Magnetic hexamers interacting in layers in the (Na,K)$_2$Cu$_3$O(SO$_4$)$_3$ minerals

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Abstract

Magnetic properties and underlying magnetic models of the synthetic $A_2$Cu$_3$O(SO$_4$)$_3$ fedotovite (A = K) and puninite (A = Na) minerals, as well as the mixed euchlorine-type NaKCu$_3$O(SO$_4$)$_3$ are reported. We show that all these compounds contain magnetic Cu$_6$ hexamer units, which at temperatures below about 100 K carry an overall spin-1 and represent magnetic molecules. Weak interactions between such molecules lead to long-range magnetic order below $T_N = 3.4$ K (A = Na), 4.7 K (A = NaK), and 2.9 K (A = K). The formation of the magnetic order is elucidated by ab initio calculations that reveal predominant inter-hexamer interactions forming a $S = 1$ square lattice within crystallographic $bc$ planes, and challenge previous description of these minerals in terms of Haldane spin chains. We emphasize the role of the anisotropy inherent to the $S = 1$ molecules in the formation of a magnetically ordered ground state with a magnon gap instead of a Haldane gap discussed in previous studies.
Introduction.

Copper compounds, including abundant minerals\(^1\) and their synthetic analogs, are fertile grounds for research on low-dimensional magnetism,\(^2\) where interesting quantum states, such as Tomonaga-Luttinger liquid\(^3\) and Bose-Einstein condensates of magnons\(^4\) can be formed. Magnetic centers are usually represented by individual spin-1/2 Cu\(^{2+}\) ions, but in a few cases these ions build clusters – magnetic molecules – that at low temperatures act as new magnetic ions with larger spin.\(^5\) This feature gives access to interesting physics beyond spin-1/2. For example, the mineral fedotovite, K\(_2\)Cu\(_3\)O(SO\(_4\))\(_3\), was recently put forward\(^6\) as material realization of a Haldane chain built by periodically arranged spin-1 ions. The significance of this model lies in its unique quantum ground state that can be approximated by dimers (valence bonds) between the neighboring atoms and features a finite excitation gap in its energy spectrum.\(^7,8\)

On the structural level, fedotovite entails Cu\(_6\) hexamer units\(^9\) that form a state with total \(S = 1\),\(^10\) naively understood as four spins up and two spins down. The hexamer units are arranged along the crystallographic \(b\) direction and may then form Haldane chains. This conjecture was supported by the experimental observation of a finite spin gap of about 0.6 meV via inelastic neutron scattering (INS), together with a Schottky like specific heat anomaly consistent with a magnetically disordered ground state.\(^6\) On the other hand, magnetic ordering was observed around 3.0 K by subsequent magnetic susceptibility measurements and neutron diffraction.\(^11\) This would indicate a conventional antiferromagnetic state and not the quantum ground state predicted by Haldane.

Here, we seek to shed light on this controversy by thermodynamic measurements and \textit{ab initio} calculations for synthetic fedotovite and its structural analogs, puninite Na\(_2\)Cu\(_3\)O(SO\(_4\))\(_3\)\(^12\) and euchlorine-type NaKCu\(_3\)O(SO\(_4\))\(_3\).\(^13\) Contrarily to the early picture that relied on a single inter-molecule interaction, our data reveal that magnetic hexamers interact in the \(bc\) plane and not along the possible Haldane chain direction. It explains why magnetic order sets in, caused by magnetic anisotropy of the \(S = 1\) units, and the Haldane picture does not hold. We quantify magnetic interactions in all three compounds and show that their large chemical flexibility leads to only a limited magnetic tunability, with long-range magnetic order observed regardless of the chemical composition.
Methods.

Synthesis. Single-phase sulfate materials were prepared by a solid-state reaction from a stoichiometric mixture of the anhydrous precursors $A_2$(SO$_4$) ($A =$ Na, K), CuSO$_4$, and CuO taken in the 1:2:1 ratio. The mixtures were ground in an agate mortar, loaded into gold plates, kept at 560 °C for 3 hours in air, and subsequently cooled for 9 hours to room temperature. The resulting solid products are inhomogeneous in texture but contain single crystals (typical crystal size 0.15×0.15×0.10 mm). The results of our single crystal XRD refinements are given in supplementary Tables S1-S5.

Powder X-ray diffraction. Powder XRD patterns were collected at room temperature in the 2θ range of 10−110 ° using the Bruker D8 diffractometer. The Profile-matching refinements were carried out using JANA2006$^{14}$. The background was fitted using Chebyshev polynomial function, and the peak shapes were described by a Pseudo-Voigt function. Results are shown Fig1.a-c and validate the preparation of single-phase materials.

Thermodynamic properties. Magnetization and heat capacity were measured on powder samples using the PPMS Dynacool (9T) from Quantum Design. For temperature-dependent magnetization measurements both zero-field-cooling (ZFC) and field-cooling (FC) protocols were used. Magnetization versus field was measured at 2K and 300K. Specific heat was measured on pressed pellets from 1.9K to 300K in zero field.

Electron spin resonance. X-band EPR experiments were carried out with a Bruker ELEXYS E580E spectrometer. Microwave power and modulation amplitude were 1 mW and 5 G, respectively. The spectra were recorded between 300 and 4 K using helium ITC503 Oxford temperature control.

First-principle calculations. Exchange couplings between the Cu$^{2+}$ ions were obtained by density-functional-theory (DFT) band-structure calculations performed in the FPLO code$^{15}$ with the Perdew-Burke-Ernzerhof flavor of the exchange-correlation potential.$^{16}$ Mapping procedure$^{17}$ was used to calculate exchange parameters $J_{ij}$ of the spin Hamiltonian,

$$H = \sum_{<ij>} J_{ij} S_i S_j$$

where the summation is over lattice bonds $<ij>$, and $S = \frac{1}{2}$ for individual Cu$^{2+}$ ions or $S = 1$ for the Cu$_6$ hexamers. Correlations effects in the Cu 3$d$ shell were treated on the mean-field level using the DFT+$U$ procedure with the on-site Coulomb repulsion $U_d = 9.5$ eV, Hund’s coupling $J_d = 1$ eV, and double-counting correction in the atomic limit.$^{18,19}$

Quantum Monte-Carlo simulations. Magnetic susceptibility and magnetization for the aforementioned spin Hamiltonian was calculated using the loop and dirloop_sse algorithms of
the ALPS simulation package on finite lattices with periodic boundary conditions and up to \( L = 48 \) or \( L = 12 \times 12 \) sites for the 1D and 2D interaction geometries, respectively.

**Results and Discussion.**

Structurally, the title series of copper sulfate minerals are built up from oxo-centered \( \text{OCu}_4 \) tetrahedra, a rather common situation for copper oxosalts, see examples and principles of the oxo-centered tetrahedral coordination in Ref. 22. They are arranged in trimers by edge sharing, leading to the \( \text{Cu}^{2+} \) hexamers highlighted in Fig.1. These clusters are linked by sulfate groups via Cu-O-O-Cu super-exchanges (SSE) along the \( b \)-axis forming 1D units, the aforementioned spin chains, but also in the \( (bc) \) plane forming 2D-layers, shown in Fig.1. Along the \( a \)-axis, the layers are separated by about 8 Å with no obvious superexchange pathways.

![Fig 1.](image)

**Fig 1.** (a,b,c) Profile-matching refinement and refinement residuals for \( A_2\text{Cu}_3\text{O(SO}_4)_3 \). (d) Crystal structure and main exchange couplings (intra-hexamer: blue lines, inter-hexamer: grey lines). blue color – \( \text{Cu}^{2+} \), red – \( \text{O}^2- \), yellow – \( \text{S}^{6+} \). The longest apical Cu-O\(_{4+1}\) bonds are shown by the dotted blue lines. (e) Lattice parameters of the \( \text{Na}_1 \text{xK}_x \) solid solution. (f) Two-dimensional square lattice of the \( S = 1 \) hexamer units with the hypothetical magnetic structure for the \( (u,0,u) \) spin components. Dotted lines denote the leading magnetic interactions between the hexamers.

The \( \text{Cu}^{2+} \) oxygen coordination of the three independent Cu1, Cu2, and Cu3 ions are strongly distorted CuO\(_{4+1}\) square pyramids, leading to a sizable mixing between \( d_{x^2-y^2} \) and \( d_{z^2} \) as magnetic orbitals. In the case of the \( d^9 \) Cu\(^{2+} \) ions, superexchange pathways are usually
restricted to four oxygen atoms in the basal plane (see the blue O₄ plaquettes in Fig. 1d), i.e. in the Cu₆ hexamers, but in the present case one should additionally consider the “long” apical Cu2-O13 (2.19 Å) and Cu3-O12 (2.32 Å) bonds, as we confirm later by the DFT calculations of the most prominent exchange couplings. On the other hand, the longer apical Cu1-O12 (2.56 Å) contacts do not play any significant role in the superexchange, because they are well above the sum of the Van der Waals radii.

Magnetic couplings within the hexamers were analyzed in some of the previous studies. Ref. 10 used energies of local magnetic excitations probed by inelastic neutron scattering to quantify 7 exchange parameters listed in Table 1 for both K₂Cu₃O(SO₄)₃ and Na₂Cu₃O(SO₄)₃. Ferromagnetic nature of J₂2 and J₃3 was assumed to avoid frustration, whereas the second-neighbor coupling J₂₃ was neglected. These results are in reasonable agreement with the susceptibility fits of Ref. 6 and with our DFT calculations, although we find weakly antiferromagnetic J₂2 and J₃₃, as well as J₂₃. Only J₁₁ is ferromagnetic but reaches almost ca. 60% of the maximal AFM exchanges. Its ferromagnetic nature is typical for the edge-sharing geometry of the two Cu₁O₅ units with the Cu₁-O-Cu₁ angles close to 90°. Interactions between the hexamers are detailed later but found, for the significant ones, even weaker than J₂₂, J₃₃, and J₂₃, so at higher temperatures magnetic behavior should be determined by individual hexamers, which show quite similar exchange parameters for K₂Cu₃O(SO₄)₃, Na₂Cu₃O(SO₄)₃, and the mixed NaKCu₃O(SO₄)₃ compound.

This similarity is reflected in the comparable INS spectra reported for fedotovite and puninite,⁶,¹⁰ but also in very similar temperature dependence of the magnetic susceptibility. All three compounds show a characteristic bend of the inverse susceptibility around 100 K (Fig. 2a) that marks the transition from the paramagnetic regime with individual Cu²⁺ ions to the collective regime, where each hexamer acts as a single spin. Curie-Weiss fits return effective magnetic moments of 1.73-2.20 μB/Cu above 100 K and 2.71-2.84 μB/hexamer below 100 K (Table 1), suggesting, respectively, the anticipated S = ½ state of individual Cu²⁺ ions and the S = 1 state of the Cu₆ hexamer at low temperatures.

This behavior indicates the separation of energy scales, with strong couplings within the hexamers and weak couplings between the hexamers. The evolution of the hexamers is independently tracked by ESR on Na₂Cu₃O(SO₄)₃ that shows powder-averaged paramagnetic resonance with two components, g⊥ = 2.1 and g∥ = 2.4, down to 100 K, with respect to the mixing of magnetic orbitals noted above. Below 100 K, the line broadens around g = 2.2 indicating the development of local fields on individual Cu²⁺ ions (Fig. 2c). The inverse of the
ESR intensity shown in supplementary Fig. S1 tracks magnetic susceptibility and also shows the slope change around 100 K.

Magnetic specific heat of Na$_2$Cu$_3$O(SO$_4$)$_3$ reveals a two-peak structure corresponding to the inter-hexamer and intra-hexamer interactions (Fig. 2e). It was obtained from the experimental specific heat by subtracting the phonon contribution roughly estimated using two Debye contributions ($i = 1$ to 2) via

$$C_{\text{latt}} = 9R \sum_{i=1}^{2} C_i \left( T / \theta_{D,i} \right)^3 \int_0^{x_{D,i}} \frac{x^4 e^x}{(e^{x-1})^2} dx$$

with $C_1 = 11(1)$, $\theta_{D,1} = 310(20)$ K, $C_2 = 18(1)$, $\theta_{D,2} = 1502(50)$ K. Full magnetic entropy of $3R \ln 2$ is recovered around 100 K (Fig. 2e), most of it contained in the second (higher-temperature) peak, whereas the first peak contains only 20% of the magnetic entropy.

With the exception of weak antiferromagnetic interactions $J_{22}$, $J_{33}$, and $J_{23}$, all intra-hexamer interactions tend to align the Cu2 and Cu3 spins parallel to each other and antiparallel to Cu1, thus giving rise to the $S = 1$ state of the hexamer. At lower temperatures, interactions between the hexamers become important, and it is these interactions that underlie the purported Haldane physics of K$_2$Cu$_3$O(SO$_4$)$_3$. Indeed, all three compounds show broad susceptibility maxima around 5-6 K indicative of low-dimensional magnetic behavior. No other features, except for the weak upturn caused by paramagnetic impurities, are seen in the magnetic susceptibility. Concurrently, specific heat shows $\lambda$-type transition anomalies at 3.4 K for Na$_2$Cu$_3$O(SO$_4$)$_3$ and 4.7 K for NaKCu$_3$O(SO$_4$)$_3$ indicating the onset of long-range magnetic order in both compounds. No clear anomaly can be seen in the case of K$_2$Cu$_3$O(SO$_4$)$_3$, although a broad feature is clearly present at 3-4 K and was previously interpreted as a Schottky anomaly. On the other hand, Fisher’s heat capacity of Ref. 11 indicated a magnetic transition, found in our work at 2.9 K. The observation of magnetic Bragg peaks below this temperature also shows that K$_2$Cu$_3$O(SO$_4$)$_3$ develops long-range magnetic order, at odds with earlier expectations of the Haldane physics in this compound. The broadened feature in the specific heat may be caused by a lower crystallinity of the potassium compound in possible relation with its fastest reactivity with moisture, due to the potassium-driven lattice dilatation.

We now analyze the inter-hexamer interactions that cause this magnetic order. All $J$’s corresponding to the Cu-Cu distances of less than 8 Å were calculated, but only two interactions, $J_{23-d1}$ and $J_{23-d2}$, are found to be significant. On the other hand, the interaction $J_{23-b}$ proposed in Ref. 6 is well below 1 K and, therefore, negligible. Both $J_{23-d1}$ and $J_{23-d2}$ connect the hexamers in the $bc$ plane.
Fig. 2 (a) $\chi'(T)$ plots measured at 1000 Oe for the (Na,K)$_2$CuO(SO$_4$)$_3$ series. The data for the K sample are corrected by subtracting a temperature-independent background contribution (b) Evidence of the low-T $\chi(T)$ bump typical of low-dimensional magnetism. (c) ESR data and $g$-components at various temperatures. (d) Temperature dependence of the specific heat at low temperatures, with $\lambda$-type peaks for Na$_2$Cu$_3$O(SO$_4$)$_3$ and NaKCu$_3$O(SO$_4$)$_3$. A similar feature is expected in K$_2$Cu$_3$O(SO$_4$)$_3$, but largely smeared out, probably due to a lower stability of this compound. (e) Phonon and magnetic contributions to the specific heat of Na$_2$Cu$_3$O(SO$_4$)$_3$. The inset shows magnetic entropy $S_{magn}$ obtained by integrating $C_p^{magn}/T$, with about 20% of the total entropy recovered at $T_N$. (f) Raw $M(H)$ data at 2 K and 300 K with the spin-flop transition highlighted via $dM/dH$ in the inset.

The diagonal couplings $J_{23-d1}$ and $J_{23-d2}$ are similar in size in all three compounds and build an effective square lattice of $S = 1$ magnetic moments associated with the hexamers (Fig. 1f). In the following, we juxtapose this square-lattice model with the experimental data.

Magnetic structure stabilized by $J_{23-d1}$ and $J_{23-d2}$ fully respects the magnetic Shubnikov group $C2'/c$ with $k = (0,0,0)$ proposed for K$_2$Cu$_3$O(SO$_4$)$_3$ on the basis of both the $S = 1$ clustering and the observed magnetic satellites in the neutron powder pattern. According to Ref. 11, the $(u,v,w)$ spin components are dominated by the $u$ and $w$ terms. In Fig. 1f, we arbitrarily choose $u = w$ for better visualization and demonstrate that the magnetic order associated with $C2'/c$ complies with the antiferromagnetic nature of $J_{23-d1}$ and $J_{23-d2}$. On the other hand, antiferromagnetic $J_{23-b}$ of Ref. 6 should lead to a different type of magnetic order and would not be consistent with neutron diffraction.
Table 1: unit cell parameters, results of the Curie-Weiss fitting, and magnetic exchanges parameters from DFT in the three studied compounds of the (Na,K)$_2$Cu$_3$O(SO$_4$)$_3$ series. When available, the intra-hexamer exchange parameters from Ref. [10] (fits to excitations energies determined by inelastic neutron scattering) and Ref. [6] (fits to the experimental susceptibility data) are given for comparison. Zero values indicate exchange couplings that are below 0.05 K and can’t be resolved by DFT.

| Compound | Space group | Na$_2$Cu$_3$O(SO$_4$)$_3$ | KNaCu$_3$O(SO$_4$)$_3$ | KCu$_3$O(SO$_4$)$_3$ |
|----------|-------------|--------------------------|--------------------------|--------------------------|
|          | C2/c        | C2/c                     | C2/c                     |
|          | a = 17.3097(9)Å | b = 17.0873(1)Å | a = 18.5753(1)Å | a = 19.6125(9)Å |
|          | b = 9.3982(5)Å  | c = 13.982(7)Å  | b = 9.3994(4)Å  | b = 9.7712(5)Å  |
|          | c = 11.936(1)$^\circ$ | V = 2172.72(19)Å$^3$ | c = 14.3701(1)$^\circ$ | c = 14.4903(7)Å |
|          |              |                         | V = 2292.62(31)Å$^3$ | V = 2578.32(17)Å$^3$ |

| Compound | Space group | Lattice parameters | Magnetic parameters |
|----------|-------------|-------------------|---------------------|
|          | C2/c        | a = 17.3097(9)Å  | $\mu_\text{eff}$ per Cu$^{2+}$ ($S$=1/2) |
|          |              | b = 9.3982(5)Å  | High Temp. 1.93 $\mu_B$, -235.2 K 1.73 $\mu_B$, -187.2 K 1.80 $\mu_B$, -216.3 K |
|          |              | c = 11.936(1)$^\circ$ | 2.45 $\mu_B$, -7.3 K 2.71 $\mu_B$, -8.4 K 2.80 $\mu_B$, -10.7 K |
|          |              | V = 2172.72(19)Å$^3$ | Low Temp. 2.84 $\mu_B$, -7.3 K 2.71 $\mu_B$, -8.4 K 2.80 $\mu_B$, -10.7 K |

| Compound | Space group | J label | J/k$_B$ (K) | J/k$_B$ (K) | J/k$_B$ (K) |
|----------|-------------|---------|-------------|-------------|-------------|
|          |             | intra-hexamer |              |              |              |
|          | Cu1-Cu1     | J$_{11}$ this work | 2.8196(7) | 159 | -164 | 2.818(2) | -157 |
|          | Cu1-Cu2     | J$_{12}$ this work | 3.3940(8) | 171 | 3.167(1) | 170 | 3.190(2) | 171 |
|          | Cu1-Cu3     | J$_{13}$ this work | 3.1114(8) | 118 | 3.393(2) | 145 | 3.416(2) | 139 |
|          | Cu2-Cu2     | J$_{22}$ this work | 3.0141(9) | 230 | 3.135(1) | 190 | 3.117(1) | 198 |
|          | Cu2-Cu3     | J$_{23}$ this work | 3.0069(8) | 230 | 3.109(2) | 29 | 2.977(2) | 19 |
|          | Cu3-Cu3     | J$_{33}$ this work | 4.1385(7) | 26 | 2.999(2) | 36 | 2.977(2) | 42 |
|          | Cu3-Cu2     | J$_{23}$ this work | 3.0069(8) | -2 | 3.019(2) | 29 | 2.977(2) | 19 |
|          | Cu1-Cu1     | J$_{11}$ this work | 5.1332(7) | 16 | 5.124(2) | 14 | 5.165 (3) | 14 |
|          | Cu1-Cu2     | J$_{12}$ this work | 6.8707(8) | 0 | 8.299(3) | 0 | 8.544(4) | 0 |
|          | Cu1-Cu3     | J$_{13}$ this work | 7.4259(8) | 0 | 8.015(5) | 0 | 8.340(5) | 0 |
|          | Cu2-Cu3     | J$_{23}$ this work | 4.3343(7) | 0 | 4.313(2) | 0 | 4.444(3) | 0 |
|          | Cu2-Cu2     | J$_{22}$ this work | 4.3616(8) | 0 | 4.288(3) | 0 | 4.289(3) | 0 |
|          | Cu3-Cu3     | J$_{33}$ this work | 4.2728(8) | 0 | 4.281(3) | 0 | 4.231(2) | 0 |
|          | Cu3-Cu2     | J$_{32}$ this work | 6.3316(8) | 9 | 6.375(3) | 11 | 6.378(3) | 9 |
|          | Cu2-Cu3     | J$_{23}$ this work | 6.3485(8) | 7 | 6.270(3) | 9 | 6.333(3) | 9 |
Another argument supporting our scenario can be derived by fitting magnetic susceptibility data with an effective spin model, where hexamers are represented by $S = 1$ units. At first glance, Haldane spin chain with $J = 3.9$ K gives a decent description of the magnetic susceptibility of Na$_2$Cu$_3$O(SO$_4$)$_3$ below 60 K (Fig. 3a), but the associated spin gap of $0.41J \sim 1.6$ K is clearly too small to account for the spin gap of 4-5 K observed experimentally.$^{10}$

![Fig. 3: (a) Comparison of the susceptibility fits for Na$_2$Cu$_3$O(SO$_4$)$_3$ using the $S = 1$ chain (Haldane chain) and $S = 1$ square-lattice models, with the latter model revealing magnetic ordering at $T_N = 3.3$ K. The inset shows magnetization curves calculated with the same parameters and depicted using the same color code at a low temperature of about 0.2 K to highlight field-induced transitions caused by the closing of the spin gap in the $S = 1$ chain and the closing of the magnon gap in the $S = 1$ square-lattice antiferromagnet. In the latter case, the field is applied along the easy direction, hence the spin-flop transition is much sharper than in the powder-averaged data of Fig. 2f. (b) Susceptibility fits for all three compounds using the $S = 1$ square-lattice model with the parameters described in the text. The arrows mark the transition temperatures $T_N$.](image)

The $S = 1$ square-lattice model proposed in our work leads to a susceptibility fit of comparable quality if the exchange coupling $J = 2.45$ K is supplied with the single-ion anisotropy $D = 0.74$ K (Fig. 3a). This single-ion anisotropy represented by the $D(S^2)$ term in the spin Hamiltonian is essential to explain two features of Na$_2$Cu$_3$O(SO$_4$)$_3$. First, the anisotropy triggers magnetic order even in the absence of magnetic couplings between the square planes. Our DFT calculations suggest that such couplings along the crystallographic $a$ direction are very weak, below 0.05 K, and can be excluded to a first approximation. Incidentally, even a purely 2D model without any interlayer couplings leads to $T_N \sim 3.3$ K in excellent agreement with the experimental value of 3.4 K, so it is mostly the anisotropy that is responsible for the long-range ordering in these materials. Single-ion anisotropy of the hexamers implies zero-field splitting of the ground-state $S = 1$ triplet, which is likely caused by anisotropic interactions between the $S = 1/2$ Cu$^{2+}$ ions.
Second, the excitation gap depends now not only on $J$, but also on $D$ and can be much larger than in the Haldane scenario. We illustrate this by calculating the low-temperature $M(H)$ curves for the exchange parameters obtained from the susceptibility fits (Fig. 3a, inset). Haldane chain shows an anomaly of $M(H)$ around 10 kOe where the spin gap is closed. On the other hand, the $S=1$ square lattice reveals a spin-flop transition around 25 kOe that corresponds to the closing of the excitation gap and manifests itself in the change of slope of the experimental $M(H)$ curve (Fig. 2f). Indeed, for the three samples, the gap closing at 2 K takes place at the critical fields $H_c$ of $\sim$4.5T ($\sim$0.57 meV) for $K_2Cu_3O(SO_4)_3$, $\sim$3.5T ($\sim$0.44 meV) for Na$_2$Cu$_3O(SO_4)_3$, and $\sim$5.8T ($\sim$0.73 meV) for NaKCu$_3O(SO_4)_3$, as estimated by the maximal $dM/dH$ inflection and the mean-field spin energy $E = g\mu_BSH$, $S = 1$, and $g = 2.2$ from low-T ESR. These values match rather well the direct measures of the excitation gap by INS.$^{6,10}$ In addition, only the square-lattice model would allow the field-induced transition at $H_c$ to be observed at 2 K. In the chain scenario, the gap is so small that at 2 K it is fully overcome by thermal fluctuations.

Similar fits with the $S = 1$ square-lattice model return $J = 3.05$ K, $D = 0.92$ K in NaKCu$_3$O(SO$_4$)$_3$ with the expected $T_N = 4.3$ K (experiment: 4.7 K) and $J = 2.48$ K, $D = 0.74$ K in K$_2$Cu$_3$O(SO$_4$)$_3$ with the expected $T_N = 3.3$ K (experiment: around 3.0 K), see Fig. 3b. These $J$ values apply to the spin Hamiltonian with $S = 1$ and are thus lower than $J_{23-d1}$ and $J_{23-d2}$ of about 10 K from DFT (Table 1), which describe interactions between the $S = \frac{1}{2}$ Cu$^{2+}$ ions.

These unexpected magnetic properties arise from the complex crystal structures of anhydrous copper oxysulfates, which are among the most common minerals in volcanic fumaroles with highly oxidizing conditions (e.g. Vesuvius, Italy; Tolbachik, Kamchatka Peninsula, Russia).$^{23}$ The impossibility of studying magnetism in natural mineral samples due to the presence of impurities requires new approaches to the synthetic procedures, which mimic natural geological processes on volcanoes.$^{24,25}$ Until recently, synthetic analogues were practically unknown, due to the instability of anhydrous sulfates in air and their proclivity to hydration.$^{26}$ A specific structural feature of fumarolic copper oxysulfate minerals is the formation of complex copper-oxygen substructures, i.e. the hexamers responsible for the magnetism that we analyzed in this work. The formation of hexamers leads to manifestations of interesting, often new, unusual magnetic phenomena.$^{2,27,28}$ In that sense, the (Na,K)$_2$Cu$_3$O(SO$_4$)$_3$ mineral series opens further perspectives concerning exotic magnetic compounds. Practically, in the lab we achieved the realization of novel synthetic compounds of this family, and their characterization is now in progress.
Concluding Remarks.

We revised here the magnetic models of the synthetic $A_2Cu_3O(SO_4)_3$ fedotovite ($A = K$) and puninite ($A = Na$) minerals, first proposed as original 1D quantum spin systems related to the Haldane conjecture of a gapped spin chain. The spin gaps of less than 1 meV are indeed observed experimentally. They arise from interactions between the Cu₆ hexamer units that below 100 K achieve an $S = 1$ state. However, these interactions do not run along the crystallographic $b$ direction, as proposed previously. Our comprehensive analysis of the experimental data and 1st principle results suggest that all compounds of the Na-to-K series are better described by a ($S = 1$) square-lattice interaction topology. This excludes the Haldane physics but highlights the importance of anisotropy of $S = 1$ macrospins.

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ASSOCIATED CONTENT.

The Supporting Information is available free of charge at https://pubs.acs.org/******. Single crystal data refinement Tables and ESR intensity versus temperature.
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REFERENCES.

(1) Pekov, I. V.; Zubkova, N. V.; Pushcharovsky, D. Y. Copper Minerals from Volcanic Exhalations - a Unique Family of Natural Compounds: Crystal-Chemical Review. *Acta Crystallogr. Sect. B* 2018, 74 (6), 502–518. https://doi.org/10.1107/S2052520618014403.

(2) Inosov, D. S. Quantum magnetism in minerals. *Adv. Phys.* 2018, 67, 149-252. https://doi.org/10.1080/00018732.2018.1571986

(3) Zaliznyak, I. A. A Glimpse of a Luttinger Liquid. *Nat. Mater.* 2005, 4 (4), 273–275. https://doi.org/10.1038/nmat1358.

(4) Zapf, V.; Jaime, M.; Batista, C. D. Bose-Einstein Condensation in Quantum Magnets. *Rev. Mod. Phys.* 2014, 86 (2), 563–614. https://doi.org/10.1103/RevModPhys.86.563.

(5) Janson, O.; Rouschatzakis, I.; Tsirlin, A. A.; Belesi, M.; Leonov, A. A.; Rößler, U. K.; van den Brink, J.; Rosner, H. The Quantum Nature of Skyrmions and Half-Skyrmions in Cu2OSeO3. *Nat. Commun.* 2014, 5 (1), 5376. https://doi.org/10.1038/ncomms6376.

(6) Fujihala, M.; Sugimoto, T.; Tohyama, T.; Mitsuda, S.; Mole, R. A.; Yu, D. H.; Yano, S.; Inagaki, Y.; Morodomi, H.; Kawae, T.; Sagayama, H.; Kumai, R.; Murakami, Y.; Tomiyasu, K.; Matsuo, A.; Kindo, K. Cluster-Based Haldane State in an Edge-Shared Tetrahedral Spin-Cluster Chain: Fedotovite K2Cu3O(SO4)3. *Phys. Rev. Lett.* 2018, 120 (7), 77201. https://doi.org/10.1103/PhysRevLett.120.077201.

(7) Affleck, I. Quantum Spin Chains and the Haldane Gap. *J. Phys. Condens. Matter* 1989, 1 (19), 3047–3072. https://doi.org/10.1088/0953-8984/1/19/001.

(8) Haldane, F. D. M. Nonlinear Field Theory of Large-Spin Heisenberg Antiferromagnets: Semiclassically Quantized Solitons of the One-Dimensional Easy-Axis Neel State. *Phys. Rev. Lett.* 1983, 50 (15), 1153–1156. https://doi.org/10.1103/PhysRevLett.50.1153.
(9) Starova, G. L.; Filatov, S. K.; Fundamensky, V. S.; Vergasova, L. P. The Crystal Structure of Fedotovite, Starova, G.L., Filatov, S.K., Fundamensky, V.S., and Vergasova, L.P. The Crystal Structure of Fedotovite, \(K_2Cu_3O(SO_4)_3\). *Mineral. Mag.* 1991, 55 (381), 613–616. https://doi.org/10.1180/minmag.1991.055.381.14.

(10) Furrer, A.; Podlesnyak, A.; Pomjakushina, E.; Pomjakushin, V. Spin Triplet Ground-State in the Copper Hexamer Compounds \(A_2Cu_3O(SO_4)_3\) (\(A = \text{Na, K}\)). *Phys. Rev. B* 2018, 98 (18), 180410. https://doi.org/10.1103/PhysRevB.98.180410.

(11) Hase, M.; Rule, K. C.; Hester, J. R.; Fernandez-Baca, J. A.; Masuda, T.; Matsuo, Y. A Possible Magnetic Structure of the Cluster-Based Haldane Compound Fedotovite \(K_2Cu_3O(SO_4)_3\). *J. Phys. Soc. Japan* 2019, 88 (9), 1–5. https://doi.org/10.7566/JPSJ.88.094708.

(12) Siidra, O. I.; Nazarchuk, E. V; Zaitsev, A. N.; Lukina, E. A.; Avdontseva, E. Y.; Vergasova, L. P.; Vlasenenko, N. S.; Filatov, S. K.; Turner, R. W.; Karpov, G. A. Copper Oxosulphates from Fumaroles of Tolbachik Volcano: Puninite, \(Na_2Cu_3O(SO_4)_3\) a New Mineral Species and Structure Refinements of Kamchatkite and Alumoklyuchevskite. *Eur. J. Mineral.* 2017, 29 (6), 499–510. https://doi.org/10.1127/ejm/2017/0029-2705.

(13) Scordari, F.; Stasi, F. The Crystal Structure of Euchlorine, \(NaKCu_3O(SO_4)_3\), Locality: Vesuvius, Italy. *Neues Jahrb. fur Mineral. Abhandlungen* 1990, 161, 241–253.

(14) Petricek, V.; Dušek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General Features. *Zeitschrift fur Krist.* 2014, 229 (5), 345–352. https://doi.org/10.1515/zkri-2014-1737.

(15) Koepernik, K.; Eschrig, H. Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme. *Phys. Rev. B* 1999, 59, 1743-1757.

(16) Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865-3868.

(17) Xiang, H.J.; Kan, E.J.; Wei, S.-H.; Whangbo, M.-H.; Gong, X.G. Predicting the spin-lattice order of frustrated systems from first principles. *Phys. Rev. B* 2011, 84, 224429.

(18) Nath, R.; Padmanabhan, M.; Baby, S.; Thirumurugan, A.; Ehlers, D.; Hemmida, M.; Krug von Nidda, H.-A.; Tsirlin, A.A. Quasi-two-dimensional \(S = 1/2\) magnetism of \(\text{Cu}[\text{C}_6\text{H}_2(\text{COO})_4][\text{C}_2\text{H}_5\text{NH}_3]_2\). *Phys. Rev. B* 2015, 91, 054409.

(19) Nath, R.; Tsirlin, A.A.; Khuntia, P.; Janson, O.; Förster, T.; Padmanabhan, M.; Li, J.; Skourski, Yu.; Baenitz, M.; Rosner, H.; Rouschatszakis, I. Magnetization and spin dynamics of the spin \(S = 1/2\) hourglass nanomagnet \(\text{Cu}_3(\text{OH})_2(\text{NIPA})_4\cdot10\text{H}_2\text{O}\). *Phys. Rev. B* 2013, 87, 214417.

(20) Todo, S.; Kato, K. Cluster algorithms for general-S quantum spin systems. *Phys. Rev. Lett.* 2001, 87, 047203.

(21) Albuquerque, A. F. *et al.* (ALPS collaboration) The ALPS project release 1.3: open source software for strongly correlated systems. *J. Magn. Magn. Mater.* 2007, 310 1187.

(22) Krivovichev, S. V.; Mentré, O.; Siidra, O. I.; Colmont, M.; Filatov, S. K. Anion-Centered Tetrahedra in Inorganic Compounds. *Chem. Rev.* 2013, 113 (8), 6459–6535. https://doi.org/10.1021/cr3004696.

(23) Vergasova, L. P.; Filatov, S. K. A Study of Volcanogenic Exhalation Mineralization. *J. Volcanol. Seismol.* 2016, 10 (2), 71–85. https://doi.org/10.1134/S0742046316020068.
(24) Kovrugin, V. M.; Siidra, O. I.; Colmont, M.; Mentré, O.; Krivovichev, S. V. Emulating Exhalative Chemistry: Synthesis and Structural Characterization of Ilinskite, Na[Cu$_5$O$_2$](SeO$_3$)$_2$Cl$_3$, and Its K-Analogue. *Mineral. Petrol.* **2015**, *421–430*. https://doi.org/10.1007/s00710-015-0369-3.

(25) Siidra, O. I.; Vladimirova, V. A.; Tsirilin, A. A.; Chukanov, N. V; Ugolkov, V. L. Cu$_9$O$_2$(VO$_4$)$_4$Cl$_2$, the First Copper Oxychloride Vanadate: Mineralogically Inspired Synthesis and Magnetic Behavior. *Inorg. Chem.* **2020**, *59*(4), 2136–2143. https://doi.org/10.1021/acs.inorgchem.9b02565.

(26) Siidra, O. I.; Borisov, A. S.; Lukina, E. A.; Depmeier, W.; Platonova, N. V; Colmont, M.; Nekrasova, D. O. Reversible Hydration/Dehydration and Thermal Expansion of Euchlorine, Ideally KNaCu$_3$O(SO$_4$)$_3$. *Phys. Chem. Miner.* **2019**, *46*(4), 403–416. https://doi.org/10.1007/s00269-018-1011-9.

(27) Fujihala, M.; Koorikawa, H.; Mitsuda, S.; Morita, K.; Tohyama, T.; Tomiyasu, K.; Koda, A.; Okabe, H.; Itoh, S.; Yokoo, T.; Ibuka, S.; Tadokoro, M.; Itoh, M.; Sagayama, H.; Kumai, R.; Murakami, Y. Possible Tomonaga-Luttinger Spin Liquid State in the Spin-1/2 Inequilateral Diamond-Chain Compound K$_3$Cu$_3$AlO$_2$(SO$_4$)$_4$. *Sci. Rep.* **2017**, *7*(1), 16785. https://doi.org/10.1038/s41598-017-16935-9.

(28) Prša, K.; Rønnow, H.M.; Zaharko, O.; Christensen, N.B.; Jensen, J.; Chang, J.; Streule, S.; Jiménez-Ruiz, M.; Berger, H.; Prester, M.; and J. Mesot, J. Anomalous Magnetic Excitations of Cooperative Tetrahedral Spin Clusters. *Phys. Rev. Lett.* **2009**, *102*, 177202. https://doi.org/10.1103/PhysRevLett.102.177202

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