Highly Anisotropic 1/3-Magnetization Plateau in a Ferrimagnet $Cs_2Cu_3(SeO_3)_4 \cdot 2H_2O$: Topology of Magnetic Bonding Required for Magnetization Plateau

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We prepared $Cs_2Cu_3(SeO_3)_4 \cdot 2H_2O$ composed of Cu^{2+} ions at square-planar coordination sites and characterized its structural and magnetic properties, to show that $Cs_2Cu_3(SeO_3)_4 \cdot 2H_2O$ is a ferrimagnet exhibiting a highly anisotropic 1/3-magnetization plateau. This unprecedented anisotropy in a magnetization plateau is the consequence of three effects, namely, the orthogonal arrangements of the corner-sharing CuO_4 square planes, the nearest-neighbor antiferromagnetic exchange, and the anisotropic g-factor of the Cu^{2+} ions. By analyzing the topology of magnetic bonding, we explored why magnetic plateaus are observed only for certain ferrimagnets and antiferromagnets.

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S1. Bond valence sum analysis

Selected geometric parameters, selected hydrogen-bond parameters and bond valence sum (BVS) data for $Cs_2Cu_3(SeO_3)_4 \cdot 2H_2O$ are given in Tables S1-S3. The BVS calculation (Table S3) are in full agreement with the expected oxidations states of all atoms and consistent with the assignment of H_2O molecule [1].

Table S1. Selected bond lengths around cations (Å)

Cs—O4^{i}	3.243 (3)	Cu1—O1^{vi}	1.949 (3)
Cs—O4^{ii}	3.243 (3)	Cu1—O1^{vii}	1.949 (3)
Cs—O4^{iii}	3.295 (3)	Cu1—O1^{viii}	1.949 (3)
Cs—O4	3.295 (3)	Cu1—O1	1.949 (3)
Cs—O4^{iv}	3.340 (3)	Cu1—O3	2.882 (5)
Cs—O4^{v}	3.340 (3)	Cu1—O3^{viii}	2.882 (5)

Cs—O2^{ii}	3.522 (3)	Cu2—O2	1.966 (3)
Cs—O2^{i}	3.522 (3)	Cu2—O2^{ix}	1.966 (3)
Cs—O2	3.649 (3)	Cu2—O1^{vii}	2.015 (3)
Cs—O2^{iii}	3.649 (3)	Cu2—O1^{x}	2.015 (3)
Se—O4	1.658 (3)	Cu2—O3	2.3766 (13)
Se—O2	1.695 (3)	Cu2—O3^{ix}	2.3766 (13)
Se—O1	1.766 (3)		

Symmetry code(s): (i) *x*, *y*-1/2, -*z*; (ii) -*x*, -*y*+1, -*z*; (iii) -*x*, -*y*+1/2, *z*; (iv) *y*-1/4, -*x*+1/4, -*z*+1/4; (v) -*y*+1/4, *x*+1/4, -*z*+1/4; (vi) -*x*+1, -*y*+3/2, *z*; (vii) -*y*+5/4, *x*+1/4, -*z*+1/4; (viii) *y*-1/4, -*x*+5/4, -*z*+1/4; (ix) -*x*+1, -*y*+1, -*z*; (x) *y*-1/4, -*x*+3/4, *z*-1/4.

Table S2. Selected hydrogen-bond parameters of *D*—H···*A*, where *D* and *A* refer to the hydrogen bond donor and acceptor atoms, respectively.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O3—H···O4^{i}	0.832 (19)	1.98 (2)	2.814 (4)	174 (6)

Symmetry code(s): (i) -*y*+5/4, *x*+3/4, *z*-1/4.

Table S3. Bond valence sums calculated for $Cs_2Cu_3(SeO_3)_4 \cdot 2H_2O$

Atom	Cs	Cu1	Cu2	Se	H	Σ
O1		$0.482_{\downarrow 4}$	$0.403_{\downarrow 2}$	1.129		2.014
O2	$0.051_{\downarrow 2*}$ $0.036_{\downarrow 2}$		$0.460_{\downarrow 2}$	1.368		1.828
O3		$0.039_{\downarrow 2}$	$0.152_{\downarrow 2}$		$0.83_{\rightarrow 2}$	2.042
O4	$0.107_{\downarrow 2}$; $0.093_{\downarrow 2}$; $0.083_{\downarrow 2}$			1.512	0.17	1.965
Σ		2.006	2.030	4.009	1	

*Symbols → and ↓ denote an increase in the corresponding contributions in rows and columns due to symmetry

S2. ac magnetic susceptibility

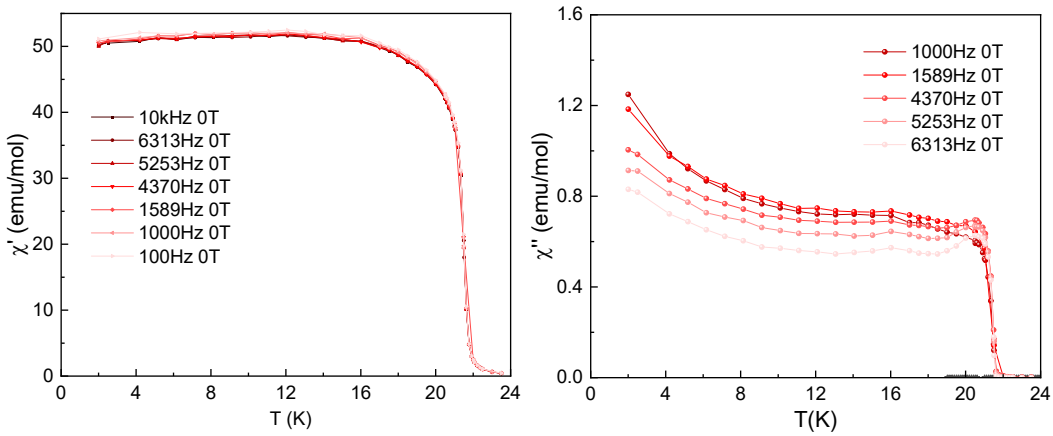


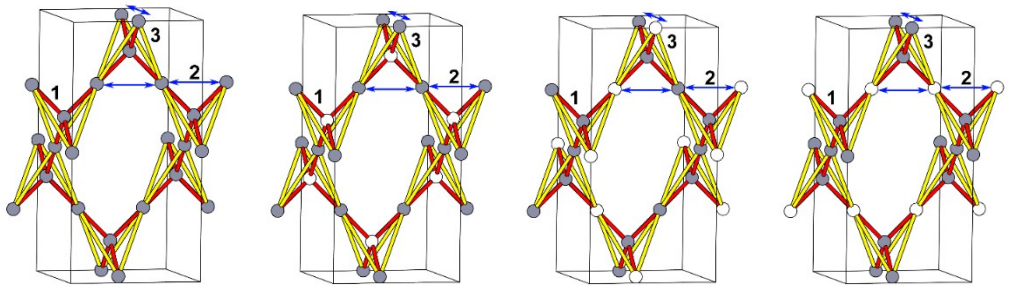
Fig. S1. Real (left panel) and imagimary (right panel) parts of ac magnetic susceptibility in $Cs_2Cu_3(SeO_3)_4 \cdot 2H_2O$.

S3. Energy mapping analysis for spin exchange

To evaluate the spin exchanges J_1 – J_3, we employ the spin Hamiltonian defined as,

$$H_{spin} = -\sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j ,$$

where the spin exchange J_{ij} between two spin sites can be J_1, J_2, or J_3. In this definition, AFM and FM exchanges are represented by negative and positive values of J_{ij}, respectively. To evaluate J_1 – J_3, we carry out the energy-mapping analysis based on DFT calculations [12-14] using the four ordered spin states shown in Fig. S1.



(a) FM (b) AF1 (c) AF2 (d) AF3

Fig. S2. Ordered spin arrangements of (a) FM, (b) AF1 (c) AF2 and (d) AF3. The grey and white circles indicate up and down spin sites of Cu^{2+} ions, respectively. The numbers 1 to 3 indicate the spin exchange paths J_1 to J_3.

References

1. Brown, I. D.; Altermatt, D. Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr. B* **1986**, 41, 244-247.