One-dimensional quantum magnetism in the anhydrous alum KTi(SO$_4$)$_2$

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Abstract

The anhydrous alum KTi(SO$_4$)$_2$, where the Ti$^{3+}$ ($d^1$, $S = 1/2$) ions form an anisotropic triangular lattice, has been prepared by a new hydrothermal route and characterized by magnetic susceptibility and neutron scattering measurements. Contrary to expectations, fits to the magnetic susceptibility indicate that the spins are isotropic (i.e. Heisenberg) and that the frustrating couplings are weak; indeed, the system is well modelled by nearly isolated chains. The inelastic neutron scattering data furthermore shows excellent agreement with an exact theoretical calculation for the one-dimensional spinon continuum. The unexpected magnetic properties of KTi(SO$_4$)$_2$ are explained in the light of density functional calculations, which reveal an unusual orbital ground state for the Ti$^{3+}$ ion.

1. Introduction

Considered a cornerstone of quantum many-body physics for many decades [1], the antiferromagnetic $S = 1/2$ Heisenberg chain model (AQHC) continues to attract experimental and theoretical attention. This enduring appeal can be traced back to the model’s richness, as well as its exact solvability. In zero magnetic field, the celebrated Bethe ansatz solution [2, 3] for the ground state is an entangled singlet characterized by algebraically decaying spin–spin correlations. Its excitations are $S = 1/2$ quasi-particles known as spinons [4, 5], which may be pictured as propagating domain walls arising from spin flips; because each flip produces an even number of spinons, they are observed in continua when using experimental techniques like inelastic neutron scattering. The recent availability of, on the one hand, large single crystals of systems which approximate the AQHC, and on the other, accurate calculations for the two and four-spinon dynamical scattering functions [6], has lead to several detailed neutron scattering measurements of spinon continua. Highlights include studies on SrCuO$_2$ [7], Cu(SO$_4$)$_2$·5(H$_2$O) [5], and KCuF$_3$ [9], where careful data treatment and analysis permit a quantitative comparison with theory. In parallel with these works, there has also been considerable interest in the effect of perturbations on the AQHC, particularly relating to quantum criticality [10, 11] and geometric frustration. Regarding the latter, the most commonly considered model is the $S = 1/2$ Heisenberg anisotropic triangular lattice (QHAT), where intra- and interchain couplings generate a network of isosceles triangles [12–14] (figure 1). Perhaps the best known realizations of this model are found in the family of Cs$_2$CuCl$_4$, where careful data treatment and analysis permit a quantitative comparison with theory. In parallel with these works, there has also been considerable interest in the effect of perturbations on the AQHC, particularly relating to quantum criticality [10, 11] and geometric frustration. Regarding the latter, the most commonly considered model is the $S = 1/2$ Heisenberg anisotropic triangular lattice (QHAT), where intra- and interchain couplings generate a network of isosceles triangles [12–14] (figure 1). Perhaps the most well-known realizations of this model are found in the family of Cs$_2$CuCl$_4$, where the ratio of the intrachain to interchain coupling $J'/J \approx 3$, neutron scattering has revealed the coexistence of a spinon continuum with a bound state induced by the interchain coupling [17, 18], as well as incommensurate spiral order at low temperatures [16].

Nearly twenty years ago, Bramwell et al proposed the anhydrous alums AM(SO$_4$)$_2$ ($A = K, Rb, M = Ti, Fe$) as an alternative set of compounds to represent both the anisotropic and isotropic ($J = J'$) triangular lattice models [21]. Among these, KTi(SO$_4$)$_2$ is the only compound which realizes the quantum limit $S = 1/2$, in this case...
Figure 1. (Right) The structure of KTi(SO₄)₂, viewed along the c’ axis. The TiO₆ octahedra are displayed in blue and the SO₄ tetrahedra in yellow. The interplane K⁺ ions have been left out for clarity. The anisotropic triangular magnetic lattice has been plotted on top of the structure, with J represented as solid black lines along (010) and J’ as dashed lines along (110), respectively. (left) A magnified view of a single TiO₆ octahedron. The isosurface represents the Ti³⁺ ground-state orbital ψ, drawn at arbitrary probability, and the black arrows denote the x’ and y’ directions in the rotated local coordinate frame. The dominant superexchange pathway proceeds through the equatorial oxygens, lying at the Ti–O distance 2.044(1) Å. The figure was obtained using the VESTA software [20].

arising from the single unpaired electron in the d-shell of Ti³⁺. KTi(SO₄)₂ is isomorphous with the naturally occurring mineral yavapaiite, KFe(SO₄)₂, which crystallizes in the monoclinic C2/m space group [22]. The structure consists of sheets of octahedrally coordinated Ti³⁺ ions bridged by (SO₄)²⁻ ions to form an anisotropic triangular lattice in the ab plane. The Ti–Ti nearest-neighbour distances along the (010) and (110) directions are 5.24 Å and 4.88 Å, respectively, with the corresponding exchanges labelled J and J’ (figure 1).

Because superexchange between neighbouring Ti³⁺ proceeds along a Ti–O–S–O–Ti pathway in both cases, J and J’ are expected to be small. Furthermore, because each nearest neighbour bond contains an inversion centre, no Dzyaloshinskii–Moriya terms are allowed (unlike in Cs₂CuCl₄). The triangular lattice [Ti(SO₄)₂] sheets are well separated by K⁺ ions along the c direction, with the interlayer distance corresponding to 7.74 Å. In [21], the magnetic susceptibility χ(T) of KTi(SO₄)₂ is found to show a broad shoulder indicating short range correlations at 7 K, followed by a sharp Curie-like increase, possibly caused by a paramagnetic impurity, at lower temperatures. Based on the small Curie constant (and hence magnetic moment) attained from fits to the high temperature data, it was speculated that the Ti³⁺ moment possesses an Ising anisotropy, as has been observed in the fully hydrated alum Cs[Ti:Al(SO₄)₂·12H₂O], where g∥ = 1.166 and g⊥ = 0.230 [23].

In this paper, we will show that KTi(SO₄)₂ is in fact an excellent realization of the AQHC. This change in interpretation has been made possible by the availability of higher quality samples synthesized by a new hydrothermal route. Standard analysis of the magnetic susceptibility yields nearly the full spin-only moment for S = 1/2, which may be understood in the context of an unusual orbital ground state revealed by DFT calculations. This ground state also explains the strong one-dimensionality of the magnetism, confirmed by fits to series expansion results for the QHAT and exact diagonalizations for the the isolated AQHC. Finally, time-of-flight neutron spectroscopy results are in near perfect agreement with the exact two- and four-spinon cross section for the AQHC, despite the use of a powder sample.

2. Synthesis and magnetic interactions

We begin by briefly discussing the sample synthesis: the literature route to KTi(SO₄)₂ involves vacuum dehydration of a stoichiometric solution of Ti₃(SO₄)₃ and K₂SO₄ followed by regrinding and annealing [21]. As stated previously, this protocol appears to also generate a large paramagnetic impurity and/or lattice defects. To prepare the present samples of KTi(SO₄)₂, we instead begin with a solution of Ti₂(SO₄)₃ and K₂SO₄ (molar ratio 3.5: 1) in H₂SO₄ (1.9 mol dm⁻³). The solution is enclosed in a 35 ml thick-walled teflon-stoppered pyrex tubes (Ace glass) and heated to 155 °C for 48 h, before slowly cooling to room temperature over 24 h. Small (~0.1 mm)³ crystals of KTi(SO₄)₂ are found on the sides of the vessel alongside a moderate amount of non-magnetic TiO₂ (anatase) powder, which may be partly removed by washing. X-ray diffraction confirms the

6 The composition of the starting solution and the reaction conditions are similar to those used in the synthesis of the monohydrate KTi(SO₄)₂·H₂O, another low dimensional magnetic system [24].
monoclinic space group of KTi(SO$_4$)$_2$, and yields room temperature lattice parameters $a = 8.2894(3)$ Å, $b = 5.2257(2)$ Å, $c = 7.8441(3)$ Å, and $\beta = 94.645(2)^\circ$. Refinements of neutron diffraction data taken at 2 K on the D1A diffractometer at the Institut Laue–Langevin (ILL) (see figure S1 in the supplementary material) indicate that $a$ and $c$ contract from their room temperature values to 8.2402(2) Å and 7.7678(1) Å, respectively. More surprisingly, $b$ shows a slight expansion to 5.23511 (9) Å. The phase fraction of anatase is estimated by the same refinement to be $\sim 10\%$.

A few clusters of crystals (in total 126.9 mg) were selected for magnetic susceptibility measurements, carried out in an applied magnetic field $H = 1000$ Oe using a Quantum Design MPMS-5 magnetometer; the temperature dependence of the molar susceptibility $\chi_m(T)$ is shown in figure 2. At high temperature, $\chi_m(T)$ follows the Curie–Weiss law $\chi_m(T) = C/(T - \theta_{CW}) + \chi_0$, where $C = N_S \mu^2_{eff}/(3k_B)$ and $\theta_{CW}$ are, respectively, the Curie and the Weiss constants, and $\chi_0$ is a $T$-independent background. Fitting in the temperature range 50–300 K yields values of $\theta_{CW} = -11(2)$ K and an effective magnetic moment $\mu_{eff} = 1.68(2)$ $\mu_B$, indicating weak antiferromagnetic couplings and a nearly full $S = 1/2$ spin–only moment ($\mu_{eff} = 1.94(3)$). The relatively large background $\chi_0 = 3 \times 10^{-4}$ originates from the core diamagnetism of KTi(SO$_4$)$_2$ and the plastic sample holder. At lower temperatures, a broad, symmetric maximum characteristic of short range order appears around the Curie and the Weiss constants, and $\chi_0$ returns to its structure, and in particular, the geometry of the Ti$^{3+}$ octahedra. In $d^1$ compounds, the interplay

![Figure 2. Magnetic susceptibility $\chi_m(T)$ of Ti–yavapaiite. The experimental data recorded at 1000 Oe is plotted with blue circles, while the fits to the Curie–Weiss law, the AQHC, and the QHAT are indicated by black dashed, red dashed, and green solid lines, respectively. The latter is only plotted down to $8 K \approx 0.8 T_p$ due to the divergence of the [5,5] Padé approximant below this temperature. The inset shows a magnified region around the low temperature peak.](image)

3. Orbital ground state and superexchange

To understand the large measured moment and apparent one-dimensionality of the magnetism in KTi(SO$_4$)$_2$, we return to its structure, and in particular, the geometry of the Ti$^{3+}$ octahedra. In $d^1$ compounds, the interplay

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7 The simulation was carried out using the ALPS package [27] on a chain of 20 spins with periodic boundary conditions.
of crystal field terms and spin–orbit coupling are crucially important for determining the single-ion magnetic properties. For perfect octahedral coordination (point group $O_h$), the $^3D$ free ion state is split into the usual set of $t_{2g}$ and $e_g$ levels, with the lone electron populating the former. The three-fold degeneracy of the crystal field ground state is lifted by LS coupling to an effective $L = -1$ orbital momentum, resulting in a non–Kramers pair of doublets in the ground state, both with $g = (L + 2S) = 0$ [23]. Lowering the symmetry to tetragonal ($D_{4h}$), the symmetry and magnitude of the magnetic moment become dependent on the sign and magnitude, $\delta$, of the tetragonal distortion; when the octahedron is axially compressed ($\delta < 0$), the orbital ground state is based on the $d_{xy}$ orbital, which yields a Kramers doublet ground state with $g = 2$, i.e. Heisenberg spins. The nearly tetragonal ($C_{2v}$) local environment of Ti$^{3+}$ in KTi(SO$_4$)$_2$ indeed appears to fulfill this condition, with two short axial and four long equatorial Ti–O distances (2.000(1) Å versus 2.044(1) Å from neutron diffraction) and O–Ti–O angles close to $90^\circ$ (figure 1). The resulting $d_{xy}$ orbital order is anticipated to produce dominant exchange along the $b$-direction, along which the Ti–O orbital overlap is large. Both the observation of a nearly full $S = 1/2$ moment and the one-dimensionality thus appear to be accounted for.

This simple picture is challenged by density-functional (DFT) calculations performed in the local density approximation (LDA) [28] using the FPLO code [29]. The orbital energies are extracted by fitting Wannier functions to the resulting d-bands, which comprise the $t_{2g}$ states around the Fermi level and the $e_g$ states 2 eV higher in energy (figure S3). Using the orthogonalized local coordinate frame with $x$, $y$, and $z$ directed along the Ti–O bonds, we find $\varepsilon_{xy} = 0.203$ eV and $\varepsilon_{xz} = \varepsilon_{yz} = 0.135$ eV. While this splitting is compatible with the crystal-field scheme for $D_{4h}$ described above, the orbitals are ordered contrary to the expectation for $\delta < 0$. Before addressing this discrepancy, we consider the effect of lowering the site symmetry to $C_{2h}$, which entails an additional small splitting between the $d_{xy}$ and $d_{yz}$ states. This splitting becomes visible when the local $y \to y'$ axis is directed along the two-fold rotation axis between two adjacent oxygen atoms in the $xy$ plane. In the new $x'y'z'$ coordinate frame, effectively the original frame with $x$ and $y$ axes turned by 45° (figure 1), the $d_{xy}$ orbital has $(x'y')^2 - (y')^2$ symmetry, and the orbital energies become $\varepsilon_{x'y'} = 0.216$, $\varepsilon_{y'y'} = 0.112$, and $\varepsilon_{z'z'} = 0.083$ eV.

The result that $\varepsilon_{x'y'} < \varepsilon_{y'y'}$ is again at odds with the geometry of the Ti$^{3+}$ octahedron, which implies $\varepsilon_{x'y'} > \varepsilon_{y'y'}$. This arrangement is expected from the scissor-like distortion of the O atoms in the $xy$ plane, where the O–Ti–O angles are 88° and 92°, respectively. The closer proximity of the O$^{2-}$ ions to $x'$, which bisects the smaller angle, then suggests $\varepsilon_{x'y'} > \varepsilon_{y'y'}$. Taking this and the unexpectedly high energy of the $(x'y')^2 - (y')^2$ orbital into account, it appears that the ions beyond the nearest-neighbour oxygens play the decisive role in the ordering of the $t_{2g}$ orbitals. This is perhaps not surprising given the small magnitude of the distortion of the Ti$^{3+}$ octahedron; the difference between axial and equatorial Ti–O bond lengths is only 0.2%. In the present case, the $d_{z'y'}$ orbital may be stabilized by the positively charged K$^+$ ions along the $x'$-direction, located at a Ti–K distance of 3.88 Å. It may also be envisaged that the second-neighbour oxygens within the SO$_4$ tetrahedra contribute; these are more remote from Ti$^{3+}$ along the $x'$-direction (Ti–O2 distance of 4.30 Å) than along the $y'$-direction (Ti–O1 distance of 3.45 Å and Ti–O3 distance of 4.09 Å). While these oxygens may also be responsible for the high energy of the $(x'y')^2 - (y')^2$ orbital in energy, this is less evident.

To investigate the orbital ground state of Ti$^{3+}$ in KTi(SO$_4$)$_2$ under more realistic conditions, we extend the above calculations by adding a Hubbard $U$ at the mean-field level (LSDA+$U$). Occupations of d-orbitals are varied as to minimize the total energy under the presence of the Hubbard term $^3$. These calculations yield an insulating state with a band gap of 2.3 eV and a ground-state orbital wave-function $\ket{\Phi} = 1/\sqrt{3} \ket{(x'y')^2 - (y')^2 + 2(x'z')}$, obtained by diagonalizing the orbital occupation matrix.

We now perform the Wannier fit to the original LDA bands using an orthonormal basis containing the $\ket{\Phi}$ orbital (figure 1) together with $\ket{\Phi_2} = 1/\sqrt{3} \ket{2(x'y')^2 - (y')^2 + 2(x'z')}$, $\ket{\Phi_3}$, and the two $e_g$ states. The energies of the $t_{2g}$ orbitals become $\varepsilon_{x'y'} = 0.064$, $\varepsilon_{y'y'} = 0.112$, and $\varepsilon_{z'z'} = 0.235$ eV; the $\ket{\Phi}$ orbital indeed has the lowest energy at the LDA level (figure S3). The nearest-neighbour Ti–Ti hopping of this state corresponding to the pathways for the exchange couplings $J$ and $J'$ are $t = -0.045$ eV and $t' = 0.023$ eV, respectively. Using the full five-band tight-binding model and adding an effective Hubbard $U_{eff} = 4$ eV and Hund’s coupling $J_{eff} = 1$ eV, we compute exchange couplings from the Kugel–Khomskii model [31, 32] and arrive at $J = 18.3$ K and $J' = 5.1$ K ($J/J' = 3.6$) in reasonable agreement with the susceptibility fits. Alternatively, we obtain $J = 16$ K and $J' = 7$ K ($J/J' = 2.3$) from LSDA+$U$ total energies of ferromagnetic and antiferromagnetic spin configurations (the so-called supercell method). However, these LSDA+$U$-based values appear to be strongly dependent on the choice of the Hubbard $U$ and on the double-counting correction method in LSDA+$U$.

KTi(SO$_4$)$_2$ may thus be said to feature a well-defined but rather unexpected orbital state described by $\ket{\Phi}$, which is triggered by the weak crystal-field splitting of the $t_{2g}$ states. This splitting is not consistent with the local distortion of the TiO$_6$ octahedron and reflects a complex interplay of ionic charges surrounding the Ti$^{3+}$ ion in the crystal structure. A similar inversion of the orbital energies with respect to crystal-field predictions for nearest-neighbour oxygens has also recently been demonstrated in the iridate compound Sr$_2$IrO$_4$ [33]. Finally,

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8 We used the on-site Hubbard repulsion $U_d = 4$ eV and Hund’s exchange $J_d = 1$ eV following our recent study of KTi(SO$_4$)$_2$·2H$_2$O in [30].
This issue has since been resolved.

4. Magnetic excitations

To address the unsettled question of the interchain couplings (and more generally, the magnetic excitations) in KTi(SO₄)₂, we carried out a time-of-flight neutron scattering on the IN5 spectrometer at the ILL. Approximately 10 g of polycrystalline KTi(SO₄)₂ (the same sample as used for neutron diffraction on D1A) were loaded in a cylindrical Cu can of diameter 11 mm, which was connected to the end of an ILL-built dilution refrigerator with a base temperature of 50 mK. Around 1 bar (at 298 K) of ⁴He exchange gas was admitted into the can to thermalize the sample at sub-Kelvin temperatures. Given the energy scale extracted from the fits to \( \chi_m(T) \), wavelengths of \( \lambda_i = 3 \, \text{Å} (E_i = 9.09 \, \text{meV}) \) and \( 5 \, \text{Å} (E_i = 3.27 \, \text{meV}) \) were selected by a pair of counter-rotating disk choppers. For both wavelengths, the choppers were spun at 17000 rpm to yield full-width half-maximum E-resolutions at the elastic line of 0.31 meV and 0.07 meV, respectively. The data were corrected for detector efficiency using a vanadium standard, the E-dependent self-attenuation of the sample, as well as background from the sample environment. Unfortunately, it was not possible to fully subtract a component arising from the beam stop, which manifests itself as strong spurious scattering at small angle in the entire energy transfer window for both wavelengths (figure 3(a))⁹.

The dynamical scattering function \( S(Q, E) = \hbar \omega \) at 50 mK for \( \lambda_i = 5 \, \text{Å} \) is shown in figure 3(a). A clear branch of excitations is observed dispersing from the vicinity of the antiferromagnetic position (0,0,0) up to \( \sim 2 \, \text{meV} \). Upon initial inspection, the powder averaging renders it difficult to distinguish whether this represents conventional magnons or a spinon continuum. However, the sharp onset of the scattering, particularly at small \( E \) (figure 4(a)), can be associated with a powder averaged one-dimensional dispersion. Furthermore, the lower bound of the spinon continuum is expected to be found at \( E_s(Q) = \frac{\pi}{2J} \cos(Qx) \), where \( Qx \) is the component of the wave-vector transfer \( Q \) along the chain direction. Choosing \( J = 1.31 \, \text{meV} \) = 15.2 K and \( Q_s \| b \), as inferred from our fits to \( \chi_m(T) \) and electronic structure calculations, we find excellent agreement with the observed dispersion. The semi-classical spin wave solution, on the other hand, indicates a zone-boundary energy of \( J_1 = 1.32 \, \text{meV} \), clearly inconsistent with the data. It also predicts an absence of scattering beyond the dispersion maximum, which a Q-integrated slice of the 3 Å data verifies is not the case (figure 4(f)).

We now attempt to put our claim that the observed scattering represents a spinon continuum on a more quantitative footing. The two- and four-spinon dynamical structure factor \( S(Q, E)_{2+4} \) for the QHCA has been obtained exactly by Caux and Hagemans [6] from an algebraic treatment based on the observation that even-spinon states are eigenstates of the AQHC Hamiltonian. Using this result as a starting point, spherical (powder) averaging was carried out assuming no dispersion or modulation of the intensity perpendicular to \( Q_s \). To achieve

⁹ This issue has since been resolved.
a uniform sampling on the constant-Q sphere, random Cartesian coordinates were selected from a Gaussian distribution and normalized to the sphere radius. The S(Q, E)\[^{pow}\] resulting from this procedure is shown in figure 3(b). The Q-dependence of the experimental S(Q, E) was extracted by integrating over a series of 0.2 meV wide strips between E = 0.5 and 2.1 meV (figures 4(a)–(d)). These strips were then fitted to the corresponding section of the powder-averaged S(Q, E)\[^{pow}\]; for each strip, the background and amplitude A(E) were adjustable parameters, while J was considered a global parameter. Regions in Q contaminated by scattering from the beam-stop were not included in the fitting range. The fitted results up to 2.1 meV ~ max E, are shown in figures 4(a)–(d), with A(E) given in figure 4(e). Excellent agreement between experiment and theory is found for all strips using J = 1.32(2) meV = 15.3(2) K. Furthermore, A(E) is broadly consistent across the full energy range, but shows a ~10% drop from its average value A = 0.079 for the highest energy strip (figure 4(e)). Although a small J could explain this small deviation [18], we will show that the likeliest explanation is the imperfect correction of the experimental data.

To verify the robustness of the AQHC with respect to our fits, we turn to the E-dependent strip through the 3 Å data set discussed above (figure 4(f)). As the scattering up to ~1 Å\(^{-1}\) contains a strong contribution from the background, we integrate S(Q, E) over the range 1.5–2.0 Å\(^{-1}\). This range furthermore covers Q \(\approx\) 1.7 Å\(^{-1}\), where J\(^{\prime}\) is expected to cause a large redistribution of intensity from the powder-averaging of the inter-chain dispersion. In order to fit S(Q, E)\[^{pow}\] to the experimental data, we convolute it pixel-by-pixel with an E-dependent resolution calculated from the expression given in [34]. Again, the agreement with the model is nearly perfect (figure 4(f)) for J = 1.38(2) meV = 16.0(2) K, close to the value extracted from our 5 Å dataset and susceptibility fit. This indicates that slight variation in A(E) observed at the longer neutron wavelength \(\lambda = 5\) Å is probably an experimental artefact, with the self-attenuation correction, which neglects the absorption in the walls of the Cu container, the most likely source of the error. Based on the above, as well as the fact that no asymmetry is observed in the dispersion, it thus appears that KT\(_2\)(SO\(_4\))\(_2\) is close to an ideal realization of the AQHC, fulfilling the condition J \(\gg\) J\(^{\prime}\).

Finally, we search for evidence of magnetic order below 1.8 K by comparing our 50 mK data to higher temperature datasets; subtraction of datasets collected in the range 1.3–10 K do not result in any systematic changes in the elastic scattering consistent with magnetic order (see figure S2, supplemental material). Using the intensity of the (001) nuclear Bragg peak, the statistical error of our data, and assuming collinear Néel order propagating with \(k = (0, 0, 0)\), we estimate an upper limit for the ordered moment of \(\mu_\parallel \sim 0.1 \mu_0\) for any magnetic moment direction. Despite the small magnitude of this estimate, magnetic order cannot be excluded in KT\(_2\)(SO\(_4\))\(_2\); in fact, strongly suppressed ordered moments (and Néel temperatures, T\(_N\)) are a general feature of one-dimensional materials. Indeed, several quasi-1D systems, including Sr\(_2\)CuO\(_3\) and Ca\(_2\)Cu\(_3\)O\(_6\), show \(\mu_\parallel < 0.1 \mu_0\) [35]. The small ordered moments and Néel temperatures can be partly understood in the context of
quantum field theory calculations, which yield $\mu_0 \sim C_1 \sqrt{J_c / J}$, where $J_c$ is an unfrustrated interchain coupling, and $T_N \sim C_2 J$.\footnote{Ignoring logarithmic corrections.} $C_1$ and $C_2$ are constants, and correspond to $\sim 1$ and $\sim 0.8$ for a cubic arrangement of spin chains\cite{36,37}. Similar calculations on stacked anisotropic triangular planes (as in KTi(SO$_4$)$_2$) show that the latter relation still holds, but that the constant $C_2$ is reduced by a factor $\sim 2$; this is presumably because the frustration within the planes reduces the effective number of nearest neighbour chains from four (in the cubic case) to two. The reduction in $C_2$ should correspondingly be $\sqrt{2}$; from this, we may estimate an interchain coupling between adjacent planes of $J_c < 0.02 J = 0.3$ K, and thus $T_N < 0.4$ K\cite{38}. This is consistent with the $J_c = 0.05 K (J_c / J \sim 300)$ extracted from our DFT calculations. Regardless of the presence or absence of magnetic order in KTi(SO$_4$)$_2$, the excitation spectrum is expected to remain largely unchanged except at very low energies $<0.25$ meV, where transverse spin waves and a gapped longitudinal spin-wave mode may occur\cite{39–43}.

5. Conclusion

To conclude, the recent preparation of high-quality samples of the anhydrous alum KTi(SO$_4$)$_2$ have allowed us to re-evaluate its magnetic properties. Fits to both magnetic susceptibility and inelastic neutron scattering data indicate that it is an excellent realization of the AQHC, with $J = 15.3(2)$ K $= 1.32(2)$ meV, and $g \sim 2$. These properties appear to arise from an unusual orbital order on the Ti$^{3+}$ site, which results in moderate antiferromagnetic superexchange along the crystallographic $b$-direction and weak exchange along other directions. A few points remain to be clarified, however, most prominently the possible presence of magnetic order at $T < 0.4$ K due to interchain couplings. This problem is most appropriately dealt with by inelastic or polarized neutron scattering at lower energies than presented here, as well as muon spin rotation.

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