Electronic structure of KTi(SO$_4$)$_2$·H$_2$O - a S=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 $\alpha = J_2/J_1 \approx 0.29$ [Chem. Mater. 20, 8 (2008)]. Here, we report a microscopically based magnetic model for this compound derived from density functional electronic structure calculations along with respective tight-binding models. Our calculations confirm the quasi one-dimensional nature of the system with antiferromagnetic $J_1$ and $J_2$, but suggest a significantly larger frustration ratio $\alpha \approx 1.1 \pm 0.2$. Based on transfer matrix renormalization group calculations we found that, 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 resolve this issue, we propose performing high-field magnetization measurements and low temperature susceptibility measurements which should allow to precisely identify the frustration ratio $\alpha$.

PACS numbers: look it up

I. INTRODUCTION

For several decades, low dimensionality 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$_2$CuO$_2$(H$_2$O)$_2$ (0 ≤ $\alpha$ ≤ 0.25); (ii) helical order with different pitch angles in LiV$_2$O$_4$, LiCu$_2$O$_2$, and NaCu$_2$O$_2$ (0 ≤ $\alpha$ ≤ 0.25); (iii) spin-Peierls transition in CuGeO$_3$ (0 ≤ $\alpha$ ≤ 0.25), (iv) dimerization of 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.

KTi(SO$_4$)$_2$·H$_2$O, a new member in the family of titanium alums has recently been synthesized. The titanium ions are in the 3+ ($d^1$) oxidation state in this material. Specific heat and susceptibility measurements indicate 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 AFM with $\alpha = 0.29$. In the well studied $J_1$-$J_2$ frustrated chain model with both interactions being AFM, the model un-
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 will 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 section II. The details of the various calculational methods are collected in section III. The results of the density functional theory based calculations, including the band structure and the accordingly derived microscopic model is described in section IV. In section V we demonstrate the effects of the crystal water in this compound by calculating the Wannier functions. The outcome of the TMRG simulations is compared to the previous experiment in section VI, which is followed by a discussion and summary in section VII.

II. CRYSTAL STRUCTURE

Throughout our calculations, we have used the recently determined experimental$^{15}$ lattice parameters in the monoclinic space group (P2$_1$/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 Krausit$^{23}$, 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 away from 90$^\circ$ 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 $t_2$ 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 KTi(SO$_4$)$_2$·H$_2$O, there is a small distortion of the octahedra and consequently splitting of the $t_2$ levels can be expected. The related case of Ti-

![FIG. 1. (Color Online) Top: Crystal structure of KTi(SO$_4$)$_2$·H$_2$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.](image-url)
OCl, another system containing Ti$^{3+}$ ion, 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 $d_{xz}$ and higher energy $d_{x^2-y^2}$ 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 $d_{xz}$ orbital, though a prolonged discussion of possible orbital fluctuations ensued afterwards. Therefore, an analysis of KTi(SO$_4$)$_2$H$_2$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)\cite{11,12}. 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 flavor of the exchange correlation potential was chosen for the scalar relativistic calculations. The strong on-site Coulomb repulsion of the Ti 3$d$ 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 3$d$ gross occupation. The AFM parts of the exchange couplings are computed as $J_{i,j}^{AFM} = 4t_i^2/U_{eff}$, by mapping the results of the LDA calculations on to a tight binding model (TBM) which is then mapped on to a Hubbard model, and subsequently to a Heisenberg model because the system belongs to the strong correlation limit\cite{13}. The AFM parts of the exchange couplings are computed as $J_{i,j}^{AFM} = 4t_i^2/U_{eff}$, by mapping the results of the LDA calculations on to a tight binding model (TBM) which is then mapped on to a Hubbard model, and subsequently to a Heisenberg model because the system belongs to the strong correlation limit $U_{eff} \gg t$ ($t$ is the leading transfer integral at half filling). The full exchange couplings are obtained by mapping 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. Maximally localized Wannier functions (WF) were calculated for the Ti $t_{2g}$ orbitals, also using FPLO, to obtain a visual insight of the relevant orbitals and superexchange interactions.

The magnetic excitation spectrum of frustrated spin chains was simulated using exact diagonalization code from the ALPS package. 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. 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 4·10$^3$ 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 KTi(SO$_4$)$_2$H$_2$O, we begin by analyzing the results from a non-magnetic 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 $\hat{z} \parallel c$, and $\hat{x}$ and $\hat{y}$ axes are rotated by 45° around $c$ with respect to the original $a$ and $b$ axes. The non-magnetic 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 3$d$ and O 2$p$ 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 KTi\((\text{SO}_4)_2\cdot\text{H}_2\text{O}\), the band width of the \( t_{2g} \) band complex is only 0.65 eV, about one third of the value for TiOCl (\( \sim 2 \) eV). This difference arises from the fact that in TiOCl, the basic octahedral structural units TiCl\(_2\)O\(_4\) 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 \( t_{2g} \) band width. In contrast, the TiO\(_6\) octahedral units in KTi\((\text{SO}_4)_2\cdot\text{H}_2\text{O}\) are neither corner- nor edge-sharing and hence the smaller \( t_{2g} \) band width.

The degeneracy between the \( t_{2g} \) orbitals is lifted due to the monoclinic symmetry of the crystal structure as seen in the non-magnetic band structure (Fig. 3). There are 2 Ti atoms per formula unit and therefore 6 \( t_{2g} \) bands close to \( E_F \). The bands are highly dispersive along \( \Gamma-Y, X-M \) 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 and the O 2p states close to \( E_F \) is less than 10% and similar to other systems where Ti occurs in the \( d^4 \) 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\((\text{SO}_4)_2\cdot\text{H}_2\text{O}\) 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 (Section 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 one unpaired electron of the Ti\(^{3+} \) ion in TiOCl is rather straightforward: the singlet \( d_{xy} \). On the other hand, for KTi\((\text{SO}_4)_2\cdot\text{H}_2\text{O}\) the pseudo octahedral ligand field splits the \( t_{2g} \) states and removes the three fold degeneracy. Nevertheless, due to the relatively small energy differences, there is no clear candidate for the choice of the half-filled orbital. The band center of the \( d_{xz} \) orbital is around \( E_F \) and is the lowest lying band of the \( t_{2g} \) complex. The center of gravity of \( d_{yz} \) and the comparably broad \( d_{xy} \) band are only slightly higher in energy than the \( d_{xz} \) at 0.15 eV and 0.25 eV, respectively. Since the three \( t_{2g} \) orbitals are quite close in energy, a subtle balance between the orbitals is expected and therefore one should carefully consider the possibility of an orbitally ordered solution. At this juncture, it is rather unclear which correlated orbital will be half filled and thereby determine the magnetic model. 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 \( d_{x^2−y^2} \) and \( d_{x^2−y^2} \) related band centers is about 0.3 eV only, compared with about 2 eV for standard cuprates. Inclusion of correlations, changes the order and results in the unpaired electron occupying the \( d_{x^2−y^2} \) orbital instead of the standard \( d_{x^2−y^2} \) in CuSb\(_2\)O\(_6\).

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 tight-binding model (TBM), which in turn is mapped onto a Hubbard model,
and subsequently to a Heisenberg model. At half filling, when $U$ is much larger than the bandwidth $w$, the spin degrees of freedom are well described by an $S=1/2$ AFM Heisenberg Hamiltonian with an exchange interaction $J_{AFM}^i \approx 4t_i^2/U_{eff}$. A $U_{eff}$ of 3.3 eV has been used to calculate the $J$'s. The frustration ratio $\alpha = J_2/J_1$ is collected in the last column.

### TABLE I. Hopping parameters (in meV) and the corresponding exchange constants (in K) from an effective one-band TBM. The hopping paths are indicated in the lower panel of Fig. 1. The transfer integral $t_1$ corresponds to hopping between the single chains, while $t_2$ corresponds to hopping within a single chain. A $U_{eff}$ of 3.3 eV has been used to calculate the $J$'s. The frustration ratio $\alpha = J_2/J_1$ is collected in the last column.

| $d_{xz}$ | $d_{yz}$ | $d_{xy}$ |
|----------|----------|----------|
| 0.047    | 0.029    | 0.037    |
| 0.028    | 0.028    | 0.037    |
| 0.081    | 0.135    | 0.256    |

| $t_1$ (eV) | $t_2$ (eV) | $J_1^{AFM}$ (K) | $J_2^{AFM}$ (K) | $\alpha$ |
|------------|------------|-----------------|-----------------|---------|
| 31         | 19         | 11.8            | 11              | 0.38    |
| 92         | 92         | 256             | 256             | 2.78    |

**FIG. 4.** (Color Online) The total exchange constants $J$'s (top panel) and the frustration ratio $\alpha$ (bottom panel) 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 eV to 4.5 eV) values. The experimental results (Ref. 14) are indicated by dashed lines.

The magnitudes of the leading hopping integrals (the paths are indicated in Fig. 1) are collected in Table I. The NN (between single chains) and NNN (along the single chains) hopping integrals $t_1$ and $t_2$ are of the same order of magnitude for the $d_{xz}$ and $d_{yz}$ orbitals. On the contrary, the TBM fit to the broad $d_{xy}$ orbital leads to a much larger $t_2$. All other $t$'s beyond NNN are less than 0.1 meV for all the three orbitals and 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 of displaying low dimensional magnetic properties. The individual exchange constants are then calculated using $J_{AFM}^i = 4t_i^2/U_{eff}$. For TiOCl, a $U_{eff}$ of 3.3 eV was shown to provide good agreement between calculated exchange constants and susceptibility measurements. The same value of $U_{eff}$ has been used here for KTi(SO$_4$)$_2$·H$_2$O, the $J$’s obtained are collected in Table I. The $J$’s for the lower energy $d_{xz}$ band and as well as the $d_{yz}$ band are of similar magnitude as compared to the experimental report. To the contrary, both the calculated NN and NNN $J$’s for the $d_{xy}$ band are much larger in energy compared to the experimental report. This large difference in the energy scale of the magnetic exchange for $d_{xy}$ band implies that this orbital might be a rather unlikely choice for full polarization (a more clear picture emerges in the following section when performing LSDA+$U$ calculations).

Since the constructed Heisenberg Hamiltonian takes into account only the antiferromagnetic component of the couplings, inclusion of ferromagnetic (FM) component could change the picture described above, especially
considering the absolute values for the AFM exchanges are quite small. In the proceeding section we report on the LSDA+$U_d$ calculations to obtain the total exchange constants $J = J_{\text{FM}} + J_{\text{AFM}}$. 

C. Density functional theory + $U$

Besides obtaining estimates for all the AFM 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 0.1 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 $U_d$ values ranging from 2.5 - 4.5 eV. 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 band width of these orbitals. Incidentally, all our attempts to spin-polarize $d_{xy}$ remained unsuccessful, though not unexpected when considering our TBM results (i.e. the much too large energy scale of $J_2$ which is inconsistent with experiments). We were also unable to stabilize different orbitally-ordered scenarios (i.e. one Ti ion with a spin-polarized $d_{xx}$ 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 $d_{xz}$ 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 map 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. 4. 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. 4 with the $J_{\text{AFM}}$ obtained from TBM in Table. 1 we can infer that there is a significant FM component to the first neighbor ($J_1^{\text{FM}}$) 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 for various transition-metal oxides, recommend a $U_d$ value of 4 eV for Ti$^{3+}$ ions. 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 $\alpha_{xz} \approx 0.94$ ($J_1^{exp} = 9.46$ K,

FIG. 5. (Color Online) Wannier functions of the three $t_{2g}$ orbitals of the Ti$^{3+}$ ion. Left panel: $d_{xz}$, middle panel: $d_{xy}$, right panel: $d_{yz}$. The blue and red lobes of the WF’s refer to the positive and negative iso-surfaces, the circles refer to the atoms. The TiO$_6$ octahedra is highlighted by the light grey Ti-O bonds. The perspective view is also aided by highlighting the crystallographic $a-b$ plane using dashed lines.

$H_{\text{AFM}}$:

\begin{equation}
H_{\text{AFM}} = \sum_{\bf R} \sum_{\bf g} \sum_{\sigma} J_{\bf R}^{\sigma} S_{\bf R}^{\sigma} S_{\bf R+\bf g}^{\sigma}
\end{equation}
$J_{xx}^{\alpha} = 2.8$ K, and $\alpha = 0.29$). The calculated value of $\alpha_{xz} = J_{zz}^{\alpha}/J_{zz}^{\alpha}$ is larger than the experimental value by a factor of 4 for the $d_{xz}$ orbital. The calculated $\alpha_{yz} (= 0.60)$ for the energetically unfavorable $d_{yz}$ orbital is also somewhat larger than the experimental value. Albeit 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 ($0.2411 < \alpha < 1.8$) of the spin-1/2 frustrated chain phase diagram.

In the following section, we attempt to understand the discrepancy between our calculations and the experiment.

V. EFFECT OF CRYSTAL WATER

A. Wannier Functions

The octahedron surrounding Ti$^{3+}$ consists of 5 O$^{2-}$ ions shared with SO$_4^{2-}$ groups, and one water molecule (see Sec. II for a more detailed discussion). From a naive consideration of average equatorial and apical Ti-O distances, the magnetically active orbital would be assigned as $d_{xy}$. In contrast, both LDA and LSDA+$U_d$ results point to $d_{xz}$ as the magnetically active orbital. In order to shed some more light on this discrepancy, we have plotted the Wannier functions for the Ti$_2$On complex (Fig. 5). 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, 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-O-Ti superexchange. The Ti $d_{xy}$ WF is composed of contributions from the $d_{xy}$ orbital as well as tails on the oxygen sites in the $xz$-plane, although these do not point towards the NN Ti atom. The $d_{yz}$ WF, on the other hand, has tails on all 6 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. We therefore infer that the orientation of the water molecule plays an important role in deciding the magnetically active orbital for obtaining the ground state in KTi(SO$_4$)$_2$H$_2$O. More detailed analysis follows in the next section.

B. Rotating the water molecule

It is normally assumed that the presence of crystal water in a compound, leads to only modest changes in the crystal field of the magnetic ion. However, it might not always be the case. Recent work on CuCl$_2$ and CuCl$_2$·2H$_2$O shows that the former is a quasi 1D-chain compound while the latter is a classical 3D AFM, although the magnetic Cu-Cl units in both compounds are structurally similar. Motivated by such reports and the results from our WF analysis, we explore the effects of the orientation of the H$_2$O molecule in KTi(SO$_4$)$_2$H$_2$O. Crystallographic data that we have used until now orient the H$_2$O molecule in the $xz$ plane. From the analysis of the WF’s we infer that the magnetically active orbital ($d_{xz}$) is selected by the hydrogen bonding of the water molecule in the $xz$-plane with the Ti $d_{xz}$ orbital. We now attempt to rotate the H$_2$O molecule to the $yz$ plane and observe the effects on the electronic structure. The symmetry of the crystal was reduced to accommodate the new orientation, though the experimental O-H distance (0.8747 Å) as well as the H-O-H bond angle (93.33°) were left untouched. The resulting non-magnetic LDA band structure is displayed in Fig. 6. The general shape of the bands as well as the various $k$-point degeneracies are similar for both the $xz$ and $yz$ oriented H$_2$O molecule.

The important changes for the fictitious $yz$ oriented system are: (a) the $d_{xx}$ band is no longer having the lowest band energy and is getting pushed upwards and therefore less occupied, (b) the $d_{yz}$ band is pulled downwards and is getting more occupied. Ergo, the orientation of the H$_2$O molecule has a profound effect on the electronic structure and plays an important role in selecting the magnetically active orbital. In contrast with the LDA result, the addition of correlations results in $d_{xz}$ as the lowest energy band, as was the case for H$_2$O —— $xz$. That said, the energy difference between singly occupied $d_{xz}$ and $d_{yz}$ is only 35 meV, 10 times smaller than the original calculation (cf. Sec. IV-C) in which the H$_2$O molecule was oriented along the $xz$-plane. Calculating the $J$’s for the fictitious system using the effective TBM resulted in $\alpha_{yz} = 0.36$ and a much larger $\alpha_{xz} = 1.11$. These results reaffirm the the importance of the water molecule in deciding not only the magnetically active orbital, but also the accordingly derived exchanges and frustration ratio in KTi(SO$_4$)$_2$H$_2$O.

C. Effect of the O-H bond length

Having observed the sensitivity of the electronic structure to the orientation of the H$_2$O molecule, our next item of interest was to check the importance of the O-H bond length on the electronic structure and magnetic proper-
ties. Recent reports on spin-1/2 kagome lattice systems\textsuperscript{36} show a dramatic impact of the O-H bond length on the exchange. It is well known that obtaining the correct O-H bond length via X-ray diffraction in a system containing heavy atoms is difficult. OH\textsuperscript{-} impurity in oxides have been shown to have an equilibrium bond length of $\approx 1$ Å.\textsuperscript{37} For KTi(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{2}O, the reported O-H bond length is 10% smaller and only 0.874 Å. 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.\textsuperscript{38} We have therefore allowed the O-H bond length to relax. Keeping the TiO\textsubscript{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.\textsuperscript{36,37} Recalculating the exchange constants using the optimized O-H distance, we obtain for $U_d = 4.0$ eV, $J_1^{zz} = 10$ K, $J_2^{zz} = 14.2$ K. The frustration ratio $\alpha_{zz} = 1.4$ is even larger than the previously calculated value using the experimental O-H bond length.\textsuperscript{38} Thus far, all of our calculations have resulted in exchanges that have the correct sign and comparable magnitudes to the previous experimental report, but nonetheless always yielded frustration ratios far greater than previously reported.\textsuperscript{15} In the following section, we make a final attempt to clarify the discrepancy between the experiment and our calculations.

VI. TMRG CALCULATIONS

As demonstrated in Ref.\textsuperscript{14}, a frustrated Heisenberg chain model with $\alpha = 0.29$ can reproduce the experimental magnetic susceptibility curve of KTi(SO\textsubscript{4})\textsubscript{2}·H\textsubscript{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. Thus, in the microscopic model, $\alpha$ should be larger than unity. The question is then, whether the large $\alpha$ 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).\textsuperscript{39} 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 $J_1 \simeq 9.6$.
This GS is robust against small frustrating to the exactly solvable gapless Heisenberg chain model. The 
are also related, although in a less trivial way. To pin-
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8}
\caption{(Color Online) Ground state magnetization of frustrated Heisenberg chains with \(\alpha = 0.29\) and \(\alpha = J_2/J_1 = 1.5\) (\(\equiv J_2/J_1\)), 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.}
\end{figure}

K and \(J_2 \simeq 2.9\) K, very close to the \(\alpha = 0.29\) reported in Ref. This. In contrast, if we proceed from the \(J_2 > J_1\) regime, we obtain \(J_1 \simeq 5.4\) K and \(J_2 \simeq 8.1\) K (\(\alpha = 1.5\)), in accord with our LSDA+U calculations. Thus, HTSE yields two ambiguous solutions.

HTSE typically diverges at temperatures 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 \(\chi^*\) 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 \(J_1 = 5.4\) 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 (Fig. 7). The difference curves evidence that both \(\alpha = 0.29\) and \(\alpha = 1.5\) provide equally good description of the experimental \(\chi(T)\) data (Fig. 6 inset).

The coexistence of the two solutions actually manifests the inner symmetry of the frustrated chain model. 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 \(\alpha = 1.5\) solutions are also related, although in a less trivial way. To pinpoint this relation, we 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 \(J_2\), up to the quantum critical point \(\alpha_c \simeq 0.2411\), where a spin gap opens. 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.

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 fitted by both \(\alpha = 0.29\) and \(\alpha = 1.5\).

Despite the similar spin gaps, the solutions \(\alpha = 0.29\) and \(\alpha = 1.5\) are physically different (unlike, e.g. \(\alpha = 0\) and \(\alpha = \infty\), that describe the same physics): spiral correlations are present in the latter case, only. Moreover, the two solutions feature substantially different correlation lengths. 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\(^2\) component of the spin, a magnetization curve reflects the energy of the lowest lying state in each S\(^2\) 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 AFM \(J_2\). However, the frustrated scenario was clearly underpinned by \(M(H)\) measurements. 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.

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 (Fig. 8). Another relevant quantity is the saturation field:

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

where \(S_{\text{max}}^z\) 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 \(H_{\text{sat}} \lesssim 16.4\) T and \(H_{\text{sat}} \lesssim 18.7\) 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\(^2\) 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 $\sim 20 \mathrm{T}$ measurement of a magnetization isotherm will be an instructive and decisive experiment to distinguish between the $\alpha = 0.29$ and $\alpha = 1.5$ scenarios.

VII. SUMMARY

In conclusion, we have studied the electronic structure of $\mathrm{KTi(SO}_4)_2\cdot\mathrm{H}_2\mathrm{O}$ 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, 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 ($\approx 10 \mathrm{K}$) of the system, we are able to obtain accurate results from our DFT calculations. Additionally, we observe a surprisingly large spin-lattice coupling with respect to the crystal water related degrees of freedom, which in turn manifests itself by playing an important role in determining the ground state of the system. 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 $\alpha \approx 1.0$ and a value of $\alpha \approx 1.4$ upon relaxing the hydrogen position in the crystal lattice. Both these values are 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 $\alpha$. Due to an intrinsic symmetry of the $J_1 - J_2$ frustrated chain model, we show that both values of $\alpha$ provide equally good fits to the experimental curve. 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 $\mathrm{KTi(SO}_4)_2\cdot\mathrm{H}_2\mathrm{O}$. Hence, we suggest performing high-field magnetization measurements on this system and as well as a.c. susceptibility experiments (to obtain the size of the spin-gap) at very low temperatures.

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