Large quantum fluctuations in the strongly coupled spin-1/2 chains of green dioptase: a hidden message from birds and trees

O. Janson, A. A. Tsirlin, M. Schmitt, and H. Rosner
Max-Planck-Institut für Chemische Physik fester Stoffe, D-01187 Dresden, Germany
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The green mineral dioptase Cu₆Si₆O₁₈·6H₂O has been known since centuries and plays an important role in esoteric doctrines. In particular, the green dioptase is supposed to grant the skill to speak with trees and to understand the language of birds. Armed with natural samples of dioptase, we were able to unravel the magnetic nature of the mineral (presumably with hidden support from birds and trees) and show that strong quantum fluctuations can be realized in an essentially framework-type spin lattice of coupled chains, thus neither frustration nor low-dimensionality are prerequisites. We present a microscopic magnetic model for the green dioptase. Based on full-potential DFT calculations, we find two relevant couplings in this system: an antiferromagnetic coupling $J_\perp$, forming spiral chains along the hexagonal $c$ axis, and an inter-chain ferromagnetic coupling $J_\parallel$ within structural Cu₂O₆ dimers. To refine the $J_\perp$ and $J_\parallel$ values and to confirm the proposed spin model, we perform quantum Monte-Carlo simulations for the dioptase spin lattice. The derived magnetic susceptibility, the magnetic ground state, and the sublattice magnetization are in remarkably good agreement with the experimental data. The refined model parameters are $J_\perp=78$ K and $J_\parallel=-37$ K with $J_\parallel/J_\perp \simeq -0.5$. Despite the apparent three-dimensional features of the spin lattice and the lack of frustration, strong quantum fluctuations in the system are evidenced by a broad maximum in the magnetic susceptibility, a reduced value of the Néel temperature $T_N \simeq 15$ K $\ll J_\perp$, and a low value of the sublattice magnetization $m=0.55 \mu_B$. All these features should be ascribed to the low coordination number of 3 that outbalances the three-dimensional nature of the spin lattice.

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I. INTRODUCTION

Since ancient times, emerald has been one of the most rare and treasured gemstones because of its bright and brilliant green color. However, by far not all gemstones that were collected as emeralds or varieties of it were indeed emeralds — many of them later appeared to be specimens of green dioptase (see Fig. 1). Nevertheless, this confusion contributed considerably to the assignment of many mysterious powers to this mineral, such as pro-
cedences should be ascribed to the low coordination number of 3 that outbalances the three-dimensional nature of the spin lattice.

The magnetic properties of green dioptase have been investigated in some experimental studies. Although these studies yield quantitatively slightly varying results, likely also related to dioptase samples originating from different locations, they essentially converge in the description of dioptase as an antiferromagnet with a rather low Néel temperature ($T_N \sim 15$ K) compared to the antiferromagnetic Curie-Weiss temperature of about 70 K. The ordered magnetic moment ($m=0.55 \mu_B$) is drastically reduced with respect to the saturation moment of 1 $\mu_B$ for Cu²⁺. Together with the broad maximum in the measured magnetic susceptibility this puts the compound in the family of spin 1/2 quantum magnets that can be described successfully in many cases by the isotropic Heisenberg model.
\[ \hat{H} = \sum_{<ij>} J_{ij} \hat{S}_i \hat{S}_j, \]  

at least for the low lying spin excitations. Here, \( J_{ij} \) represents the exchange interaction between spins located at the lattice sites \( i \) and \( j \).

Although this model looks deceivingly simple at the first glance, neither its solution for a seemingly ordinary situation nor the assignment of appropriate exchange integrals \( J_{ij} \) for a specific material are trivial in any way. It is obvious that the crystal structure of a compound is the key to understand its magnetic properties. On the other hand, an assignment of interaction parameters solely based on structural considerations can be completely misleading like in the case of \((\text{VO})_2\text{P}_2\text{O}_7\). In recent years, even careful investigations based on accurate experimental data, but within a limited spectrum of methods, have suggested controversially discussed magnetic models for several compounds. A prominent example for this problem are the two closely related spin-1/2 \( J_1\)-\( J_2 \) chain compounds \( \text{Li}_2\text{Cu}_2\text{O}_2 \) and \( \text{LiCu}_2\text{O}_2 \), for which consensus about their location in the magnetic phase diagram was established only recently.

Thus, to establish the appropriate magnetic model for a new, complex material, the application of independent methods seems of crucial importance. In particular, the search for the relevant sector in the phase diagram can largely benefit from a detailed microscopic analysis based on modern band structure theory in combination with numerical methods to solve subsequently the corresponding Heisenberg Hamiltonian, at least in an approximate way.

In particular, for green dioptase a magnetic model with antiferromagnetic (AFM) nearest-neighbor (NN) coupling \( J_e \) along the spiral chains (see Fig. 1 middle) and AFM coupling \( J_d \) within the structural \( \text{Cu}_2\text{O}_5 \) dimers was suggested on empirical grounds and evaluated using quantum Monte-Carlo simulations (QMC) to fit the experimental magnetic susceptibility. This study places the compound in proximity to a quantum critical point due to a competition between chain-like ordering along \( c \) and magnetic dimer formation caused by the AFM \( J_d \). In contrast to Ref. 24, the results of our microscopic study place the compound in a different region of the phase diagram and assign the strong quantum fluctuations and the related magnetic properties to the small effective coordination number of the magnetic \( \text{Cu}^{2+} \) sites.

II. METHODS

Electronic structure calculations were performed using the full potential non-orthogonal local-orbital minimum basis scheme \( \text{fplo}9.00-33 \). For the scalar relativistic calculations within the local density approximation (LDA) the exchange and correlation potential of Perdew and Wang was chosen. A well-converged \( k \)-mesh of 8×8×8 points was used for LDA calculations. Wan- nier functions (WF) were calculated for the antibonding \( \text{Cu} 3d_{xz-\gamma^*} \) states. Strong correlations are treated in a mean-field way within the LSDA+U approach. For the double counting correction (DCC) we applied the two limiting cases: the around-mean-field (AMF) approach and the fully-localized limit (FLL). The on-site Coulomb repulsion \( U_{3d} \) was varied within the physically reasonable ranges: \( U_{3d}=5.5-7.5 \) eV for AMF and \( U_{3d}=6.5-9.5 \) eV for FLL. The intra-atomic Hund’s coupling \( J_{3d} \) was fixed to 1 eV. To allow for various spin ordering arrangements, the original hexagonal symmetry was reduced to the spacegroup \( P1 \). For the LSDA+U calculations, we used \( k \)-meshes of 4×4×4 points. The calculations were carefully checked for convergence. For the structural input, we used the crystal structure from Ref. 4.

Quantum Monte-Carlo (QMC) simulations were performed using the programs \texttt{looper} and \texttt{dirloop.sse} of the software package \texttt{ALPS}. The magnetic susceptibility was simulated for \( N=10752 \) sites clusters, containing 256 coupled chains of 42 sites each. In the temperature range \( T/J_e = 0.15-4.50 \), we used 25 000 sweeps for thermalization and 300 000 sweeps after thermalization. The resulting statistical errors (<0.1%) are far below the experimental inaccuracy. To evaluate the dependence of the static structure factor on the cluster size, we performed a series of simulations starting with a \( N=24 \) sites cluster and consequently increasing it up to \( N=8232 \) sites. Magnetization curves were simulated on \( N=1536 \) sites clusters at \( T=0.025J_e \) using 50 000 sweeps for thermalization and 500 000 sweeps after thermalization. Statistical errors did not exceed 0.5%.

The experimental data were collected on a natural sample of green dioptase. A green transparent crystal was mechanically detached from the calcite matrix and used for magnetic measurements without alignment in the magnetic field. The magnetic susceptibility was measured with a Quantum Design MPMS SQUID in the temperature range 2–380 K in applied fields up to 5 T.

III. RESULTS

A. Electronic structure and magnetic model

The electronic structure of the green dioptase was calculated within the LDA. The atom-resolved density of states (DOS) is depicted in Fig. 2. The width of the valence band is about 10 eV, similar to other cuprates. States at the Fermi level evidence a metallic solution in contrast to the green transparent crystals indicating an insulating behavior. This well known shortcoming of the LDA approach originates from the underestimation of the strong Coulomb repulsion in the \( \text{Cu} 3d \) shell. The insulating ground state can be restored by adding the missing part of correlation (i) via mapping onto a Hubbard model
FIG. 1. (Color online) Left: Crystal structure of the green dioptase. The Cu$_2$O$_6$ dimers are shown in yellow and form a 3D network. SiO$_4$ tetrahedra are shown blue. The crystal water is depicted by O (blue) and H (gray) atoms with O–H bonds. Middle: the magnetic model of the green dioptase. Cu atoms are depicted as orange spheres, other atoms are not shown. The leading antiferromagnetic coupling $J_c$ (red) forms spiral chains running along $c$ perpendicular to the projection plane. The ferromagnetic coupling $J_d$ (blue) within the structural Cu$_2$O$_6$ dimers couples the chains into a three-dimensional framework. Right: section of the spiral chain along $c$ (bottom) and a natural sample of green dioptase grown on calcite (top).

FIG. 2. (Color online) Total and atom-resolved LDA density of states for the green dioptase. The antibonding Cu–O $d\sigma$ states form a well separated band complex at the Fermi level.
be derived using the second order perturbation theory expression $J_{ij}^{AFM}=4t_{ij}^2/U_{eff}$. Since the original TB-model is a one-band model, only the antiferromagnetic contribution to the total magnetic exchange is accounted for in this approach. Thus, the resulting antiferromagnetic contributions for the leading couplings are $J_c^{AFM}=184$ K and $J_d^{AFM}=125$ K. Since exchange integrals $J_{ij}^{AFM}$ are proportional to $t_{ij}^2$, all further exchanges are smaller than 7 K (less than 4% of the leading exchange) and can be neglected in first place.

Due to their close vicinity to 90° the intra-dimer Cu–O–Cu bond angle of 97.4° and inter-dimer angle of 107.6° require a careful estimation of the ferromagnetic contributions to the total exchange integrals, neglected in the effective one-band TB model approach presented above. Thus, we performed LSDA+U calculations of magnetic supercells with various collinear spin arrangements. The mapping of total energy differences onto a classical Heisenberg model results in an AFM exchange along the spirals chains $J_c=110$ K and a FM intra-dimer exchange $J_d=-66$ K for a typical value of $U_d=6.5$ eV within the AMF DCC scheme.

In agreement with the expectations according to the Goodenough-Kanamori-Anderson rules, the LSDA+U calculations evidence considerable FM contributions to both relevant exchange integrals $J_c$ and $J_d$. In particular, the total value of $J_c$ is strongly reduced compared to the estimate from the one-band model ($J_c^{AFM}=184$ K), yielding $J_c^{FM}=-74$ K. For $J_d$, the closer proximity of the Cu–O–Cu angle to 90° leads to an even larger FM contribution $J_d^{FM}=-191$ K which exceeds the AFM part $J_d^{AFM}$, resulting in a significantly FM total coupling $J_d$ within the structural dimers.

Since the choice of DCC is non-trivial and can have a large impact on the resulting exchange parameters, we compare the AMF results to FLL calculations. For the green diopside, we find that both DCC schemes yield similar results (Fig. 1). The only apparent difference is related to the values of $U_{3d}$: for FLL, about 2 eV larger $U_{3d}$ values are required in order to obtain the same exchange integrals as AMF. The FM nature of $J_d$ remains stable in the whole range of $U_{3d}$ and for the two DCC schemes.

Although the qualitative microscopic model is well justified by varying the $U_{3d}$ parameter in a rather wide range, the strong dependence of the resulting exchange integrals on $U_{3d}$ impedes an accurate estimation of the absolute size and the ratio of the two couplings. In the next section, we refine the values of the exchange integrals by alternative methods.

To summarize the microscopic analysis, we obtain a model with two leading interactions: an AFM $J_c$ running along the spiral (in the $c$ direction) and an FM $J_d$ inside structural Cu$_2$O$_6$ dimers. We should note that a related magnetic model was proposed in Ref. 24. It is based on the same relevant exchange interactions, but implies an AFM intra-dimer coupling $J_d$ in contrast to the FM nature of this coupling in our model. Remarkably, a model...
we find that the ratio \( J_d/J_c \) can be varied in a rather wide range \((-0.8...-0.4)\) yielding a very good fit to the experimental data for the paramagnetic phase\textsuperscript{11}. To improve our refinement of \( J_d/J_c \), we have to address the magnetic ordering temperature \( T_N \), which can be traced by a clear kink in the simulated curves. The reference to \( T_N \) yields \( J_d/J_c \) close to \(-0.5\). The respective fit is shown in Fig. 5 (top). The resulting \( J_d/J_c \) of 78 K agrees well with the DFT estimates: 110 K for \( U_{sd}=6.5 \) eV within the AMF scheme \((J_d/J_c=-0.6)\) and even better with 85 K yielded by \( U_{sd}=8.5 \) eV for the FLL scheme \((J_d/J_c=-0.55)\). Moreover, \( g = 2.26 \) and \( \chi_0 = -6.9 \times 10^{-5} \) emu/mol are consistent with estimates from the Curie-Weiss fit \((2.30\) and \(-7.2 \times 10^{-5}\) emu/mol, respectively).

For a further test of our model, we will address its ground state properties. First, the propagation vector \( \vec{q} \) of the AFM ordered GS coincides with the experimentally observed \( \vec{q}=(0,0,2/3\pi)\) in the whole range \(-1\leq J_d/J_c \leq -0.2\). In this GS, the neighboring spins along the spiral chains \((J_c)\) align antiferromagnetically, while the ordering within the edge-sharing dimers \((J_d)\) is FM. This justifies the validity of our microscopic model, but does not allow for a more accurate refinement of the proposed value for the \( J_d/J_c \) ratio. For a further comparison, we use the sublattice magnetization \((m)\) that has been previously estimated in neutron diffraction experiments and amounts to \( 0.55 \mu_B \). Unfortunately, the theoretical estimation of \( m \) is not straightforward for two reasons. First, the simulations
do not yield the magnetic moment in the ordered state directly. Instead, it can be estimated based on the static structure factor or on spin correlations. Second, 3D coupling is crucial for the magnetic ordering of the green dioptase, thus sizable finite size effects are expected even for rather large clusters. To account for these effects, we use the general procedure from Ref. 42 and estimate the magnetic moment $m$ based on a finite-size scaling of the static structure factor, taken for the propagation vector of the ordered structure. The results of simulations for various $J_d/J_c$ ratios are shown in Fig. 5 (bottom). Remarkably, the theoretical $m$ for $J_d/J_c=−0.5$ is in good agreement with the experimental value.

Finally, we can introduce a magnetic field term to our Hamiltonian and simulate the behaviour of magnetization $M$ as a function of the reduced magnetic field $0\leq h^* \leq 5J_d$. Such a simulation could be an additional test for our model, since high-field magnetization experiments were recently announced.2 Therefore, we simulate $M(h^*)$ curves for $J_d/J_c=−0.5 \pm 0.2$ and scale them using the expression

$$M(h) = M \left(\frac{k_BJ_c}{g\mu_B}h^*\right),$$ (3)

adopting the $J_c$ and $g$ values from the fits to $\chi(T)$. The resulting curves shown in Fig. 6 have similar shape and only slightly different values of the saturation field.\(^\texttt{35-37}\) Therefore, the experimental $M(h)$ dependence is unlikely to facilitate a further refinement of the model parameters due to practical resolution limits at high magnetic fields. In addition, the predicted value of the saturation field remains challenging for present-day experimental facilities.

IV. DISCUSSION

In our model, the spin lattice of the green dioptase comprises AFM couplings $J_c$ between the corner-sharing CuO$_4$ plaquettes and FM couplings $J_d$ between the edge-sharing plaquettes (Fig. 1). This situation is not surprising, because the corner-sharing connection normally leads to 180° superexchange, while the edge-sharing connection corresponds to the Cu–O–Cu angle close to 90°. However, the crystal structure of the green dioptase shows a tiny difference between the superexchange pathways. The twisted configuration of the corner-sharing plaquettes leads to the Cu–O–Cu angle of 107.6° for $J_c$ that is substantially larger than 97.4° for $J_d$. The smaller angle for $J_d$ still fits to the general trend, predicted by Goodenough-Kanamori-Anderson rules.\(^\texttt{35-37}\) On the other hand, the green dioptase is very close to the “critical regime” of the Cu–O–Cu superexchange. Then, even a weak structural change could lead to a strong modification of the exchange couplings, making an empirical assignment of the parameter region difficult. For example, the earlier theoretical analysis assumed AFM coupling for both $J_c$ and $J_d$.\(^\texttt{24}\) Therefore, we used a quantitative microscopic approach and demonstrated that this empirical assumption is not consistent with the electronic structure of the compound.

To examine whether small changes in the crystal structure may lead to a modification of the microscopic model, the consideration of structurally closely related
compounds is a natural approach. The dehydration transforms the green dioptase into the black dioptase Cu$_6$Si$_6$O$_{18}$ that essentially keeps the 3D framework-type crystal structure (Fig. I) but lacks water molecules. The Cu–O–Cu angles amount to 110.7° and 97.3° for $J_c$ and $J_d$, respectively. Thus, based on basic structural arguments, the signs of the two couplings should persist, while the absolute values are likely increased. This prediction is in line with the experimental data, indicating a large Weiss temperature $\theta$ of 180 K of the black dioptase compared to $\theta$ = 43 K in the green dioptase (Sec. III B). In addition, neutron diffraction studies evidence similar magnetic structures for the black and green dioptase. On the other hand, a very recent study of black dioptase based on extended Hückel calculations and a 1D fit to the magnetic susceptibility assigns the compound to the model family of AFM chain compounds with very weak interchain interactions.

Further examples of the dioptase structure are given by the hydrated and anhydrous Cu germanates Cu$_6$Ge$_6$O$_{18}$ · $x$H$_2$O with $x$ = 0 and 6. These compounds were previously considered as coupled frustrated spin chains, because a sizable next-nearest-neighbor coupling along the spiral chains was assumed. This assumption is rather empirical and mainly motivated by the chemical similarity to the well-known spin-Peierls compound CuGeO$_3$ with its frustrated spin chains of edge-sharing CuO$_4$ plaquettes. However, the pronounced difference in the crystal structures strongly impedes a reliable transfer of the well established magnetic model of the chain compound CuGeO$_3$ to the Ge-dioptase Cu$_6$Ge$_6$O$_{18}$. Based on the results for the Si-dioptase, we would expect sizable AFM $J_c$, while $J_d$ is either FM or AFM. In the case that the FM and AFM contributions to $J_d$ are close to cancel each other, the inter-chain coupling is effectively switched off, and long-range couplings along the spiral chains could alter the physics. The above empirical analysis gives no clear evidence for significant long-range couplings, but further microscopic studies should challenge this conclusion. Thus, since the minor structural changes in the dioptase family might be crucial for changes in the leading magnetic couplings and the understanding of their magnetic properties, a detailed comparative study is underway.

Taking the green dioptase as an example, we have derived the basic features of the dioptase spin lattice. This spin lattice is unfrustrated, hence we should preclude any references to the frustrated spin chain model, at least for the green dioptase Cu$_6$Si$_6$O$_{18}$ · 6H$_2$O. It is worth to mention that the dioptase structure does not give rise to the star lattice (decorated honeycomb lattice), as it may seem on the first glance. Such confusion could arise from a specific projection of the crystal structure, where the spiral chains look like flat frustrated triangles (compare to the middle panel of Fig. I).

After shortly outlining what the dioptase spin lattice is not, it is more important to establish what it actually is: uniform AFM spin chains aligned along the c direction are arranged on the honeycomb lattice, i.e., each chain is coupled to three neighboring chains, and the system is geometrically 3D (Fig. I). However, the total coordination number is as low as three: each atom has two $J_c$ bonds and one $J_d$ bond only. Thus, the couplings in the ab plane form a kind of a “sparse” honeycomb lattice. The reduction in the coordination number has strong effect on the magnetic properties.

Experimental data for the green dioptase evidence strong quantum fluctuations: the broad susceptibility maximum at $T_{\text{max}}/J_c \simeq 0.64$, the low Néel temperature ($T_N/J_c \simeq 0.2$), and the reduced sublattice magnetization $\langle S \rangle = 0.55 \mu_B$ compared to 1 $\mu_B$ for the classical spin-$1/2$ systems. Strong quantum fluctuations are usually observed in low-dimensional and/or frustrated spin systems. For example, the archetypal two-dimensional spin model of the square lattice reveals the susceptibility maximum at $T_{\chi_{\text{max}}} / J \simeq 1.0$ and a sublattice magnetization of $0.6 \mu_B$. To reduce the ordering temperature down to $T_N / J = 0.2$, a very weak interlayer coupling $J_{\perp} / J \sim 10^{-4}$ is required. Thus, the quantum fluctuations in the dioptase spin lattice are even stronger than in the square lattice, despite the 3D geometry.

Quantum fluctuations in a 3D spin system can arise from the magnetic frustration (see Ref. [52] for an instructive example). However, the dioptase spin lattice is neither low-dimensional, nor frustrated, hence its quantum behavior has a different origin. We suggest that the long-range magnetic ordering in dioptase is impeded by the low coordination number of the lattice, because the low number of bonds reduces the exchange energy that should stabilize the ordered ground state. The dioptase lattice can thus be compared to low-dimensional spin systems with similar coordination numbers. For example, the honeycomb lattice having three bonds per site reveals the low sublattice magnetization of $0.54 \mu_B$ and $T_{\chi_{\text{max}}} / J \simeq 0.7$ (compare to 0.6 $\mu_B$ and 1.0 for the square lattice with four bonds per site). The apparent similarity between the dioptase and the honeycomb lattice clearly shows that the coordination number is the actual criterion of the “low-dimensionality”, as long as the magnitude of quantum fluctuations (the tendency towards the quantum behavior) is considered. Although the conclusion is a natural consequence of simple energy considerations, this is often overlooked. While neither the dioptase crystal structure, nor its spin model look low-dimensional, the essential physics is governed by strong quantum fluctuations, typical for low-dimensional magnets. The above considerations should stimulate further studies of dioptase-structure materials and the respective spin model.

V. SUMMARY AND OUTLOOK

Based on density functional calculations, quantum Monte-Carlo simulations and magnetic measurements we have derived a new magnetic model for the natural min-
eral green dioptase Cu$_6$Si$_6$O$_{18}$·6H$_2$O on a microscopic basis. We have shown that green dioptase can be well described by a quantum spin 1/2 Heisenberg model with essentially two relevant interactions: an NN AFM intra-chain coupling $J_c \sim 78$ K within the spiral chains running along the crystallographic c direction, and a NN FM intra-dimer (inter-chain) coupling $J_d \sim -37$ K within the structural Cu$_2$O$_4$ dimers. The calculated temperature dependence of the magnetic susceptibility, the magnetic ground state, the ordering temperature and the sublattice magnetization for the suggested model parameters are in very good agreement with the experimental data. From our results we conclude that the dioptase spin lattice is neither low-dimensional nor frustrated, but exhibits large quantum fluctuations due to a small effective coordination number of its magnetic sites despite the three-dimensional lattice geometry.

Our approach demonstrates the great potential of the combination of modern band structure methods and numerical simulations with magnetic measurements for a reliable modeling of the magnetic properties for complex compounds. An empirically based assignment of interaction parameters for structurally complex systems can be easily misleading and restrict studies to inappropriate regions of the magnetic phase diagram. Since minor structural changes may cause drastic changes in the leading magnetic couplings, especially for couplings via bonds close to 90° relevant in the dioptase family, a detailed comparative study for the hydrous and anhydrous Si- and Ge-dioptase compounds is in progress.

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\* janson@cpfs.mpg.de
\* rosner@cpfs.mpg.de

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To prove that, we plotted the orbital-resolved DOS for individual atoms. The states corresponding to the O atoms bridging two Cu atoms in a dimer show a clearly planar character. For the O atoms linking two neighboring dimers, the contributions from O 2$p^x$ and O 2$p^z$ are comparable, because the O 2$p^z$ states correspond to the O 2$p^x$ states of the neighbor-dimer, while the states from O 2$p^y$ are negligible.

We should note, that a good fit to the experimental magnetic susceptibility is by no means an evidence that the model itself is correct, since essentially different sets of parameters for the same spin lattice and even for different lattices can yield similar macroscopic magnetic behavior. For the ordered phase, anisotropy plays a crucial role. Since the simulated model is isotropic, the temperature range corresponding to the AFM ordered phase (below $T_N < 15$ K) was excluded from the fit.

For non-frustrated spin lattice in dioptase, the value of the saturation field depends on $J_c$ and $g$, but is not affected by the $J_d/J_c$ ratio in case of a FM $J_d$. K. H. Breuer, W. Eysel, and R. Mueller, Z. Krist. 187, 15 (1989).

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