Electronic structure of KTi(SO$_4$)$_2$·H$_2$O: An $S = \frac{1}{2}$ frustrated chain antiferromagnet

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The compound KTi(SO$_4$)$_2$·H$_2$O was recently reported as a quasi-one-dimensional spin-$1/2$ compound with competing antiferromagnetic nearest-neighbor exchange $J_1$ and next-nearest-neighbor exchange $J_2$ along the chain with a frustration ratio $\alpha = J_2/J_1 \approx 0.29$. Here, we report a microscopic model for this compound derived from density functional theory (DFT) based electronic structure calculations along with respective tight-binding models. Our (LSDA + $U_Q$) calculations confirm the quasi-one-dimensional nature of the system with antiferromagnetic $J_1$ and $J_2$, but suggest a significantly larger frustration ratio $\alpha_{DFT} \approx 0.94 - 1.4$, depending on the choice of $U_Q$ and structural parameters. Based on transfer matrix renormalization group (TMRG) calculations we find $\alpha_{TMRG} = 1.5$. Due to an intrinsic symmetry of the $J_1$-$J_2$ model, our larger frustration ratio $\alpha$ is also consistent with the previous thermodynamic data. To identify the frustration ratio $\alpha$ unambiguously, we propose performing high-field magnetization and low-temperature susceptibility measurements.

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I. INTRODUCTION

For several decades, low-dimensional magnetism has attracted great interest in solid state physics and chemistry. Since the influence of quantum fluctuations becomes especially pronounced for low-dimensional spin-$1/2$ systems, these systems have been investigated extensively, both theoretically and experimentally. Quantum fluctuations become even more important in determining the ground state and the nature of the low-lying excitations if the system under consideration exhibits strongly frustrated interactions.

Whereas pure geometrical frustration, i.e., triangular, kagomé, or pyrochlore lattices, can be realized by special symmetries in two or more dimensions, frustration in one-dimensional systems (linear chains) is generally realized by competing interactions. The simplest frustrated one-dimensional model is the $J_1$-$J_2$ model with nearest-neighbor (NN) exchange $J_1$ and next-nearest-neighbor (NNN) exchange $J_2$, where $J_2$ is antiferromagnetic. The phase diagram of this seemingly simple model is very rich. Depending on the frustration ratio $\alpha = J_2/J_1$, a variety of ground states are observed in corresponding quasi-1D systems: (i) ferromagnetically ordered chains in Li$_3$CuO$_2$ \cite{1,2} ($0 > \alpha > -0.25$); (ii) helical order with different pitch angles in LiVCuO$_3$, LiCu$_2$O$_2$, and NaCuO$_2$ \cite{3-9} ($\alpha < -0.25$); and (iii) spin-Peierls transition in CuGeO$_3$ \cite{10,11} ($\alpha \gtrsim 0.2411$), i.e., with both exchange couplings antiferromagnetic.

The possibility of subtle interplay between spin, orbital, charge and lattice degrees of freedom due to the threefold orbital degeneracy of Ti$^{3+}$ in octahedral environments, makes Ti$^{3+}$ based oxides an interesting class of materials to study. Exotic features like the orbital-liquid state in LaTiO$_3$ and the presence of strong orbital fluctuations in YTiO$_3$ have been reported.\cite{12,13} While an abundance of experimental work exists on low-dimensional spin-$1/2$ cuprates (with Cu$^{2+}$), materials based on spin-$1/2$ titanates (with Ti$^{3+}$) are rather sparse. A well known example of low-dimensional titanates is the new class of inorganic spin-Peierls materials TiOX ($X = \text{Cl, Br}$).\cite{14} Quasi-one-dimensional magnetism was observed in TiOCl and TiOBr along with a first-order transition to a dimerized nonmagnetic ground state (spin-Peierls-like) below 67 and 27 K, respectively. The main difference between $S = 1/2$ titanates and vanadates as compared to the cuprates ($3d^1$ versus $3d^4$) is that the unpaired electron resides in the $t_{2g}$ complex for the former, while occupying the $e_g$ complex for the latter. This usually results in narrow bands at the Fermi level ($E_F$) for the titanates and vanadates as compared to the cuprates, which in turn leads to small values for the exchange couplings and brings several experimental conveniences.

The susceptibility scale for the magnetic contribution to the specific heat is of the order of $T/J$, separating magnetic and phonon contribution in the specific heat ($C_P$) measurements is thus relatively easy. For the same reason, magnetization measurements can reach the saturation moment in experimentally attainable fields, thereby providing more information about the exchange parameters and the frustration regime. Thus, in many respects, spin-$1/2$ compounds with a singly occupied $t_{2g}$ orbital are an ideal object to study the physics of quasi-one-dimensional frustrated chains.

KTi(SO$_4$)$_2$·H$_2$O, a new member in the family of titanium alums has recently been synthesized.\cite{15} The titanium ions are in the Ti$^{3+} (d^1)$ oxidation state in this material. Specific heat and susceptibility measurements suggest that KTi(SO$_4$)$_2$·H$_2$O is a $S = 1/2$ frustrated chain system. Fits to the susceptibility data using exact diagonalization on up to 18 spins resulted in estimates for leading exchanges $J_1 = 9.46$ K and $J_2 = 2.8$ K, both antiferromagnetic (AFM) with a frustration ratio $\alpha = 0.29$. In the well-studied $J_1$-$J_2$ frustrated chain model with both interactions being AFM, the model undergoes a quantum phase transition at $\alpha \sim 0.2411$ to a twofold degenerate gapped phase, and for $\alpha \gtrsim 0.2411$ the system will exhibit spontaneous dimerization.\cite{16-22} In light of this result, KTi(SO$_4$)$_2$·H$_2$O would be expected to occupy the highly
interesting region of the phase diagram, with a small gap \( \Delta < J_1/20 \).\textsuperscript{15,22}

Here, we report the results of an electronic structure analysis from first principles, carried out to obtain a microscopic picture of the origin of the low-dimensional magnetism in KTi(SO\(_4\))\(_2\)-H\(_2\)O. The magnetically active orbital is identified using band-structure calculations followed by subsequent analysis of the exchange couplings. The calculated \( J \)'s have the same sign as the experiments (i.e., AFM), but the estimated frustration ratio \( \alpha \) is considerably larger compared to the experimental findings. We explore in detail the reasons for this discrepancy and propose an alternative solution that fits the experimental data, as well as being consistent with our band structure calculations. To this end, we have simulated the temperature dependence of magnetic susceptibility using the transfer matrix renormalization group (TMRG) method to unambiguously identify the exchange couplings that describe the microscopic magnetic model for KTi(SO\(_4\))\(_2\)-H\(_2\)O. On the basis of these results, we suggest performing high-field magnetization measurements, which should be a decisive experiment to identify the precise frustration ratio \( \alpha \). The influence of crystal water on the observed ground state is also discussed in detail.

The remainder of the manuscript is organized as follows. The crystal structure of KTi(SO\(_4\))\(_2\)-H\(_2\)O is described in Sec. II. The details of the various calculational methods are collected in Sec. III. The results of the density functional theory based calculations, including the band structure and the accordingly derived microscopic model, is described in Sec. IV. The outcome of the TMRG simulations is compared to the previous experiment in Sec. V, which is followed by a discussion and summary in Sec. VI.

II. CRYSTAL STRUCTURE

Throughout our calculations, we have used the recently determined experimental\textsuperscript{15} lattice parameters in the monoclinic space group (\( \text{P}2_1/m \)) of KTi(SO\(_4\))\(_2\)-H\(_2\)O: \( a = 7.649 \) Å, \( b = 5.258 \) Å, \( c = 9.049 \) Å and \( \beta = 101.742^\circ \). The crystal structure, which is isomorphous to that of the mineral krasusite,\textsuperscript{23} KFe(SO\(_4\))\(_2\)-H\(_2\)O, is displayed in Fig. 1. Isolated pairs of chains (“double chains”) of TiO\(_6\) octahedra run along the crystallographic \( b \) axis. The octahedra are distorted and have no edge-sharing or corner-sharing oxygen atoms. The SO\(_4\) tetrahedra corner share with three adjacent TiO\(_6\) octahedra, forming an isosceles triangle. These triangles edge share to make up the double chains. The single chains are displaced with respect to each other both laterally and vertically. Large K\(^+\) ions isolate the double chains along \( a \), while along \( c \) the chains are separated by water molecules that share the oxygen atom with the TiO\(_6\) octahedra. The water molecules are oriented in the \( ac \) plane. All of the octahedral O-Ti-O bond angles deviate slightly from 90° and there are three pairs of Ti-O bond lengths of 2.001 Å, 2.056 Å (in the \( ab \) plane), and 2.043 Å (along \( c \)). The shortest Ti-Ti distance is 4.93 Å and is between nearest neighbors (NN) on the adjacent chains (\( t_1 \) in Fig. 1). Within the chains, neighboring Ti are 5.23 Å apart (\( t_2 \) in Fig. 1). By analogy with the \( J_1 - J_2 \) Heisenberg model, we will call the magnetic interactions corresponding to the shorter distance (NN) \( J_1 \) and the longer distance (next-nearest neighbors, NNN) \( J_2 \). In case of a perfect octahedral environment, the three \( t_{2g} \) states would be degenerate and thus warrant additional effects (i.e., lattice distortion, spin/charge/orbital ordering) to lift the degeneracy and allow for an \( S = 1/2 \) singlet ground state for a Ti\(^{3+}\) ion.\textsuperscript{14,24} In KTi(SO\(_4\))\(_2\)-H\(_2\)O, there is a small distortion of the octahedra and, consequently, splitting of the \( t_{2g} \) levels can be expected. The related case of TiOCl, another system containing Ti\(^{3+}\) ions, also possesses a distorted arrangement of TiCl\(_2\)O\(_4\) octahedra, though the distortions are much larger with equatorial Ti-O and Ti-Cl bond lengths of 2.25 Å and 2.32 Å, respectively, and an apical Ti-O bond length of 1.95 Å. Consequently, the \( t_{2g} \) orbitals in TiOCl were thought to split into a lower energy \( d_{xy} \) and higher energy \( d_{xz,yz} \) orbitals. Electronic structure calculations confirmed this interpretation and revealed the magnetically active orbital for the \( S = 1/2 \) chains in TiOCl was indeed the lower energy \( d_{xy} \) orbital.\textsuperscript{14,25}
though a prolonged discussion of possible orbital fluctuations ensued afterwards. Therefore an analysis of KTi(SO₄)₂·H₂O from the structural point of view alone is not sufficient to determine the ground state of the system. Detailed calculations are necessary to understand the correct orbital and magnetic ground state of the system.

III. CALCULATIONAL DETAILS

The DFT calculations were performed using a full potential nonorthogonal local orbital code (FPLO) within the local (spin) density approximation [L(S)DA].²⁶,²⁷ The energies were converged on a dense k mesh with 300 points for the conventional cell in the irreducible wedge of the Brillouin zone. The Perdew and Wang flavor²⁸ of the exchange correlation potential was chosen for the scalar relativistic calculations. The strong on-site Coulomb repulsion of the Ti 3d orbital was taken into account using the L(S)DA + U method, applying the “atomic limit” double counting term. The projector on the correlated orbitals was defined such that the trace of the occupation number matrices represent the 3d gross occupation. Maximally localized Wannier functions (WF) were calculated for the Ti 3d orbitals to acquire the transfer integrals, also using FPLO.²⁹ The exchange couplings are computed using an LDA based model approach, by mapping the results of the LDA calculations onto a tight-binding model (TBM), which is then mapped onto a multiorbital Hubbard model, and subsequently to a Heisenberg model because the system belongs to the strong correlation limit $U_{\text{eff}} \gg t$ ($t$ is the leading transfer integral at half-filling and $U_{\text{eff}}$ is the effective on-site Coulomb repulsion). Another method of evaluating the exchange couplings is to map the LSDA + $U_d$ total energies of various supercells with collinear spin configurations to a classical Heisenberg model. The supercells used to calculate $J_1$ and $J_2$ were sampled using 300 and 100 k points, respectively.

The magnetic excitation spectrum of frustrated spin chains was simulated using exact diagonalization code from the ALPS package.³⁰ We used periodic boundary conditions and considered finite lattices comprising up to $N = 32$ spins.

The magnetic susceptibility of infinite frustrated spin chains was simulated using the transfer matrix renormalization group (TMRG) technique.³¹ For each simulation, we kept 120–160 states, the starting inverse temperature was set to 0.05$J_1$, and the Trotter number was varied between $4 \times 10^3$ and $16 \times 10^3$. The results were well converged for the whole temperature range of the experimental curve from Ref. 15.

IV. ELECTRONIC STRUCTURE CALCULATIONS

A. Local density approximation

Since there exists no previous report on the electronic structure of KTi(SO₄)₂·H₂O, we begin by analyzing the results from a nonmagnetic LDA calculation. In a simplified, fully ionic model, each Ti$^{3+}$ ion is surrounded by a slightly distorted octahedron of O$^2-$ ions. The pseudo octahedral coordination dictates a set of local axes for the conventional $e_g$ and $t_{2g}$ orbitals. The local coordinate system is chosen as $\hat{z} | c$, and $\hat{x}$ and $\hat{y}$ axes are rotated by 45° around $c$ with respect to the original $a$ and $b$ axes. The nonmagnetic total and orbital resolved density of states (DOS) are collected in Fig. 2. The presented part of the valence band is predominantly comprised of Ti 3d and O 2$p$ states belonging to TiO₆ octahedra. The states belonging to sulfur (not shown) lie mainly below $-8$ eV. The contribution from K, S, and H sites are negligible in the displayed energy range. (Bottom) Ti 3d orbital resolved DOS. The $t_{2g}$ and $e_g$ complexes are split by a ligand-field splitting of about 2 eV. The $d_{xz}$, orbital and the $d_{yz}$ orbital are very close and split from the broad $d_{xy}$ (larger bandwidth) orbital.

![FIG. 2. (Color online) (Top) Total and partial DOS obtained within LDA for KTi(SO₄)₂·H₂O. The valence panel is predominantly comprised of Ti 3d and O 2p states. The sulfur states (not shown here) lie mainly below $-8$ eV. The contribution from K, S, and H sites are negligible in the displayed energy range. (Bottom) Ti 3d orbital resolved DOS. The $t_{2g}$ and $e_g$ complexes are split by a ligand-field splitting of about 2 eV. The $d_{xz}$, orbital and the $d_{yz}$ orbital are very close and split from the broad $d_{xy}$ (larger bandwidth) orbital.](image-url)
and the O 2p states close to $E_F$ is less than 10% and similar to other systems where Ti occurs in the $d^1$ configuration. This scenario is different from the cuprates ($d^9$) where 30% of the contribution to the states at $E_F$ stems from O 2p. This fundamental difference in the strength of the hybridization between the transition metal ions and the oxygen ligands comes from the relative energies ($\Delta$) of the oxygen p and the transition metal d bands. In cuprates, the highest (half-filled) $d_{x^2−y^2}$ orbital and the uppermost (filled) oxygen p orbitals are rather close in energy ($\Delta \sim 2$ eV) resulting in a strong pd hybridization. In titanates, on the contrary, the $t_{2g}$ orbitals lie much higher in energy than the uppermost (filled) oxygen p orbitals ($\Delta \geq 3$ eV) and therefore exhibit significantly less pd hybridization. Upon hole doping, the holes would formally appear in the oxygen p orbitals for cuprates and in one of the $t_{2g}$ orbitals for titanates, characterizing them as charge-transfer and Mott-Hubbard systems, respectively.

Experimentally, KTi(SO$_4$)$_2$H$_2$O is an insulator, but a metallic solution is obtained within LDA. Such metallic results from LDA are well known and understood to arise from the inadequate treatment of the strong Coulomb correlation of the 3d orbitals. Therefore the orbital dependence of the Coulomb and exchange interactions are taken into account in a mean-field-like approximation using the LSDA + $U$ approach (Sec. IV C). As mentioned previously in Sec. II, the distorted octahedra in TiOCl split the $t_{2g}$ states into a lower lying singlet ($a_1$) and a higher energy doublet ($d_{x^2−y^2}$). Presuming no further symmetry breaking, adding correlations, the choice of the orbital for occupying the unpaired electron of the Ti$^{3+}$ ion in TiOCl is rather straightforward: the singlet $d_{x^2−y^2}$. On the other hand, for KTi(SO$_4$)$_2$H$_2$O the pseudo-octahedral ligand field fully splits the $t_{2g}$ states and removes the threefold degeneracy. The on-site energy from the Wannier functions for the $d_{x^2−y^2}$ orbital is close to $E_F$ and is the lowest lying band of the $t_{2g}$ complex. The on-site energies of $d_{xz}$ and the broader $d_{yz}$ band (by a factor of 2) are only slightly higher in energy than the $d_{xz}$ band by 0.04 and 0.2 eV, respectively. Since the three $t_{2g}$ orbitals are quite close in energy, a subtle balance between the orbitals is expected and the choice for the half-filled orbital is not clear a priori. Moreover, one should also carefully consider the possibility of an orbitally ordered solution. Even the undoped, low-dimensional $S = 1/2$ cuprates that possess an extensive literature, where the magnetic model is generally understood to be governed by the half-filled $d_{x^2−y^2}$ orbital, can sometimes show surprises. For example, the CuO$_6$ octahedral environment in the insulating $S = 1/2$ quasi-1D system CuSb$_2$O$_6$ is less distorted than usual, so that the cubic degeneracy for the $e_g$ ligand-field states are only slightly lifted. The energy difference between the narrow $d_{x^2−y^2}$ and the broad $d_{3z^2−r^2}$ related band centers is about 0.5 eV only, compared with about 2 eV for standard cuprates. Inclusion of correlations, changes the order of the bands and the broad band wins with the unpaired electron occupying the $d_{3z^2−r^2}$ orbital instead of the standard $d_{x^2−y^2}$ in CuSb$_2$O$_6$. In comparison to CuSb$_2$O$_6$, the crystal field splitting in KTi(SO$_4$)$_2$H$_2$O is even smaller: 0.3 eV versus 0.04–0.2 eV, respectively. Thus it is pertinent to do a careful analysis and consider different scenarios beyond just the crystal field to arrive at a definitive answer.

We take into account the strong electronic correlations of the Ti 3d states via two possible ways: (a) mapping the results from LDA first to a multiorbital tight-binding model (TBM) using the Wannier functions basis to obtain the transfer integrals ($t_i$). At half-filling, when $U$ is much larger than the bandwidth, the spin degrees of freedom are well described by an $S = 1/2$ Heisenberg Hamiltonian with an antiferromagnetic part of the exchange interactions $J_i^{AFM} \simeq 4t_i^2/U_{eff}$. The ferromagnetic contributions are evaluated by considering the Kugel-Khomskii model, which considers all the 3d levels and the intra-atomic exchange interaction ($J_{eff}$). (b) Another way is by performing LSDA + $U_d$ total energy calculations for various collinear spin configurations and mapping the energy differences onto a classical Heisenberg model to obtain the total exchanges $J_i$. At this juncture, the difference between the two parameters used to incorporate the effects of strong correlations, $U_{eff}$ and $U_d$, must be clarified. The former is applied to LDA bands, which include the effects of hybridization between the metal atoms and ligands, while $U_d$ is applied to atomiclike 3d orbitals. This necessitates using different values for these two parameters.

### B. Wannier functions

Wannier functions are essentially a real-space picture of localized orbitals and can be used to enhance the understanding of bonding properties via an analysis of factors such as their shape and symmetry. Before analyzing the WF’s (shown in Fig. 4), one should keep in mind that the two nearest-neighbor (NN) Ti atoms do not belong to the same chain but to the pair-chain displaced along the c axis (see lower panel of Fig. 1). By fitting (using exact diagonalization) the low-temperature magnetic susceptibility, the recent experimental report suggests that the AF-NN interaction $J_1$ is larger than the AF-NNN interaction $J_2$. Therefore one expects to observe large tails at oxygen sites from the WF’s bending towards the NN Ti atoms, as this facilitates the Ti-O-Ti superexchange. Foremost, we observe that the WF’s resemble the atomiclike $d$ orbitals. There is a lot of oxygen hybridization tails, but...
not a strong $t_{2g}-\epsilon_g$ mixing (refer to Table I). The Ti $d_{xy}$ WF is composed of contributions from the $d_{xy}$ orbital as well as tails on the oxygen sites in the $xy$ plane, although these do not point towards the NN Ti atom. The $d_{yz}$ WF, on the other hand, has tails on all six oxygen sites of the TiO$_6$ octahedra, and all point towards the NN Ti atom. Interestingly, the $d_{xz}$ WF not only has tails on the oxygen sites bending towards the NN Ti, but also has tails on one of the hydrogen site belonging to the crystal water molecule. Such an effect is arising from the hybridization effect of the O and H orbitals. The effects of hybridization involving the H atom in the $d_{xz}$ WF is comparatively less than the $d_{xz}$, since no extended tails are observed on the H site.

C. Tight-binding model using Wannier functions

Though LDA fails in reproducing the insulating ground state of KTi(SO$_4$)$_2$·H$_2$O system, it still provides valuable information about the orbitals involved in the low-energy physics, as well as their corresponding interactions strengths. As mentioned previously, the strong Coulomb correlations favor full polarization, and a detailed analysis is necessary to identify the ground state for the fully polarized $d$ orbital.

### TABLE I. The NN and NNN transfer integrals $t_1$ and $t_2$ and on-site energies $\epsilon_0$ obtained using the WF technique for all the five $d$ orbitals of Ti. All the $t$'s are in meV while $\epsilon_0$ is in eV.

<table>
<thead>
<tr>
<th>$t_1$ (meV)</th>
<th>$x_z$</th>
<th>$y_z$</th>
<th>$x_y$</th>
<th>$x^2 - y^2$</th>
<th>$3z^2 - r^2$</th>
<th>$\epsilon_0$</th>
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<td>7.8</td>
<td>53.4</td>
<td>0.045</td>
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<td>$y_z$</td>
<td>3.7</td>
<td>1.7</td>
<td>3.1</td>
<td>9.5</td>
<td>32.8</td>
<td>0.087</td>
</tr>
<tr>
<td>$x_y$</td>
<td>1.1</td>
<td>1.4</td>
<td>31.1</td>
<td>21.1</td>
<td>6.1</td>
<td>0.243</td>
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<tr>
<td>$x^2 - y^2$</td>
<td>7.8</td>
<td>9.5</td>
<td>2.3</td>
<td>12.8</td>
<td>23.1</td>
<td>0.209</td>
</tr>
<tr>
<td>$3z^2 - r^2$</td>
<td>53.4</td>
<td>32.8</td>
<td>55.4</td>
<td>128</td>
<td>231</td>
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<table>
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<th>$x_y$</th>
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<tr>
<td>$3z^2 - r^2$</td>
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<td>49.7</td>
<td>2.6</td>
<td>77.6</td>
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Noting that the magnitude of the leading hopping integrals $t_1$ and $t_2$ (the paths are indicated in Fig. 1) are collected in Table I. All other $t$'s beyond NNN are less than 1 meV for all the five orbitals and therefore can be neglected for the chain physics. The two main hopping terms are thus confined to interactions between the Ti sites within each $S=1/2$ “double chain”, consistent with the experimental observations$^{15}$ of displaying low-dimensional magnetic properties. Given that the matrix subspace of the $t_{2g}$ manifold is diagonally dominant (see Table II), it is conceivable that the inter-$t_{2g}$ mixing is small enough such as to justify an orbital by orbital tight-binding fit for this orbital subspace, discarding the coupling between different $t_{2g}$ Wannier functions. An exception is the $t_{1, xz-yz}$ hopping, which is of the same size as the $t_{2g}$ off-diagonal elements. However, this orbital is of minor importance in our final analysis (see below), and hence the general argument holds to a good approximation. Although we do not refrain ourselves to such a TB analysis, it would yield very similar results to our Wannier functions analysis. Albeit we obtain some large hoppings between the $t_{2g}$ and $\epsilon_g$ manifolds, these transfer integrals do not influence the exchange constants much due to the large differences in their on-site energies as shown below. The individual exchange constants ($J_{ij}$) are calculated.

### TABLE II. The FM ($J_1^{FM}$, $J_2^{FM}$), AFM ($J_1^{AFM}$, $J_2^{AFM}$), and the total exchange integrals ($J_1$, $J_2$) calculated applying the Kugel-Khomskii model [Eq. (1)] for the Ti $t_{2g}$ orbitals, using $U_{eff} = 3.3$ eV and $J_{eff} = 1$ eV. The $J$ values are in units of degrees of Kelvin. For comparison, the experimental values are $J_1^{exp} = 9.46$ K and $J_2^{exp} = 2.8$ K.$^{15}$ The last column is the frustration ratio $\alpha$ evaluated as $J_2/J_1$. We have additionally calculated the dependence of $J$’s to the choice of $U_{eff}$ and $J_{eff}$, which are collected in Supplemental Material.

<table>
<thead>
<tr>
<th>$J_1^{FM}$</th>
<th>$J_2^{FM}$</th>
<th>$J_1^{AFM}$</th>
<th>$J_2^{AFM}$</th>
<th>$J_1$</th>
<th>$J_2$</th>
<th>$\alpha$</th>
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<td>21</td>
<td>11</td>
<td>-0.4</td>
<td>10.6</td>
</tr>
<tr>
<td>$d_{yz}$</td>
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<td>-2.7</td>
<td>17.8</td>
<td>10</td>
<td>-1.3</td>
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<td>-7.0</td>
<td>-6.9</td>
<td>243</td>
<td>-6.0</td>
<td>237</td>
</tr>
</tbody>
</table>
using the expression of the Kugel-Khomskii model,\(^3\)

\[ J_{ij,\alpha} = \frac{4t_{ij,\alpha\alpha}^2}{U_{\text{eff}}} - \sum_{\beta} \left(\frac{4t_{ij,\alpha\beta}^2}{U_{\text{eff}}} + \Delta_{\alpha\beta}^2\right) \left(\frac{4t_{ij,\alpha\beta}^2}{U_{\text{eff}}} + \Delta_{\alpha\beta} - J_{\text{eff}}\right) \]

\( = J_{\text{AFM}} - J_{\text{FM}}. \tag{1} \)

where \( i \) and \( j \) denote the sites, \( \alpha \) is the magnetically active orbital at site \( i \), \( \beta \) is one of five \( d \) orbitals at site \( j \) and \( t_{ij,\alpha\beta} \) is the transfer integral of orbital \( \alpha \) at site \( i \) to orbital \( \beta \) at site \( j \), \( \Delta_{\alpha\beta} \) are the crystal field splittings between orbitals \( \alpha \) and \( \beta \). \( U_{\text{eff}} \) and \( J_{\text{eff}} \) denote the on-site Coulomb repulsion and Hund’s coupling, respectively. The first term in the above equation is the AFM superexchange and describes the AFM coupling due to the hopping between active \( d \) orbitals. The second term is the sum of the exchange interactions between the active orbital \( \alpha \) and the rest of the \( d \) complex, and thus ferromagnetic (FM). For TiOCl, a \( U_{\text{eff}} \sim 3.3 \text{ eV} \) was shown to provide good agreement between calculated exchange constants and susceptibility measurements.\(^3\) The same value of \( U_{\text{eff}} = 3.3 \text{ eV} \) with a \( J_{\text{eff}} = 1 \text{ eV} \) has been used here for KTi(SO\(_4\))\(_2\)·H\(_2\)O, and the \( J \)’s obtained thus are collected in Table II. Only the exchanges for the \( t_{2g} \) complex are shown here, since the single unpaired Ti 3\( d \) electron is very unlikely to occupy the higher-lying \( \epsilon_g \) states. The \( J \)’s are predominantly AFM for the lower energy \( d_{xz} \) and as well as the slightly higher lying \( d_{yz} \) band, and furthermore, the \( J \)’s are of similar order of magnitude as compared to the experimental report (\( J_{1\text{exp}} = 9.46 \text{ K} \), \( J_{2\text{exp}} = 2.8 \text{ K} \)).\(^5\) To the contrary, the calculated NN and NNN \( J \)’s for the \( d_{xy} \) band are much smaller and larger in energy respectively, compared to the experimental report. This large difference in the energy scale of the magnetic exchanges for the \( d_{xy} \) band implies that this orbital might be a rather unlikely choice for full polarization (an even more clear picture emerges in the following section when performing LSDA + \( U \) calculations). Furthermore, we have checked the robustness of our calculated \( J \)’s as a function of the parameters \( U_{\text{eff}} \) and \( J_{\text{eff}} \) in the physically relevant sector. We varied \( U_{\text{eff}} \) in the range of 2 to 4 eV and \( J_{\text{eff}} \) in the range of 0.5 to 1 eV and find that \( \alpha_{d_{xz}} \) and \( \alpha_{d_{yz}} \) were (i) very robust in the entire parameter region, varying at maximum by about 10%, and (ii) always significantly larger than \( \alpha_{\text{exp}} \) (see Supplemental Material\(^3\) for further details). In contrast, \( \alpha_{d_{xy}} \) changes strongly in the relevant parameter range, but remains far too large in the entire region and thus incompatible with the experimental findings.

D. Density functional theory +\( U \)

Besides obtaining estimates for the various couplings in the system, the TBM also allows for approximating the number of Ti-Ti neighbors that needs to be considered when performing the more involved and time consuming LSDA + \( U \) supercell calculations. Since the AFM exchanges obtained from the TBM beyond the NNN are less than 1 meV and because FM interactions beyond second neighbors should also be small, we constructed two supercells to obtain the values of the short-ranged exchanges \( J_1 \) and \( J_2 \). Using different initial density matrices for the Ti 3\( d \) orbitals, one can correlate (fill the spin-up band with one electron and leave the spin-down band empty), the bands belonging to different irreducible representations. For KTi(SO\(_4\))\(_2\)·H\(_2\)O, we tried to spin polarize each of the three \( t_{2g} \) bands. We considered \( U_{\text{d}} \) values ranging from 2.5–4.5 eV.\(^3\) First, let us consider the \( d_{xz} \) and \( d_{yz} \) orbitals, which gave similar AFM exchange constants in our TBM. In all of our LSDA + \( U_d \) calculations, the scenario in which the \( d_{xz} \) band was spin polarized had the lowest energy. Spin-polarizing \( d_{yz} \) required an additional energy of 350 meV per Ti\(^{3+} \) ion. This energy scale is comparable to the bandwidth of these orbitals. Incidentally, all our attempts to spin polarize \( d_{xy} \) resulted in the system converging to the lowest energy \( d_{xz} \) solution. We were also unable to stabilize different orbitally ordered scenarios (i.e., one Ti ion with a spin-polarized \( d_{xz} \) orbital and the NN Ti ion with a spin-polarized \( d_{yz} \) orbital). This alludes to the fact that the (local) magnetic ground state in KTi(SO\(_4\))\(_2\)·H\(_2\)O is very likely determined by the Ti 3\( d_{xz} \) orbital. The next question to answer is whether the exchange constants obtained for the \( d_{xz} \) orbitals are consistent with the experimental findings. We obtain effective exchange constants by performing LSDA + \( U_d \) calculations of differently ordered spin configurations (FM, AFM, and ferrimagnetic) and mapping the energies to a Heisenberg model. Among the considered spin configurations, the AFM spin configuration was always more favorable (lower total energy) than the FM. The exchange constants and the frustration ratio \( \alpha \) are collected in Fig. 5. For comparison, we have displayed the values for both \( d_{xz} \) and \( d_{yz} \) orbitals. For the range of \( U_d \) values considered here, \( J_{d_{xz}}^{\text{exp}} \) is comparable to experimental findings while \( J_{d_{yz}}^{\text{exp}} \) is larger by almost an order of magnitude. Comparing the total \( J \)’s in Fig. 5 with the \( J_{\text{AFM}} \) obtained from TBM in Table I, we can infer that there is a significant FM component to the NN (\( J_1^{\text{FM}} \)) while the FM component to the NNN (\( J_2^{\text{FM}} \)) is quite negligible. Though the \( J \)’s do not vary very much for \( U_d = 2.5 \) to 4.5 eV, an appropriate \( U_d \) value needs to be chosen for comparison with experiments. Spin- and orbital-unrestricted Hartree-Fock calculation of the on-site Coulomb interaction

FIG. 5. (Color online) The total exchange constants (top) and the frustration ratio (bottom) as a function of \( U_d \) for \( d_{xz} \) and \( d_{yz} \) orbitals. The NN total exchange \( J_1 \) (full symbols) and NNN total exchange \( J_2 \) (empty symbols) do not vary much for the considered range of \( U_d \) (2.5 to 4.5 eV) values. The experimental results (Ref. 15) are indicated by thick dashed lines.
ELECTRONIC STRUCTURE OF $\text{KTi(SO}_4\text{)}_2\cdot\text{H}_2\text{O}$ . . .  

The small energy scale of the leading couplings leads to sizable error bars for the $J_1$ and $J_2$ values estimated from LSDA + $U_d$ calculations. To refine the model parameters, we use the analytical expressions for the high-temperature part of the magnetic susceptibility of a frustrated Heisenberg chain, the high-temperature series expansion (HTSE). 40 Typical for a local optimization procedure, the results are dependent on the initial values. If we start from the $J_1 > J_2$ limit, HTSE yields $J_1 \approx 9.6 \text{ K}$ and $J_2 \approx 2.9 \text{ K}$, very close to the $\alpha = 0.29$ reported in Ref. 15. In contrast, if we proceed from the $J_2 > J_1$ regime, we obtain $J_1 \approx 5.4 \text{ K}$ and $J_2 \approx 8.1 \text{ K} (\alpha = 1.5)$, in accord with our LSDA + $U_d$ calculations. Thus HTSE yields two ambiguous solutions.

HTSE typically converges only for temperatures higher or comparable with the magnetic energy scale ($T \gtrsim J$). To verify, whether both solutions agree with the experimental $\chi(T)$ at lower temperatures, we simulate the temperature dependence of reduced magnetic susceptibility $\chi^*$ using TMRG, and fit the resulting $\chi^*(T/\max(J_1, J_2))$ dependencies to the experimental curve. In this way, we again find that besides the previously reported $\alpha = 0.29$ solution, the $\alpha = 1.5$ curve with $J_1 = 5.4 \text{ K}, J_2 = 8.1 \text{ K}, g = 1.74,$ and $\chi_0 = 5.9 \times 10^{-5} \text{ emu/mol}$ also yields an excellent fit to the experimental magnetic susceptibility (see Fig. 6). The difference curves evidence that both $\alpha = 0.29$ and 1.5 provide a good description of the experimental $\chi(T)$ data. Note that the fit for $\alpha = 1.5$ is slightly better (see Fig. 6, inset), but is likely not significant enough to prefer one of the two solutions.

The coexistence of the two solutions actually manifests the inner symmetry of the frustrated chain model. As a trivial example, the uniform chain limit can be described with $\alpha = 0$ ($J_1 \neq J_2 = 0$) as well as $\alpha = \infty$ ($J_1 = 0, J_2 \neq 0$). The $\alpha = 0.29$ and 1.5 solutions are also related, although in a less trivial way. To pinpoint this relation, we briefly revisit the phase diagram of the frustrated chain model. The $\alpha = 0$ limit corresponds to the exactly solvable gapless Heisenberg chain model. This GS is robust against small frustrating

For various transition-metal oxides, recommend a $U_d$ value of 4 eV for Ti$^{3+}$ ions. 36 Using that value of $U_d$ as a benchmark, we obtain, $J_1^{\text{exp}} \approx 12 \text{ K}, J_2^{\text{exp}} \approx 13.4 \text{ K},$ and $\alpha_{\text{exp}} \approx 0.94 \pm 0.15$ ($J_1^{\exp} = 9.46 \text{ K}, J_2^{\exp} = 2.8 \text{ K},$ and $\alpha = 0.29$). The error bar is calculated from the difference in the $\alpha$ values between 3 $\leq U_d \leq 4$. The calculated value of $\alpha_{\text{exp}} = J_1^{\text{exp}}/J_2^{\text{exp}}$ is larger than the experimental value by a factor of 3 for the $d_z^2$ orbital. The calculated $\alpha_{\text{exp}} = 0.60 \pm 0.01$ for the energetically unfavorable $d_z^2$ orbital is also significantly larger than the experimental value. Altogether the $S = 1/2$ frustrated chain magnetism in KTi(SO$_4$)$_2$·H$_2$O is established in both LDA and LSDA + $U_d$ calculations, our results for $\alpha$ are not consistent with the experiments. Nonetheless, both our calculation and experiment suggest an $\alpha$ in the highly interesting region ($0.241 < \alpha < 1.8$) of the spin-1/2 frustrated chain phase diagram.

One reason for the overestimation of $\alpha$ in our calculations might be related to the O-H bond length in KTi(SO$_4$)$_2$·H$_2$O. Recent reports on Cu$^{2+}$ spin-1/2 kagome lattice systems (Ref. 37) show that shortening of the O-H bond length can have dramatic impact on the NN magnetic exchange, including the sign change from AFM to FM. However, it is well known that obtaining the correct O-H bond length via x-ray diffraction in a system containing heavy atoms is at best difficult. OH$^-$ groups in oxides have been shown to have a typical equilibrium bond length of $\approx 1$ Å. 38 For KTi(SO$_4$)$_2$·H$_2$O, the reported O-H bond length is only 0.874 Å, thus more than 10% smaller than this value. Therefore one possible reason for the larger frustration ratio $\alpha$ in LSDA + $U_d$ calculations as compared to experiments might arise from the possibly underestimated O-H bond length. 39

We have therefore allowed the O-H bond length to relax (keeping the H-O-H angle fixed). Keeping the TiO$_6$ octahedra rigid, we relaxed the H position with respect to the total energy and obtained an optimized O-H bond length of about 1 Å, in accordance with the empirical expectations. 37,38 Recalculating the exchange constants using the optimized O-H distance, we obtain for $U_d = 4.0$ eV, $J_1^{\text{calc}} = 10 \text{ K}, J_2^{\text{calc}} = 14.2 \text{ K}$. The frustration ratio $\alpha_{\text{calc}} = 1.4 \pm 0.2$ is even larger (by 50%) than the previously calculated value using the experimental O-H bond length. This change in $\alpha$ with respect to the H position is quite dramatic, while it must be noted that the obtained $J$’s are of the same order as the experiment. It is generally accepted that total energy calculations provide accurate atomic positions. It is thus highly desirable to determine the hydrogen position precisely. In the following section, we attempt to understand the discrepancy between our calculations and the experiment.

V. TMRG CALCULATIONS

As demonstrated in Ref. 15, a frustrated Heisenberg chain model with $\alpha = 0.29$ can reproduce the experimental magnetic susceptibility curve of KTi(SO$_4$)$_2$·H$_2$O. The small $\alpha = 0.29$ implies that $J_1$ is large, while $J_2$ is small. This is at odds with our LSDA + $U_d$ calculations, where the antiferromagnetic exchange between NNN Ti atoms appears to be more efficient than the NN exchange, resulting in $\alpha > 1$. The question is then, whether the large $\alpha$ regime conforms to the experimental behavior.

We have therefore allowed the O-H bond length to relax (keeping the H-O-H angle fixed). Keeping the TiO$_6$ octahedra rigid, we relaxed the H position with respect to the total energy and obtained an optimized O-H bond length of about 1 Å, in accordance with the empirical expectations. 37,38 Recalculating the exchange constants using the optimized O-H distance, we obtain for $U_d = 4.0$ eV, $J_1^{\text{calc}} = 10 \text{ K}, J_2^{\text{calc}} = 14.2 \text{ K}$. The frustration ratio $\alpha_{\text{calc}} = 1.4 \pm 0.2$ is even larger (by 50%) than the previously calculated value using the experimental O-H bond length. This change in $\alpha$ with respect to the H position is quite dramatic, while it must be noted that the obtained $J$’s are of the same order as the experiment. It is generally accepted that total energy calculations provide accurate atomic positions. It is thus highly desirable to determine the hydrogen position precisely. In the following section, we attempt to understand the discrepancy between our calculations and the experiment.

FIG. 6. (Color online) Fits to the magnetic susceptibility. The experimental data are adopted from Ref. 15. The magnetic susceptibility of frustrated Heisenberg chains with $\alpha = 0.29$ and 1.5 ($\alpha = J_2/J_1$) was simulated using TMRG. The simulated curves were fitted to the experiment by varying the fitting parameters $J_1, g,$ and the temperature-independent contribution $\chi_0$. (Inset) Difference curves for both solutions. $\Delta \chi$ is the difference between the simulated and the experimental value.
$J_2$, up to the quantum critical point $\alpha_c \simeq 0.2411$, where a spin gap opens.\textsuperscript{17} For larger $\alpha$ values, the spin gap rapidly increases and reaches its maximum value $\Delta \simeq 0.43 J_1$ at $\alpha \simeq 0.6$. Further enhancement of $\alpha$ reduces the spin gap. In the large $\alpha$ limit ($J_2 \gg J_1$), the spin gap exhibits an exponential decay.\textsuperscript{22}

Thus, for a certain value of the spin gap $\Delta$, there are two possible $\alpha$ values: (i) with a dominant $J_1$, i.e., from the $\alpha = 0.2411$–0.6 range and (ii) with a sizable $J_2$ ($\alpha = 0.6$–$\infty$). Since $\Delta$ plays a decisive role for the shape of $\chi(T)$, both solutions yield similar macroscopic magnetic behavior. This explains the seemingly unusual fact that the experimental data for KTi(SO$_4$)$_2$·H$_2$O can be well fitted by both $\alpha = 0.29$ and $1.5$.

Unlike, e.g., $\alpha = 0$ and $\infty$, that describe the same physics, the solutions $\alpha = 0.29$ and $1.5$ are physically different despite the similar spin gaps. Spiral correlations are present in the latter case only.\textsuperscript{22} Moreover, the two solutions feature substantially different correlation lengths.\textsuperscript{22} Thus the two solutions can be distinguished by measuring a characteristic experimental feature (“smoking gun”).

For spin systems, a measurement of magnetization isotherms is technically simple, but very informative, especially for systems with weak magnetic couplings. Since the magnetic field linearly couples to the $S^z$ component of the spin, a magnetization curve reflects the energy of the lowest lying state in each $S^z$ sector. This often suffices to distinguish between ambiguous solutions. For instance, HTSE for the $J_1 - J_2$ square lattice system BaCdVO(PO$_4$)$_2$ yielded, besides the frustrated solution with an AFM $J_2$, also a nonfrustrated solution with FM $J_2$. However, the frustrated scenario was clearly underpinned by $M(H)$ measurements.\textsuperscript{41} In a recent work, $M(H)$ measurements for $A_2$CuP$_2$O$_7$ ($A = \text{Li, Na}$) resolved previous controversies concerning the magnetic dimensionality of these compounds.\textsuperscript{42}

We argue that for the frustrated Heisenberg chain model, the characteristic behavior of magnetization curve on the verge of saturation can be used to distinguish between different scenarios. In particular, the $\alpha = 0.29$ magnetization curve exhibits a well pronounced upward bending, while only a feeble bending is visible in the $\alpha = 1.5$ GS magnetization (see Fig. 7). Another relevant quantity is the saturation field:

$$H_{sat} = (g\mu_B)^{-1}E(S^z_{\text{max}}) - E(S^z_{\text{max}} - 1),$$

where $S^z_{\text{max}}$ corresponds to the fully polarized state. The energies are estimated using exact diagonalization for finite chains of $N = 32$ spins. Adopting $J_1$, $J_2$, and $g$ values from the HTSE fits, we obtain $H_{sat} \simeq 16.4$ T and $H_{sat} \simeq 18.7$ T for $\alpha = 0.29$ and $\alpha = 1.5$, respectively. Both values of saturation field lie in the experimentally accessible field range. A somewhat problematic point could be the low-energy scale of KTi(SO$_4$)$_2$·H$_2$O, which renders the typical measurement temperature of $\sim 1.5$ K as relatively high, hence the states with different $S^z$ could be substantially mixed. Still, the $\alpha = 0.29$ magnetization isotherms will retain fingerprints of the characteristic bending. Therefore we believe that a high-field (up to $\sim 20$ T) measurement of a magnetization isotherm will be an instructive and decisive experiment to distinguish between the $\alpha = 0.29$ and $1.5$ scenarios.

FIG. 7. (Color online) Ground-state magnetization of frustrated Heisenberg chains with $\alpha = 0.29$ and $\alpha = J_2/J_1 = 1.5$ ($\alpha = J_2/J_1$), simulated using exact diagonalization on finite lattices (rings) of $N = 24$ spins. Note the characteristic upward bending of the $\alpha = 0.29$ curve. (Inset) Finite-size dependence of the ground-state magnetization.

VI. SUMMARY

In conclusion, we have studied the electronic structure of KTi(SO$_4$)$_2$·H$_2$O in detail using DFT based calculations. The results of both the TBM and LSDA + $U_d$ calculations confirm beyond doubt the low-dimensional nature of the material with NN and NNN exchanges $J_1$ and $J_2$ confined to the double-chains running along the $b$ axis. We also confirm the AFM nature of the exchanges, consistent with the experimental report, with the Ti $3d_{xz}$ orbital being the magnetically active one, holding the single unpaired electron of the Ti$^{3+}$ ion. The magnitude of the calculated $J$’s are of the right order compared to the experiment, though we observe a strong dependence to the $t_{2g}$ orbital choice. Notwithstanding the small energy scale ($\sim 10$ K) of the system, we are able to obtain the correct order of the $J$’s from our DFT calculations. Additionally, we observe a sizable dependence of the estimated exchanges from the O–H bond length. This feature is clearly elucidated by calculating the Wannier functions, which show the effects of hydrogen bonding to the corresponding $t_{2g}$ orbital, which is oriented in the same plane as the crystal water molecule. Using the experimental position for hydrogen, we obtain a frustration ratio $\alpha \approx 0.94 \pm 0.15$ and a value of $\alpha \approx 1.4 \pm 0.2$ upon relaxing the hydrogen position in the crystal lattice (from LSDA + $U_d$, $U_d = 3.5 \pm 0.5$ eV). Both these values are significantly larger than the experimental value $\alpha_{exp} = 0.29$. In order to understand the origin of this discrepancy between the experiment and our calculations, we simulated the temperature dependence of the susceptibility using both the small and large values of $\alpha$. Due to an intrinsic symmetry of the $J_1 - J_2$ frustrated chain model, we show that both values of $\alpha$ provide similarly good fits to the experimental curve. Thus our calculated value of $\alpha$ is in line with the TMRG estimate of $\alpha_{TMRG} = 1.5$. Consequently, we calculated magnetization curves as a means to unambiguously distinguish the two solutions and show two features, which can be used to identify the appropriate $\alpha$ that defines the magnetic
ground state of KTi(SO$_4$)$_2$·H$_2$O. Hence we suggest performing high-field magnetization measurements on this system as well as susceptibility experiments (to obtain the size of the spin gap) at very low temperatures.

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