Chem. Mater. **2008,** *20,* 8–10

A New Realisation of the $S = 1/2$ Frustrated Chain Antiferromagnet

G. J. Nilsen,*,†,‡,§ H. M. Rønnow,† A. M. Läuchli,‖
F. P. A. Fabbiani,⊥ J. Sanchez-Benitez,# K. V. Kamenev,#
and A. Harrison‡,∇

Laboratory for Quantum Magnetism, Institute of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland, School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, United Kingdom, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, Institute for Numerical Research in the Physics of Materials, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland, Rutherford Appleton Laboratory, Chilton OX11 OQX, United Kingdom, School of Electrical Engineering and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom, and Institut Laue Langevin, 6 rue Jules Horowitz, 38042 Grenoble, France

Received August 16, 2007
Revised Manuscript Received October 26, 2007

Model magnets with $S = 1/2$ have been much sought-after in recent decades, mainly because of theoretical predictions of novel quantum ground states. Although the search so far has primarily focused on materials based on Cu^{2+}, the chemistry of Ti^{3+} (d^1) has remained rather underexplored in this context. The primary reason for this is the instability of Ti^{3+} with respect to oxidation. Nonetheless, aqueous Ti^{3+} can be stabilized in reducing conditions, as well as with ligands for which it has an affinity, such as SO_4^{2-}. A family of materials known as the titanium alums, with general formula $ATi(SO_4)_2 \cdot xH_2O$ ($A = Na$, K, Rb, Cs and $x = 0,12$) provide an example of compounds grown from such solutions. In the $x = 12$ case, the magnetic Ti^{3+}ion is isolated by coordinating H_2O molecules, making it an excellent candidate for crystal field studies.[1–3] The anhydrous version of K-titanium alum, on the other hand, consists of layers of Ti^{3+} ions coordinated and interlinked by SO_4^{2-} and provides a good realization of the $S = 1/2$ Ising model on the triangular lattice.[4] These compounds are part of a larger group of materials $AB(SO_4)_2 \cdot xH_2O$, where $B = Ti$ can be substituted for either Al or another trivalent first-row transition metal. Although only the $x = 0$, 12 endmembers are known in the case of Ti, several intermediate species with $x = 1$, 4, 6, 11 are known to occur naturally for $B =$ Al, Fe. Here, we present the synthesis, crystal structure, and magnetic properties of a new model magnet $KTi(SO_4)_2 \cdot H_2O$ (i.e., $x = 1$). Specifically, we demonstrate that $KTi(SO_4)_2 \cdot H_2O$ has the Krausite structure of its $B = Fe$ analogue and represents a realistation of the currently much sought-after $S = 1/2$ Heisenberg frustrated chain model (FCM). More generally, our discovery brings the promise of a new class of $S = 1/2$ model magnet.

$KTi(SO_4)_2 \cdot H_2O$ was discovered in an exploration of the aqueous $K^+{-}Ti^{3+}{-}SO_4^{2-}$ system under hydrothermal conditions. K_2SO_4, $Ti_2(SO_4)_3$, and H_2SO_4 were combined in the molar ratio 2:7:15 inside a PTFE lined bomb, which was heated to 155 °C for 48 h. It was then cooled slowly (10° h^{-1}) to room temperature, yielding small ($\sim$0.1 mm^3) bluish purple crystals in addition to amorphous impurity. The product, which appeared to be air stable, was finally washed with water and propanone and dried overnight. In 52 repetitions of the reactions, only amorphous product was formed in all but four cases. It was eventually found that placing a small glass liner inside the PTFE container resulted in a better success rate, with 6 of 25 attempts yielding the desired product.

A crystal of dimensions 0.19 mm × 0.15 mm × 0.08 mm was selected for single-crystal diffraction. All data were collected at 150(2) K on a Bruker SMART APEX CCD diffractometer equipped with an Oxford Cryosystems low-temperature device. The structure was solved by direct methods and full matrix least-squares structure refinement against F^2 was performed using CRYSTALS.[6] Non-hydrogen atoms were modeled with anisotropic displacement parameters. Hydrogen atoms were located on a difference map and their positions were refined subject to distance restraints. The coordination of water rather than hydroxyl was primarily inferred from magnetic susceptibility measurements, which confirmed the oxidation state of Ti as Ti^{3+}. These measurements were carried out down to 1.8 K in a field of 100 Oe on a polycrystalline sample containing up to $\sim$5% of amorphous impurity using a Quantum Design $MPMS_2$ SQUID magnetometer. The specific heat was measured on a 2 mg cluster of crystals in the temperature range 480 mK to 300 K using a Quantum Design PPMS fitted with a ^3He insert.

$KTi(SO_4)_2 \cdot H_2O$ was found to crystallize in the monoclinic $P2_1/m$ space group, with lattice parameters $a = 7.6492(3)$ Å, $b = 5.2580(2)$ Å, $c = 9.0485(3)$ Å, and $\beta = 101.742(2)°$. The structure (Figure 1) is isomorphous with that of the naturally occurring mineral Krausite ($KFe(SO_4)_2 \cdot H_2O$)[7] and consists of double chains of Ti octahedra, connected by SO_4^{2-} groups along the b axis. The pairs of chains are

---

[*] Corresponding author. E-mail: goran.nilsen@epfl.ch.
[†] IPMC, Ecole Polytechnique Fédérale de Lausanne.
[‡] School of Chemistry, University of Edinburgh.
[§] Paul Scherrer Institut.
[‖] IRRMA, Ecole Polytechnique Fédérale de Lausanne.
[⊥] Rutherford Appleton Laboratory.
[#] School of Electrical Engineering and CSEC, University of Edinburgh.
[∇] Institut Laue Langevin.

(1) Dionne, G. F.; MacKinnon, J. A. **1968**, *172*, 325.
(2) Bleaney, B.; Bogle, G. S.; Cooke, A. H.; Duffus, R. J.; O'Brien, M. C. M.; Stevens, K. W. H. *Proc. Phys. Soc. A* **1954**, *68*, 57.
(3) Bose, A.; Chakravarty, A. S.; Chatterjee, R. *Proc. R. Soc. London, Ser. A* **1960**, *255*, 145.
(4) Bramwell, S. T.; Carling, S. G.; Harding, C. J.; Harris, K. D. M.; Kariuki, B. M.; Nixon, L.; Parkin, I. P. *J. Phys.: Condens. Matter* **1996**, *8*, 123.
(5) Momma, K.; Izumi, F. In *Commission of Crystallographic Computing Newsletter*; Parsons, S., Cranswick, L., Eds.; International Union of Crystallography: Chester, U.K., 2006; Vol. 7, p 106.
(6) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.
(7) Graeber, E. J.; Morosin, B.; Rosenzweig, A. *Am. Mineral* **1965**, *50*, 1929.

10.1021/cm7023263 CCC: $40.75

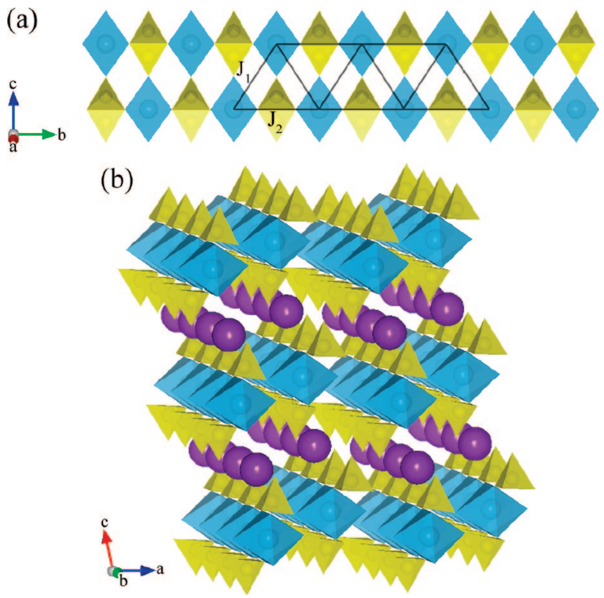

Figure 1. (a) View of the double chains showing the connectivity between the magnetic Ti^{3+} ions (at the center of the blue octahedra) via the SO_4^{2-} tetrahedra (yellow). (b) Three-dimensional arrangement of the double chains seen along the *b* axis. The structures were generated using the VESTA visualisation package.[5]

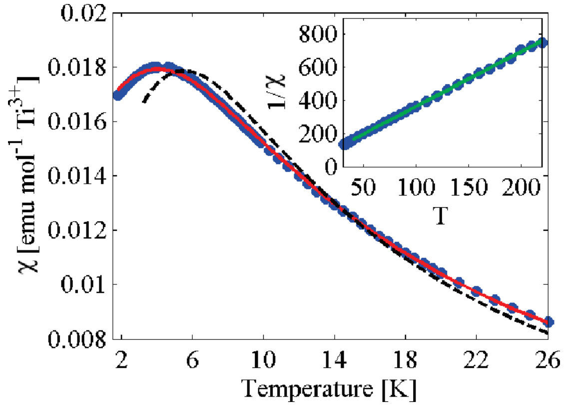

Figure 2. Low-temperature susceptibility of $KTi(SO_4)_2 \cdot H_2O$. Exact diagonalization data for $g = 1.80(2)$, $\alpha = 0.29$, and $J_1 = 9.48(2)$ K are indicated by the solid line. The dashed line represents a fit in the same region (3–300 K) at the Bonner–Fisher limit ($\alpha = 0$) with $J = 8.51(9)$ K and $g = 1.901(1)$. The inset shows the Curie–Weiss fit of the high-temperature region of the data.

separated in the *a* direction by K^+ ions and in the *c* direction by interpenetrating H_2O molecules bound to the octahedra.

The magnetic ions are connected in a so-called railroad trestle motif (Figure 1a), with diagonal separations of 4.929 Å and horizontal separations of 5.258 Å. Superexchange is expected to be mediated by the SO_4^{2-} groups, which doubly bridge both nearest and next-nearest neighbor pairs of magnetic ions. The sign of the exchange is anticipated to be antiferromagnetic from the Goodenough−Kanamori rules. The the distances between the chains in the *a* and *c* directions are 7.598 and 5.869 Å, respectively, suggesting that any magnetic exchange in $KTi(SO_4)_2 \cdot H_2O$ should be essentially confined to the chains.

The temperature dependence of the magnetic susceptibility of $KTi(SO_4)_2 \cdot H_2O$ is indicated in Figure 2. A fit to the high temperature ($T > 40$ K) region using the Curie–Weiss law yields $\mu_{eff} = 1.557(3)\ \mu_B$ (i.e., $g = 1.80$) and $\theta = -9.8(7)$ K, (i.e., weak antiferromagnetic coupling). The presence of amorphous impurity, which contains diamagnetic Ti^{4+}, means that the value for μ_{eff} should be treated as a lower bound. For some Ti^{3+} compounds, a significant reduction in the magnetic moment is caused by spin–orbit coupling to degenerate orbital states. In Cs-titanium alum for instance, values of $g_{\parallel} = 1.14$ and $g_{\perp} = 1.25$ are reported[2] and ascribed to coupling to the low-lying excited orbital doublet, which arises in a trigonal crystal field. In the case of $KTi(SO_4)_2 \cdot H_2O$, however, we believe that such degeneracies are lifted by lower-symmetry components in the crystal field, with sufficient splittings such that the orbital moment is largely quenched.[1]

When the temperature is lowered, a broad maximum in the susceptibility characteristic of short-range order along the magnetic chains is observed around $T = 4.5$K. No signs of long-range ordering are observed down to the lowest temperature, indicating that the interchain exhange is weak. A fit to the Bonner–Fisher curve[8] for the $S = 1/2$ Heisenberg chain was attempted, but was found to describe the peak shape and position poorly. This highlights the influence of additional terms in the Hamiltonian. One likely candidate for such a term based on the connectivity between the magnetic ions is a frustrating next nearest neighbor interaction. Hence, the Hamiltonian may be written

$$H = J_1 \sum_{n,n+1}^{N} S_n S_{n+1} + J_2 \sum_{n,n+2}^{N} S_n S_{n+2}$$

where J_1 and J_2 are the nearest neighbor and next-nearest neighbor exchange parameters, respectively. The frustrated chain model can show a range of exotic quantum ground states,[9] depending on the value of the frustration parameter $\alpha = J_2/J_1$, as well as the respective signs of J_1 and J_2. When J_1, $J_2 > 0$ and $\alpha > 0.2411$, for instance, a singlet liquid ground state with a gap Δ to the lowest excited triplet is expected.[10–12] This gap persists for $\alpha \rightarrow \infty$, although there is a crossover to a regime with spiral correlations for $\alpha > 1.8$.[13] In the case where $J_1 < 0$, $J_2 > 0$ and $|\alpha| > 0.25$, classical helical order is expected.

Because no analytical expression exists for the susceptibility of the frustrated chain model, exact diagonalization was performed on up to 18 spins for a range of α using the ALPS package.[14] The fits of the calculated data to the experimentally measured susceptibility are shown in Figure 2. The best correspondence between experiment and calculation is found for $\alpha = 0.29(1)$, $g = 1.80(1)$, and $J_1 = 9.48(2)$K, which implies that the system is in the dimer spin liquid phase, corresponding to a predicted gap to the lowest triplet of $\Delta < J_1/20$.[15]

As a complement to the magnetic susceptibility measurement, specific heat was measured in the temperature range 480 mK to 300 K. The data again show a broad feature at

---

(8) Bonner, J. C.; Fisher, M. E. *Phys. Lett.* **1964**, 135.
(9) Bursill, R.; Gehring, G. A.; Farnell, D. J. J.; Parkinson, J. B.; Xian, T.; Zeng, C. *J. Phys.: Condens. Matter* **1995**, *7*, 8605.
(10) Majumdar, C. K.; Ghosh, D. K. *J. Math. Phys.* **1969**, *10*, 1388.
(11) Haldane, F. D. M. *Phys. Rev. B* **1982**, *25*, 4925.
(12) Okamoto, K.; Nomura, K. *Phys. Lett. A* **1992**, *169*, 433.
(13) Somma, R. D.; Aligia, A. A. *Phys. Rev. B* **2001**, *64*, 024410.
(14) Alet, F. *J. Phys. Soc. Jpn. Suppl.* **2005**, *74*, 30.
(15) White, S. R.; Affleck, I. *Phys. Rev. B* **1996**, *54*, 9862.

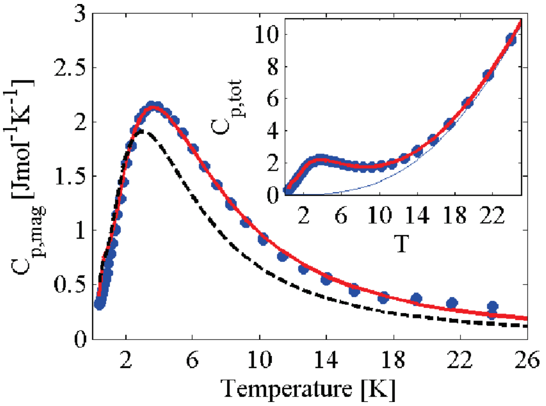

Figure 3. Magnetic specific heat, $C_{p,mag}$, fitted as described in the text to ED data (solid line) and the Bonner–Fisher curve (dashed line, $J = 7.9(7)$ K). The inset shows ED fit with phonon contribution of the form $C_{p,phonon} = \beta T^3 + \gamma T^5 + \delta T^7$.

around $T = 3$ K (Figure 3) corresponding to the point at which the maximum overlap between buildup of short-range correlations (and hence the magnetic density of states) and thermal population of available states is achieved. Also in the specific heat, no anomalies or other indications of long-range order are observed. The curve was fitted for $T < 50$ K using the expression $C_{p,tot} = C_{p,mag} + C_{p,phonon}$, where $C_{p,mag}$ was calculated by exact diagonalization, and $C_{p,phonon}$ was approximated using a power series in odd powers of T up to order T.[7] Again, the Bonner–Fisher curve fails to capture the main features of the peak. Parameters of $\alpha = 0.29(2)$ and $J_1 = 9.53(7)$ K were found to provide the best description of the data, thus confirming the results from the susceptibility fit.

In summary, we have reported the synthesis and crystal structure of $KTi(SO_4)_2.H_2O$, a novel frustrated magnet with the Krausite structure. Both specific heat and magnetic susceptibility measurements on $KTi(SO_4)_2 \cdot H_2O$ indicate a promising realization of the $S = 1/2$ frustrated chain model with $J_1 = 9.46(2)$ K, $\alpha = 0.29(1)$, and hence $J_2 = 2.8$ K. Other experimental systems that map onto this model include Cu[2-(2-aminomethyl)]Br_2 ($\alpha = 0.2$),[16] $(N_2H_5)CuCl_3$ ($\alpha = 4$),[17,18] $SrCuO_2$ ($\alpha < -10$),[19,20] $LiCu_2O_2$ ($\alpha = -1$),[21,22] $LiCuVO_4$ ($\alpha = -0.78$),[23] and Li_2CuZrO_4 ($\alpha = -0.3$).[24] The structures of many of these, however, consist of edge-sharing CuO_2 chains, which leads to weak, often ferromagnetic, nearest-neighbor exchange (∠Cu−O−Cu → 90), and stronger next-nearest neighbor Cu−O−O−C exchange. Hence, the highly interesting region of the phase diagram defined by $0.2411 < \alpha < 1.8$ is essentially inaccessible in this type of system; in fact, $KTi(SO_4)_2 \cdot H_2O$ is the only known material to fall within this α range.

Acknowledgment. We acknowledge F.C. Coomer for assistance during the initial stages of the synthesis.

Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

CM7023263

---

(16) Kikuchi, H.; Nagasawa, H.; Ajiro, Y.; Asano, T; Goto, T. *Physica B* **2000**, *284*, 1631.
(17) Brown, D. B.; Donner, J. A.; Hall, J. W.; Wilson, S. R.; Wilson, R. B.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1979**, *18*, 2635.
(18) Maeshima, N.; Hagiwara, M.; Narumi, Y.; Kindo, K.; Kobayashi, T. C.; Okunishi, K. *J. Phys.: Condens. Matter* **2003**, *15*, 3607.
(19) Zaliznyak, I. A.; Woo, H.; Perring, T. G.; Broholm, C. L.; Frost, C. D.; Takagi, H. *Phys. Rev. Lett.* **2004**, *93*, 087202.
(20) Matsuda, M.; Katsumata, K. *J. Magn. Magn. Mater.* **1995**, *140*, 1671.
(21) Drechsler, S.-L.; Tristan, N.; Klingeler, R.; Büchner, B.; Richter, J.; Mlek, J.; Volkova, O; Vasiliev, A.; Schmitt, M.; Ormeci, A.; Loison, C.; Schnelle, W.; Rosner, H. *J. Phys.: Condens. Matter* **2007**, *19*, 145230.
(22) Masuda, T.; Zheludev, A.; Bush, A.; Markina, M.; Vasiliev, A. *Phys. Rev. Lett.* **2004**, *92*, 177201.
(23) Enderle, M.; Mukherjee, C.; Fåk, B.; Kremer, R. K.; Broto, J.-M.; Rosner, H.; Dreschler, S.-L.; Richter, J.; Malek, J.; Prokofiev, A.; Assmus, W.; Pujol, S.; Raggazzoni, J.-L.; Rakoto, H.; Rheinstädter; Rønnow, H. M. *Europhys. Lett.* **2005**, *70*, 237.
(24) Drechsler, S.-L.; Volkova, O.; Vasiliev, A. N.; Tristan, N.; Richter, J.; Schmitt, M.; Rosner, H.; Mlek, J.; Klingeler, R.; Zvyagin, A.; Büchner, B. *Phys. Rev. Lett.* **2004**, *94*, 039705.