

## An organically templated iron sulfate with a distorted Kagome lattice exhibiting unusual magnetic properties

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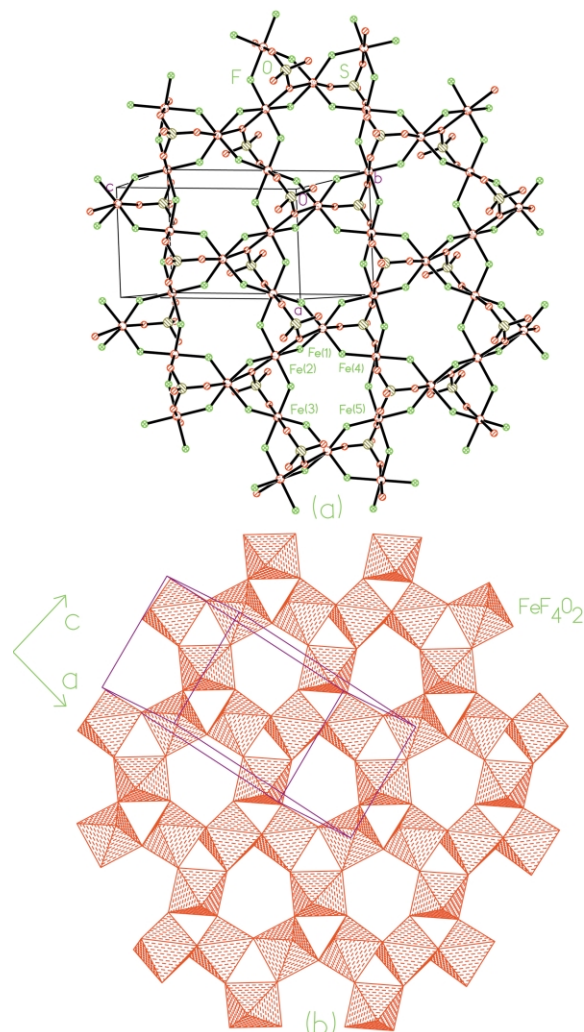
A layered iron sulfate of the composition  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3][\text{Fe}^{\text{II}}_3\text{F}_6(\text{SO}_4)_2]$ , possessing a distorted Kagome lattice, prepared hydrothermally, is found to exhibit magnetic hysteresis like a ferrimagnet besides the characteristics of a frustrated system, like those of a spin glass.

Iron compounds with the Kagome lattice such as the jarosites constitute a well-known case of geometrically frustrated magnetic systems.<sup>1,2</sup> In the last few years, there has been considerable effort to prepare and characterize the magnetic properties of materials with the Kagome lattice, but a complete understanding has not been possible, partly because of the difficulties in preparing pure stoichiometric compounds.<sup>3</sup> Recent studies suggest that some of the iron-containing Kagome compounds show long-range antiferromagnetic ordering at low temperatures while a few others show only spin-glass behaviour.<sup>1,2,4</sup> Thus, hydronium jarosite exhibits spin-glass behaviour but no long-range antiferromagnetic ordering.<sup>4</sup> It has been predicted recently that in the presence of distortion, a Kagome lattice may exhibit unusual magnetic properties including ferrimagnetism.<sup>5,6</sup> As part of our effort to synthesize novel inorganic open-framework structures by employing the sulfate tetrahedron as a primary building unit,<sup>7</sup> we have been able to prepare an organically templated iron fluorosulfate  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3][\text{Fe}^{\text{II}}_3\text{F}_6(\text{SO}_4)_2]$ , **I**, by hydrothermal synthesis.† **I** has a slightly distorted Kagome lattice, the distortion arising from the presence of three edge-sharing  $\text{Fe}^{\text{II}}$  octahedra in the place of all corner-sharing octahedra in the layered network. This unusual iron compound does indeed exhibit features of a magnetically frustrated system, but also shows magnetic hysteresis just below the spin freezing temperature.

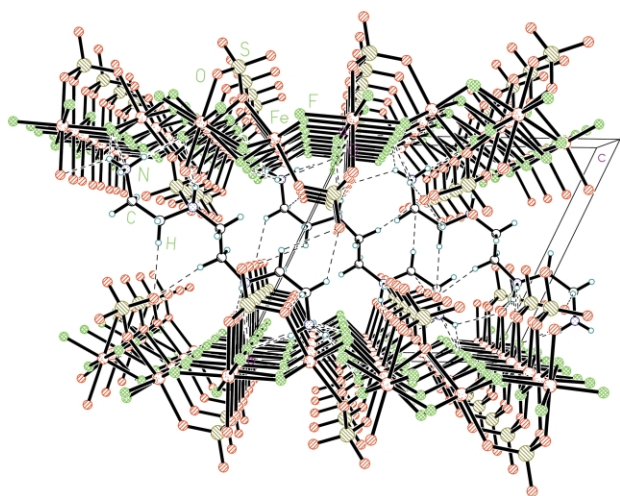
The asymmetric unit of **I** contains 31 non-hydrogen atoms out of which 21 belong to the inorganic framework and 10 belong to the extra framework amine molecule.‡ There are five crystallographically distinct Fe atoms and two S atoms with all the Fe atoms having octahedral geometry. The Fe atoms have fluorine and oxygen neighbors to form  $\text{FeF}_4\text{O}_2$  octahedra. The structure of **I**, consists of anionic framework layers of  $[\text{Fe}_3\text{F}_6(\text{SO}_4)_2]$ . Due to the presence of 50% edge-sharing octahedra, two types of triangular lattices are created. One type of three-ring trio is formed by the vertex-sharing of the  $\text{FeF}_4\text{O}_2$  octahedra creating a perfect three-membered ring, which is capped by the sulfate tetrahedron, as in a jarosite. On the other hand, the three-ring trio formed by two edge-sharing and one corner-sharing octahedra, creates a distorted triangular lattice which is bridged by the sulfate tetrahedron Fig. 1. The presence of three-connected and two-connected sulfate tetrahedra in this structure lattice is rather unusual.

The problem of non-stoichiometry, generally encountered in jarosites, due to the presence of OH groups, has been avoided in the compound under study by replacing the OH sites by fluorine atoms. While the fluoride ion has been used earlier as a mineralizing agent in hydrothermal synthesis, using it to control site defects is rather new. The anionic layers of the vertex/edge-sharing  $\text{FeF}_4\text{O}_2$  octahedra and the bi-capping and tri-capping tetrahedral  $\text{SO}_4$  units are linked together by Fe–F/O–Fe and Fe–

O–S bonds. All the  $\text{FeF}_4\text{O}_2$  units share four of their Fe–F vertices with similar neighbors, with the Fe–F–Fe bonds creating vertex-shared trimers, except Fe(1) and Fe(2) which in addition share a tri-coordinated oxygen creating an edge/vertex-shared trimer in the *ac*-plane. The  $\text{SO}_4$  tetrahedra cap the vertex-sharing trimers using the three canted oxygens, while they bridge the edge-sharing trimers. The distorted three- and six-rings of the octahedra give rise to unsymmetrical hexagons as shown in Fig. 1(b). We thus obtain a structure with a distorted Kagome lattice. It should be recalled that the normal Kagome lattice contains only vertex-shared octahedra and hence sym-



**Fig. 1** (a) Ball and stick representation of a section of  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3][\text{Fe}^{\text{II}}_3\text{F}_6(\text{SO}_4)_2]$ , **I**, showing the presence of the 3 and 6-rings. Note the bi-capping and tri-capping of sulfate tetrahedra in the 3-membered rings. (b) Polyhedral view of the 2D network of corner/edge-sharing iron octahedra in **I** in the *ac*-plane. Note the distorted 3 and 6-membered ring formed due to the presence of edge sharing iron octahedra.



**Fig. 2** View down the crystallographic *a*-axis showing the packing of layers in **I**. Note the pillaring role of tetra-protonated amine molecules and the interaction between the amine and the inorganic framework leading to a 3D assembly. Dotted line represents the various hydrogen bond interactions.

metrical hexagons of the hexagonal tungsten bronze type.<sup>8</sup> The layers in **I** are stacked one over the other along the *b*-axis in AAAA fashion and are held together by hydrogen bonding interaction with tetra-protonated amine molecules which reside in the interlamellar space Fig. 2.

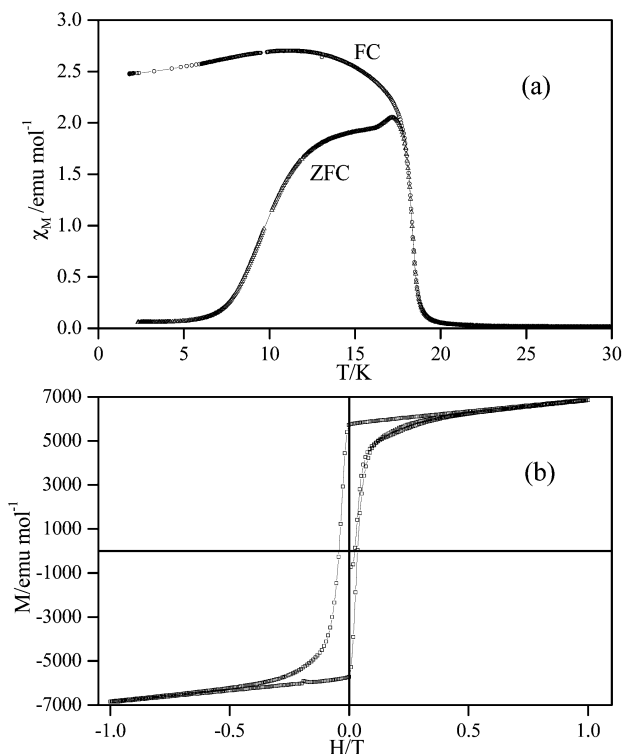
The Fe–O bond distances in **I** are in the range 2.166(5)–2.247(5) Å, [(Fe(1)–O)<sub>av</sub> = 2.218, (Fe(2)–O)<sub>av</sub> = 2.1965, (Fe(3)–O)<sub>av</sub> = 2.166, (Fe(4)–O)<sub>av</sub> = 2.185 and (Fe(5)–O)<sub>av</sub> = 2.208 Å]. The Fe–F bond distances are in the range 1.981(4)–2.131(4) Å [(Fe(1)–F)<sub>av</sub> = 2.0612, (Fe(2)–F)<sub>av</sub> = 2.06, (Fe(3)–F)<sub>av</sub> = 2.065, (Fe(4)–F)<sub>av</sub> = 2.043 and (Fe(5)–F)<sub>av</sub> = 2.037 Å]. The S–O bond distances are in the range 1.453(5)–1.511(5) Å, [(S(1)–O)<sub>av</sub> = 1.48 and (S(2)–O)<sub>av</sub> = 1.479]. The values of bond angles and distances indicate a near perfect octahedral and tetrahedral geometry for Fe and S respectively. Bond valence calculations<sup>9</sup> [Fe(1) = 1.87, Fe(2) = 1.89, Fe(3) = 1.93, Fe(4) = 1.96 and Fe(5) = 1.97] and the average bond distance values indicate that the valence state of all the Fe atoms to be +2. Accordingly, Mössbauer spectra showed the presence of a signal due to Fe<sup>2+</sup> and precluded the presence of mixed valence iron. The position of fluorine atoms is also supported by BVS calculations [F(1) = 0.72, F(2) = 0.70, F(3) = 0.743, F(4) = 0.62, F(5) = 0.61 and F(6) = 0.65].

In Fig. 3(a), we present the temperature-dependent DC magnetic susceptibility data of **I**, to demonstrate divergence between the zero-field-cooled (ZFC) and field-cooled (FC) samples. This behavior is characteristic of a frustrated ground-state as in spin glasses,<sup>3,10</sup> and exhibited by iron compounds possessing the Kagome lattice.<sup>1,2,4</sup> Interestingly **I** also shows magnetic hysteresis below *T<sub>f</sub>* (18 K) as shown in Fig. 3(b). The occurrence of hysteresis, suggesting the presence of ferrimagnetic interactions, is indeed a novel feature of Kagome lattice in **I**. Such hysteresis is not exhibited by normal Kagome lattices<sup>1,2,4</sup> and can therefore be attributed to the distortion caused by the presence of the edge-sharing octahedra in **I**.

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## Notes and references

† *Synthesis*: the synthesis was carried out in a Teflon-lined acid digestion bomb with an internal volume of 23 cm<sup>3</sup> under autogenous pressure by heating the starting mixture at 180 °C for 4 days. Compound **I** was prepared from the reaction mixture of ferric citrate (1 mmol), H<sub>2</sub>SO<sub>4</sub>(98%) (6 mmol), TETA (60%)(2 mmol), HF (48%) (4 mmol), H<sub>2</sub>O (30 mmol) and *n*-butanol (30 mmol). The product containing pale yellowish needle shaped crystals was monophasic (yield 25%). TGA of **I** reveals the loss of amine and HF at 360 °C [obs = 34.4%, calc = 36%], followed by the loss of SO<sub>3</sub> and the remaining fluorine [obs = 31.4%, calc = 32%] in the 490–700 °C range.



**Fig. 3** (a) DC susceptibility data showing divergence between the ZFC and FC (at 100 Oe) behaviour. (b) Magnetic hysteresis at 10 K.

‡ *Crystal data*: [H<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>][Fe<sup>II</sup><sub>3</sub>F<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>], **I**, *M<sub>r</sub>* = 623.95, triclinic, space group = *P* $\bar{1}$  (no. 2), *a* = 7.4013(5), *b* = 11.0392(7), *c* = 12.0779(8) Å,  $\alpha$  = 114.981(2),  $\beta$  = 92.838(2),  $\gamma$  = 91.614(2)°, *V* = 892.09(10) Å<sup>3</sup>, *Z* = 2,  $\mu$  = 2.750 mm<sup>-1</sup>,  $\rho_{\text{calcd}}$  = 2.323 Mg m<sup>-3</sup>. A total of 3678 reflections were collected in the  $\theta$  range 1.9–23.3 and merged to give 2496 unique data (*R*<sub>int</sub> = 0.0310) of which 1842 with *I* > 2 $\sigma$ (*I*) were considered to be observed. Final *R* = 0.0478, *R*<sub>w</sub> = 0.1059 and *S* = 1.062 were obtained for 269 parameters. CCDC reference number 186592. See <http://www.rsc.org/suppdata/cc/b2/b204615f/> for crystallographic data in CIF or other electronic format.

Single crystal data were collected on a Siemens SMART-CCD diffractometer [graphite-monochromated Mo<sub>K $\alpha$</sub>  radiation,  $\lambda$  = 0.71073 Å (*T* = 298K)]. An absorption correction based on symmetry-equivalent reflections was applied using SADABS.<sup>11</sup> The structures were solved using SHELXS-86<sup>12</sup> and SHELXTL-PLUS.<sup>13</sup>

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