting fields. Therefore we compare our results for the isotropic Heisenberg model with experiments for $H \perp b$. We find that dimer spins should be about 2.7% polarized each (see Section S6), *i.e.*, dimers are essentially in the singlet state whereas the single “monomer” spins are almost fully polarized in the 1/3 plateau. This is qualitatively consistent with recent $^{63,65}\text{Cu}$ NMR [18].

At this stage, the values of all J_i are fixed and we have a parameter-free prediction of the magnetic susceptibility χ . Fig. 3 (c) compares our computations [16] with our measurement of the magnetic susceptibility of azurite for $H \perp b$, which is very similar to the original experiment of Ref. [1]. Our parameter set (Table I, line **3**) leads to a small, but qualitative improvement compared to the original one of [1] (see Table I, line **4**): we reproduce a double-peak-like structure at the correct temperatures whereas only a single peak [7] is obtained with the parameters of [1].

Analogous to the magnetic susceptibility, we also have a parameter-free prediction for the magnetic specific heat. At zero field, two anomalies have been observed in the specific heat at $T = 18$ K [1] and $T = 4$ K [1, 6]. Fig. 3 (d) compares the field-dependence of the experimental specific heat with results calculated [16] for the parameters of Table I, line **3**. The sharp peak in the experimental curves slightly below 2 K [1, 12] signals an ordering transition which is out of reach of a one-dimensional model. Nevertheless, not only are the numerical values of the specific heat for $2 \text{ K} < T \lesssim 10 \text{ K}$ comparable between theory and experiment, but also important features are reproduced correctly: (i) a low-temperature peak appears for $H = 0$ at $T \approx 3$ to 4 K. Note that this low-temperature peak at $H = 0$ is absent [8] for the original parameter set of Ref. [1] (compare the dashed curve in the lower panel of Fig. 3 (d)). (ii) The low-temperature peak is gradually suppressed by an applied field, as emphasized by down arrows in the figure. (iii) In the temperature range $7 \text{ K} \leq T \leq 10 \text{ K}$, the specific heat increases not only with temperature but also with increasing magnetic field (marked by up arrows).

Fig. 3 (e) shows our numerical result [17] (see also Section S2) for the transverse dynamic structure factor on the 1/3 plateau as a function of momentum transfer k along the chain direction and energy E . The peak values of the dynamic structure factor trace two dispersion curves nicely. Comparison with the corresponding INS results [6] (white symbols in Fig. 3 (e)) shows that the computed ratio of the bandwidths is extremely close to the experimental value of about 1/6 [31]. Also the total intensities in the peaks compare favorably with the experimental results [6].

To summarize, we have shown that the combination of first principles DFT with state-of-the-art many-body calculations successfully provides a microscopic model for the frustrated magnet azurite, which explains a wide

range of experiments [1, 2, 6, 18]. We believe that attempts to fit such a range of experiments, using at least four exchange constants J_i , are bound to fail. Hence, the guiding DFT computations were essential. There are several issues for further experimental and theoretical study (see Section S8). In particular, the implications of the full three-dimensional model which we have derived remain to be explored.

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SUPPLEMENTARY MATERIAL

S1. Density functional calculations

Structure relaxations were performed with the Car-Parrinello projector augmented wave (CP-PAW) method [20]. We employed a plane wave cutoff of 30 Ryd for the plane wave part and of 120 Ryd for the density, respectively, and we used the following sets of (s,p,d) projector functions per angular momentum: Cu(2,2,2), O(2,2,1), C(2,2,1) and H(2,0,0). We employed a $(4 \times 4 \times 4)$ k mesh and the $P21/c$ symmetry was preserved during the relaxation with the help of 60 constraints. The relaxation with the generalized gradient approximation (GGA) functional [32] resulted in small bond length changes of up to 4% and in angle changes up to 2° compared to the experimental data from Ref. [3].

The relative strengths of the exchange pathways in azurite have been obtained by using the electronic structure technique of muffin-tin orbital (MTO) based NMTO-downfolding [24, 33].

DFT calculations were performed with the full potential local orbital method [26] (FPLO), version 8.50, and the full potential augmented plane wave (FLAPW) method as implemented in the WIEN2k [21] code, which has been used to crosscheck the FPLO results for selected supercells. Total energies for different spin configurations were obtained in the GGA+U formalism, employing both the atomic limit (AL) as well as the around mean field (AMF) double counting correction. The AL double counting correction turned out to be the better choice for the calculation of a realistic set of model parameters for azurite because the ratios J_i/J_2 are strongly dependent on U in the case of the AMF double counting correction and can even adopt unphysical values ($J_1, J_3 > J_2$).

Table SI shows the complete set of exchange coupling

U [eV]	J_1	J_2	J_3	J_4	J_5	J_6	J_7	J_m	J_d
4	34.1	145.4	35.4	5.9	2.9	16.2	-1.7	5.9	-1.7
6	21.3	82.8	21.2	3.8	1.5	8.6	-1.8	3.9	-0.8
8	13.5	42.8	12.5	2.7	0.6	4.4	-1.7	2.6	-0.4

TABLE SI. Exchange constants in K derived from FPLO GGA+U calculations with the atomic limit double counting correction. Slater parameters are chosen as $F_0 = U$, $F_2 = 8.6$ eV and $F_4 = 5.4$ eV, *i.e.*, $J_H = (F_2 + F_4)/14 = 1$ eV.

parameters J_i , obtained with the FPLO code (version 8.50) employing the GGA+U functional with atomic limit double counting correction. The calculations were repeated for three choices of the Coulomb correlation strength, $U = 4$ eV, 6 eV and 8 eV. The Hund's rule coupling J_H was chosen as $J_H = 1$ eV. The dominant coupling exhibits a proportionality to $1/U$. Note that the relative importance of the monomer-monomer coupling increases as U is increased.

J_2 is antiferromagnetic and the dominant interaction. One can therefore apply perturbative considerations in J_i/J_2 and argue that interchain excitations can be neglected to a first approximation (see Section S4). The essential items are that the interchain exchange constants J_4 to J_7 are small compared to J_2 and that they connect only to dimers of the neighboring chains (compare Figs. 1 (c) and (d)).

This suggests to reduce the set of interaction parameters to a minimal model including J_1 , J_2 , J_3 , and J_m only. In order to determine the effective values of these exchange constants quantitatively, we performed a least-square fit for the energy differences including only J_1 , J_2 , J_3 , and J_m in the model and set all other parameters to zero. It should be noted that the exchange constants obtained in this way are effective parameters, which contain the effect of the remaining parameters not included in the model as statistical average. Furthermore, it is also important that the procedure of statistical averaging is done over a sufficiently large manifold, since otherwise the effective parameters are to some degree arbitrary. The results are shown in Table SII. It can be seen that in the minimal model the effective parameters J_1 and J_3 show a strong asymmetry, which is not present in the full set of interaction parameters shown in Table SI. This is mainly due to integrating out of the fairly large coupling parameter J_6 in the model, which couples Cu monomer with Cu dimer atoms and in this way provides an effective asymmetry of J_1 and J_3 (inclusion of J_6 in addition to the minimal model again results in nearly identical J_1 and J_3 values).

U [eV]	J_1	J_2	J_3	J_m
4	50.5	151.1	35.7	3.4
6	30.0	85.4	21.0	3.0
8	17.9	43.9	12.0	2.4

TABLE SII. Effective exchange constants in K for a minimal model including only J_1 , J_2 , J_3 , and J_m obtained via statistical averaging (see text).

S2. DMRG calculations

The theoretical magnetization curve in Fig. 3 (b) has been obtained with the static density-matrix renormalization group (DMRG) method [15, 34] using $m = 300$ states per block and four sweeps in each magnetization sector. The theory curves in Figs. 3 (c), 3 (d), and S1 have been obtained using transfer-matrix DMRG (TMRG [16, 35]) for the infinite system and $m = 300$. Note that these are in agreement with previous TMRG computations [7, 8] for the parameters of Ref. [1].

The transverse dynamic structure factor of Fig. 3 (e) has been computed by dynamic DMRG [17] for the parameters of Table I, line **3**, using open chains with $N = 60$ sites, up to $m = 200$ states per block and two sweeps per energy point. Note that for a meaningful comparison of scattering intensities with experiment, we had to take the precise positions of the copper atoms in azurite into account and use the same momentum perpendicular to the chain direction as in the experiment [6].

S3. Experiment

The specific heat of a plate-like azurite single crystal with the total mass of 0.36 mg was measured, employing an ac-calorimetry according to Ref. [36]. The data were taken in the temperature range $1.6 \text{ K} \leq T \leq 30 \text{ K}$ and in magnetic fields up to 8 T. The experiments were performed using a home-built AC-calorimeter especially designed for small plate-like samples. The sample holder, consisting of a resistive thermometer (Cernox CX-1080-BG) and a heater, is attached to a ^4He -bath cryostat equipped with a superconducting magnet.

The magnetic susceptibility of azurite was measured in the temperature range between $2 \text{ K} \leq T \leq 300 \text{ K}$ and in magnetic fields up to $H = 4 \text{ T}$ using a Quantum Design SQUID magnetometer. The orientation of the single crystal (mass 55.26 mg) with respect to the external field was $H \perp b$ -axis. The data were corrected for the temperature-independent diamagnetic core contribution, according to Ref. [37] and the magnetic contribution of the sample holder. The latter was determined from an independent measurement.

S4. Perturbative treatment of interchain coupling

For a large and antiferromagnetic J_2 , one can use perturbative arguments to integrate out the copper dimers and generate effective interactions between the monomer copper atoms. In the limit of infinite J_2 , the two spins on the corresponding dimer bond are in their singlet state $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. In this limit, the only interaction between the monomer spins is J_m . However, one can use degenerate perturbation theory in J_i/J_2 to generate further interactions between the monomer spins.

The second-order contribution to the monomer-monomer interactions within a chain is known [28] to be given by

$$\tilde{J}_m = \frac{(J_1 - J_3)^2}{2J_2}. \quad (1)$$

This effective interaction enhances the bare interaction J_m between the monomers along the chain provided that $J_1 \neq J_3$.

The interactions J_4 and J_7 connect dimers of neighboring chains (see Fig. 1 (d)). Accordingly, they contribute to interchain monomer-monomer exchange only in third order in perturbation theory and generate exchanges $\propto J_1^2 J_4/J_2^2$, $J_1 J_3 J_4/J_2^2$, $J_1^2 J_7/J_2^2$ and $J_1 J_3 J_7/J_2^2$. Using the values of the J_i in Table I, line 1, these effective interchain exchanges are estimated to be at most on the order of 0.3 K $\approx J_m/10$ and thus can be neglected safely.

By contrast, J_5 and J_6 contribute in second order perturbation theory to interchain coupling since they connect dimers with monomers of the neighboring chains (see Fig. 1 (c)). The contribution from J_5 is given by $(J_1 + J_3) J_5/(2J_2)$. Inserting the numbers from Table I, line 1, this again turns out to be on the order of 0.2 K $\approx J_m/10$, *i.e.*, also J_5 is sufficiently small to be neglected safely.

The exchange constant J_6 also contributes terms proportional to $J_1 J_6/J_2$ and $J_3 J_6/J_2$ to interchain effective monomer-monomer coupling. Inserting again the values of J_1 , J_2 , J_3 , and J_6 in Table I, line 1 into the second-order expression, we now obtain a contribution on the order of 1.4 K $\approx J_m/2$ to the effective interchain monomer-monomer coupling. On the one hand, this is still sufficiently small not to give rise to relevant dispersion of the excitations perpendicular to the chains, in agreement with inelastic neutron scattering on azurite [6]. On the other hand, this value is too large to neglect J_6 completely.

In fact, in a mean-field picture, the monomer moments influence the effective monomer-monomer exchange along the neighboring chains. The reason is that the interchain couplings connect the monomer spins only to one of the dimer spins on the neighboring chains, thus breaking the symmetry of the exchange process along the chains and giving rise to corrections to (1). In this mean-field pic-

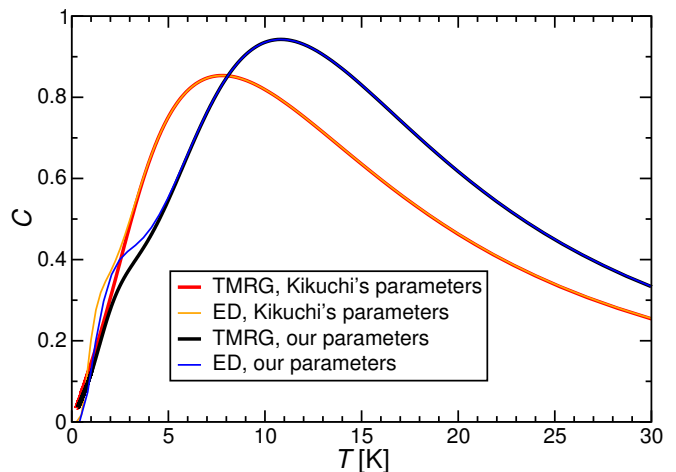


FIG. S1. TMRG and ED results for the zero-field specific heat per spin. The ED computations were performed for $N = 18$ spins. We show results both for our new parameter set, Table I, line 3, as well as for Kikuchi's original parameter set Table I, line 4 $J_1 = 19$ K, $J_2 = 24$ K, $J_3 = 8.6$ K, and $J_m = 0$ [1].

ture, the interchain coupling J_6 has the same effect as the intrachain coupling J_1 .

These arguments suggest that one may go from the full three-dimensional model to an effective chain model by neglecting J_4 , J_5 , and J_7 , and adding J_6 to J_1 . The difference between lines 1 and 2 of Table I or Tables SI and SII can indeed be understood at least qualitatively in this way although the reduction has been performed in a completely different manner.

S5. Specific heat

Experimentally, two anomalies have been observed in the magnetic specific heat at $T \approx 18$ K [1] and $T \approx 4$ K [1, 6] (compare also top panel of Fig. 3 (d)). Fig. S1 shows TMRG results for the specific heat per spin C in zero magnetic field. For our new parameter set, Table I, line 3 (black line in Fig. S1), we find a maximum of C at a temperature slightly above 10 K and a low-temperature feature at $T \approx 3$ K. Although this does not reproduce the experimental temperatures exactly, it is in better agreement with the experimental findings than the results for the original parameter set of Ref. [1] (red line in Fig. S1).

Fig. S1 includes exact diagonalization (ED) results for rings with $N = 18$ spins. We observe that finite-size effects have no visible effect for $T \gtrsim 6$ K.

N	monomer $\langle S_i^z \rangle$	dimer $\langle S_i^z \rangle$
18	0.47342867	0.01328567
24	0.47343148	0.01328426
30	0.47343154	0.01328423
36	0.47343154	0.01328423

TABLE SIII. Structure of the $M = 1/3$ plateau state for rings with N sites and the parameters in line **3** of Table I.

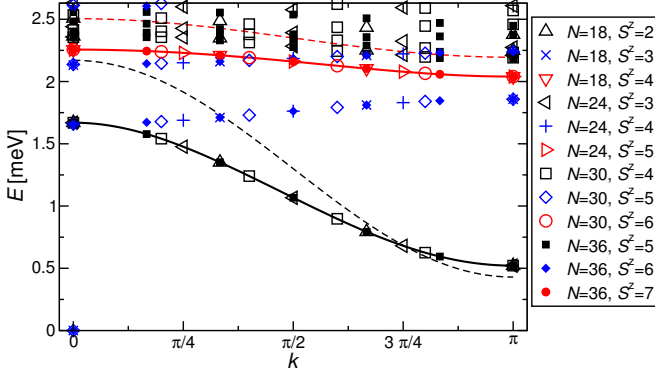


FIG. S2. Excitation spectrum at $H = 14$ T as computed by exact diagonalization with the parameters in Table I, line **3**. Solid black (red) lines connect the lowest excitations with spin quantum numbers smaller (larger) by one than that of the $1/3$ plateau state. Dashed lines indicate the location of the experimental result [6] for the corresponding excitations.

S6. Structure of the $1/3$ plateau

The $1/3$ plateau state of azurite has been characterized using NMR [18], which amounts to a measurement of the expectation values $\langle S_i^z \rangle$. This NMR study showed that the dimer spins are essentially in their singlet state with just 10% spin polarization on the dimers. Correspondingly, the monomer spins are almost polarized on the $1/3$ plateau.

Using ED for rings with $N = 18, 24, 30,$ and 36 sites and our parameters line **3** of Table I, we find the structure of the $M = 1/3$ plateau state presented in Table SIII. We observe that the numerical results for the expectation values converge rapidly with system size and read off that the dimer spins are about 2.7% polarized each. This is only slightly smaller than the 10% observed in Ref. [18]. We note that the NMR experiment [18] involved a rotation around the crystallographic a -axis and speculate that this gives rise to non-commuting fields which enhance the dimer polarization as compared to the ideal Heisenberg model.

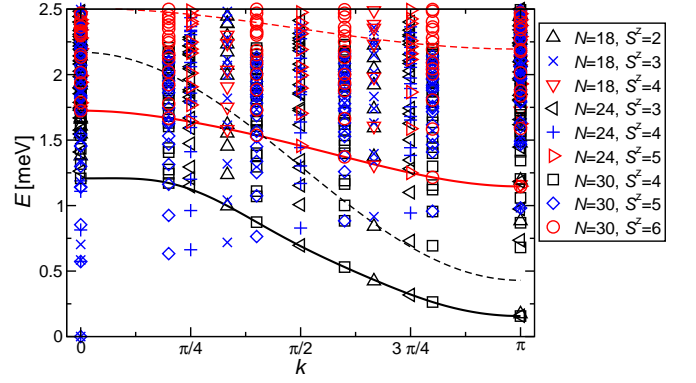


FIG. S3. Same as Fig. S2, but for Kikuchi's original parameter set Table I, line 4, $J_1 = 19$ K, $J_2 = 24$ K, $J_3 = 8.6$ K, and $J_m = 0$ [1].

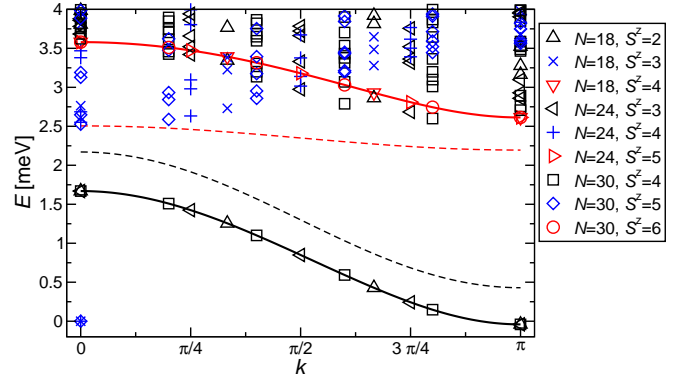


FIG. S4. Same as Fig. S2, but for the parameter set of Gu and Su [7, 8]: $J_1 = 23$ K, $J_2 = 43.7$ K, $J_3 = -9.3$ K, and $J_m = 0$.

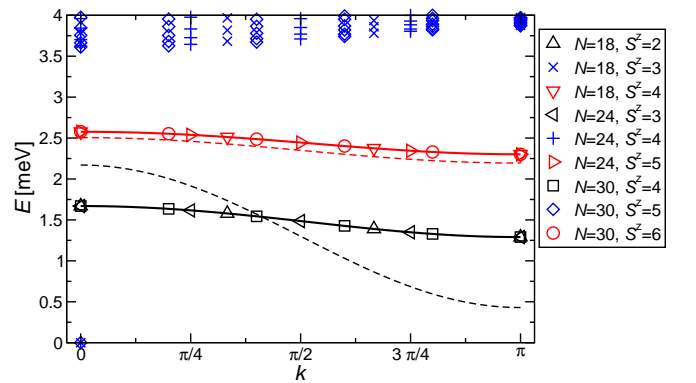


FIG. S5. Same as Fig. S2, but for a first parameter set proposed in Ref. [6]: $J_1 = 1$ K, $J_2 = 55$ K, $J_3 = -20$ K, and $J_m = 0$.

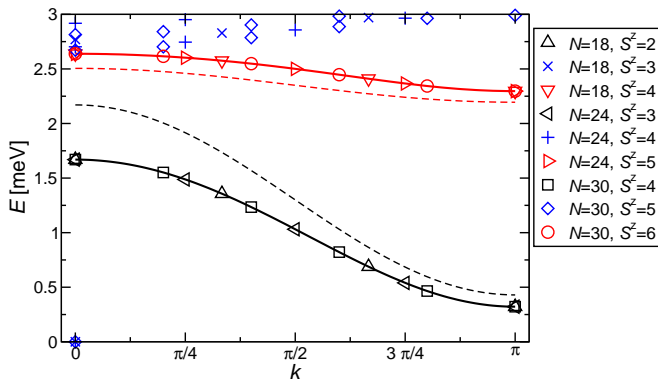


FIG. S6. Same as Fig. S2, but for the second parameter set proposed in Ref. [6]: $J_1 = 1$ K, $J_2 = 55$ K, $J_3 = -20$ K, and $J_m = 6.5$ K.

S7. Excitation spectrum on the 1/3 plateau

The excitation spectrum above the 1/3 plateau of azurite has been probed by inelastic neutron scattering at $H = 14$ T [6]. These experiments observed two cosine-like bands of magnetic excitations with a minimum energy at the antiferromagnetic wave vector $k = \pi$. The two bands are sketched by the dashed lines in Figs. S2–S6. They are centered around ≈ 1.3 meV and ≈ 2.35 meV and have a width of 20.2 K and 3.6 K, respectively. In particular the ratio of the bandwidths of the upper and lower bands is $1.8/10.1 \approx 1/5.6$.

Figs. S2–S6 show the excitation spectrum as a function of momentum k along the chain direction on the 1/3 plateau computed by exact diagonalization with periodic boundary conditions. Black, blue, and red symbols correspond to excitations with $\Delta S^z = -1, 0$, and 1 , respectively. The blue symbol at $k = 0$ and energy $E = 0$ corresponds to the ground state of the 1/3 plateau. A Fourier analysis of the lowest $\Delta S^z = \pm 1$ excitations for $N = 30$ sites yields the solid lines in Figs. S2–S6. One observes that the lowest $\Delta S^z = \pm 1$ excitations collapse onto these lines for all sizes N , demonstrating that the main effect of a finite system size N on these excitations is a discretization of the allowed values of the momentum k (see also [9]).

First let us look at our final parameter set Table I, line **3**. The lowest black and red excitation in Fig. S2, *i.e.*, the two solid curves correspond to the two dispersion curves already observed in Fig. 3 (e). Note that energy and momentum resolution in Fig. 3 (e) is essentially limited by the open ends of the finite-size chains which were used for the dynamic DMRG computations. Evidently, inspection of the momentum-resolved bare energy levels shown in Fig. S2 yields better energy-momentum resolution at the expense of losing information about the neutron intensities of the excitations. Indeed, in Fig. S2 we see a large number of excitations at energies above 2 meV and

only the dynamic structure factor of Fig. 3 (e) shows that they have very little contribution to the inelastic neutron cross section. From the bare energy levels of Fig. S2, we read off a bandwidth ratio of $1/5.3$ which is very close to the experimental value [6].

Fig. S3 shows the expected excitation spectrum for Kikuchi’s original parameter set Table I, line **4** [1]. Note that we have computed only the 20 lowest excitations in some sectors for $N \geq 24$ and that the density of states is already quite large at energies above 1 meV in the present case. Hence, some levels may be missing in Fig. S3 at energies $E > 2$ meV for $S^z \leq N/6$ and $N \geq 24$. We nevertheless keep this region in order to be able to show the location of the excitations observed by inelastic neutron scattering on azurite [6] (dashed lines). In the present case it is not so easy to distinguish two cosine-like bands in the numerical results. If one uses the lowest black and red energy level, respectively, one finds a bandwidth ratio close to $1/1.9$, quite far off the experimental result [6].

Further proposals of parameters sets [6–8] contain a ferromagnetic J_3 . Ref. [10] already pointed out that a ferromagnetic J_3 is hard to reconcile with the crystal structure of azurite given the $d_{x^2-y^2}$ character of the relevant copper orbitals. We will nevertheless look at the excitation spectra for these parameter sets and demonstrate that they are either inconsistent or at least yield less good agreement with the neutron scattering experiments [6] than our final parameter set given in Table I, line **3**.

The parameter set of Gu and Su [7, 8] $J_1 = 23$ K, $J_2 = 43.7$ K, $J_3^{xy} = -6.9$ K, $J_3^z = -11.73$ K, $J_m = 0$ has an artificially large magnetic anisotropy in the supposedly ferromagnetic J_3 . Replacing this by an average value $J_3 = -9.3$ K, we find the excitation spectrum shown in Fig. S4. Not only is the bandwidth ratio of approximately $1/1.8$ again far away from the experimental result [6], but in this case the upper excitation branch is about 1 meV (≈ 10 K) too high in energy.

Finally, Ref. [6] tried to invert perturbative results for the effective monomer-monomer and dimer-dimer exchanges along the chain in order to propose $J_1 = 1$ K, $J_2 = 55$ K and a ferromagnetic $J_3 = -20$ K. We discuss two variants of these parameters, starting in Fig. S5 with $J_m = 0$. In this case, we find a bandwidth ratio $1/1.4$ which is clearly inconsistent with the experimental result. However, it was already proposed in Ref. [6] to improve this behavior by adding a $J_m = 6.5$ K. The result with such a J_m included is shown in Fig. S6. While inclusion of $J_m = 6.5$ K improves the agreement with experiment [6], the result is not quite as good for our final parameter set Table I, line **3**. In particular, the bandwidth ratio is just $1/4$.

To summarize the discussion of this subsection, we have demonstrated that our final parameter set Table I, line **3** yields the best agreement with inelastic neutron scattering on the 1/3 plateau [6] among the proposals

of Refs. [1, 6–8]. In particular, inelastic neutron scattering is inconsistent with the parameters proposed in Refs. [1, 7, 8].

S8. Perspectives

There are some further refinements of the model for azurite to be implemented in future investigations. Firstly, we have argued interchain coupling to be unimportant for a basic description of azurite, but, although small, it is present and likely to be responsible for the following features: (i) The strong curvature at the lower edge of 1/3 plateau in the theoretical magnetization curve of Fig. 3 (b) versus the smoother behavior observed in the experiment for $H \perp b$ is characteristic for one- versus higher-dimensional physics [38–40]. (ii) An ordering transition at temperatures slightly below 2 K [1, 12–14] is evident in Fig. 3 (d), *i.e.*, interchain coupling affects thermodynamic properties at temperatures of a few Kelvin. In view of the success of the effective one-dimensional model Table I, line **3**, we are confident that our prediction of Table I, line **1** for the exchange ratios of the full three-dimensional model is also reliable. Indeed, it would be very interesting to compare the predictions of this three-dimensional model for the zero-field ordered state with the corresponding recent experimental observations [14]. However, this will require very different methods from the present work and thus is an interesting topic for future investigations.

Secondly, we have neglected magnetic anisotropy in the theoretical model although experiments [1] show that it is present in azurite and affects magnetic properties for a magnetic field parallel to the crystallographic b -axis at an energy scale of a few Kelvin.

Finally, we would like to emphasize that we find all J_i antiferromagnetic with similar values of J_1 and J_3 , thus placing azurite in a highly frustrated parameter regime. This is reflected by the almost localized nature of the dimer excitations. These excitations will become low-energy excitations in magnetic fields around 32 T, and one expects related unusual thermodynamic behavior like an enhanced magnetocaloric effect [5, 41]. This calls for additional thermodynamic measurements close to the saturation field of azurite.

[1] H. Kikuchi, Y. Fujii, M. Chiba, S. Mitsudo, T. Idehara, T. Tonegawa, K. Okamoto, T. Sakai, T. Kuwai, and H. Ohta, Phys. Rev. Lett. **94**, 227201 (2005).
 [2] H. Kikuchi, Y. Fujii, M. Chiba, S. Mitsudo, T. Idehara, T. Tonegawa, K. Okamoto, T. Sakai, T. Kuwai, K. Kindo, A. Matsuo, W. Higemoto, K. Nishiyama, M. Horvatić, and C. Berthier, Progr. Theor. Phys. Suppl. **159**, 1 (2005).

[3] F. Zigan and H. D. Schuster, Z. Kristallogr. **135**, 416 (1972).
 [4] C. Lacroix, P. Mendels, and F. Mila, *Introduction to Frustrated Magnetism*, Springer Series in Solid-State Sciences (Springer, Heidelberg, 2011) Vol. 164.
 [5] O. Derzhko, J. Richter, A. Honecker, and H.-J. Schmidt, Low Temp. Phys. **33**, 745 (2007).
 [6] K. C. Rule, A. U. B. Wolter, S. Süllow, D. A. Tennant, A. Brühl, S. Köhler, B. Wolf, M. Lang, and J. Schreuer, Phys. Rev. Lett. **100**, 117202 (2008).
 [7] B. Gu and G. Su, Phys. Rev. Lett. **97**, 089701 (2006).
 [8] B. Gu and G. Su, Phys. Rev. B **75**, 174437 (2007).
 [9] H.-J. Mikeska and C. Luckmann, Phys. Rev. B **77**, 054405 (2008).
 [10] J. Kang, C. Lee, R. K. Kremer, and M.-H. Whangbo, J. Phys.: Condens. Matter **21**, 392201 (2009).
 [11] H. Kikuchi, Y. Fujii, M. Chiba, S. Mitsudo, T. Idehara, T. Tonegawa, K. Okamoto, T. Sakai, T. Kuwai, and H. Ohta, Phys. Rev. Lett. **97**, 089702 (2006).
 [12] H. Forstater, G. Taylor, and R. B. King, J. Chem. Phys. **31**, 929 (1959).
 [13] M. C. R. Gibson, K. C. Rule, A. U. B. Wolter, J.-U. Hoffmann, O. Prokhnenko, D. A. Tennant, S. Gerischer, M. Kraken, F. J. Litterst, S. Süllow, J. Schreuer, H. Luetkens, A. Brühl, B. Wolf, and M. Lang, Phys. Rev. B **81**, 140406(R) (2010).
 [14] K. C. Rule, M. Reehuis, M. C. R. Gibson, B. Ouladdiaf, M. J. Gutmann, J.-U. Hoffmann, S. Gerischer, D. A. Tennant, S. Süllow, and M. Lang, Phys. Rev. B **83**, 104401 (2011).
 [15] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).
 [16] X. Wang and T. Xiang, Phys. Rev. B **56**, 5061 (1997).
 [17] E. Jeckelmann, Phys. Rev. B **66**, 045114 (2002).
 [18] F. Aimo, S. Krämer, M. Klanjšek, M. Horvatić, C. Berthier, and H. Kikuchi, Phys. Rev. Lett. **102**, 127205 (2009).
 [19] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
 [20] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
 [21] P. Blaha, K. Schwarz, C. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k: An augmented plane wave plus local orbitals program for calculating crystal properties*. (TU Wien, Austria, 2001).
 [22] E. L. Belokoneva, Yu. K. Gubina, and J. B. Forsyth, Phys. Chem. Minerals **28**, 498 (2001).
 [23] The orbital assignment is given in the local reference frame of Cu where the ab plane corresponds to the CuO₄ plane with a parallel to a Cu-O bond.
 [24] O. K. Andersen and T. Saha-Dasgupta, Phys. Rev. B **62**, R16219 (2000).
 [25] R. Valentí, T. Saha-Dasgupta, and C. Gros, Phys. Rev. B **66**, 054426 (2002).
 [26] K. Koepnik and H. Eschrig, Phys. Rev. B **59**, 1743 (1999); <http://www.FPL0.de>.
 [27] T. Chanier, M. Sargolzaei, I. Opahle, R. Hayn, and K. Koepnik, Phys. Rev. B **73**, 134418 (2006).
 [28] A. Honecker and A. Läuchli, Phys. Rev. B **63**, 174407 (2001).
 [29] H. C. Kandpal, I. Opahle, Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Phys. Rev. Lett. **103**, 067004 (2009).
 [30] H. Ohta, S. Okubo, T. Kamikawa, T. Kunimoto, Y. Inagaki, H. Kikuchi, T. Saito, M. Azuma, and M. Takano, J. Phys. Soc. Jpn. **72**, 2464 (2003).
 [31] We would like to emphasize that we have made no further

adjustments to the magnetic field $H = 14$ T although the critical field at the lower edge of the $M = 1/3$ plateau is reproduced less accurately than other features (compare Fig. 3 (b)). Therefore, we attach more importance to the bandwidth ratio than the absolute position of the excitation bands.

- [32] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [33] O. K. Andersen, T. Saha-Dasgupta, and S. Ezhov, Bull. Mater. Sci. **26**, 19 (2003).
- [34] U. Schollwöck, Rev. Mod. Phys. **77**, 259 (2005).
- [35] R. J. Bursill, T. Xiang, and G. A. Gehring, J. Phys.: Condens. Matter **8**, L583 (1996).
- [36] P. F. Sullivan and G. Seidel, Phys. Rev. **173**, 679 (1968).
- [37] O. Kahn, *Molecular Magnetism*. (Wiley-VCH, New York, 1993).
- [38] G. I. Dzhaparidze and G. I. Nersesyan, JETP Lett. **27**, 334 (1978).
- [39] V. L. Pokrovsky and A. L. Talapov, Phys. Rev. Lett. **42**, 65 (1979).
- [40] E. G. Batyev and L. S. Braginskii, Soviet Physics JETP **60**, 781 (1984).
- [41] A. Honecker, S. Hu, R. Peters, and J. Richter, J. Phys.: Condens. Matter **23**, 164211 (2011).