

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

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The compound $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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 $\alpha = J_2/J_1 \approx 0.29$ [G. J. Nilsen, H. M. Rønnow, A. M. Läuchli, F. P. A. Fabbiani, J. Sanchez-Benitez, K. V. Kamenev, and A. Harrison, *Chem. Mater.* **20**, 8 (2008)]. Here, we report a microscopically based magnetic model for this compound derived from density functional theory (DFT) based electronic structure calculations along with respective tight-binding models. Our (LSDA + U_d) calculations confirm the quasi-one-dimensional nature of the system with antiferromagnetic J_1 and J_2 , but suggest a significantly larger frustration ratio $\alpha_{\text{DFT}} \approx 0.94$ –1.4, depending on the choice of U_d and structural parameters. Based on transfer matrix renormalization group (TMRG) calculations we find $\alpha_{\text{TMRG}} = 1.5$. Due to an intrinsic symmetry of the J_1 - J_2 model, our larger frustration ratio α is also consistent with the previous thermodynamic data. To identify the frustration ratio α 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_2CuO_2 ^{1,2} ($0 \geq \alpha \geq -0.25$); (ii) helical order with different pitch angles in LiVCuO_4 , LiCu_2O_2 , and NaCu_2O_2 ³⁻⁹ ($\alpha < -0.25$); and (iii) spin-Peierls transition in CuGeO_3 ^{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 YTlO_3 have been reported.^{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 ($X = \text{Cl}, \text{Br}$).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 $3d^9$) 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. Since the temperature scale for the magnetic contribution to the specific heat is of the order of 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.

$\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, a new member in the family of titanium alums has recently been synthesized.¹⁵ The titanium ions are in the $\text{Ti}^{3+}(d^1)$ oxidation state in this material. Specific heat and susceptibility measurements suggest that $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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.¹⁶⁻²² In light of this result, $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ would be expected to occupy the highly

interesting region of the phase diagram, with a small gap $\Delta < J_1/20$.^{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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. 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 α 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. 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 α . 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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 experimental¹⁵ lattice parameters in the monoclinic space group ($P2_1/m$) of $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$: $a = 7.649 \text{ \AA}$, $b = 5.258 \text{ \AA}$, $c = 9.049 \text{ \AA}$ and $\beta = 101.742^\circ$. The crystal structure, which is isomorphous to that of the mineral krausite,²³ $\text{KFe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, 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 \AA , 2.056 \AA (in the ab plane), and 2.043 \AA (along c). The shortest Ti-Ti distance is 4.93 \AA and is between nearest neighbors (NN) on the adjacent chains (t_1 in Fig. 1). Within the chains, neighboring Ti are 5.23 \AA 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

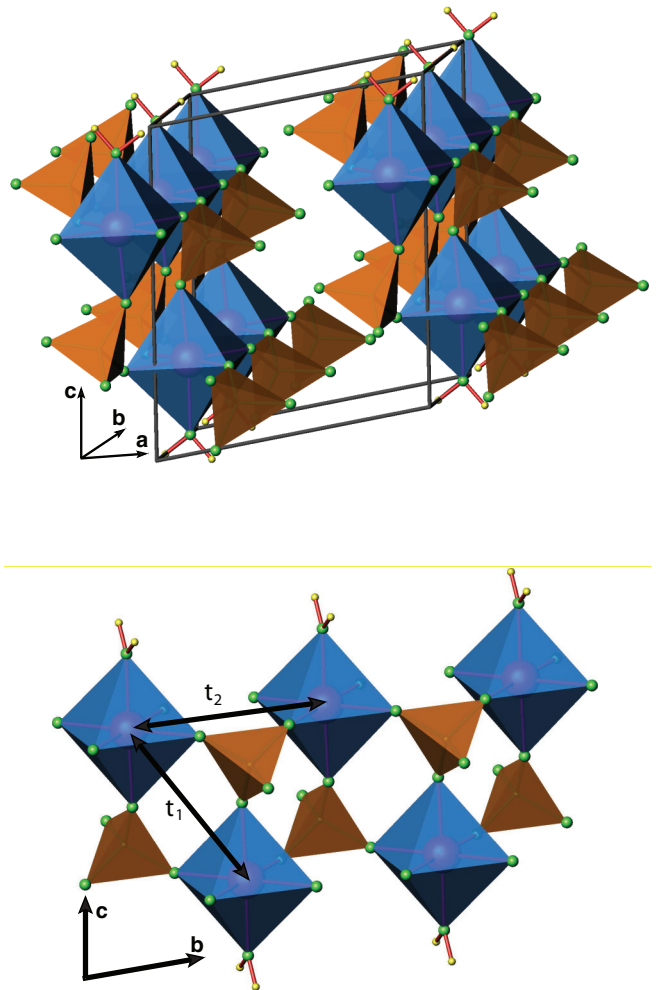


FIG. 1. (Color online) (Top) Crystal structure of $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. Double chains of TiO_6 octahedra run along the b axis. The octahedra are connected on either sides by SO_4 tetrahedra. Water molecules are bound to the octahedra and separating the double chains along the c axis. The potassium atoms (not shown here) separate the double chains along the a axis. (Bottom) An isolated segment of the double chain. The nearest-neighbor (NN) and next-nearest-neighbor (NNN) hopping paths are represented as t_1 and t_2 , respectively.

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.²⁴ In $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, 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_2O_4 octahedra, though the distortions are much larger with equatorial Ti-O and Ti-Cl bond lengths of 2.25 \AA and 2.32 \AA , respectively, and an apical Ti-O bond length of 1.95 \AA . 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,^{14,25}

though a prolonged discussion of possible orbital fluctuations ensued afterwards. Therefore an analysis of $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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_{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 $0.05J_1$, and the Trotter number was varied between 4×10^3 and 16×10^3 . 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, 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

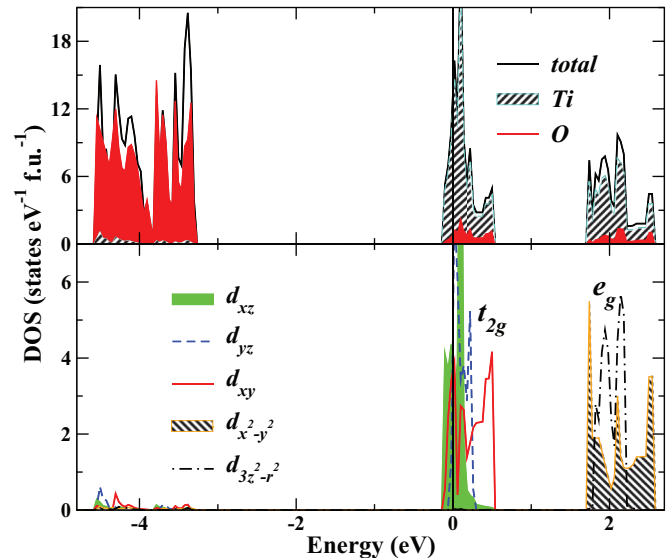


FIG. 2. (Color online) (Top) Total and partial DOS obtained within LDA for $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. The valence panel is predominantly comprised of Ti- $3d$ and O- $2p$ states. The sulfur states (not shown here) lie mainly below -8 eV. The contribution from K, S, and H sites 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.

presented part of the valence band is predominantly comprised of Ti $3d$ and O $2p$ states belonging to TiO_6 octahedra. The states belonging to sulfur (not shown) lie below -8 eV and are therefore well separated from the TiO_6 states. The weight close to the Fermi level (E_F) is mainly from the Ti t_{2g} states, which contain two electrons (one for each Ti in the unit cell) and are separated by a ligand-field splitting of about 2 eV from the higher lying (empty) e_g states. For an octahedral arrangement of oxygen anions around a $3d$ transition metal cation, a 2 eV ligand-field split is rather typical. For TiOCl (~ 2 eV).²⁵ This difference arises from the fact that in TiOCl , the basic octahedral structural units TiCl_2O_4 are arranged such that they are corner sharing in the a direction and edge-sharing along the b direction, leading to a larger interaction between the octahedral units and hence a larger t_{2g} bandwidth. In contrast, the TiO_6 octahedral units in $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ are neither corner- nor edge-sharing and hence the smaller t_{2g} bandwidth.

The degeneracy between the t_{2g} orbitals is lifted due to the monoclinic symmetry of the crystal structure as seen in the nonmagnetic band structure (see Fig. 3). There are 2 Ti atoms per formula unit and therefore 6 t_{2g} bands close to E_F . The bands are predominantly dispersive along Γ - Y , X - M , and XZ - MZ directions, which are along the crystallographic y axis and remain rather flat along the other high-symmetry directions. This implies that the main interaction between the Ti^{3+} ions is along the “double chain,” while sizably smaller interactions are expected between the adjacent double chains. The band belonging to the d_{xz} orbital is lower in energy as compared to the d_{yz} and d_{xz} (nearly empty and larger band width) orbitals (also see Fig. 2). The mixing between the Ti $3d$

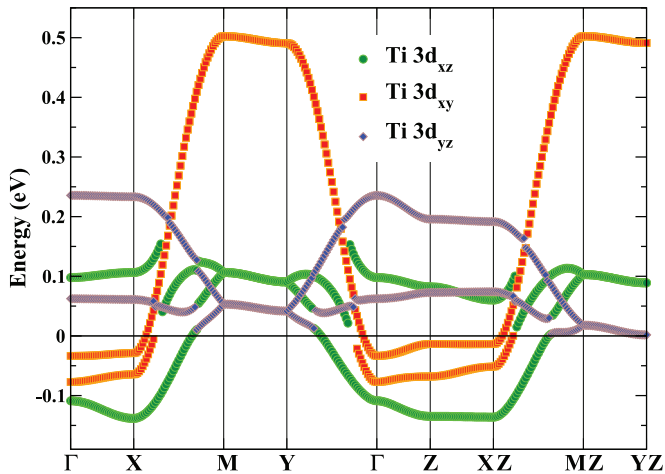


FIG. 3. (Color online) Band structures with band character close to the Fermi level obtained within LDA. The bands are dispersive along Γ -Y and X-M direction—the crystallographic y direction along which the “double chains” propagate. There are two Ti atoms in the unit cell and therefore 6 t_{2g} bands crossing the Fermi energy.

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 (Δ) 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, $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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 (d_{xy}) and a higher energy doublet ($d_{xz,yz}$). 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_{xy} . On the other hand, for $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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_{xz} orbital is close to E_F and is the lowest lying band of the t_{2g} complex. The on-site energies of d_{yz} and the broader d_{xy} 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_2O_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 0.3 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_2O_6 .³² In comparison to CuSb_2O_6 , the crystal field splitting in $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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 $J_i^{\text{AFM}} \simeq 4t_i^2/U_{\text{eff}}$. The ferromagnetic contributions are evaluated by considering the Kugel-Khomskii model,³³ 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 report¹⁵ 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-O-Ti superexchange. Foremost, we observe that the WF’s resemble the atomiclike d orbitals. There is a lot of oxygen hybridization tails, but

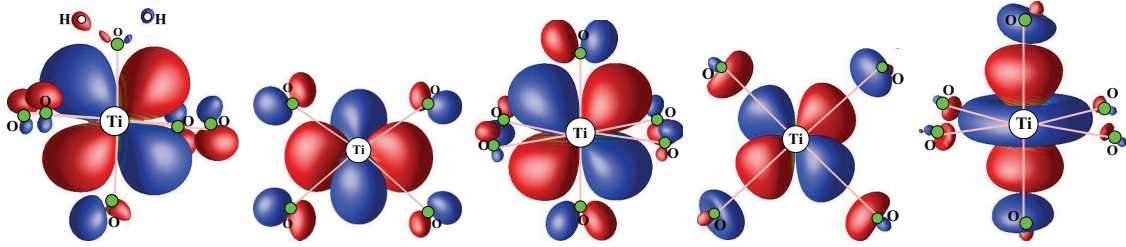


FIG. 4. (Color online) Wannier functions of all the five $3d$ orbitals of the Ti^{3+} ion. (Left to right) d_{xz} , d_{xy} , d_{yz} , $d_{x^2-y^2}$, $d_{3z^2-r^2}$. The blue and red lobes of the WF's refer to the positive and negative isosurfaces, the circles refer to the atoms. The TiO_6 octahedra are highlighted by the light pink Ti-O bonds. For d_{xy} and $d_{x^2-y^2}$, only the plaquette Ti-O bonds are shown.

not a strong t_{2g} - e_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_{yz} 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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 ϵ_0 obtained using the WF technique for all the five d orbitals of Ti. All the t 's are in meV while ϵ_0 is in eV.

	xz	yz	xy	$x^2 - y^2$	$3z^2 - r^2$
t_1 (meV)	t_{2g}			e_g	
xz	44.2	5.3	3.7	7.8	53.4
yz	5.3	38.2	1.7	9.5	32.8
xy	3.7	1.7	3.1	2.3	55.4
$x^2 - y^2$	7.8	9.5	2.3	1.6	12.8
$3z^2 - r^2$	53.4	32.8	55.4	12.8	23.1
t_2 (meV)	t_{2g}			e_g	
xz	27.8	5.4	1.1	3.5	9.1
yz	5.4	26.7	2.4	22.6	3.0
xy	1.1	2.4	131	6.1	49.7
$x^2 - y^2$	3.5	22.6	6.1	211	2.6
$3z^2 - r^2$	9.1	3.0	49.7	2.6	77.6
(eV)	xz	yz	xy	$x^2 - y^2$	$3z^2 - r^2$
ϵ_0	0.045	0.087	0.243	2.097	1.992

Therefore, to obtain a microscopic picture of the magnetic interactions, we have constructed an effective five-orbital TBM including all the five $3d$ orbitals of Ti. There are two Ti atoms in the unit cell, resulting in altogether ten bands. Ti centered WF's adapted to the various $3d$ orbital characters are constructed, and the transfer integrals (t_{ij}) of the TBM are evaluated as non-diagonal matrix elements in this Wannier basis. The magnitudes 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 observations¹⁵ 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 $t_{1,xy-xy}$ 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 e_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 $U_{\text{eff}} = 3.3$ eV and $J_{\text{eff}} = 1$ eV. The J values are in units of degrees of Kelvin. For comparison, the experimental values are $J_1^{\text{exp}} = 9.46$ K and $J_2^{\text{exp}} = 2.8$ K.¹⁵ The last column is the frustration ratio α 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.

	J_1^{AFM}	J_1^{FM}	J_1	J_2^{AFM}	J_2^{FM}	J_2	α
d_{xz}	27	-6.0	21	11	-0.4	10.6	0.5
d_{yz}	20.5	-2.7	17.8	10	-1.3	8.7	0.5
d_{xy}	0.1	-7.0	-6.9	243	-6.0	237	34

using the expression of the Kugel-Khomskii model,³³

$$J_{ij,\alpha} = \frac{4t_{ij,\alpha\alpha}^2}{U_{\text{eff}}} - \sum_{\beta} \frac{4t_{ij,\alpha\rightarrow\beta}^2 J_{\text{eff}}}{(U_{\text{eff}} + \Delta_{\alpha\beta})(U_{\text{eff}} + \Delta_{\alpha\beta} - J_{\text{eff}})} \quad (1)$$

$$= J_{\text{AFM}} - J_{\text{FM}},$$

where i and j denote the sites, α is the magnetically active orbital at site i , β is one of five d orbitals at site j , $t_{ij,\alpha\rightarrow\beta}$ are the transfer integrals of orbital α at site i to orbital β at site j , $\Delta_{\alpha\beta}$ are the crystal field splittings between orbitals α and β . U_{eff} and J_{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 α and the rest of the d complex, and thus ferromagnetic (FM). For TiOCl, a $U_{\text{eff}} \sim 3.3$ eV was shown to provide good agreement between calculated exchange constants and susceptibility measurements.²⁵ The same value of $U_{\text{eff}} = 3.3$ eV with a $J_{\text{eff}} = 1$ eV has been used here for $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, 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 $3d$ electron is very unlikely to occupy the higher-lying e_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 ($J_1^{\text{exp}} = 9.46$ K, $J_2^{\text{exp}} = 2.8$ K).¹⁵ 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_{eff} and J_{eff} in the physically relevant sector. We varied U_{eff} in the range of 2 to 4 eV and J_{eff} in the range of 0.5 to 1 eV and find that α_{xz} and α_{yz} were (i) very robust in the entire parameter region, varying at maximum by about 10%, and (ii) always significantly larger than α_{exp} (see Supplemental Material³⁴ for further details). In contrast, α_{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_d 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 $3d$ 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, we tried to spin polarize

each of the three t_{2g} bands. We considered U_d values ranging from 2.5–4.5 eV.³⁵ 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is very likely determined by the Ti $3d_{xz}$ orbital. The next question to answer is whether the exchange constants obtained for the d_{xz} orbital 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 α 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, $J_1^{d_{xz}}$ is comparable to experimental findings while $J_2^{d_{xz}}$ is larger by almost an order of magnitude. Comparing the total J 's in Fig. 5 with the J^{AFM} obtained from TBM in Table I, we can infer that there is a significant FM component to the NN (J_1^{FM}) while the FM component to the NNN (J_2^{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

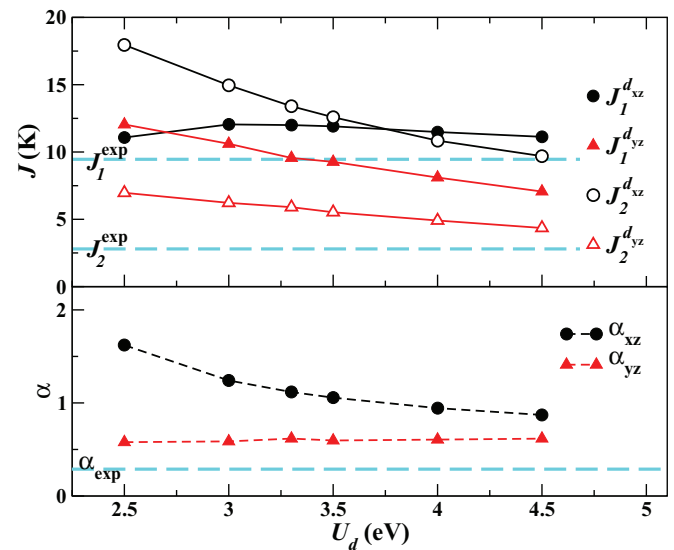


FIG. 5. (Color online) The total exchange constants (top) and the frustration ratio α (bottom) as a function of U_d for d_{xz} and d_{yz} orbitals. The NN total exchange J_1 (full symbols) and NNN total exchange J_2 (empty symbols) do not vary much for the considered range of U_d (2.5 to 4.5 eV) values.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

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, $J_1^{d_{xz}} \approx 12$ K, $J_2^{d_{xz}} \approx 13.4$ K, and $\alpha_{xz} \approx 0.94 \pm 0.15$ ($J_1^{\text{exp}} = 9.46$ K, $J_2^{\text{exp}} = 2.8$ K, and $\alpha = 0.29$). The error bar is calculated from the difference in the α values between $3 \leq U_d \leq 4$. The calculated value of $\alpha_{xz} = J_2^{xz}/J_1^{xz}$ is larger than the experimental value by a factor of 3 for the d_{xz} orbital. The calculated $\alpha_{yz} = 0.60 \pm 0.01$ for the energetically unfavorable d_{yz} orbital is also significantly larger than the experimental value. Albeit the $S = 1/2$ frustrated chain magnetism in $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is established in both LDA and LSDA + U_d calculations, our results for α are not consistent with the experiments. Nonetheless, both our calculation and experiment suggest an α in the highly interesting region ($0.2411 < \alpha < 1.8$) of the spin-1/2 frustrated chain phase diagram.

One reason for the overestimation of α in our calculations might be related to the O-H bond length in $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. 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 ≈ 1 Å.³⁸ For $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, 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 α 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, $J_1^{xz} = 10$ K, $J_2^{xz} = 14.2$ K. The frustration ratio $\alpha_{xz} = 1.4 \pm 0.2$ is even larger (by 50%) than the previously calculated value using the experimental O-H bond length. This change in α 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. 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 α regime conforms to the experimental behavior.

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 $J_1 \approx 9.6$ K and $J_2 \approx 2.9$ 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 $J_1 \approx 5.4$ K and $J_2 \approx 8.1$ 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 ($T \geq J$). To verify, whether both solutions agree with the experimental $\chi(T)$ at lower temperatures, we simulate the temperature dependence of reduced magnetic susceptibility χ^* 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 $J_1 = 5.4$ K, $J_2 = 8.1$ K, $g = 1.74$, and $\chi_0 = 5.9 \times 10^{-5}$ 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 $\alpha = +0$ ($J_1 \neq 0, J_2 = 0$) 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

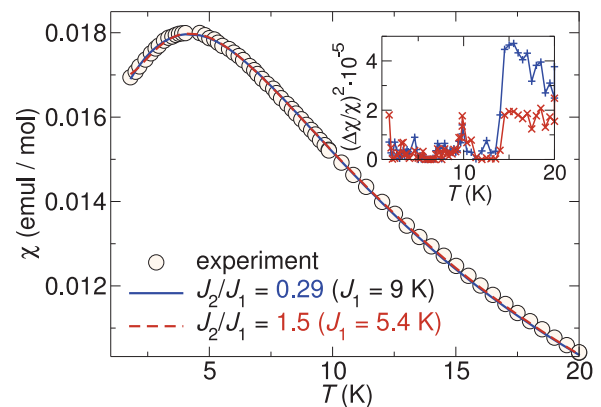


FIG. 6. (Color online) Fits to the magnetic susceptibility. The experimental data are adopted from Ref. 15. The magnetic susceptibility of frustrated Heisenberg chains with $\alpha = 0.29$ and 1.5 ($\alpha \equiv J_2/J_1$) was simulated using TMRG. The simulated curves were fitted to the experiment by varying the fitting parameters J_1 , g , and the temperature-independent contribution χ_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.¹⁷ For larger α 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 α reduces the spin gap. In the large α limit ($J_2 \gg J_1$), the spin gap exhibits an exponential decay.²²

Thus, for a certain value of the spin gap Δ , there are two possible α values: (i) with a dominant J_1 , i.e., from the $\alpha = 0.2411$ – 0.6 range and (ii) with a sizable J_2 ($\alpha = 0.6$ – ∞). Since Δ 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ can be well fitted by both $\alpha = 0.29$ and 1.5 .

Unlike, e.g., $\alpha = 0$ and ∞ , 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.²² Moreover, the two solutions feature substantially different correlation lengths.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 $\text{BaCdVO}(\text{PO}_4)_2$ 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.⁴¹ In a recent work, $M(H)$ measurements for $\text{A}_2\text{CuP}_2\text{O}_7$ ($A = \text{Li, Na}$) resolved previous controversies concerning the magnetic dimensionality of these compounds.⁴²

We argue that for the frustrated Heisenberg chain model, the characteristic behavior of magnetization 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:

$$H_{\text{sat}} = (g\mu_B)^{-1} [E(S_{\text{max}}^z) - E(S_{\text{max}}^z - 1)], \quad (2)$$

where S_{max}^z 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 $H_{\text{sat}} \simeq 16.4$ T and $H_{\text{sat}} \simeq 18.7$ 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 $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, which renders the typical measurement temperature of ~ 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 ~ 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.

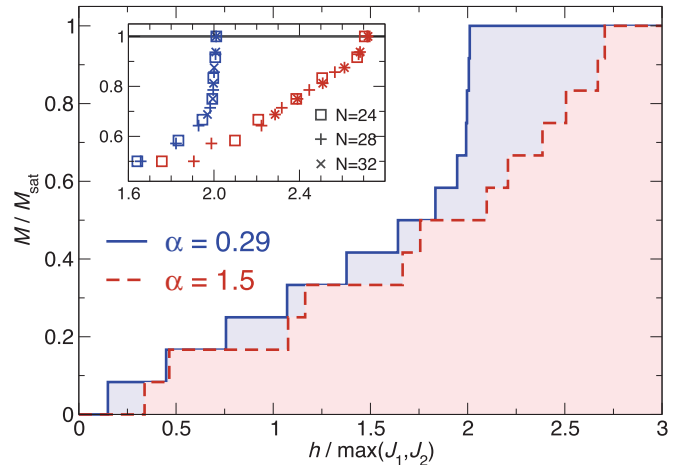


FIG. 7. (Color online) Ground-state magnetization of frustrated Heisenberg chains with $\alpha = 0.29$ and $\alpha = J_2/J_1 = 1.5$ ($\alpha \equiv J_2/J_1$), simulated using exact diagonalization on finite lattices (rings) of $N = 24$ spins. Note the characteristic upward bending of the $\alpha = 0.29$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

VI. SUMMARY

In conclusion, we have studied the electronic structure of $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ 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 (≈ 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 $\alpha_{\text{exp}} = 0.29$. 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 α . Due to an intrinsic symmetry of the $J_1 - J_2$ frustrated chain model, we show that both values of α provide similarly good fits to the experimental curve. Thus our calculated value of α is in line with the TMRG estimate of $\alpha_{\text{TMRG}} = 1.5$. 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 α that defines the magnetic

ground state of $\text{KTi}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. 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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- ¹W. E. A. Lorenz, R. O. Kuzian, S.-L. Drechsler, W.-D. Stein, N. Wizen, G. Behr, J. Málek, U. Nitzsche, H. Rosner, A. Hiess, W. Schmidt, R. Klingeler, M. Loewenhaupt, and B. Büchner, *Europhys. Lett.* **88**, 37002 (2009).
- ²U. Nitzsche, S.-L. Drechsler, and H. Rosner (unpublished).
- ³A. A. Gippius, E. N. Morozova, A. S. Moskvina, A. V. Zalesky, A. A. Bush, M. Baenitz, H. Rosner, and S.-L. Drechsler, *Phys. Rev. B* **70**, 020406 (2004).
- ⁴S.-L. Drechsler, J. Málek, J. Richter, A. S. Moskvina, A. A. Gippius, and H. Rosner, *Phys. Rev. Lett.* **94**, 039705 (2005).
- ⁵M. Enderle, C. Mukherjee, B. Fak, R. Kremer, J. Broto, H. Rosner, S.-L. Drechsler, J. Richter, J. Málek, A. Prokofiev *et al.*, *Europhys. Lett.* **70**, 237 (2005).
- ⁶T. Masuda, A. Zheludev, A. Bush, M. Markina, and A. Vasiliev, *Phys. Rev. Lett.* **92**, 177201 (2004).
- ⁷L. Capogna, M. Mayr, P. Horsch, M. Raichle, R. K. Kremer, M. Sofin, A. Maljuk, M. Jansen, and B. Keimer, *Phys. Rev. B* **71**, 140402(R) (2005).
- ⁸S.-L. Drechsler, J. Richter, A. Gippius, A. Vasiliev, A. Bush, A. Moskvina, Y. Prots, W. Schnelle, and H. Rosner, *Europhys. Lett.* **73**, 83 (2006).
- ⁹Quan-Lin Ye, Yasuharu Kozuka, Hirofumi Yoshikawa, Kunio Awaga, Shunji Bandow, and Sumio Iijima, *Phys. Rev. B* **75**, 224404 (2007).
- ¹⁰J. Riera and A. Dobry, *Phys. Rev. B* **51**, 16098 (1995).
- ¹¹M. Hase, I. Terasaki, and K. Uchinokura, *Phys. Rev. Lett.* **70**, 3651 (1993).
- ¹²G. Khaliullin and S. Maekawa, *Phys. Rev. Lett.* **85**, 3950 (2000).
- ¹³T. Kiyama, H. Saitoh, M. Itoh, K. Kodama, H. Ichikawa, and J. Akimitsu, *J. Phys. Soc. Jpn.* **74**, 1123 (2005).
- ¹⁴A. Seidel, C. A. Marianetti, F. C. Chou, G. Ceder, and P. A. Lee, *Phys. Rev. B* **67**, 020405(R) (2003).
- ¹⁵G. J. Nilsen, H. M. Rønnow, A. M. Läuchli, F. P. A. Fabbiani, J. Sanchez-Benitez, K. V. Kamenev, and A. Harrison, *Chem. Mater.* **20**, 8 (2008).
- ¹⁶R. Jullien and F. D. M. Haldane, *Bull. Am. Phys. Soc.* **28**, 344 (1983).
- ¹⁷K. Okamoto and K. Nomura, *Phys. Lett. A* **169**, 433 (1992).
- ¹⁸S. Eggert, *Phys. Rev. B* **54**, R9612 (1996).
- ¹⁹C. K. Majumdar and D. K. Ghosh, *J. Math. Phys.* **10**, 1388 (1969).
- ²⁰C. K. Majumdar and D. K. Ghosh, *J. Math. Phys.* **10**, 1399 (1969).
- ²¹F. D. M. Haldane, *Phys. Rev. B* **25**, 4925 (1982).
- ²²S. R. White and I. Affleck, *Phys. Rev. B* **54**, 9862 (1996).
- ²³E. J. Graeber, B. Morosin, and A. Rosenzweig, *Am. Mineral.* **50**, 1929 (1965).
- ²⁴Note that the orbital angular momentum remains unquenched in the 2T ground-state term, transforming as $-\mathbf{L}$ for $L = 1$. Spin-orbit coupling results in a pair of nonmagnetic Kramers doublets in the effective $J = 3/2$ ground state and a magnetic Kramers doublet excited state. However, the spin-orbit coupling for Ti is rather small compared to the ligand-field split due to the small distortion of the TiO_6 octahedra. Thus we do not include the spin-orbit coupling in our calculations.
- ²⁵T. Saha-Dasgupta, R. Valenti, H. Rosner, and C. Gros, *Europhys. Lett.* **67**, 63 (2004).
- ²⁶K. Koepnik and H. Eschrig, *Phys. Rev. B* **59**, 1743 (1999).
- ²⁷I. Opahle, K. Koepnik, and H. Eschrig, *Phys. Rev. B* **60**, 14035 (1999).
- ²⁸J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- ²⁹H. Eschrig and K. Koepnik, *Phys. Rev. B* **80**, 104503 (2009).
- ³⁰A. F. Albuquerque, F. Alet, P. Corboz, P. Dayal, A. Feiguin, S. Fuchs, L. Gamper, E. Gull, S. Gürtler, A. Honecker, R. Igarashi, M. Körner, A. Kozhevnikov, A. Läuchli, S. R. Manmana, M. Matsumoto, I. P. McCulloch, F. Michel, R. M. Noack, G. Pawłowski, L. Pollet, T. Pruschke, U. Schollwöck, S. Todo, S. Trebst, M. Troyer, P. Werner, and S. Wessel, *J. Magn. Magn. Mater.* **310**, 1187 (2007).
- ³¹X. Wang and T. Xiang, *Phys. Rev. B* **56**, 5061 (1997).
- ³²D. Kasinathan, K. Koepnik, and H. Rosner, *Phys. Rev. Lett.* **100**, 237202 (2008).
- ³³I. Kugel and D. I. Khomskii, *Sov. Phys. Usp.* **25**, 231 (1982); V. V. Mazurenko, F. Mila, and V. I. Anisimov, *Phys. Rev. B* **73**, 014418 (2006).
- ³⁴See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.88.224410> for α as a function of U_{eff} and J_{eff} .
- ³⁵The effective on-site exchange J_d has been set to 1 eV.
- ³⁶T. Mizokawa and A. Fujimori, *Phys. Rev. B* **54**, 5368 (1996); One should note that the value of U_d is depending on the basis set, the choice of the double counting scheme, etc. Thus $U_d = 4$ eV should be considered as an approximation, only.
- ³⁷O. Janson, J. Richter, and H. Rosner, *Phys. Rev. Lett.* **101**, 106403 (2008).
- ³⁸V. Szalay, L. Kovács, M. Wöhlecke, and E. Libowitzky, *Chem. Phys. Lett.* **354**, 56 (2002).
- ³⁹The electron density of hydrogen, the lightest atom with only one electron, is generally localized away from the nucleus and hence it is difficult to detect the exact position of the H nucleus from x-ray diffraction measurements. The relatively high electron density between the oxygen and hydrogen atoms makes the O-H bonds to appear too short.
- ⁴⁰A. Bühler, U. Löw, and G. S. Uhrig, *Phys. Rev. B* **64**, 024428 (2001).
- ⁴¹R. Nath, A. A. Tsirlin, H. Rosner, and C. Geibel, *Phys. Rev. B* **78**, 064422 (2008).
- ⁴²S. Lebernegg, A. A. Tsirlin, O. Janson, R. Nath, J. Sichelschmidt, Yu. Skourski, G. Amthauer, and H. Rosner, *Phys. Rev. B* **84**, 174436 (2011).