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1996 J. Phys.: Condens. Matter 8 L123

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## LETTER TO THE EDITOR

# The anhydrous alums as model triangular-lattice magnets

S T Bramwell<sup>†||</sup>, S G Carling<sup>‡</sup>, C J Harding<sup>§</sup>, K D M Harris<sup>†¶</sup>,  
B M Kariuki<sup>†¶</sup>, L Nixon<sup>†</sup> and I P Parkin<sup>†</sup>

<sup>†</sup> Department of Chemistry, University College London, Christopher Ingold Laboratories, 20 Gordon Street, London WC1H 0AJ, UK

<sup>‡</sup> The Royal Institution of Great Britain, 21 Albermarle Street, London W1X 4BS, UK

<sup>§</sup> Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

Received 2 January 1996

**Abstract.** We show that materials based on the yavapaiite layered structure are of potential interest as realizations of a model quasi-two-dimensional triangular-lattice antiferromagnet. The structure type is such that magnetic ions occupy a regular or very slightly distorted triangular lattice in well separated layers. We report the magnetic susceptibility versus temperature behaviour of three compounds:  $\text{RbFe}(\text{SO}_4)_2$ , which has an equilateral triangular lattice, and  $\text{KFe}(\text{SO}_4)_2$  and  $\text{KTi}(\text{SO}_4)_2$  which both have isosceles triangular lattices. A comparison of the behaviour of these three compounds identifies the effect of distortion and the spin value on the properties of the triangular-lattice antiferromagnet.  $\text{KTi}(\text{SO}_4)_2$ , which we have made for the first time, has  $S = 1/2$ , and may prove to be the best example of the  $S = 1/2$  triangular-lattice antiferromagnet yet discovered.

The fully frustrated triangular-lattice antiferromagnet is a statistical mechanical system of considerable interest. With classical Ising spins and near-neighbour interactions, the ground state has power-law decay of correlations, and the magnetic susceptibility diverges as  $1/T$  [1]. With classical isotropic spins, the frustration is relieved to some extent by the adoption, at  $T = 0$  K, of a three-sublattice non-collinear spin structure in which each spin makes an angle of  $120^\circ$  with its neighbours. At finite temperature there is a weak cusp in the uniform magnetic susceptibility which is believed to mark a defect-mediated transition [2]. The properties of this system, and its relatives with an admixture of Ising or  $XY$ -interactions, were originally elucidated by the pioneering work of Miyashita, Kawamura and co-workers [2–5]. Both the classical two-dimensional triangular-lattice antiferromagnet, and the related stacked triangular-lattice antiferromagnet magnet exhibit exceedingly rich temperature–field phase diagrams which have attracted great interest and led to much controversy [6–10].

With quantum spins, the situation is further complicated by the possibility that quantum fluctuations reduce the sublattice order at  $T = 0$  K. For  $S \gg 1/2$ , the reduction is unlikely to be significant, but for  $S = 1/2$  it has been speculated that ground-state order might be completely destroyed [11]. Fazekas and Anderson [12] suggested that the  $S = 1/2$  system has a ground state of the resonating-valence-bond (RVB) type, which is of interest in connection with the theory of high-temperature superconductivity [13]. For the  $S = 1/2$  Heisenberg triangular-lattice antiferromagnet, it is now generally believed that the ground state is in fact ordered, but with a much reduced moment at  $T = 0$  K [14, 15]. However,

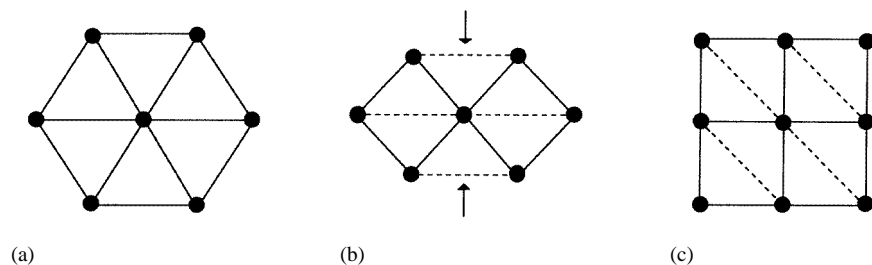
<sup>||</sup> Author to whom any correspondence should be addressed.

<sup>¶</sup> Present address: School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.

Ising-like or other perturbations to the basic Heisenberg Hamiltonian could stabilize an exotic ground state.

Experimentally, the stacked triangular lattice is quite well represented by  $ABX_3$ -type compounds [16, 17], but, with the exception of  $VX_2$  ( $X = \text{Cl, Br, I}$ ) [16], there are relatively few realizations of essentially two-dimensional systems. In particular the only known examples of the interesting  $S = 1/2$  triangular-lattice antiferromagnet are  $\text{NaTiO}_2$  [18] and  $\text{LiNiO}_2$  [18, 19]. These strongly coupled systems display mysterious magnetic properties and are doubtless best described in terms of extended bonding. In such systems it is difficult to be sure of the applicability of a Heisenberg spin Hamiltonian, and it would be desirable to develop new  $S = 1/2$  systems with localized and weakly coupled spins. In general a number of controversies could be addressed experimentally with the aid of new model triangular-lattice antiferromagnets.

In this letter, we report the discovery of a series of compounds which appear to be ideal for this purpose. They are part of an extensive series of general formula  $AM(\text{XO}_4)_2$ , related to the mineral yavapaiite,  $\text{KFe}(\text{SO}_4)_2$  [20]. In general A is a univalent (e.g.  $\text{Na}^+$ ) or divalent (e.g.  $\text{Ba}^{2+}$ ) cation, M is a trivalent (e.g.  $\text{Fe}^{3+}$ ) or tetravalent (e.g.  $\text{Mo}^{4+}$ ) cation, and  $\text{XO}_4$  is a divalent (e.g.  $\text{SO}_4^{2-}$ ) or trivalent (e.g.  $\text{PO}_4^{3-}$ ) oxy-anion. Subject to the requirement of charge balance, practically any combination of such species can be realized [21–23]. The general structure type is one in which M ions lie in triangular arrays in well separated layers formed by the  $\text{XO}_4$  groups, and the A ions occupy the interlayer space. There are usually either one or three layers per unit cell [22]. With a very large interlayer spacing of  $>8 \text{ \AA}$ , all of the compounds should closely approximate a two-dimensional magnetic model. As there are  $O(10^4)$  possible compounds which adopt this structure, we have chosen to confine our initial investigation to the series of anhydrous sulphate alums  $AM(\text{SO}_4)_2$ , with  $A = \text{Na, K, Rb, Cs}$  and  $M = \text{Ti, V, Cr, Fe}$ . Our reason for studying the sulphates is that we expect  $\text{Ti}^{3+}$  with spin  $S = 1/2$  to be stable in the presence of sulphate ligands. In fact we have succeeded in preparing the Ti compounds for the first time using air-sensitive techniques.



**Figure 1.** (a) The equilateral triangular (ET) lattice, as adopted by  $\text{RbFe}(\text{SO}_4)_2$ . (b) The isosceles triangular (IT) lattice, indicating the direction of the in-plane distortion in  $\text{KTi}(\text{SO}_4)_2$  and  $\text{KFe}(\text{SO}_4)_2$ . (c) The square lattice with diagonal bonds, which is topologically the same as (b).

There are several structural subtleties associated with the anhydrous alums, which we will address in detail in a future publication. However, we can broadly classify the compounds into two main types, depending upon the lattice occupied by the magnetic  $M^{3+}$  ions. The first type, adopted by  $\text{RbFe}(\text{SO}_4)_2$ , has an undistorted equilateral triangular lattice (figure 1(a)), while the second type, adopted by  $\text{KFe}(\text{SO}_4)_2$  and  $\text{KTi}(\text{SO}_4)_2$  has a triangular lattice which is slightly compressed along one of the in-plane twofold axes such that each triangle becomes isosceles, with two shorter bonds and one longer bond (see figure 1(b)). We

may define a parameter  $\Delta$  as the fractional difference in bond length:  $\Delta = d_{\text{long}}/d_{\text{short}} - 1$ . Typically  $\Delta \approx \text{O}(0.1)$  (see figure 1). We shall refer to the equilateral triangular lattice as the ET lattice and the isosceles triangular lattice as the IT lattice.

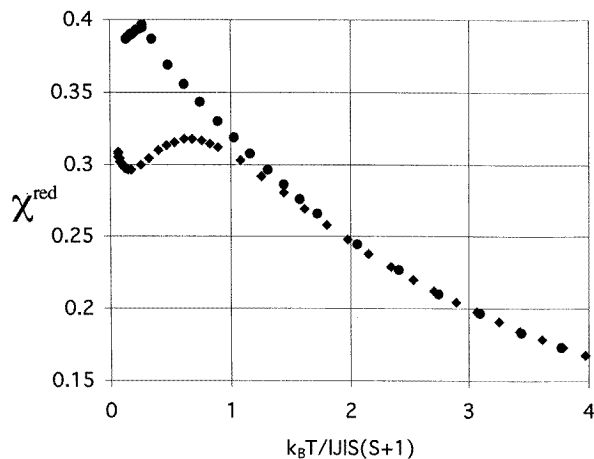
With near-neighbour magnetic couplings the IT lattice is topologically the same as a square lattice with diagonal bonds, and is characterized by two exchange constants:  $J_1$ , the square-lattice coupling, and  $J_2$ , the diagonal coupling (figure 1(c)). With  $J_2 = 0$  one has an unfrustrated square lattice, with  $J_2 = J_1$  a fully frustrated triangular lattice, and with  $J_1 = 0$  an assembly of uncoupled chains. In the intermediate case  $J_1 > J_2$ , the system is clearly less frustrated than the equilateral triangular lattice. In fact it can be shown [24] that for the Ising model, long-range order occurs below a temperature  $k_B T_c \approx 2.89 (J_1 - J_2)$ . For  $J_1 < J_2$  there is no long-range order, even though frustration is relieved within the ‘chains’. The XY-model on the same lattice was studied by Zhang *et al* [25] and termed the ‘row model’. They found that a simple antiferromagnetic ground state was stable for  $J_1/J_2 > 0.5$ . Possible experimental realizations of this situation are provided by oxides with the trirutile structure, e.g.  $\text{CoSb}_2\text{O}_6$  [26]. For  $J_1/J_2 < 0.5$  the classical ground state was found to be a spiral phase. One might expect quantum effects to be particularly important in this latter case, as they are for an isolated one-dimensional chain. Whilst the IT lattice compounds would be expected to have  $J_2 \neq J_1$ , we cannot know without direct measurement whether  $J_1 > J_2$  or  $J_1 < J_2$ : exchange constants depend on a subtle balance of large energy terms and are influenced by bond angles and atom positions, as well as by interatomic distances.

We have measured the magnetic susceptibility of several members of the series of anhydrous alums and have discovered that in general the Fe and Ti compounds show appreciable antiferromagnetic coupling, whereas the V materials are only very weakly coupled ( $J/k_B < 1$  K), and the Cr compounds are ferromagnetic. In this letter we restrict our attention to the three compounds  $\text{RbFe}(\text{SO}_4)_2$ ,  $\text{KFe}(\text{SO}_4)_2$ , and  $\text{KTi}(\text{SO}_4)_2$ . The two Fe compounds have spin  $S = 5/2$  and would be expected to approximate a classical spin model on the ET and IT lattices respectively. The Ti compound has  $S = 1/2$  and would be expected to approximate a quantum spin model on the IT lattice. A comparative study of these materials may therefore reveal the effect of both the in-plane distortion and the spin value on the magnetic properties of the triangular-lattice antiferromagnet. We have not yet discovered a Ti compound with the ET lattice.

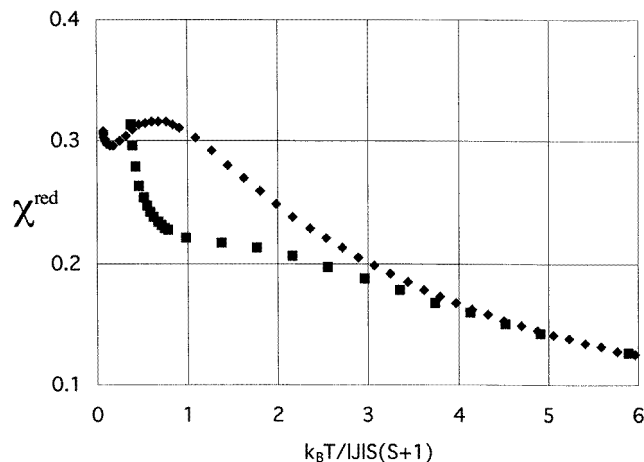
**Table 1.** Structural and magnetic data for selected anhydrous alums, giving (1) the space group (s.g.), (2) the lattice constants, (3) the ‘type’ of lattice: ET or IT, as defined in the text, (4) the degree of distortion  $\Delta$ , defined as the fractional difference in the edge length of the triangular plaquettes which for all IT lattices considered have two shorter bonds and one longer bond, (5) the Weiss constant  $\theta$  and  $g$ -value derived from a linear regression analysis of the magnetic susceptibility data, and (6) an effective exchange constant  $JS(S+1)/k_B$  (K) derived from the fitted Weiss constant according to the model described in the text.

Compound	s.g.	Lattice constants ( $\text{\AA}$ deg $^{-1}$ )						Type	$\Delta$	$\theta$ (K)	$g$	$JS(S+1)/k_B$
		$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$					
$\text{RbFe}(\text{SO}_4)_2$	$P321$	4.85	4.85	8.43	90	90	120	ET	0.00	$-29.12(6)$	$2.012(1)$	$-14.56(3)$
$\text{KFe}(\text{SO}_4)_2$	$C2/m$	8.16	5.16	7.94	90	94	90	IT	0.10	$-55.5(4)$	$1.986(4)$	$-27.8(4)$
$\text{KTi}(\text{SO}_4)_2$	$C2/m$	8.22	5.20	7.94	90	94	90	IT	0.06	$-10.2(1)$	$1.618(7)$	$-5.1(1)$

The Fe materials were made by published methods [22], and the Ti salt was made for the first time by vacuum dehydration of a stoichiometric solution of  $\text{K}_2\text{SO}_4$  and  $\text{Ti}_2(\text{SO}_4)_3$ , with grinding and annealing at  $350^\circ\text{C}$  in the absence of air. The crystal structures of



**Figure 2.** Circles: reduced magnetic susceptibility versus reduced temperature for  $\text{RbFe}(\text{SO}_4)_2$  (ET lattice,  $S = 5/2$ ). Diamonds: reduced magnetic susceptibility versus reduced temperature for  $\text{KFe}(\text{SO}_4)_2$  (IT lattice,  $S = 5/2$ ).



**Figure 3.** Squares: reduced magnetic susceptibility versus reduced temperature for  $\text{KTi}(\text{SO}_4)_2$  (IT lattice,  $S = 1/2$ ). Diamonds: reduced magnetic susceptibility versus reduced temperature for  $\text{KFe}(\text{SO}_4)_2$  (IT lattice,  $S = 5/2$ ).

$\text{RbFe}(\text{SO}_4)_2$ ,  $\text{KFe}(\text{SO}_4)_2$  and  $\text{KTi}(\text{SO}_4)_2$  were determined by Rietveld refinement of the powder x-ray diffraction profiles. The structure of  $\text{KTi}(\text{SO}_4)_2$  has not been reported before, whereas the refined structures of  $\text{RbFe}(\text{SO}_4)_2$  and  $\text{KFe}(\text{SO}_4)_2$  were in agreement with those reported previously [20, 21]. Relevant structural information is summarized in table 1. The magnetic susceptibility was measured in the range 1.8 K to 300 K using a Quantum Design SQUID magnetometer at the Royal Institution of Great Britain, and a Faraday balance at the Open University, Milton Keynes, UK. The magnetic data were transformed into an inverse magnetic susceptibility  $1/\chi$  versus temperature  $T$ , and analysed by linear regression

according to the Curie–Weiss law [27] using

$$\frac{1}{\chi} = \frac{T}{C} - \frac{\theta}{C} \quad C = \frac{Ng^2\mu_B^2 S(S+1)}{3k_B}.$$

The results of the fits, taking the effective  $g$ -value  $g$  and the Curie–Weiss constant  $\theta$  as the adjustable parameters, are given in table 1. The Curie–Weiss constants were further analysed using the following equation [27]:

$$\theta = \frac{1}{3}zJS(S+1)$$

to give an effective near-neighbour exchange constant  $J$ , assuming six nearest neighbours (i.e.  $z = 6$ ). Note that the assumption  $z = 6$  is at best approximate for materials with the IT lattice. The exchange constant  $J$  so defined is appropriate to the Hamiltonian

$$H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

where the sum is taken counting each bond once, and therefore corresponds to the definition used by Kawamura and Miyashita [2] in their Monte Carlo study of the classical Heisenberg antiferromagnet on the triangular lattice. To further facilitate comparison with theory we present our experimental data (figures 2 and 3), in the form of the reduced magnetic susceptibility  $\chi^{\text{red}}$  versus reduced temperature  $T^{\text{red}}$ .  $\chi^{\text{red}}$  is a dimensionless quantity defined as follows:

$$\chi^{\text{red}} = \frac{\chi|J|}{Ng^2\mu_B^2/3}$$

which is again directly comparable to the quantity measured in the Monte Carlo simulations [2], and  $T^{\text{red}}$  is defined as

$$T^{\text{red}} = \frac{k_B T}{|J|S(S+1)}.$$

We first discuss the two Fe compounds  $\text{RbFe}(\text{SO}_4)_2$  and  $\text{KFe}(\text{SO}_4)_2$ , which have the ET and IT structures respectively.  $\text{Fe}^{3+}$ , with a  ${}^6\text{S}$  ground term [28], is expected to be an isotropic ion which leads to an almost pure Heisenberg interaction [29]. Indeed for both compounds the fitted  $g$ -values are close to 2.0 as expected for an ion with no orbital moment. The reduced magnetic susceptibility versus reduced temperature curves for the two compounds, shown in figure 2, have a distinctly different form below  $T^{\text{red}} \approx 1$ . That of  $\text{RbFe}(\text{SO}_4)_2$  is characterized by a single weak cusp at  $T_c \approx 4.2(2)$  K ( $T^{\text{red}} \approx 0.29(2)$ ) and in this region is strikingly similar to the Monte Carlo simulation result of Kawamura and Miyashita [2] for the classical Heisenberg antiferromagnet on a triangular lattice. In the layered magnets the cusp undoubtedly marks a three-dimensional ordering transition, but as is the case for unfrustrated layered magnets [30], we expect two-dimensional fluctuations to dominate the thermal behaviour except in a very narrow region both above and below  $T_c$ . Our results at the cusp temperature,  $T_c^{\text{red}} = 0.29$ ,  $\chi_c^{\text{red}} = 0.4$ , may be compared with the simulation result (figure 14 of [2])  $T_c = 0.33$ ,  $\chi_c = 0.35$ . The differences between these results are probably mainly due to quantum fluctuations. We may tentatively conclude that  $\text{RbFe}(\text{SO}_4)_2$  is a nearly ideal realization of a two-dimensional Heisenberg magnet on the triangular (ET) lattice. The magnetic susceptibility curve for the IT lattice magnet  $\text{KFe}(\text{SO}_4)_2$ , in contrast to that of  $\text{RbFe}(\text{SO}_4)_2$ , has a broad hump at 18(1) K,  $T^{\text{red}} \approx 0.65$ , a point of inflection at 11(1)K,  $T^{\text{red}} \approx 0.40$ , a fairly sharp minimum at 5.0(5) K,  $T^{\text{red}} \approx 0.18$ , and an upturn at lower temperatures. The broad hump is characteristic of a build-up of short-range order, and is consistent with our expectations for the IT lattice described above. As  $J_1/J_2$  increases from 0 to  $\infty$  we would expect the magnetic susceptibility to change

from a hump into a cusp (at  $J_1/J_2 = 1$ ) and back into a hump again. The magnetic susceptibility measurements do not clearly distinguish the case where  $J_1/J_2 > 1$  from that where  $J_1/J_2 < 1$ . However, a very recent neutron diffraction study [31] has shown that it is the minimum at 5 K that is associated with a weak sublattice ordering of the Fe spins. This is perhaps more consistent with  $\text{KFe}(\text{SO}_4)_2$  being chain like,  $J_1/J_2 < 1$ , than square-lattice like,  $J_1/J_2 > 1$ , as in the latter case we might expect the point of inflection at 11 K to mark the ordering temperature.

$\text{KTi}(\text{SO}_4)_2$ , with  $\text{Ti}^{3+}$ ,  $S = 1/2$ , has the IT structure and thus can be compared with  $\text{KFe}(\text{SO}_4)_2$  ( $S = 5/2$ ). The reduced magnetic susceptibility of both compounds is plotted versus temperature in figure 3. It can be seen that the magnetic susceptibility of the Ti material falls significantly below that of its Fe analogue at low temperature. This is as would be expected, as the quantum restriction on energy levels is more severe in the  $S = 1/2$  case. The magnetic susceptibility curve of  $\text{KTi}(\text{SO}_4)_2$  does not have a distinct maximum, but rather a shoulder at about  $T \approx 7$  K,  $T^{\text{red}} \approx 1.4$ , and an upturn at  $T \approx 3$  K,  $T^{\text{red}} \approx 0.6$ , which cannot be ascribed to a paramagnetic component. Our recent neutron diffraction study [31] revealed no long-range order in  $\text{KTi}(\text{SO}_4)_2$  down to 1.2 K,  $T^{\text{red}} \approx 0.24$ . We have also studied the closely related compound  $\text{RbTi}(\text{SO}_4)_2$ , which shows a more distinct upturn in the magnetic susceptibility and a weak ordering transition. Unfortunately, whilst this compound is structurally and magnetically similar to  $\text{KTi}(\text{SO}_4)_2$ , we have not yet been able to establish its exact crystal structure, and we refrain from further analysis of its magnetic properties at this stage. The fitted  $g$ -value of 1.6 for  $\text{Ti}^{3+}$  in  $\text{KTi}(\text{SO}_4)_2$  is significantly less than the spin-only value of 2.0 [32]. The reduction in  $g$  is likely to result from the combined effects of exchange and spin-orbit coupling [27, 28]. A possibility which arises for  $\text{Ti}^{3+}$  compounds is that Curie-Weiss behaviour reflects the spin-orbit splitting of the ground state of *uncoupled* ions. However, we can eliminate this possibility as magnetic Bragg peaks have been observed for  $\text{RbTi}(\text{SO}_4)_2$ . The large deviation of the  $g$ -value of  $\text{Ti}^{3+}$  from 2.0 suggests substantial exchange or single-ion anisotropy, and makes  $\text{KTi}(\text{SO}_4)_2$  and other anhydrous titanium sulphate alums possible candidates for Ising-like  $S = 1/2$  systems. However, we note that the low-temperature upturn in the magnetic susceptibility is characteristic of the classical Ising-Heisenberg model on the ET lattice [3], but is not, to our knowledge, characteristic of an RVB state [12].

In conclusion, the yavapaiite layered structure is notable for its great versatility in accommodating magnetic cations on a triangular lattice. We therefore expect the series to offer considerable scope for the realization of triangular-lattice magnets with various different spin values and exchange pathways. Further investigations are progress to explore these possibilities.

It is a pleasure to thank M F Collins for bringing to our attention the work of Zhang *et al* [25], J E Greedan for pointing out the analogy with the trirutile structure oxides [26], and A M Buckley for discussions which led to this investigation. LN would like to thank the University of London Provost Fund for a Studentship.

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