# Frustrated Magnetism in a 2-D Ytterbium Fluoride

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## **Further Synthetic Details**

**General methods.** All reagents were obtained from commercial suppliers without further purification. Deionized water with a resistivity of 18.2 M $\Omega$ ·cm was used for all syntheses. Hydrothermal reactions were carried out in 23 mL Teflon-lined pressure vessels (Parr 4749).

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Experiment	<b>m</b> Yb(NO₃)₃	$\mathbf{m}_{H_2SO_4}$	Reaction products	Notes
number.	(mmol)	(mmol)	(identified by PXRD)	
1	1.0	3.9	<b>1-Yb</b> , KYb <sub>3</sub> F <sub>10</sub> ,	
2	1.0	11.8	1-Yb	Crystals are too
				small for SCXRD
3	1.0	15.7	<b>1-Yb</b> , YbF₃	
4	1.0	31.4	YbF₃	
5	2.0	2.0	<b>1-Yb</b> , YbF₃	
6	2.0	3.9	<b>1-Yb</b> , YbF₃	
7	2.0	7.8	1-Yb	Crystals are too
				small for SCXRD
8	2.0	15.7	1-Yb	Reaction condition
				used in this work

Table S1. List of control experiments for the synthesis of 1-Yb.<sup>a</sup>

<sup>a</sup> All the control experiments use 5.0 mmol KF and 4.0 mL deionized water. The mixture was all sealed in stainless-steel Parr vessel equipped with 23 mL Teflon liner and reacted in preheated oven at 230 °C for 18 hours.



### Single crystal X-ray diffraction and analysis

**Figure S1.** Crystals of KYb<sub>2</sub>F<sub>5</sub>SO<sub>4</sub> in paratone oil under optical microscope

**Crystallographic Analyses.** A single crystal of KYb<sub>2</sub>F<sub>5</sub>SO<sub>4</sub> was mounted on a loop with paratone oil. The crystals were cooled and kept at T = 100(2) K during the data collection. The crystals were then optically aligned on a Bruker D8 Quest X-ray diffractometer using a digital camera. Diffraction data were obtained by irradiating the crystals with an X-ray source (Mo K $\alpha$ ,  $\lambda$  = 0.71073 Å) with high brilliance and high-performance focusing multilayered optics. APEX 3 was used for determination of the unit cells, data collection, and integration of the data. Numerical absorption corrections were also applied with SADABS.<sup>1</sup> A quarter sphere of data was collected for all crystals. The structure was solved with the ShelXT structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface.<sup>2</sup> The model was refined with version 2014/7 of ShelXL2014 using Least Squares minimization.<sup>3</sup>

Compound	$KYb_2F_5SO_4$
Empirical formula	$KYb_2F_5SO_4$
$D_{calc.}$ / g cm <sup>-3</sup>	5.705
<i>m</i> / mm <sup>-1</sup>	28.719
Formula Weight	576.24
Color	colorless
Shape	Prism
Size / mm <sup>3</sup>	0.128 × 0.064 × 0.063
T/K	100(2)
Crystal System	Orthorhombic
Space Group	Pbcm
a/Å	6.4616(14)
b/Å	13.292(4)
c / Å	7.8111(18)
<i>α</i> / °	90
β/゜	90
γ/°	90
V / Å <sup>3</sup>	670.9(3)
Z	4
Ζ'	0.5
F(000)	1008
Radiation	ΜοΚα (λ=0.71073)
2θ range for data collection(°)	6.306 to 66.328
Index Ranges	-9 ≤ h ≤ 9, -20 ≤ k ≤ 20, -11≤ 1 ≤ 12
Reflections Collected	10025
Independent Reflections	1356 [ $R_{int} = 0.0610, R_{sigma} = 0.0383$ ]
Data/Restraints/Parameters	1356/0/72
Goodness-of-Fit on F2	1.111
Final R Indexes [I>= $2\sigma$ (I)]	R1=0.0210, wR2=0.0529
Final R Indexes [all data]	R1=0.0216, wR2=0.0533
Largest Diff. Peak/Hole (e / ų)	2.21/-1.79
Completeness to 20	100%

Table S2. Crystal data and structure refinement for  $KYb_2F_5SO_4$ 

Atoms	Wyckoff	x/a	y/b	z/c	U <sub>eq</sub>
_	position				
Yb1	4 <i>d</i>	0.15834(3)	0.20591(2)	1/4	0.00424(7)
Yb2	4c	0.64022(3)	1/4	1/2	0.00433(7)
K1	4 <i>d</i>	0.38709(16)	0.49834(9)	1/4	0.01202(19)
S1	4 <i>d</i>	0.87957(17)	0.43329(9)	1/4	0.00510(19)
O1	4 <i>d</i>	0.9316(5)	0.5413(3)	1/4	0.0072(6)
O2	4 <i>d</i>	0.0755(5)	0.3761(3)	1/4	0.0066(6)
O3	8e	0.7570(4)	0.5920(2)	0.0953(3)	0.0072(4)
F1	4c	0.0197(5)	1/4	0	0.0071(5)
F2	4 <i>d</i>	0.4566(4)	0.2951(2)	1/4	0.0073(5)
F3	8e	0.3900(3)	0.14377(17)	0.4313(2)	0.0078(4)
F4	4 <i>d</i>	0.7888(5)	0.3045(2)	3/4	0.0067(5)

 Table S3. Atomic coordinates



**Figure S2.** Demonstration of fluoride bridging mode in **1-Yb**. The fluorine atoms with  $\mu_2$  bridging mode are brown and fluorine atoms with  $\mu_3$  bridging mode are green.



Figure S3. Demonstration of four different triangles in 1-Yb. These four types of triangles are designated as triangle 1, 2, 3 and 4, and number in the center of each triangles indicate the type of the triangle.

		<u> </u>				
Tria	Angle 1	Degree / °	Angle 2	Degree / °	Angle 3	Degree
ngle						/ °
1	∠Yb2-Yb1-	59.759(16)	∠Yb1-Yb2-	60.120(8)	∠Yb1-Yb2-	60.120(8)
	Yb2		Yb2		Yb2	
2	∠Yb1-Yb2-	62.682(16)	∠Yb1-Yb1-	58.659(8)	∠Yb1-Yb1-	58.659(8)
	Yb1		Yb2		Yb2	
3	∠Yb2-Yb1-	63.294(17)	∠Yb1-Yb2-	58.353(8)	∠Yb1-Yb2-	58.353(8)
	Yb2		Yb2		Yb2	
4	∠Yb1-Yb2-	66.432(17)	∠Yb1-Yb1-	56.784(8)	∠Yb1-Yb1-	56.784(8)
	Yb1		Yb2		Yb2	

Table S4. Internal angles of four types of triangles in 1-Yb.

## Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns were obtained with a PANalytical X'Pert PRO Alpha-1 diffractometer using 1.8 kW Ceramic copper tube source. The simulations of PXRD patterns from SCXRD results are performed by software CrystalDiffract 6.



**Figure S4.** Experimental (black line) and the simulated (red line, simulated from singlecrystal X-ray result) powder X-ray diffraction patterns for **1-Yb**. No obvious difference between the position of peaks is observed which demonstrates the bulk purity of assynthesized compound.

#### Fourier-transformation infrared spectroscopy (FT-IR)

Fourier-transformation infrared (FT-IR) spectroscopy of 1-Yb was acquired in powders form on a Bruker ALPHA FTIR spectrometer from 400 to 4000 cm<sup>-1</sup>. The sample was dried under vacuum using Schlenk techniques for two hours prior to the FT-IR measurement.



**Figure S5.** FT-IR results for **1-Yb**. No obvious peak was observed from 3600 cm<sup>-1</sup> to 2700 cm<sup>-1</sup> which ruled out the existence of water or hydroxy group in **1-Yb**. The IR vibrations of  $SO_4^{2-}$  are documented to be located around 451 (v<sub>2</sub>), 618 (v<sub>4</sub>), 981 (v<sub>1</sub>) and 1104 (v<sub>3</sub>) cm<sup>-1</sup>, and when the  $SO_4^{2-}$  tetrahedron is distorted, both v<sub>3</sub>, and v<sub>4</sub> vibrations could have two or three peaks and v<sub>1</sub> and v<sub>2</sub> could be active.<sup>4</sup> The v<sub>2</sub>, v<sub>3</sub>, v<sub>4</sub>,vibrations of sulfate groups were clearly observed in **1-Yb** with v<sub>3</sub> and v<sub>4</sub> are split into two and three peaks, respectively. The peak centered at 1024 cm<sup>-1</sup> could be the active v<sub>1</sub> vibration mode since a large shoulder area can be observed. Therefore, the IR spectrum further validates the SCXRD results of **1-Yb**.

#### **Physical property measurements**

Magnetic susceptibility measurements and isothermal magnetization measurements M(H) were performed on the **1-Yb** using a Quantum Design physical property measurement system (PPMS) vibrating sample magnetometer (VSM) in a range of magnetic fields  $0 \le \mu_0 H \le 5.5 T$  and temperatures  $1.8 \le T \le 300 K$ . The reported ESD's are based on the linear fit and do not reflect underlying experimental error. Heat-capacity measurements were carried out on a Quantum Design physical property measurement system (PPMS) instrument in a range of measuring magnetic fields,  $0 \le \mu_0 H \le 1 T$  and temperatures  $0.1 \le T \le 4 K$ . To ensure sample thermalization at low temperatures, powder measurements were made on pellets of 1-Yb mixed with silver powder, the contribution of which was measured separately and subtracted to obtain the specific heat  $C_p$ .



Figure S6. The temperature dependence of specific heat divided by temperature under different magnetic field in **1-Yb**.

#### References

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