

Supporting Information

for

# Magnetization Plateaus by the Field-Induced Partitioning of Spin Lattices

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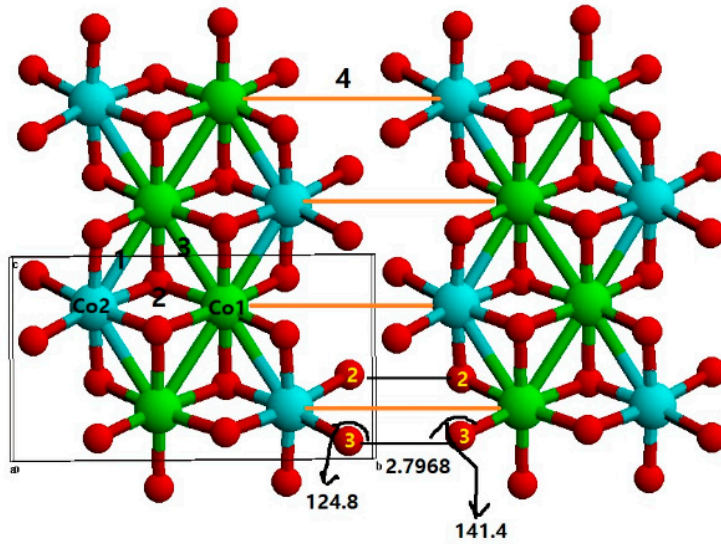
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## S1. CoGeO<sub>3</sub>

### (a) Spin exchange paths



CoGeO<sub>3</sub> (a, 2b, c)

J1: Co(1)..Co(2), 3.0433 (x4 x 4) = (16)

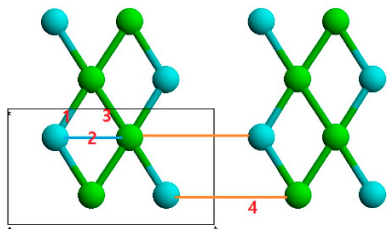
J2: Co(1)..Co(2), 3.2618 (x2 x 4) = (8)

J3: Co(1)..Co(1), 3.0793 (x2 x 4) = (8)

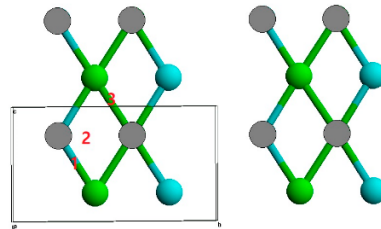
Inter layer

J4: Co(1)..Co(2), 5.7562 (x4 x 2) = (8)

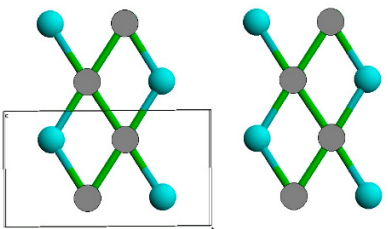
### (b) Ordered spin states using a (a, 2b, c) superstructure



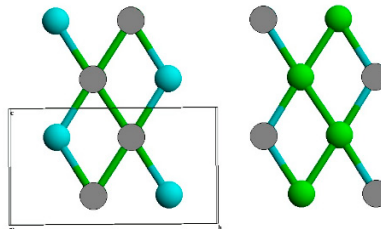
(a) FM



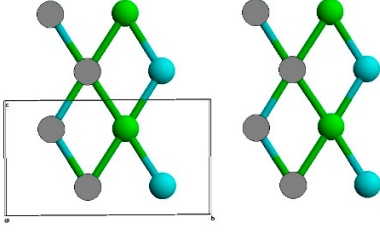
(b) AF1



(c) AF2



(d) AF3



(e) AF4

Figure S1. Ordered spin arrangements of (a) FM, (b) AF1, (c) AF2, (d) AF3 and (e) AF4 states.

### (c) Energies of the ordered spin states in terms of the spin exchanges

$$E_{\text{FM}} = (-16J_1 - 8J_2 - 8J_3 - 8J_4)(N^2/4)$$

$$E_{\text{AF1}} = (+16J_1 - 8J_2 + 8J_3 - 8J_4)(N^2/4)$$

$$E_{\text{AF2}} = (+16J_1 + 8J_2 - 8J_3 + 8J_4)(N^2/4)$$

$$E_{\text{AF3}} = (+16J_1 + 8J_2 - 8J_3 - 8J_4)(N^2/4)$$

$$E_{\text{AF4}} = (-16J_1 + 8J_2 + 8J_3 + 8J_4)(N^2/4)$$

### (d) Spin exchanges in terms of the ordered spin state energies

$$J_4 = (1/16)(E_{\text{AF2}} - E_{\text{AF3}})(4/N^2)$$

$$J_3 = (1/32)[(E_{\text{AF4}} - E_{\text{FM}}) - (E_{\text{AF2}} - E_{\text{AF1}})](4/N^2)$$

$$J_2 = (1/16)[\{(E_{\text{AF4}} - E_{\text{FM}})(4/N^2)\} - 16J_3 - 16J_4]$$

$$J_1 = (1/32)[(E_{\text{AF3}} - E_{\text{AF4}})(4/N^2) + 16J_3 + 16J_4]$$

### (e) Ordered spin state energies and spin exchanges from DFT+U calculations

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U calculations

	U = 3 eV	U = 4 eV
FM	61.13	65.07
AF1	15.66	15.69
AF2	3.22	2.61
AF3	4.11	3.25
AF4	0	0

(a, 2b, c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

Plane wave cutoff energy = 450 eV

kpoint set = (6x4x8)

	U = 3 eV	U = 4 eV
J <sub>1</sub>	54.45	60.29
J <sub>2</sub>	185.03	198.14
J <sub>3</sub>	125.52	134.02
J <sub>4</sub>	4.60	3.33

#### (f) Ordered spin state energies and spin exchanges from DFT+U+SOC calculations

Table S2. Relative energies (meV/Co) with respect to the spin orientation //c obtained from DFT+U(4eV)+SOC calculations.

	//a	//b	//c
Co1	0.27	0	1.19
Co2	0.21	0.68	0

\*The Co<sup>2+</sup> sites other than the one under investigation were replaced with Zn<sup>2+</sup> ions.

Table S3. Relative energies (in meV/FU) and spin exchange parameters (in K) obtained from DFT+U(4eV)+SOC calculations

	U = 4 eV
FM	62.25
AF1	4.84
AF2	0
AF3	7.35
AF4	0.31

	U = 4 eV
J <sub>1</sub>	74.39
J <sub>2</sub>	134.27
J <sub>3</sub>	147.19
J <sub>4</sub>	37.88

## S2. $\text{Ba}_3\text{Mn}_2\text{O}_8$

### (a) Spin exchange paths using a (2a, b, 2c) supercell

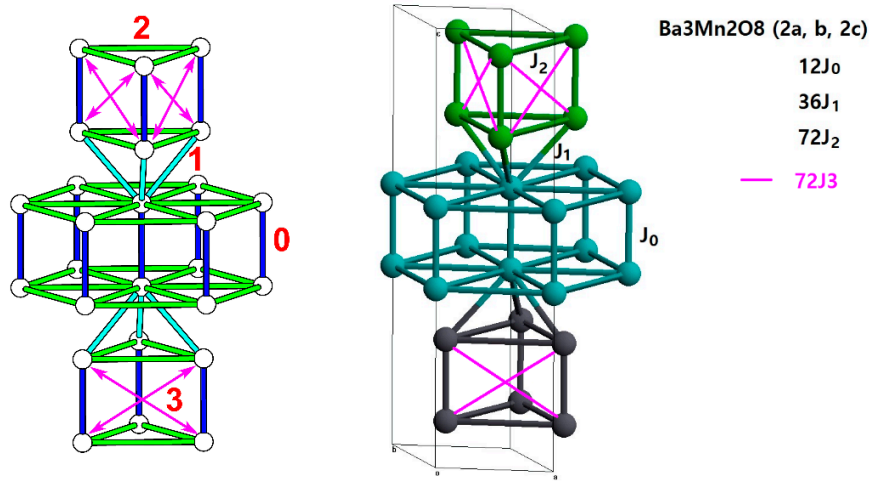
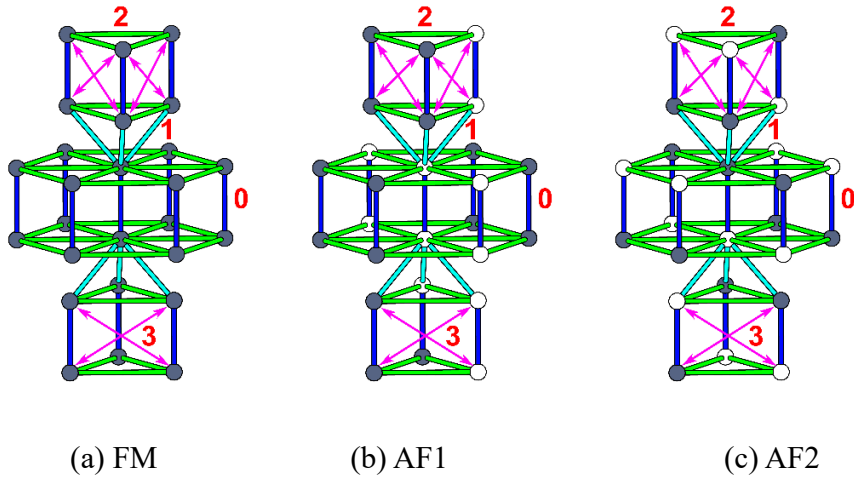
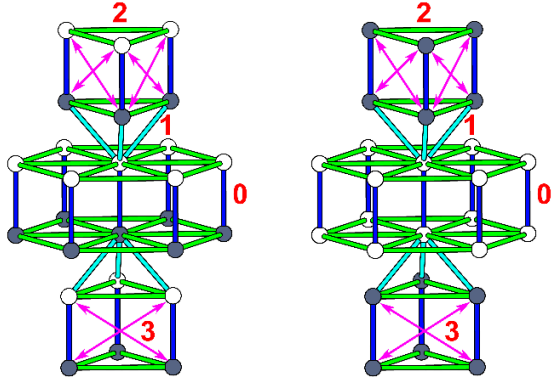


Figure S1. Spin exchange paths in  $\text{Ba}_3\text{Mn}_2\text{O}_8$ . The numbers 0 to 3 represent the spin exchange paths  $J_0$  to  $J_3$ , respectively. The white circles indicate the  $\text{Mn}^{2+}$  ions sites.

### (b) Ordered spin states





(d) AF3

(e) AF4

Figure S2. Ordered spin arrangements of (a) FM, (b) AF1, (c) AF2, (d) AF3 and (e) AF4 state. The gray and white circles indicate the up and down spin sites of  $\text{Mn}^{2+}$  ions, respectively.

### (c) Energies of the ordered spin states in terms of the spin exchanges

$$E_{\text{FM}} = (-12J_0 - 36J_1 - 72J_2 - 72J_3)(N^2/4)$$

$$E_{\text{AF1}} = (-12J_0 - 4J_1 + 24J_2 + 24J_3)(N^2/4)$$

$$E_{\text{AF2}} = (+12J_0 + 4J_1 + 24J_2 - 24J_3)(N^2/4)$$

$$E_{\text{AF3}} = (+12J_0 + 36J_1 - 72J_2 + 72J_3)(N^2/4)$$

$$E_{\text{AF4}} = (-12J_0 + 36J_1 - 72J_2 - 72J_3)(N^2/4)$$

### (d) Spin exchanges in terms of the ordered spin state energies

$$J_1 = (1/72)(E_{\text{AF4}} - E_{\text{FM}})(4/N^2)$$

$$J_3 = (1/192)[\{(E_{\text{AF3}} - E_{\text{AF4}}) - (E_{\text{AF2}} - E_{\text{AF1}})\}(4/N^2) + 8J_1]$$

$$J_0 = (1/24)[(E_{\text{AF3}} - E_{\text{AF4}})(4/N^2) - 144J_3]$$

$$J_2 = (1/96)[(E_{\text{AF2}} - E_{\text{AF3}})(4/N^2) + 32J_1 + 96J_3]$$

### (e) Ordered spin state energies and spin exchanges from DFT+U calculations

Table S1. Relative energies (in meV/FU) and spin exchange parameters (in K) obtained from DFT+U calculations

	U = 2 eV	U = 3 eV	U = 4 eV
FM	13.55	9.77	7.23
AF1	7.35	6.15	5.70
AF2	0	0	0.47
AF3	0.68	0.02	0
AF4	10.10	7.45	5.78

(2a, b, 2c) super cell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

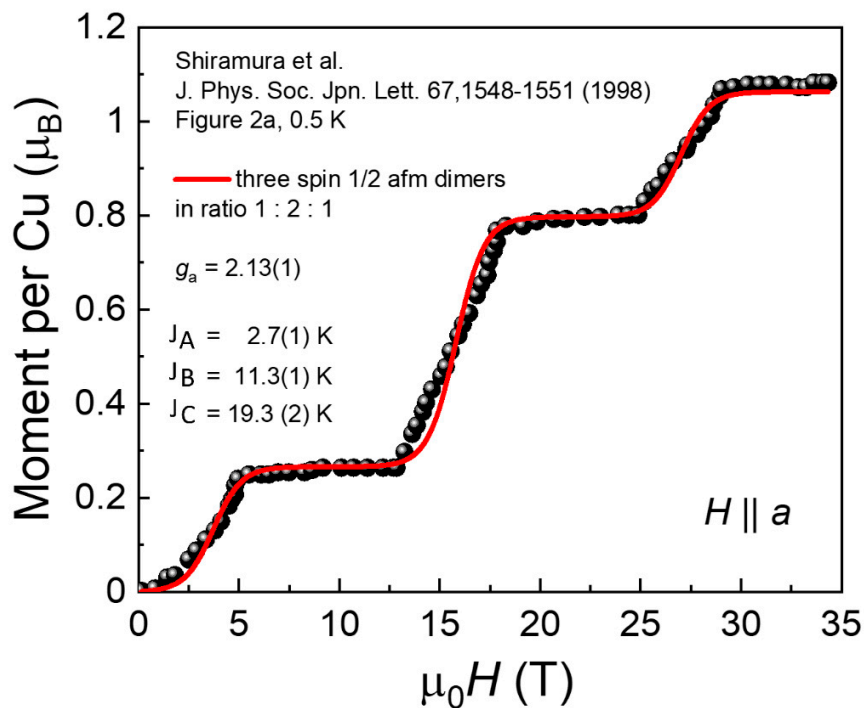
Plane wave cutoff energy = 450 eV

kpoint set = (6x6x3)

	U = 2 eV	U = 3 eV	U = 4 eV
J <sub>0</sub>	21.98	18.21	15.23
J <sub>1</sub>	3.34	2.24	1.40
J <sub>2</sub>	2.50	1.32	0.39
J <sub>3</sub>	0.89	0.56	0.26

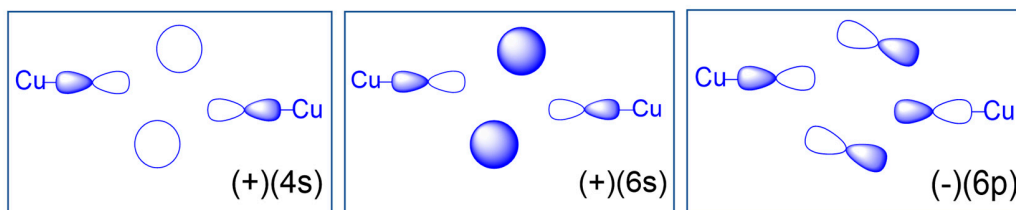


### S3. Supplementary figures

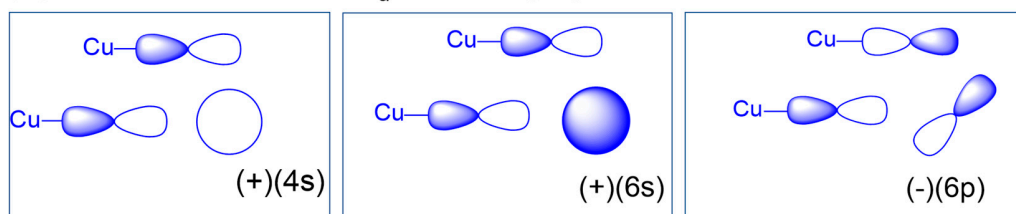


**Figure S1.** Magnetization curve of  $\text{NH}_4\text{CuCl}_3$  obtained by using  $H \parallel a$  (black dots) simulated by assuming that dimers A, B and C are all singlet dimers (solid red curve).

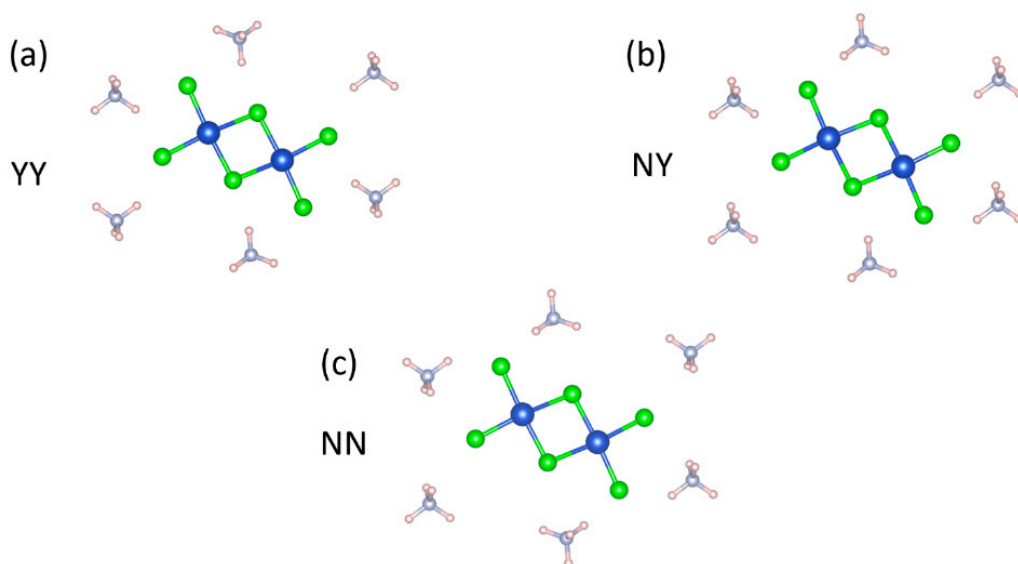
(a) Interactions in the  $J_2$  exchange path



(b) Interactions in the  $J_a'$  exchange path



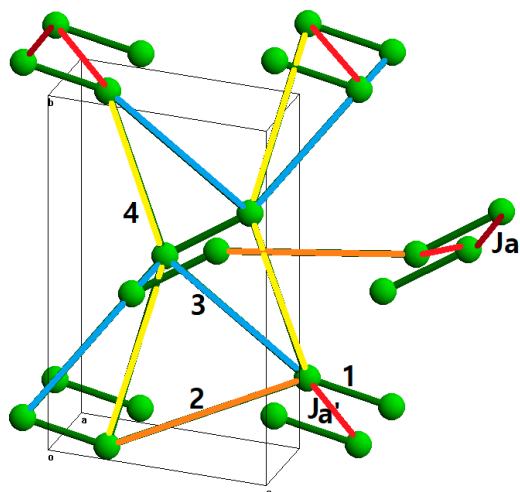
**Figure S2.** Orbital interactions of the (+) and (-) d-states of  $(\text{CuCl}_4)_2$  dimer with the frontier orbitals of the  $\text{A}^+$  cations making  $\text{Cl}\dots\text{A}^+\dots\text{Cl}$  bridge in the (a)  $J_2$  and (b)  $J_a'$  exchange path. For simplicity, the (+) and (-) states are represented by showing only the Cl 3p-orbital of the Cu-Cl bond making the  $\text{Cl}\dots\text{A}^+\dots\text{Cl}$  bridge.



**Figure S3.** Orientations of the six  $\text{NH}_4^+$  cations surrounding each  $\text{Cu}_2\text{Cl}_6^{2-}$  anion in  $\text{NH}_4\text{CuCl}_3$  with the (a) YY, (b) NY and (c) NN arrangements of the  $\text{NH}_4^+$  cations.

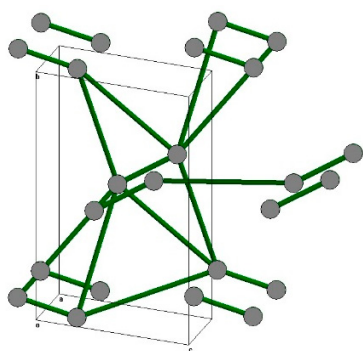
#### S4. $\text{KCuCl}_3$

##### (a) Spin exchange paths

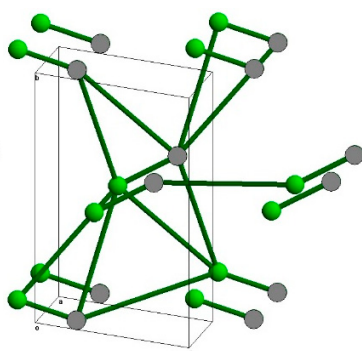


J1(x8): 3.4510  
J2(x8): 8.1392  
J3(x16): 7.8433  
J4(x16): 7.3327  
Ja(x16): 4.0340  
Ja'(x8): 3.9089

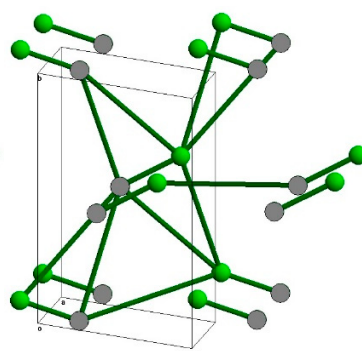
##### (b) Ordered spin states using a (2a, b, 2c) superstructure



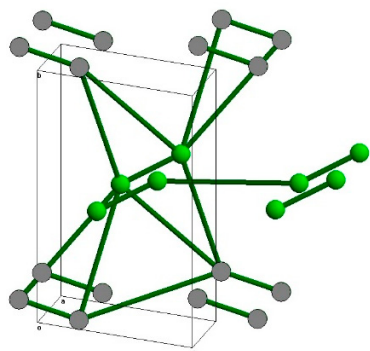
(a) FM



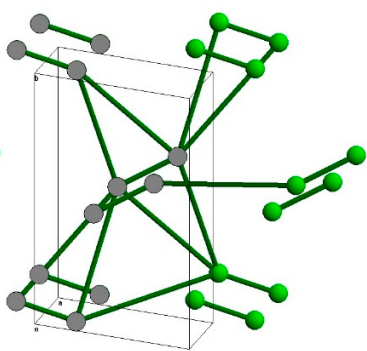
(b) AF1



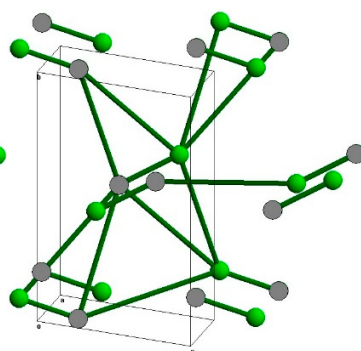
(c) AF2



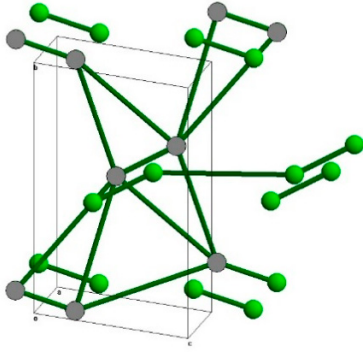
(d) AF3



(e) AF4



(f) AF5



(g) AF6

Figure S1. Ordered spin arrangements of (a) FM, (b) AF1, (c) AF2, (d) AF3, (e) AF4, (f) AF5 and (g) AF6 states.

**(c) Energies of the ordered spin states in terms of the spin exchanges**

$$E_{\text{FM}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF1}} = (+8J_1 + 8J_2 - 16J_3 + 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF2}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF3}} = (-8J_1 - 8J_2 + 16J_3 + 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF4}} = (-8J_1 + 8J_2 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF5}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 + 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF6}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 + 16J_a + 8J_{a'}) (N^2/4)$$

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_4 = (1/64)(4/N^2)[(E_{\text{AF3}} - E_{\text{FM}}) - (E_{\text{AF2}} - E_{\text{AF1}})]$$

$$J_3 = (1/32)[(E_{\text{AF3}} - E_{\text{FM}})(4/N^2) - 32J_4]$$

$$J_2 = (1/16)[\{(E_{\text{AF4}} - E_{\text{FM}})(4/N^2)\} - 16J_4 - 16J_3]$$

$$J_{a'} = (1/32)(4/N^2)[(E_{\text{AF6}} - E_{\text{FM}}) - (E_{\text{AF5}} - E_{\text{AF2}})]$$

$$J_a = (1/32)[(E_{\text{AF5}} - E_{\text{AF2}})(4/N^2) + 16J_{a'}]$$

$$J_1 = (1/16)[(E_{\text{AF1}} - E_{\text{FM}})(4/N^2) - 32J_4 - 16J_2 - 16J_{a'}]$$

**(e) Ordered spin state energies and spin exchanges from DFT+U calculations**

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U calculations

	U = 4 eV
FM	5.65
AF1	0.89
AF2	0
AF3	4.72
AF4	4.52
AF5	1.20
AF6	4.94

(2a, b, 2c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

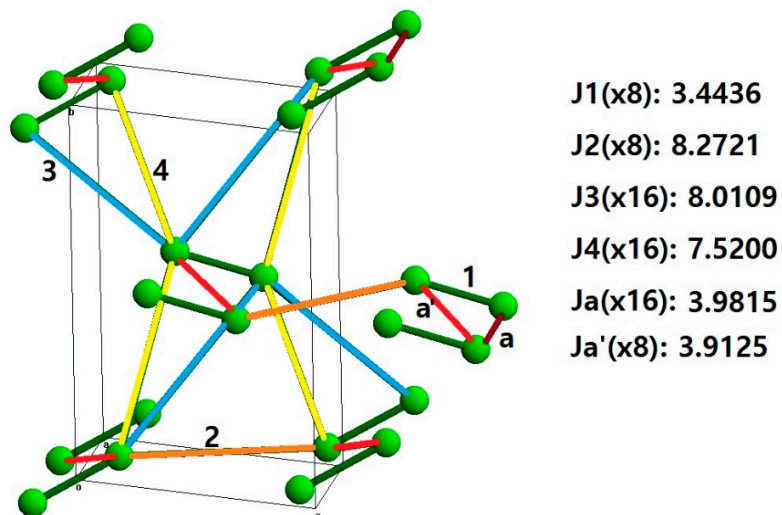
Plane wave cutoff energy = 450 eV

kpoint set = (8x4x4)

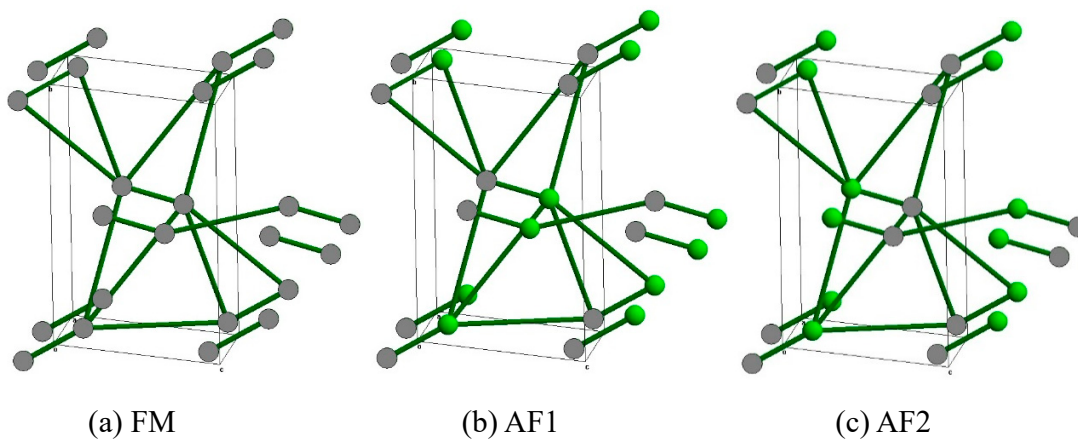
	U = 4 eV
J <sub>1</sub>	144.97
J <sub>2</sub>	30.65
J <sub>3</sub>	21.10
J <sub>4</sub>	0.38
J <sub>a</sub>	-5.73
J <sub>a'</sub>	44.15

## S5. $\text{TiCuCl}_3$

### (a) Spin exchange paths



### (b) Ordered spin states using a $(2a, b, 2c)$ superstructure



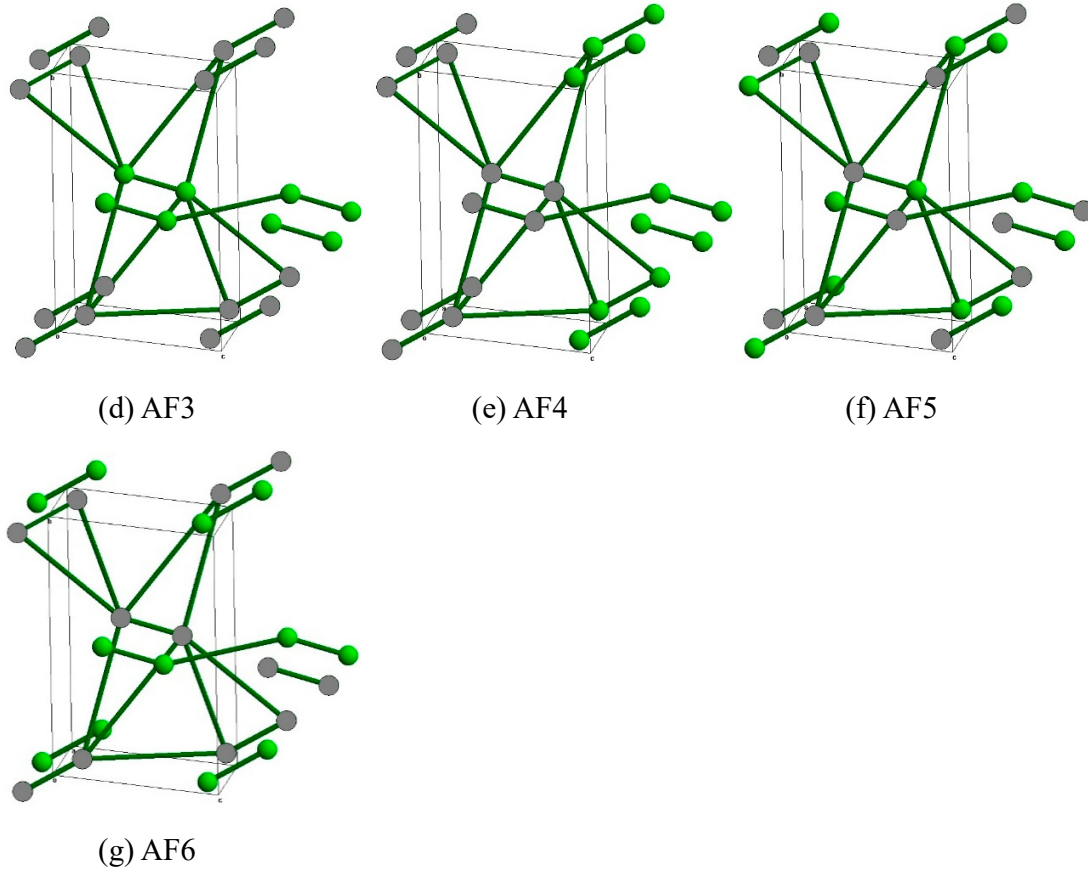


Figure S1. Ordered spin arrangements of (a) FM, (b) AF1, (c) AF2, (d) AF3, (e) AF4, (f) AF5 and (g) AF6 states.

**(c) Energies of the ordered spin states in terms of the spin exchanges**

$$E_{\text{FM}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF1}} = (+8J_1 + 8J_2 - 16J_3 + 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF2}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF3}} = (-8J_1 - 8J_2 + 16J_3 + 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF4}} = (-8J_1 + 8J_2 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF5}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 + 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF6}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 + 16J_a + 8J_{a'}) (N^2/4)$$

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_4 = (1/64)(4/N^2)[(E_{AF3} - E_{FM}) - (E_{AF2} - E_{AF1})]$$

$$J_3 = (1/32)[(E_{AF3} - E_{FM})(4/N^2) - 32J_4]$$

$$J_2 = (1/16)[\{(E_{AF4} - E_{FM})(4/N^2)\} - 16J_4 - 16J_3]$$

$$J_{a'} = (1/32)(4/N^2)[(E_{AF6} - E_{FM}) - (E_{AF5} - E_{AF2})]$$

$$J_a = (1/32)[(E_{AF5} - E_{AF2})(4/N^2) + 16J_{a'}]$$

$$J_1 = (1/16)[(E_{AF1} - E_{FM})(4/N^2) - 32J_4 - 16J_2 - 16J_{a'}]$$

### (e) Ordered spin state energies and spin exchanges from DFT+U calculations

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U calculations

	U = 4 eV
FM	8.67
AF1	1.85
AF2	0
AF3	6.56
AF4	5.72
AF5	2.47
AF6	6.77

(2a, b, 2c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

Plane wave cutoff energy = 450 eV

kpoint set = (8x4x4)

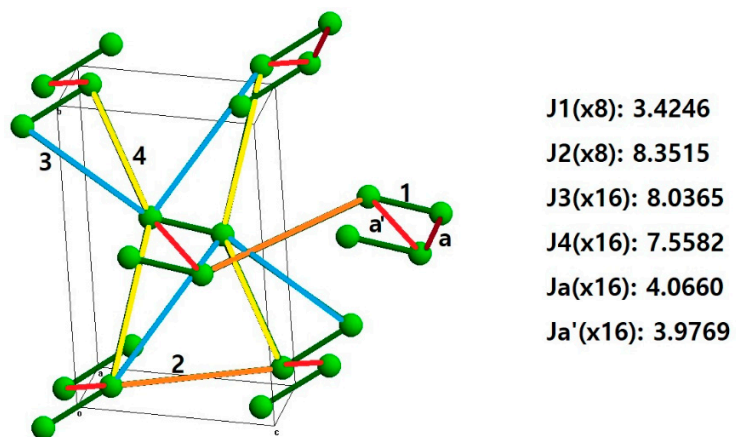
	U = 4 eV
J <sub>1</sub>	121.2



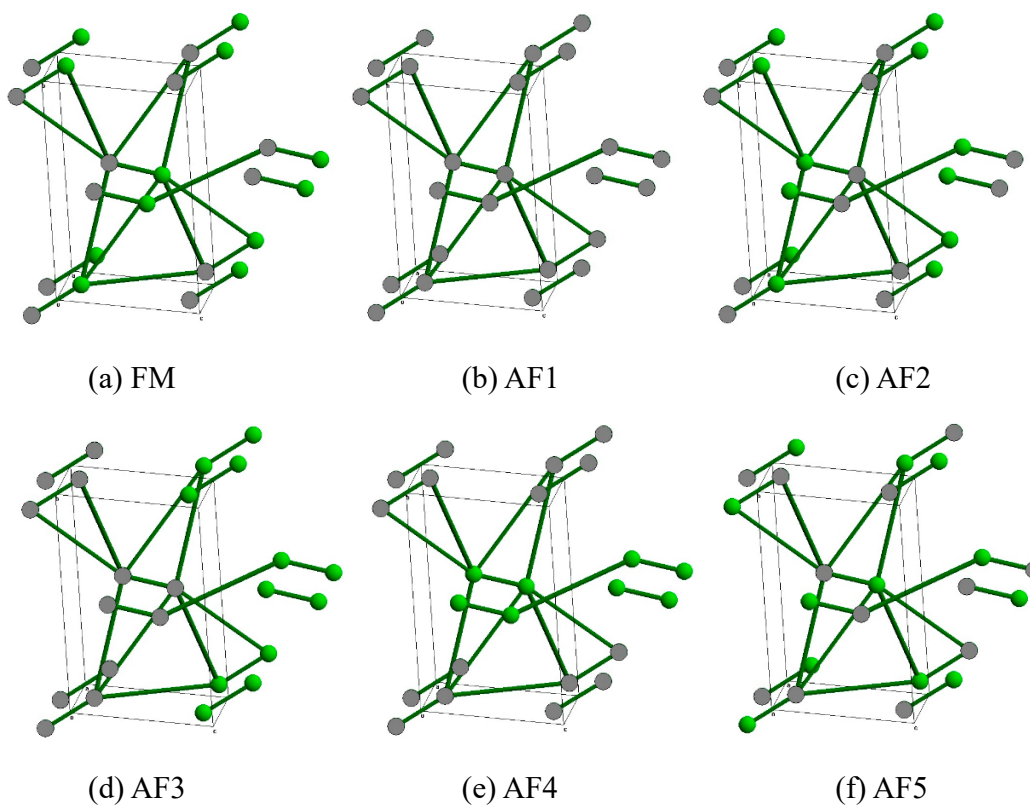
J <sub>2</sub>	87.7
J <sub>3</sub>	45.9
J <sub>4</sub>	3.1
J <sub>a</sub>	-6.6
J <sub>a</sub> '	101.5

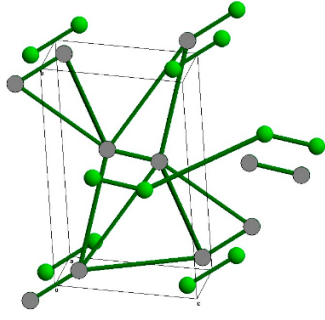
## S6. Unoptimized and optimized YY structures of $\text{NH}_4\text{CuCl}_3$

### (a) Spin exchange paths



### (b) Ordered spin states using a (2a, b, 2c) superstructure





(g) AF6

Figure S1. Ordered spin arrangements of (a) FM, (b) AF1, (c) AF2, (d) AF3, (e) AF4, (f) AF5 and (g) AF6 states.

**(c) Energies of the ordered spin states in terms of the spin exchanges**

$$E_{\text{FM}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF1}} = (+8J_1 + 8J_2 - 16J_3 + 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF2}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF3}} = (-8J_1 - 8J_2 + 16J_3 + 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF4}} = (-8J_1 + 8J_2 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF5}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 + 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF6}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 + 16J_a + 8J_{a'}) (N^2/4)$$

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_4 = (1/64)(4/N^2)[(E_{\text{AF3}} - E_{\text{FM}}) - (E_{\text{AF2}} - E_{\text{AF1}})]$$

$$J_3 = (1/32)[(E_{\text{AF3}} - E_{\text{FM}})(4/N^2) - 32J_4]$$

$$J_2 = (1/16)[\{(E_{\text{AF4}} - E_{\text{FM}})(4/N^2)\} - 16J_4 - 16J_3]$$

$$J_{a'} = (1/32)(4/N^2)[(E_{\text{AF6}} - E_{\text{FM}}) - (E_{\text{AF5}} - E_{\text{AF2}})]$$

$$J_a = (1/32)[(E_{\text{AF5}} - E_{\text{AF2}})(4/N^2) + 16J_{a'}]$$

$$J_1 = (1/16)[(E_{\text{AF1}} - E_{\text{FM}})(4/N^2) - 32J_4 - 16J_2 - 16J_{a'}]$$

**(e) Ordered spin state energies and spin exchanges from DFT+U calculations**

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U (4eV) calculations

	Unoptimized	Optimized
FM	6.01	5.93
AF1	0.55	0.65
AF2	0	0
AF3	5.47	5.26
AF4	5.56	5.33
AF5	0.09	0.11
AF6	6.14	6.08

(2a, b, 2c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

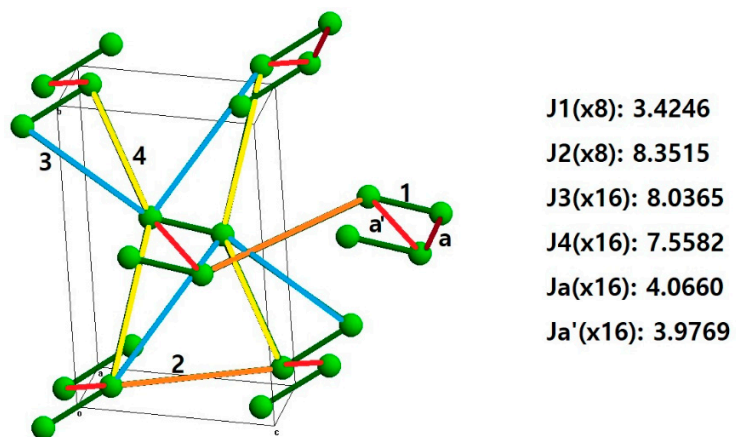
Plane wave cutoff energy = 450 eV

kpoint set = (8x4x4)

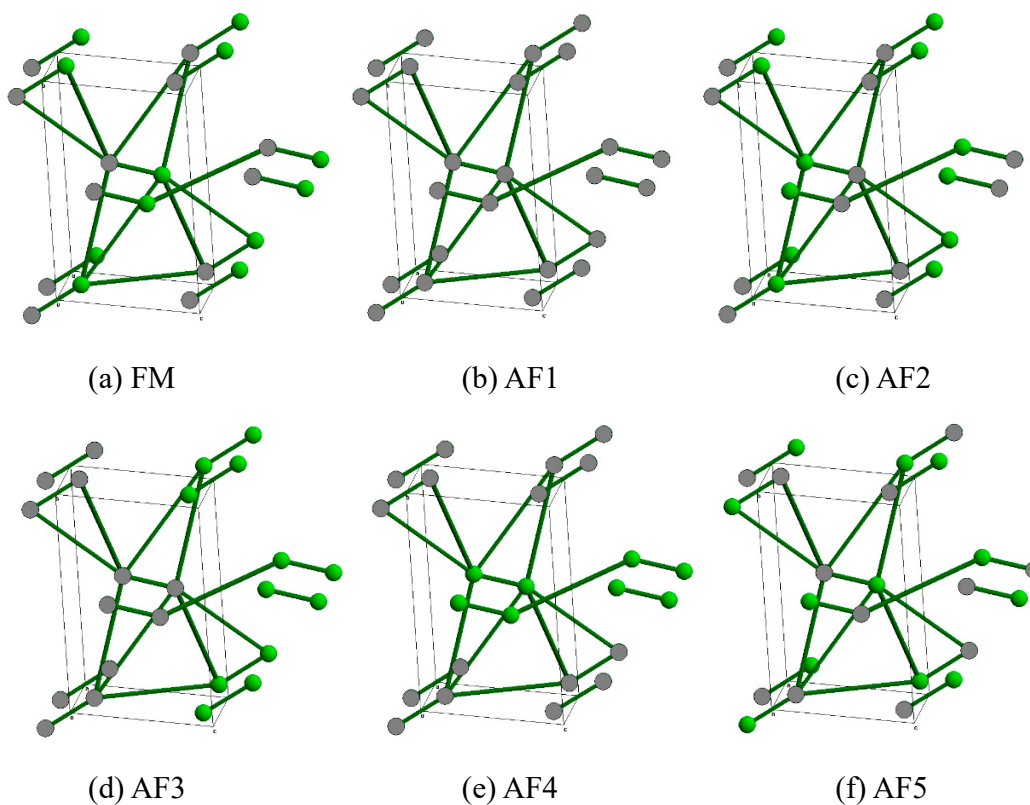
	Unoptimized	Optimized
J <sub>1</sub>	246.20	233.57
J <sub>2</sub>	8.16	12.28
J <sub>3</sub>	12.70	15.20
J <sub>4</sub>	-0.13	0.22
J <sub>a</sub>	-2.60	-3.10
J <sub>a'</sub>	-0.90	-1.01

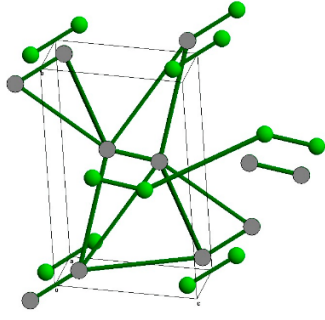
## S7. Unoptimized and optimized NY structures of $\text{NH}_4\text{CuCl}_3$

### (a) Spin exchange paths



### (b) Ordered spin states using a (2a, b, 2c) superstructure





(g) AF6

Figure S1. Ordered spin arrangements of (a) FM, (b) AF1, (c) AF2, (d) AF3, (e) AF4, (f) AF5 and (g) AF6 states.

**(c) Energies of the ordered spin states in terms of the spin exchanges**

$$E_{\text{FM}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF1}} = (+8J_1 + 8J_2 - 16J_3 + 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF2}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF3}} = (-8J_1 - 8J_2 + 16J_3 + 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF4}} = (-8J_1 + 8J_2 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF5}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 + 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF6}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 + 16J_a + 8J_{a'}) (N^2/4)$$

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_4 = (1/64)(4/N^2)[(E_{\text{AF3}} - E_{\text{FM}}) - (E_{\text{AF2}} - E_{\text{AF1}})]$$

$$J_3 = (1/32)[(E_{\text{AF3}} - E_{\text{FM}})(4/N^2) - 32J_4]$$

$$J_2 = (1/16)[\{(E_{\text{AF4}} - E_{\text{FM}})(4/N^2)\} - 16J_4 - 16J_3]$$

$$J_{a'} = (1/32)(4/N^2)[(E_{\text{AF6}} - E_{\text{FM}}) - (E_{\text{AF5}} - E_{\text{AF2}})]$$

$$J_a = (1/32)[(E_{\text{AF5}} - E_{\text{AF2}})(4/N^2) + 16J_{a'}]$$

$$J_1 = (1/16)[(E_{\text{AF1}} - E_{\text{FM}})(4/N^2) - 32J_4 - 16J_2 - 16J_{a'}]$$

**(e) Ordered spin state energies and spin exchanges from DFT+U calculations**

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U (4eV) calculations

	Unoptimized	Optimized
FM	5.12	4.48
AF1	0.49	0.39
AF2	0	0
AF3	4.62	3.88
AF4	4.69	4.06
AF5	0.07	0.08
AF6	5.26	4.59

(2a, b, 2c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

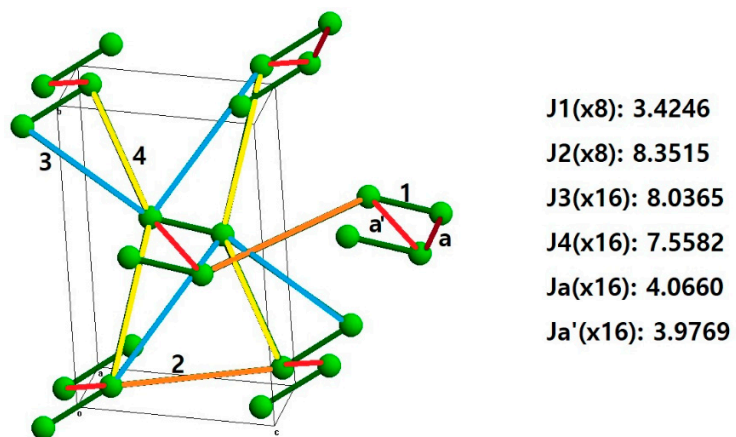
Plane wave cutoff energy = 450 eV

kpoint set = (8x4x4)

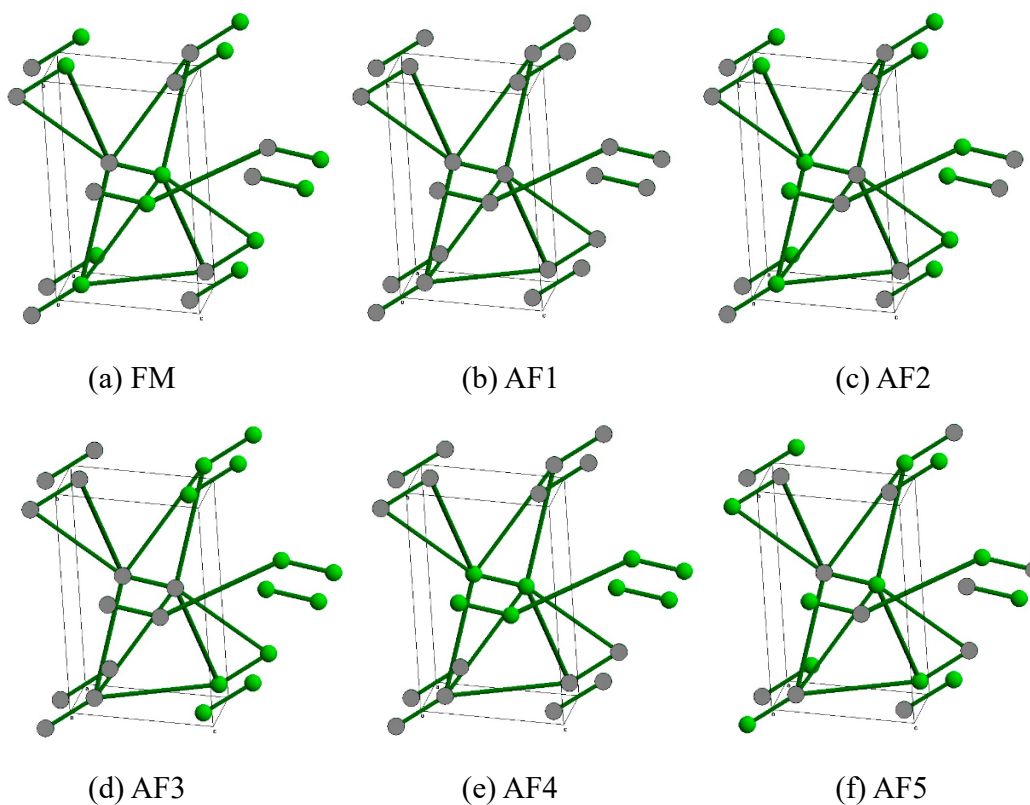
	Unoptimized	Optimized
J <sub>1</sub>	207.68	179.90
J <sub>2</sub>	8.60	5.18
J <sub>3</sub>	11.50	11.47
J <sub>4</sub>	0.20	2.51
J <sub>a</sub>	-2.52	-2.25
J <sub>a'</sub>	-1.59	-0.71

## S8. Unoptimized and optimized NN structures of $\text{NH}_4\text{CuCl}_3$

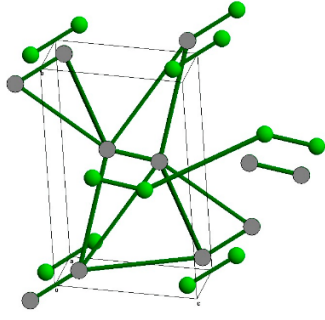
### (a) Spin exchange paths



### (b) Ordered spin states using a (2a, b, 2c) superstructure







(g) AF6

Figure S1. Ordered spin arrangements of (a) FM, (b) AF1, (c) AF2, (d) AF3, (e) AF4, (f) AF5 and (g) AF6 states.

**(c) Energies of the ordered spin states in terms of the spin exchanges**

$$E_{\text{FM}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF1}} = (+8J_1 + 8J_2 - 16J_3 + 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF2}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 - 16J_a + 8J_{a'}) (N^2/4)$$

$$E_{\text{AF3}} = (-8J_1 - 8J_2 + 16J_3 + 16J_4 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF4}} = (-8J_1 + 8J_2 - 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF5}} = (+8J_1 + 8J_2 + 16J_3 - 16J_4 + 16J_a - 8J_{a'}) (N^2/4)$$

$$E_{\text{AF6}} = (-8J_1 - 8J_2 - 16J_3 - 16J_4 + 16J_a + 8J_{a'}) (N^2/4)$$

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_4 = (1/64)(4/N^2)[(E_{\text{AF3}} - E_{\text{FM}}) - (E_{\text{AF2}} - E_{\text{AF1}})]$$

$$J_3 = (1/32)[(E_{\text{AF3}} - E_{\text{FM}})(4/N^2) - 32J_4]$$

$$J_2 = (1/16)[\{(E_{\text{AF4}} - E_{\text{FM}})(4/N^2)\} - 16J_4 - 16J_3]$$

$$J_{a'} = (1/32)(4/N^2)[(E_{\text{AF6}} - E_{\text{FM}}) - (E_{\text{AF5}} - E_{\text{AF2}})]$$

$$J_a = (1/32)[(E_{\text{AF5}} - E_{\text{AF2}})(4/N^2) + 16J_{a'}]$$

$$J_1 = (1/16)[(E_{\text{AF1}} - E_{\text{FM}})(4/N^2) - 32J_4 - 16J_2 - 16J_{a'}]$$

**(e) Ordered spin state energies and spin exchanges from DFT+U calculations**

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U (4eV) calculations

	Unoptimized	Optimized
FM	4.03	2.35
AF1	0.44	0.19
AF2	0	0.01
AF3	3.57	1.91
AF4	3.63	2.06
AF5	0.06	0
AF6	4.19	2.39

(2a, b, 2c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

Plane wave cutoff energy = 450 eV

kpoint set = (8x4x4)

	Unoptimized	Optimized
J <sub>1</sub>	160.31	91.81
J <sub>2</sub>	8.03	3.58
J <sub>3</sub>	10.44	7.26
J <sub>4</sub>	0.26	2.90
J <sub>a</sub>	-2.52	-0.41
J <sub>a'</sub>	-2.03	-1.06

# S9. $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$

## (a) Spin exchange paths

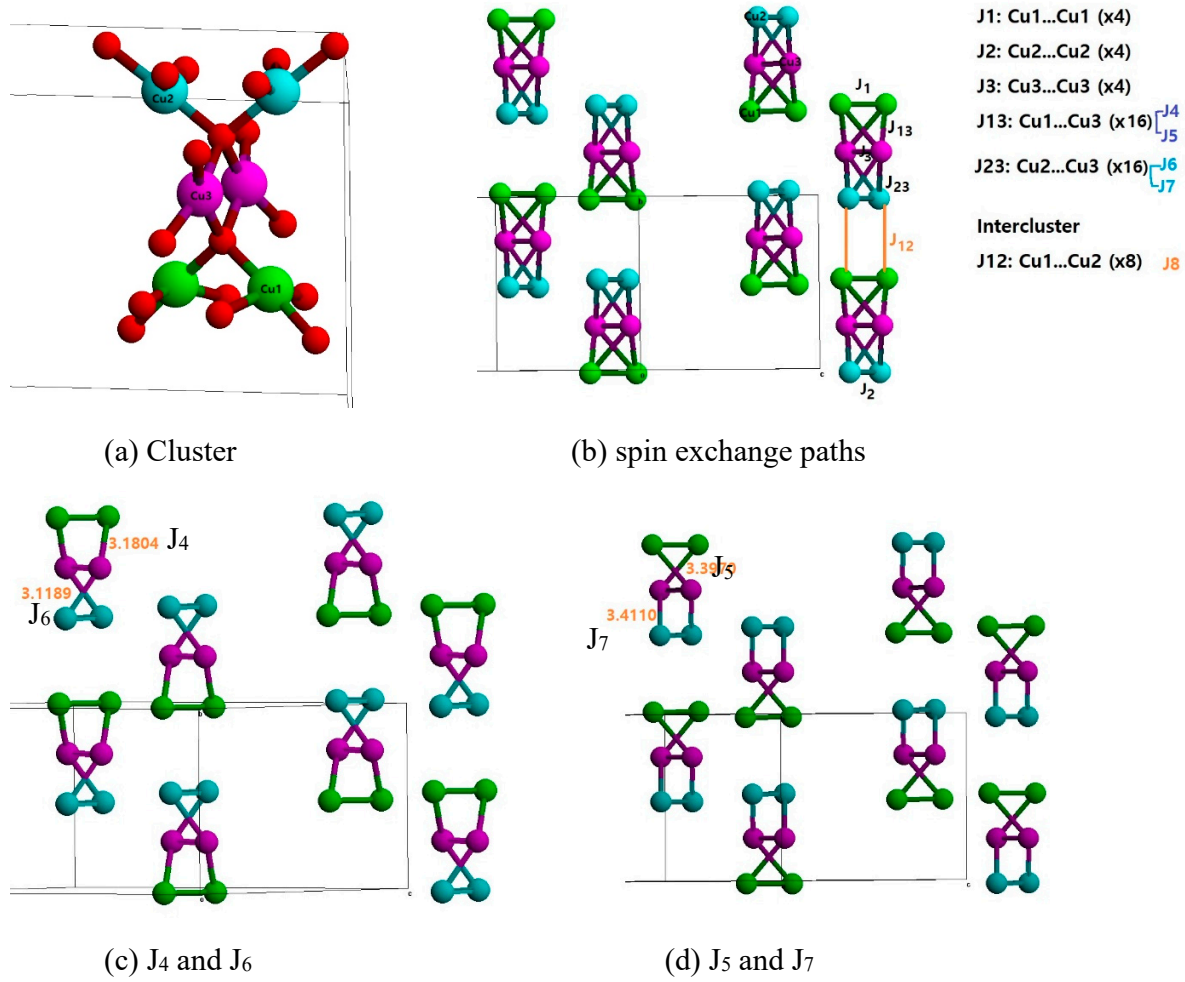


Figure S1.

$$\text{FM} = -4J_1 - 4J_2 - 4J_3 - 8J_4 - 8J_5 - 8J_6 - 8J_7 - 8J_8$$

$$\text{AF1} = -4J_1 + 4J_2 - 4J_3 - 8J_4 - 8J_5$$

$$\text{AF2} = -4J_1 - 4J_2 + 4J_3 - 8J_8$$

$$\text{AF3} = +4J_1 - 4J_2 - 4J_3 - 8J_6 - 8J_7$$

$$\text{AF4} = -4J_1 - 4J_2 - 4J_3 - 8J_4 - 8J_5 + 8J_6 + 8J_7 - 8J_8$$

$$\text{AF5} = -4J_1 - 4J_2 - 4J_3 + 8J_4 + 8J_5 + 8J_6 + 8J_7 - 8J_8$$

$$\text{AF6} = -4J_1 - 4J_2 - 4J_3 + 8J_4 + 8J_5 - 8J_6 - 8J_7 + 8J_8$$

$$\text{AF7} = -4J_1 + 4J_2 + 4J_3 - 8J_6 + 8J_7$$

$$\text{AF8} = +4J_1 - 4J_2 + 4J_3 + 8J_4 - 8J_5$$

**(b) Ordered spin states**

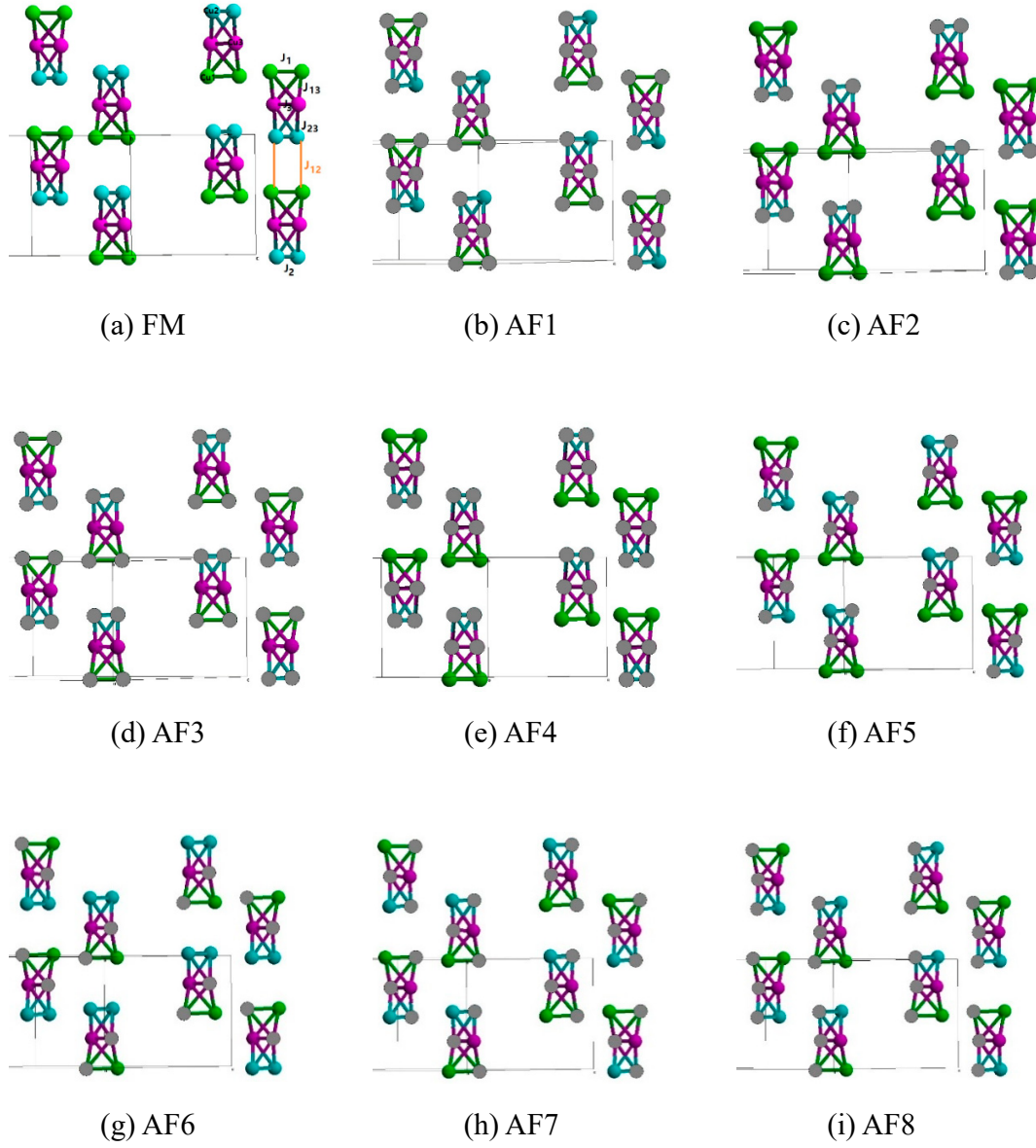


Figure S2. Ordered spin arrangements

**(c) Energy differences between ordered spin states in terms of the spin exchanges**

Final	J <sub>1</sub>	J <sub>2</sub>	J <sub>3</sub>	J <sub>4</sub>	J <sub>5</sub>	J <sub>6</sub>	J <sub>7</sub>	J <sub>8</sub>
AF2 - FM	0	0	0	0	0	16	16	16
AF3 - AF4	0	0	0	0	0	16	16	-16
AF1 - AF2	0	8	0	0	0	-8	-8	-8
AF7 - AF6	0	8	0	0	0	-8	8	-8
AF3 - FM	0	0	0	16	16	16	16	0
AF7 - AF8	0	0	0	16	-16	-16	16	0
AF5 - AF4	0	8	8	-8	-8	0	16	-8
AF6 - AF5	8	-8	0	8	-8	8	-8	0

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_8 = (1/32)(4/N^2)[(E_{AF2} - E_{FM}) - (E_{AF3} - E_{AF4})]$$

$$J_7 = (1/16)(4/N^2)[(E_{AF7} - E_{AF6}) - (E_{AF1} - E_{AF2})]$$

$$J_6 = (1/16)[(E_{AF3} - E_{AF4})(4/N^2) - 16J_7 + 16J_8]$$

$$J_2 = (1/8)[(E_{AF7} - E_{AF6})(4/N^2) + 16J_6 - 8J_7 + 8J_8]$$

$$J_5 = (1/32)[\{(E_{AF3} - E_{FM}) - (E_{AF7} - E_{AF8})\}(4/N^2) - 32J_6]$$

$$J_4 = (1/16)[\{(E_{AF7} - E_{AF8})(4/N^2)\} + 16J_5 + 16J_6 - 16J_7]$$

$$J_3 = (1/8)[\{(E_{AF5} - E_{AF4})(4/N^2)\} - 8J_2 + 8J_4 + 8J_5 - 16J_7 + 8J_8]$$

$$J_1 = (1/8)[\{(E_{AF6} - E_{AF5})(4/N^2)\} + 8J_2 - 8J_4 + 8J_5 - 8J_6 + 8J_7]$$

**(e) The energies of the ordered spin states and the spin exchanges from DFT+U calculations**

Table S1. Relative energies (in meV/FU) and spin exchange parameters (in K) obtained from DFT+U calculations

	$\Delta E$ (meV/FU)	
	U = 3 eV	U = 4 eV
FM	100.75	83.15
AF1	64.62	54.45
AF2	41.38	34.69
AF3	0	0
AF4	42.20	35.69
AF5	37.84	33.43
AF6	36.78	32.81
AF7	32.61	29.02
AF8	40.30	35.66

(a, b, c) unit cell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

Plane wave cutoff energy = 450 eV

kpoint set = (2x 8 x 4)

	U = 3 eV	U = 4 eV
J <sub>1</sub>	899.26	744.73
J <sub>2</sub>	841.58	637.49
J <sub>3</sub>	-552.51	-524.04
J <sub>4</sub>	622.14	495.29
J <sub>5</sub>	537.11	457.58
J <sub>6</sub>	542.33	429.91
J <sub>7</sub>	635.91	546.27
J <sub>8</sub>	199.23	148.09

## S10. Azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ : Evaluation of the interlayer spin exchanges

### (a) Spin exchange paths

In the main text, the diamond triangle is defined by  $J_2$ ,  $J_1$  and  $J_3$ . However,  $J_1$  is very close to  $J_3$ . Thus, we simplify our analysis by an ideal diamond triangle defined by  $J_2$ ,  $J_1$  and  $J_1$ .

The intra-diamond exchanges  $J_1$  and  $J_2$  together with the inter-diamond exchange  $J_3$  form layers. (In the main text,  $J_3$  is referred to as  $J_4$ .)

There are two inter-layer exchanges  $J_4$  and  $J_5$ . (In the main text,  $J_4$  and  $J_5$  are referred to as  $J_5$  and  $J_6$ , respectively.)

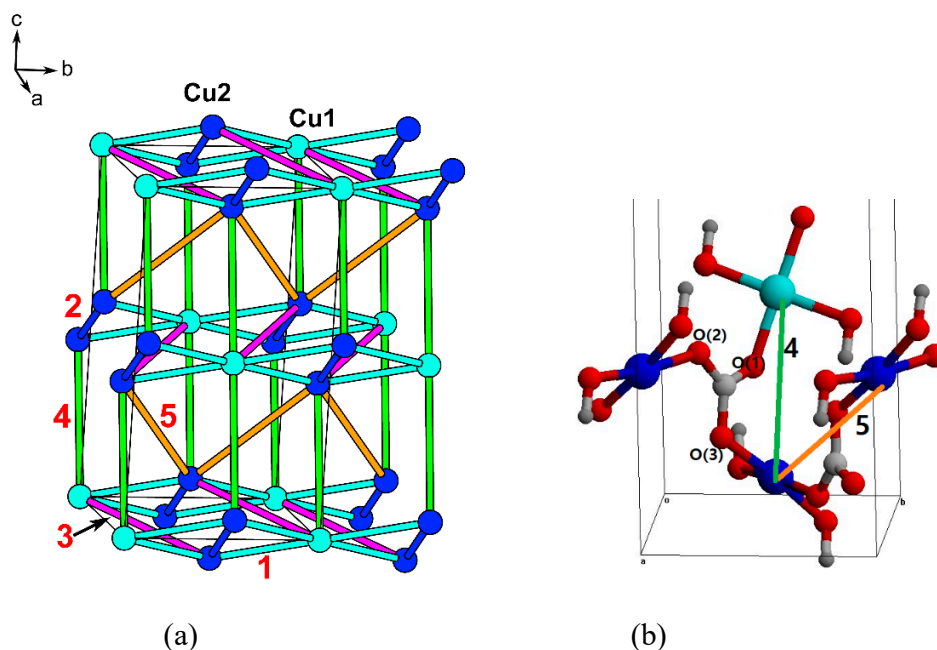


Figure S1. (a) Spin exchange paths,  $J_1$  to  $J_5$  and (b) Interlayer paths,  $J_4$  and  $J_5$ .

Table S1. Geometrical parameters of interlayer paths  $J_4$  and  $J_5$

	Cu...Cu	O...O	$\angle\text{Cu-O...O, O...O-Cu}$
$J_4$	4.5391	2.2120	83.05, 147.38
$J_5$	5.0959	2.2298	98.23, 141.53

**(b) Ordered spin states using a (2a, 2b, c) super cell containing 8 FUs**

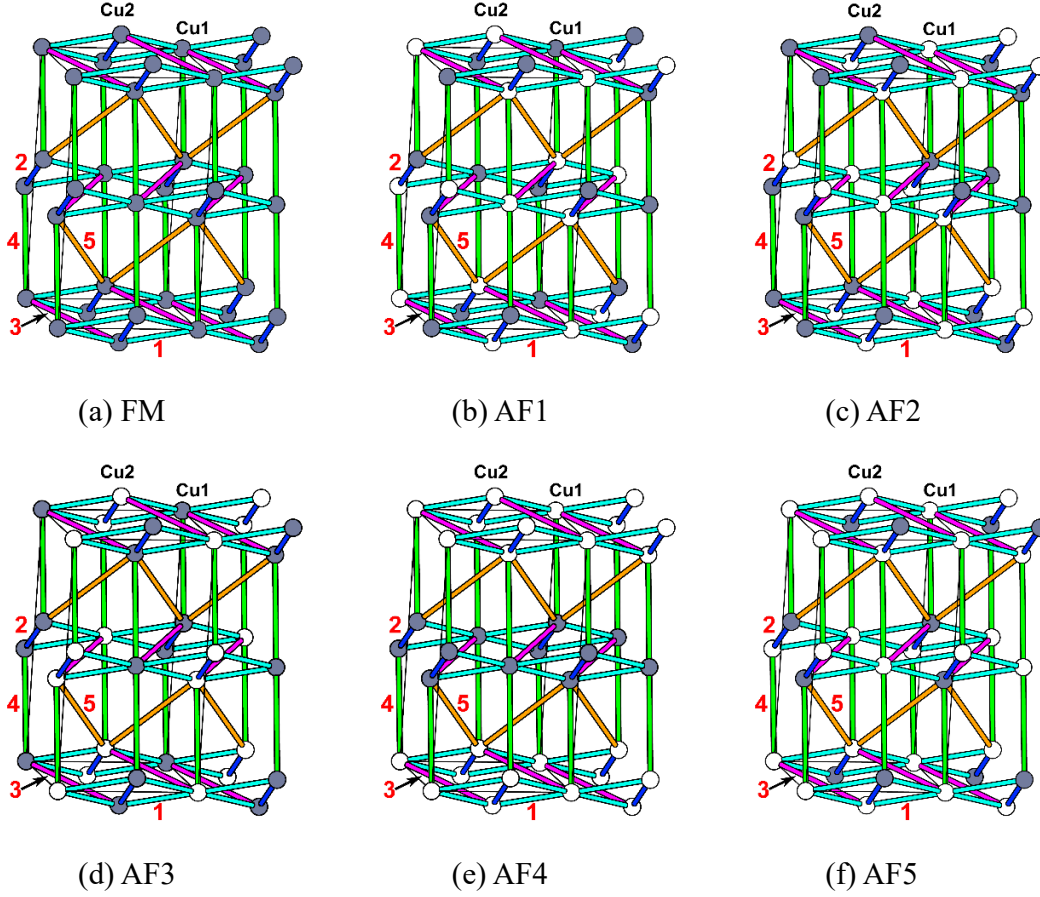


Figure S2. Ordered spin arrangements of FM and AF( $i$ )( $i = 1$  to 5).

**(c) Energies of the ordered spin states in terms of the spin exchanges**

Table S2. Values of  $n_i$  in the energy expressions,  $E_{\text{spin}} = \sum_{i=1}^5 n_i J_i S^2$ , for the ordered spin states FM and AF $_i$  ( $i = 1 - 5$ ).

	$J_1$	$J_2$	$J_3$	$J_4$	$J_5$
FM	-32	-8	-16	-16	-16
AF1	0	8	-16	0	0
AF2	0	8	16	0	0
AF3	32	-8	-16	-16	-16



AF4	-32	-8	-16	16	16
AF5	0	8	0	0	16

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_3 = (1/32)(4/N^2)(AF2 - AF1)$$

$$J_1 = (1/64)(4/N^2)(AF3 - FM)$$

$$J_2 = (1/32)[\{(AF1 - FM) - (AF4 - AF2)\}(4/N^2) - 64J_1 - 32J_3]$$

$$J_4 = (1/16)[\{(AF4 - AF5)(4/N^2)\} + 32J_1 + 16J_2 + 16J_3]$$

$$J_5 = (1/16)[\{(AF5 - AF2)(4/N^2)\} + 16J_3]$$

**(e) Ordered spin state energies and spin exchanges from DFT+U calculations**

Table S3. Relative energies (in meV/FU) and spin exchange interactions (in K) obtained from DFT+U calculations

	U = 3 eV	U = 4 eV
FM	29.20	22.62
AF1	4.07	3.17
AF2	0	0
AF3	13.11	10.04
AF4	28.01	21.98
AF5	2.85	2.34

(2a, 2b, c) super cell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

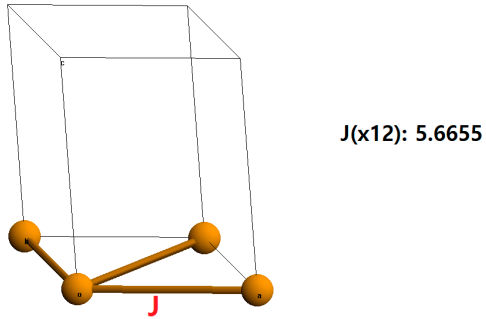
Plane wave cutoff energy = 450 eV

kpoint set = (6x4x6)

	U = 3 eV	U = 4 eV
J <sub>1</sub>	93.29	73.00
J <sub>2</sub>	382.64	297.93
J <sub>3</sub>	47.20	36.74
J <sub>4</sub>	32.77	25.10
J <sub>5</sub>	-18.95	-17.65

## S11. $\text{RbFe}(\text{MoO}_4)_2$

### (a) Spin exchange paths



### (b) Ordered spin states using a (2a, 2b, c) superstructure

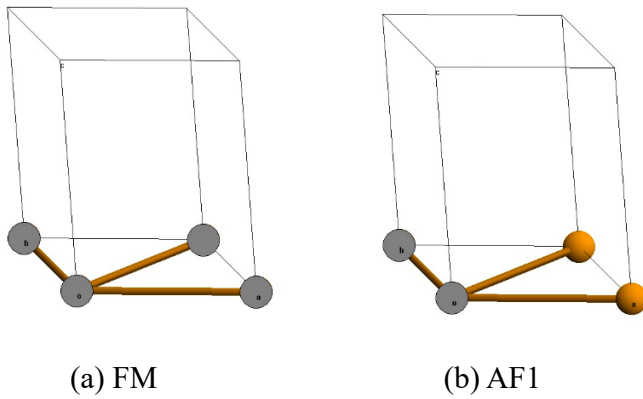


Figure S1. Ordered spin arrangements of (a) FM and (b) AF1 states.

### (c) Energies of the ordered spin states in terms of the spin exchanges

$$E_{\text{FM}} = (-12J)(N^2/4)$$

$$E_{\text{AF1}} = (+4J)(N^2/4)$$

### (d) Spin exchanges in terms of the ordered spin state energies

$$J = (1/16)(4/N^2)(E_{\text{AF1}} - E_{\text{FM}})$$

### (e) Ordered spin state energies and spin exchanges from DFT+U calculations

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U calculations

	U = 4 eV
FM	3.18
AF1	0

(2a, 2b, c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

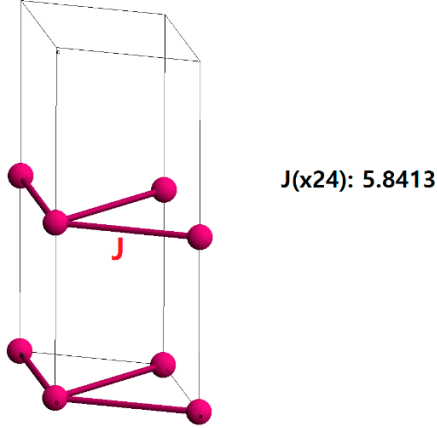
Plane wave cutoff energy = 450 eV

kpoint set = (6x6x9)

	U = 4 eV
J	1.47

## S12. Ba<sub>3</sub>CoSb<sub>2</sub>O<sub>9</sub>

### (a) Spin exchange paths



### (b) Ordered spin states using a (2a, 2b, c) superstructure

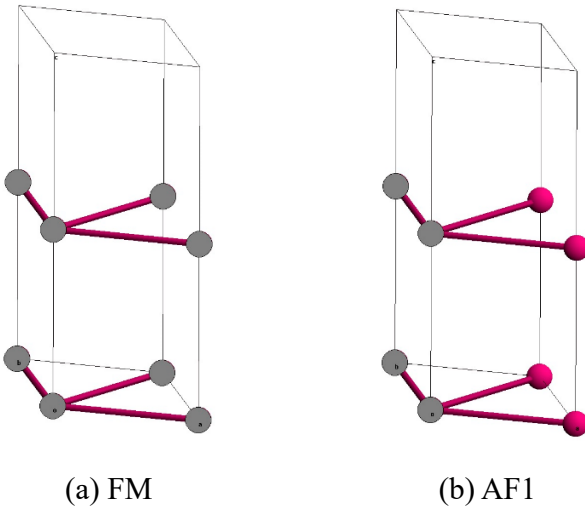


Figure S1. Ordered spin arrangements of (a) FM and (b) AF1 states.

### (c) Energies of the ordered spin states in terms of the spin exchanges

$$E_{\text{FM}} = (-24J)(N^2/4)$$

$$E_{\text{AF1}} = (+8J)(N^2/4)$$

### (d) Spin exchanges in terms of the ordered spin state energies

$$J = (1/32)(4/N^2)(E_{\text{AF1}} - E_{\text{FM}})$$

**(e) Ordered spin state energies and spin exchanges from DFT+U calculations**

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U calculations

	U = 4 eV
FM	4.81
AF1	0

(2a, 2b, c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

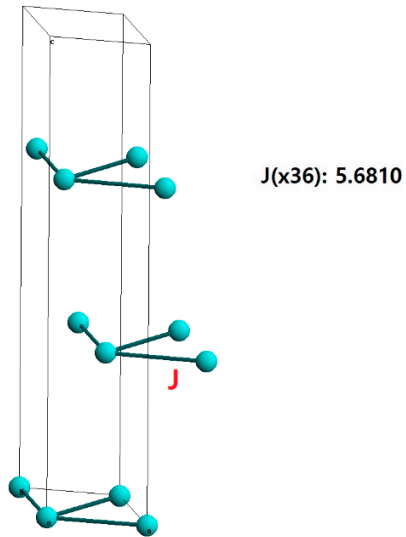
Plane wave cutoff energy = 450 eV

kpoint set = (6x6x4)

	U = 4 eV
J	6.20

### S13. Ba<sub>2</sub>LaNiTe<sub>2</sub>O<sub>12</sub>

#### (a) Spin exchange paths



#### (b) Ordered spin states using a (2a, 2b, c) superstructure

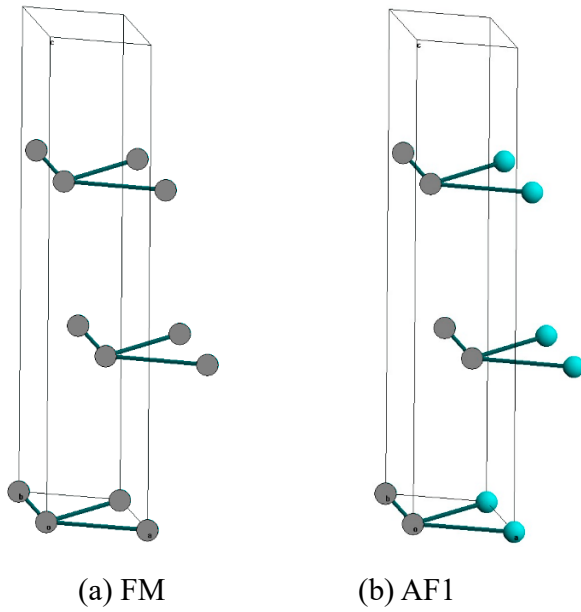


Figure S1. Ordered spin arrangements of (a) FM and (b) AF1 states.

#### (c) Energies of the ordered spin states in terms of the spin exchanges

$$E_{\text{FM}} = (-36J)(N^2/4)$$

$$E_{AF1} = (+12J)(N^2/4)$$

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J = (1/48)(4/N^2)(E_{AF1} - E_{FM})$$

**(e) Ordered spin state energies and spin exchanges from DFT+U calculations**

Table S1. Relative energies (in meV/FU) of the broken-symmetry states and the spin exchange parameters (in K) obtained from DFT+U calculations

	U = 4 eV
FM	19.33
AF1	0

(2a, 2b, c) supercell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

Plane wave cutoff energy = 450 eV

kpoint set = (6x6x2)

	U = 4 eV
J	56.04



# S14. $\text{Y}_2\text{Cu}_7(\text{TeO}_3)_6\text{Cl}_6(\text{OH})_2$

## (a) Spin exchange paths

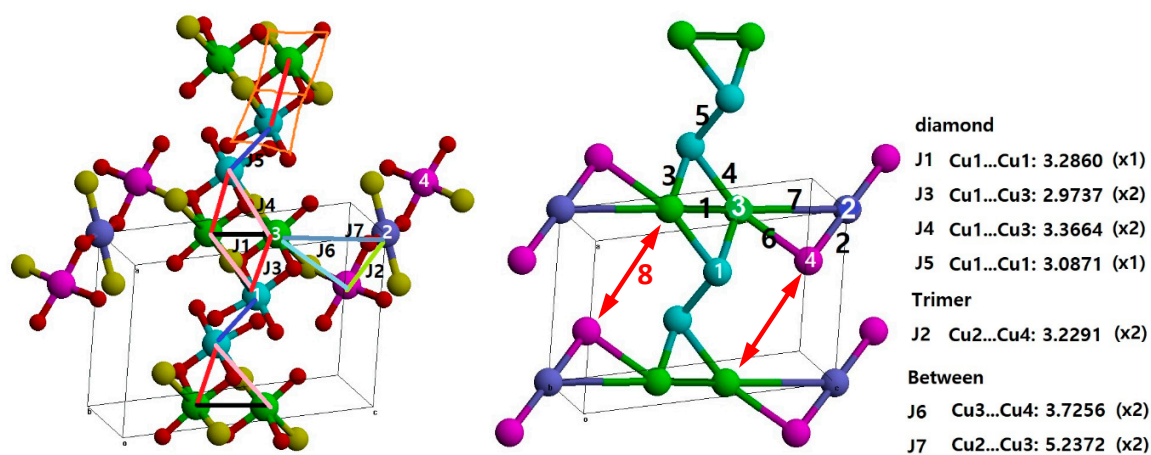
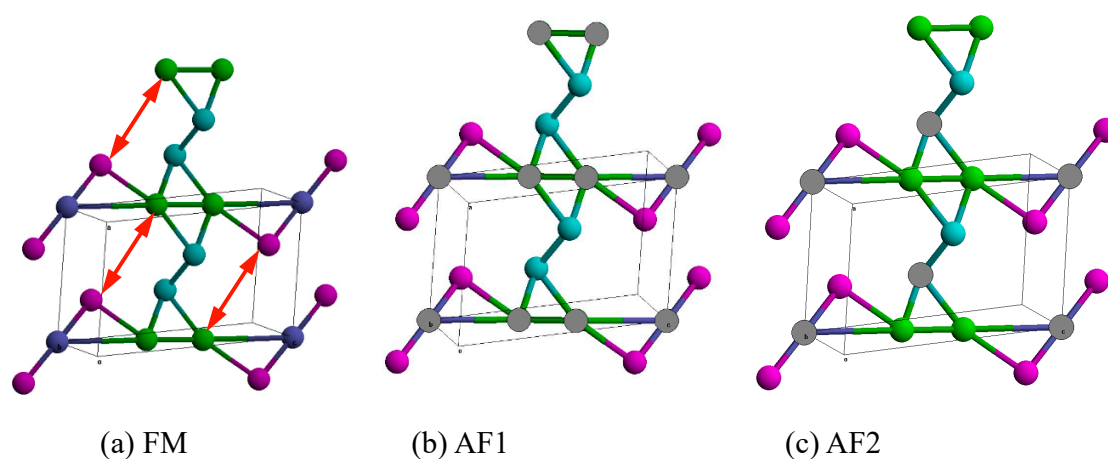


Figure S1. Spin exchange paths,  $J_1$  to  $J_8$ . The cyan, purple, green and magenta circles represent the Cu1, Cu2, Cu3 and Cu4 ions, respectively. [ $J_8$  Cu3...Cu4 = 6.2263 (x2)]

## (b) Ordered spin states using a (2a, b, c) supercell



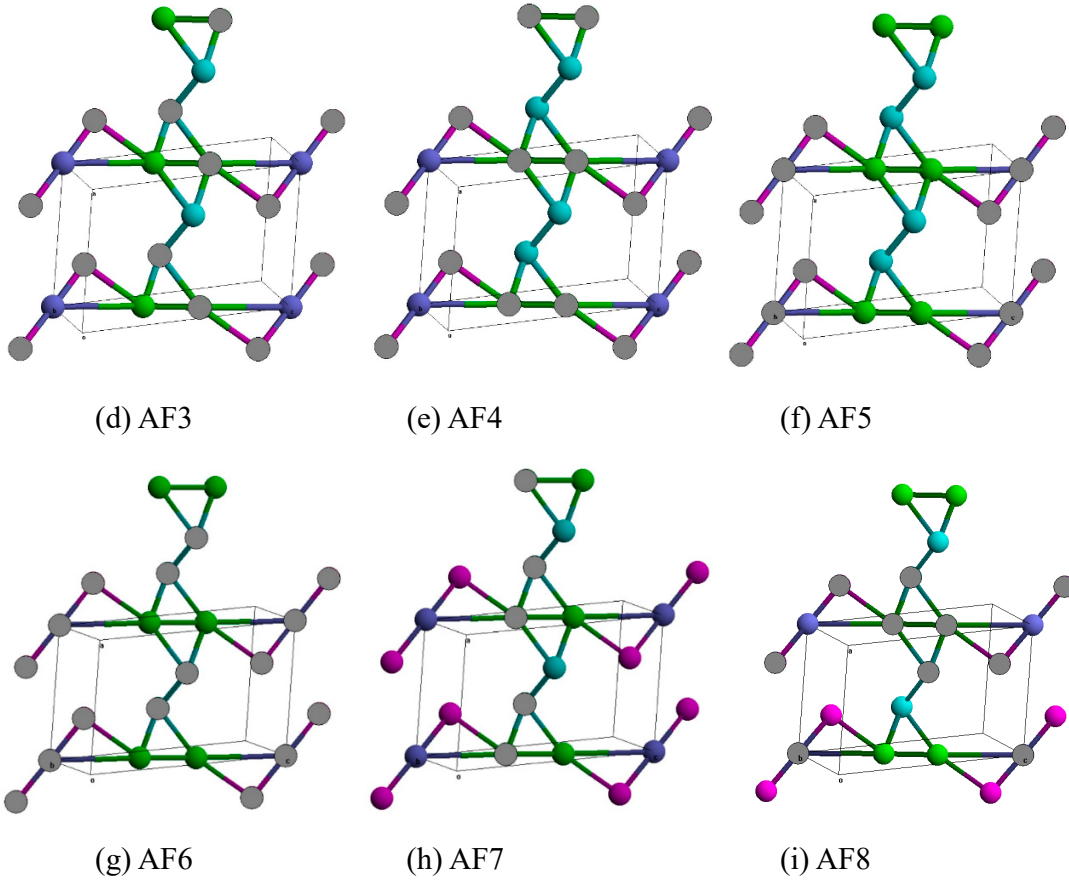


Figure S2. Ordered spin arrangements of FM, AF1 – AF8 states. The shaded and unshaded circles indicate the up and down spin sites, respectively.

### (c) Energies of the ordered spin states in terms of the spin exchanges

Table S1. Coefficients of  $n_i$  of  $E = \sum_{i=1}^7 n_i J_i S^2$  per (2a, b, c) supercell.

	$J_1$	$J_2$	$J_3$	$J_4$	$J_5$	$J_6$	$J_7$	$J_8$
FM	-2	-4	-4	-4	-2	-4	-4	-4
AF1	-2	4	4	4	-2	4	-4	4
AF2	-2	4	0	0	2	-4	4	-4
AF3	2	4	4	-4	2	0	0	0
AF4	-2	4	4	4	-2	-4	4	-4
AF5	-2	-4	-4	-4	-2	4	4	4
AF6	-2	-4	4	4	-2	4	4	4
AF7	2	-4	-4	4	2	0	0	0

AF8	-2	4	-4	-4	2	-4	4	4
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**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_7 = (1/16)(4/N^2)[(AF5 - FM) - (AF1 - AF4)]$$

$$J_2 = (1/8)[\{(AF5 - FM) - (AF6 - AF4)\}(4/N^2) - 8J_7]$$

$$J_3 = (1/16)[\{(AF6 - AF7) - (AF5 - AF3)\}(4/N^2) - 8J_2]$$

$$J_4 = (1/8)[(AF6 - AF5)(4/N^2) - 8J_3]$$

$$J_8 = (1/8)[\{(AF7 - AF2) - (AF3 - AF8)\}(4/N^2) + 8J_2 + 12J_3 - 4J_4]$$

$$J_6 = (1/8)[(AF5 - FM)(4/N^2) - 8J_7 - 8J_8]$$

$$J_1 = (1/4)[(AF3 - AF8)(4/N^2) - 8J_3 - 4J_6 + 4J_7 + 4J_8]$$

$$J_5 = (1/4)[(AF2 - AF4)(4/N^2) + 4J_3 + 4J_4]$$

**(e) Relative energies of the ordered spin states and the spin exchanges from DFT+U calculations**

Table S2. Relative energies (meV/FU) of the ordered spin states obtained from DFT+U calculations

	U = 3 eV	U = 4 eV
FM	66.28	53.93
AF1	1.62	1.95
AF2	56.27	46.82
AF3	20.76	17.90
AF4	46.15	39.02
AF5	21.81	17.36
AF6	0	0
AF7	44.98	36.32
AF8	23.25	19.00

(2a, b, c) super cell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

Plane wave cutoff energy = 450 eV

kpoint set = (4x6x4)

Table S3. Spin exchange parameters (in K) from DFT+U calculations

	U = 3 eV	U = 4 eV
J <sub>1</sub>	7.08	1.73
J <sub>2</sub>	-19.20	-25.47
J <sub>3</sub>	276.63	220.24
J <sub>4</sub>	-23.58	-18.90
J <sub>5</sub>	18.39	20.38
J <sub>6</sub>	6.70	3.84
J <sub>7</sub>	-0.35	-2.85
J <sub>8</sub>	509.34	423.26

# S15. $\text{Cu}_5(\text{VO}_4)_2(\text{OH})_4$

## (a) Spin exchange paths

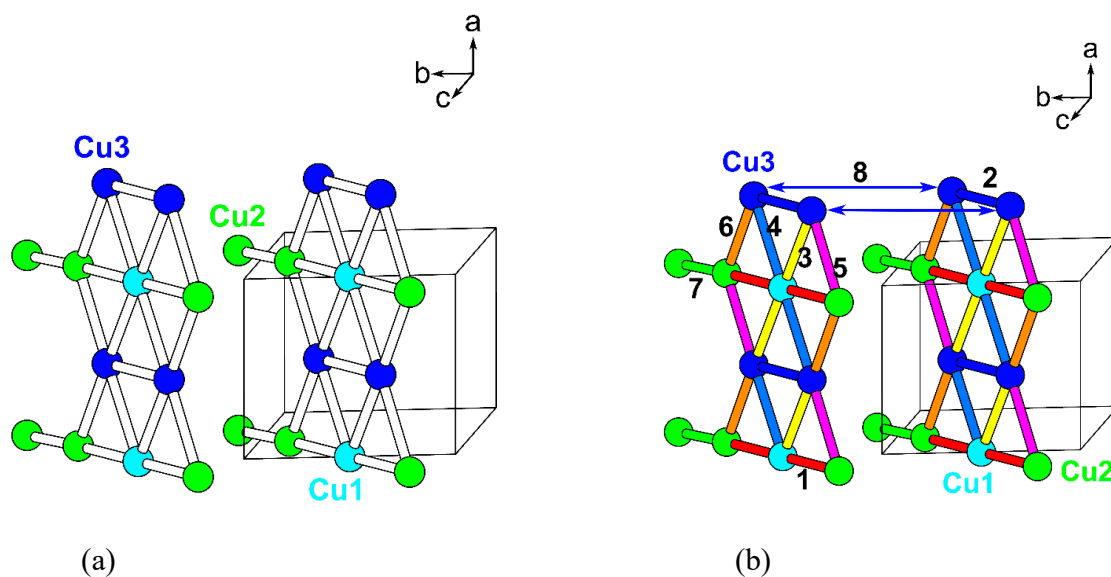


Figure S1. (a) Two Cu<sub>5</sub>-layers in (2a, 2b, c) super cell and (b) spin exchange paths. The numbers 1 to 8 indicate the spin exchange paths J<sub>1</sub> to J<sub>8</sub>, respectively. The J<sub>8</sub> is interlayer spin exchange between Cu(2) cations.

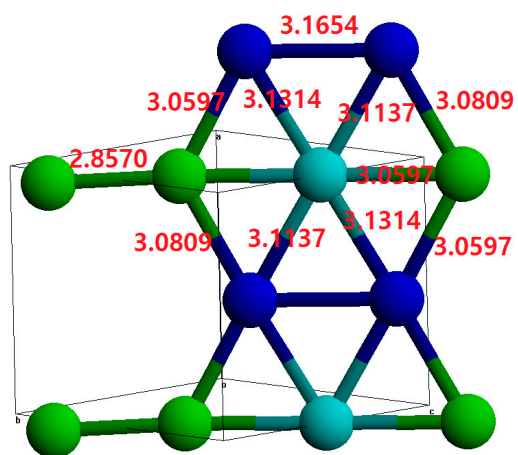
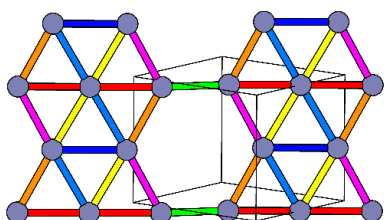
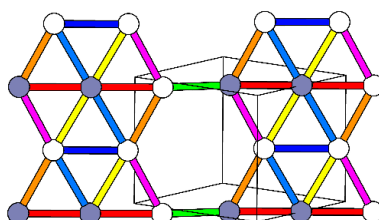


Figure S2. Cu-Cu bond distances associated with the intralayer spin exchange paths J<sub>1</sub> to J<sub>7</sub>.

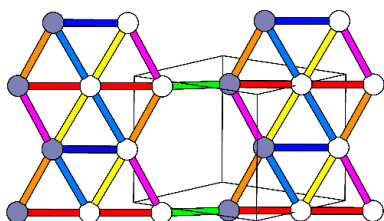
**(b) Ordered spin states using a (2a, 2b, c) super cell**



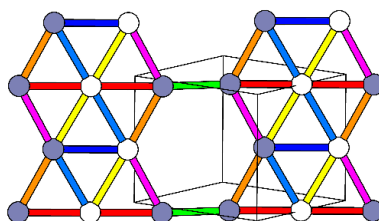
(a) FM



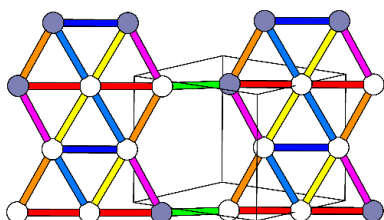
(b) AF1



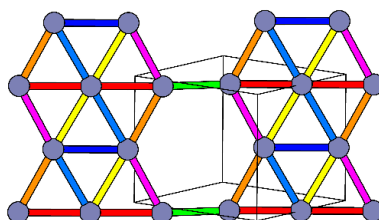
(c) AF2



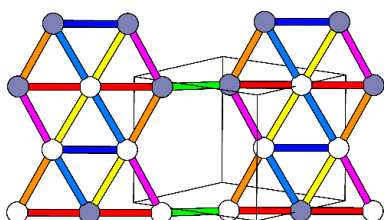
(d) AF3



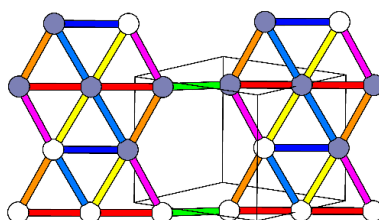
(e) AF4



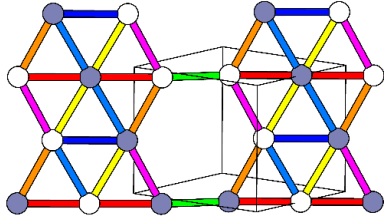
(f) AF5



(g) AF6



(h) AF7



(i) AF8

Figure S3. Ordered spin arrangements of FM and AF(i) (i = 1 to 8). The spin arrangements of the  $J_8$  are AFM except for the FM state.

### (c) Energies of the ordered spin states in terms of the spin exchanges

Table S1. Coefficients  $n_i$  of  $E_i = \sum_{i=1}^8 n_i J_i S^2$

	$J_1$	$J_2$	$J_3$	$J_4$	$J_5$	$J_6$	$J_7$	$J_8$
FM	-16	-8	-16	-16	-16	-16	-8	-8
AF1	0	-8	16	16	0	0	8	8
AF2	0	8	0	0	-16	-16	8	8
AF3	16	8	0	0	0	0	-8	8
AF4	0	-8	0	0	16	-16	8	8
AF5	-16	-8	-16	-16	-16	-16	-8	8
AF6	16	-8	0	0	0	0	-8	8
AF7	-16	8	16	-16	16	-16	-8	8
AF8	16	8	16	-16	-16	16	-8	8

### (d) Spin exchanges in terms of the ordered spin state energies

$$J_8 = (1/16)(4/N^2)(E_{AF5} - E_{FM})$$

$$J_2 = (1/16)\{(4/N^2)[(E_{AF3} - E_{FM}) - (E_{AF6} - E_{AF5})] - 16J_8\}$$

$$J_5 = (1/32)[(4/N^2)(E_{AF4} - E_{AF2}) + 16J_2]$$

$$J_1 = (1/32)\{(4/N^2)[(E_{AF4} - E_{AF5}) - (E_{AF1} - E_{AF3})] - 16J_2 - 32J_5\}$$

$$J_6 = (1/32)[(4/N^2)(E_{AF8} - E_{AF7}) - 32J_1 + 32J_5]$$

$$J_7 = (1/16)[(4/N^2)(E_{AF4} - E_{AF3}) + 16J_1 + 16J_2 - 16J_5 + 16J_6]$$

$$J_3 = (1/32)[(4/N^2)(E_{AF7} - E_{AF5}) - 16J_2 - 32J_5]$$

$$J_4 = (1/32)[(4/N^2)(E_{AF1} - E_{AF7}) - 16J_1 + 16J_2 + 16J_5 - 16J_6 - 16J_7]$$

**(e) Relative energies of the ordered spin states and spin exchanges from DFT+U calculations**

Table S2. Relative energies (in meV/FU) obtained from DFT+U calculations

	U = 3 eV	U = 4 eV	U = 5 eV
FM	68.15	55.06	44.29
AF1	26.52	22.25	18.60
AF2	40.85	33.16	26.84
AF3	13.60	12.24	11.03
AF4	0	0	0
AF5	67.57	55.20	44.99
AF6	12.65	11.56	10.55
AF7	27.96	23.83	20.14
AF8	35.45	30.29	25.94

(2a, 2b, c) super cell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

Plane wave cutoff energy = 450 eV

kpoint set = (6x4x8)

Table S3. Spin exchange parameters (in K) obtained from DFT+U calculations

	U = 3 eV	U = 4 eV	U = 5 eV
J <sub>1</sub>	240.93	193.76	154.66
J <sub>2</sub>	-11.02	-7.83	-5.51



J <sub>3</sub>	3.80	-2.55	-6.09
J <sub>4</sub>	-27.06	-24.32	-21.36
J <sub>5</sub>	231.42	188.40	152.93
J <sub>6</sub>	-52.92	-42.80	-35.35
J <sub>7</sub>	103.30	96.66	88.75
J <sub>8</sub>	6.76	-1.62	-8.12

## S16. $\text{Na}_2\text{Cu}_7(\text{SeO}_3)_4\text{O}_2\text{Cl}_4$

### (a) Spin exchanges

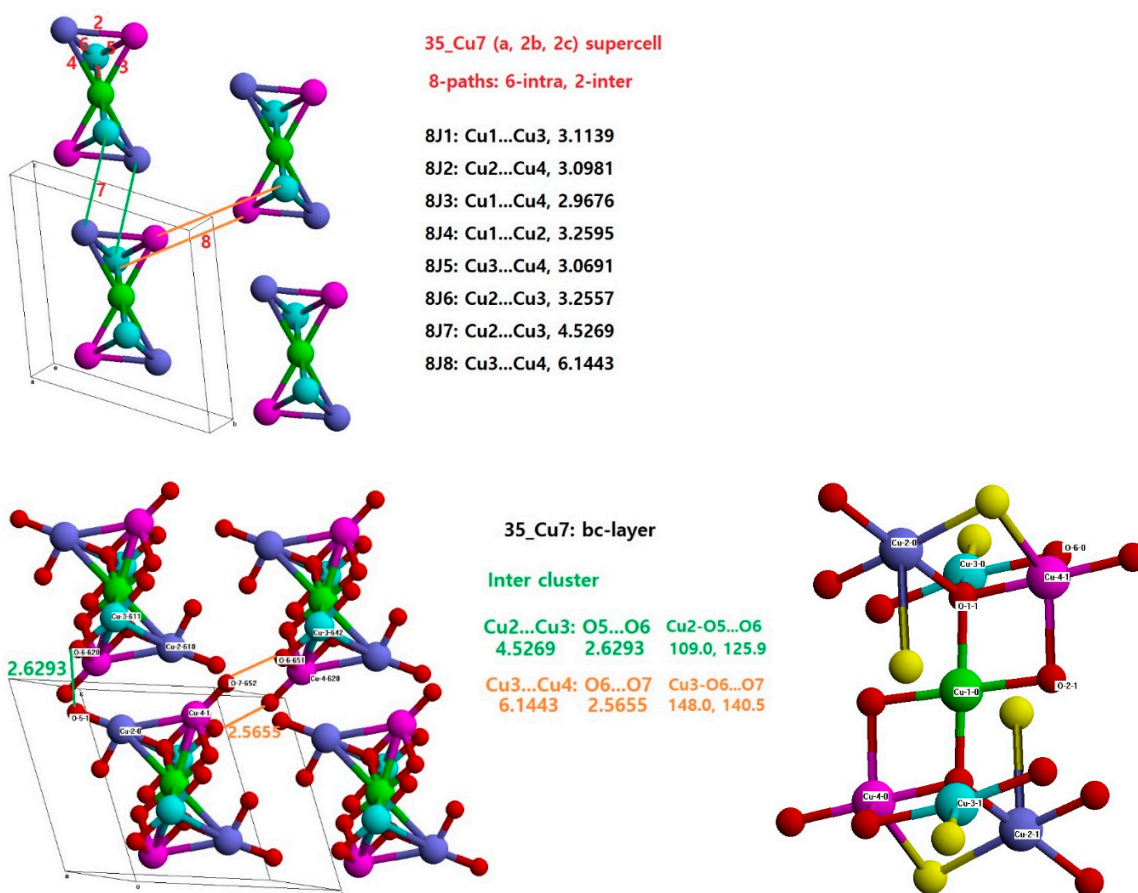


Figure S1. Spin exchange paths

	Cu...Cu	$\angle\text{Cu-O-Cu}$	O...O	$\angle\text{Cu-O...O}$
J <sub>1</sub>	3.1139	107.7		
J <sub>2</sub>	3.0981	108.3		
J <sub>3</sub>	2.9676	94.7, 101.7		
J <sub>4</sub>	3.2595	116.8		
J <sub>5</sub>	3.0691	95.5, 105.6		
J <sub>6</sub>	3.2557	115.3		
J <sub>7</sub>	4.5269		2.6293	109.0, 125.9
J <sub>8</sub>	6.1443		2.5655	148.0, 140.5

**(b) Ordered spin states using a (a, 2b, 2c) supercell**

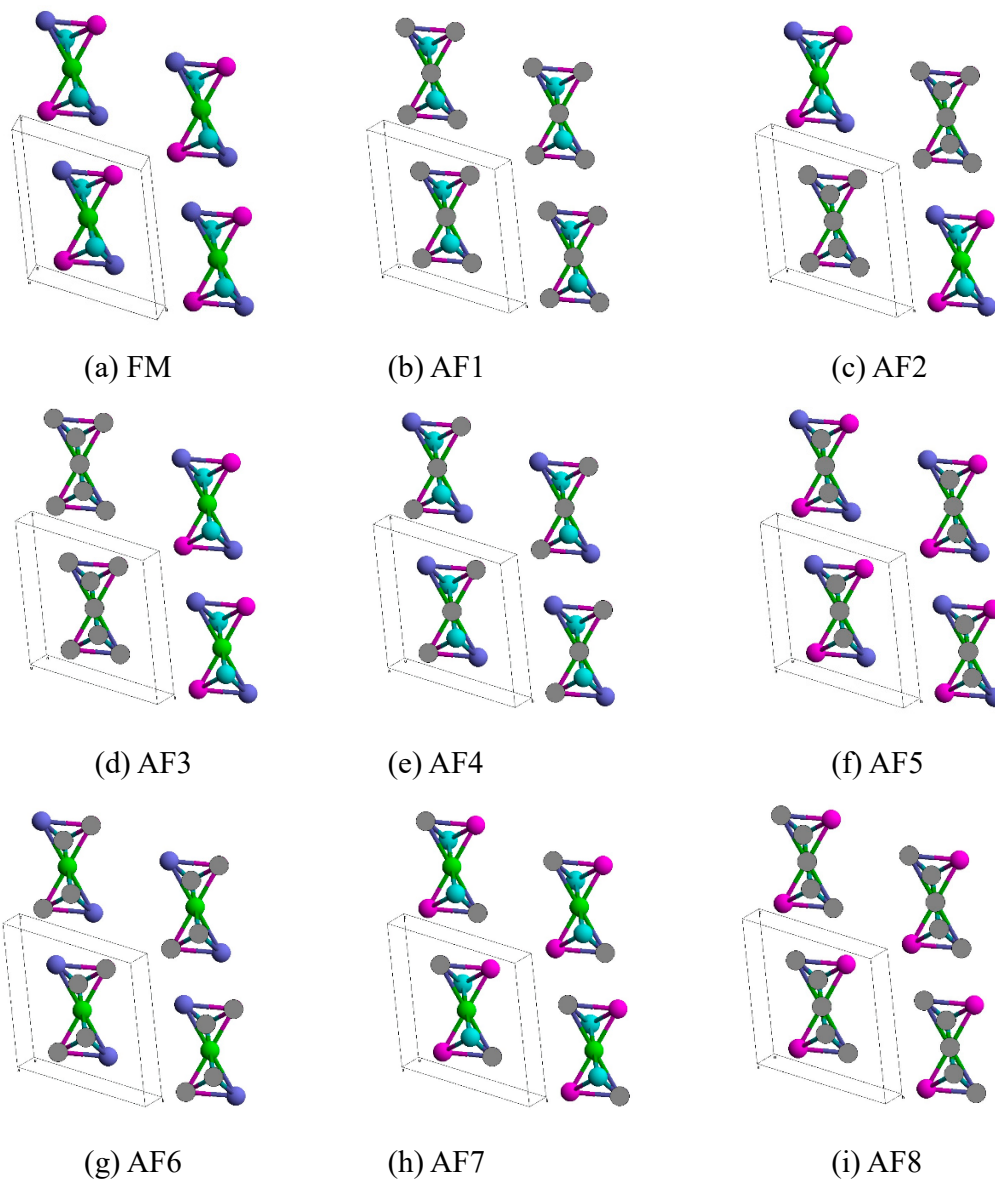


Figure S2. Ordered spin arrangements of FM and AF(i) ( $i = 1$  to 8). The green, purple, cyan and magenta indicate the Cu1, Cu2, Cu3 and Cu4 ions. The shaded and unshaded circles represent the up and down spin sites of Cu ions, respectively.

**(c) Energies of the ordered spin states in terms of the spin exchanges**

Table S1. Coefficients  $n_j$  of  $E_i = \sum_{j=1}^8 n_j J_j S^2$  The  $E_i$  ( $i= 1$  to  $9$ ) =  $E_{FM}$  and  $E_{AF1}$  to  $E_{AF8}$

	$J_1$	$J_2$	$J_3$	$J_4$	$J_5$	$J_6$	$J_7$	$J_8$
$E_{FM}$	-8	-8	-8	-8	-8	-8	-8	-8
$E_{AF1}$	8	-8	-8	-8	8	8	-8	-8
$E_{AF2}$	-8	-8	-8	-8	-8	-8	8	-8
$E_{AF3}$	-8	-8	-8	-8	-8	-8	-8	8
$E_{AF4}$	8	8	-8	8	8	-8	-8	8
$E_{AF5}$	-8	-8	8	8	8	8	8	8
$E_{AF6}$	8	8	8	-8	-8	8	8	-8
$E_{AF7}$	-8	8	-8	8	-8	8	8	-8
$E_{AF8}$	-8	8	8	-8	8	-8	-8	8

**(d) Spin exchanges in terms of the ordered spin state energies**

$$J_7 = (1/16)(4/N^2)(E_{AF2} - E_{FM})$$

$$J_8 = (1/16)(4/N^2)(E_{AF3} - E_{FM})$$

$$J_6 = (1/32)[\{(E_{AF1} - E_{AF4}) - (E_{AF3} - E_{AF7})\}(4/N^2) - 16J_7 + 32J_8]$$

$$J_4 = (1/32)[\{(E_{AF5} - E_{AF8}) - (E_{AF3} - E_{AF7})\}(4/N^2) - 32J_6 - 32J_7 + 16J_8]$$

$$J_3 = (1/32)[\{(E_{AF5} - E_{AF7}) - (E_{AF1} - E_{AF6})\}(4/N^2) - 16J_7 - 16J_8]$$

$$J_5 = (1/16)[\{(E_{AF1} - E_{AF6}) - (E_{AF5} - E_{AF8})\}(4/N^2) + 16J_3 + 16J_4 + 16J_6 + 32J_7]$$

$$J_1 = (1/16)[(E_{AF6} - E_{AF8})(4/N^2) + 16J_5 - 16J_6 - 16J_7 + 16J_8]$$

$$J_2 = (1/16)[(E_{AF8} - E_{AF5})(4/N^2) + 16J_4 + 16J_6 + 16J_7]$$

**(e) Relative energies of the ordered spin states and the spin exchanges from DFT+U calculations**

Table S2. Relative energies (meV/FU) of the ordered spin states obtained from DFT+U calculations

	$U = 3 \text{ eV}$	$U = 4 \text{ eV}$
--	--------------------	--------------------

E <sub>FM</sub>	94.86	73.60
E <sub>AF1</sub>	103.05	86.09
E <sub>AF2</sub>	134.24	107.45
E <sub>AF3</sub>	119.29	95.43
E <sub>AF4</sub>	105.88	88.92
E <sub>AF5</sub>	34.34	29.79
E <sub>AF6</sub>	120.70	102.63
E <sub>AF7</sub>	172.85	144.25
E <sub>AF8</sub>	0	0

(a, 2b, 2c) super cell

PBE functional for the exchange-correlation

SCF convergence criterion =  $10^{-6}$  eV

Plane wave cutoff energy = 450 eV

kpoint set = (6x4x2)

Table S3. Spin exchange parameters (in K) obtained from DFT+U calculations

	U = 3 eV	U = 4 eV
J <sub>1</sub>	-311.62	-274.35
J <sub>2</sub>	-54.00	-64.19
J <sub>3</sub>	672.71	545.29
J <sub>4</sub>	-243.88	-211.77
J <sub>5</sub>	765.01	625.92
J <sub>6</sub>	-150.03	-150.89
J <sub>7</sub>	-58.46	-47.10
J <sub>8</sub>	115.01	92.28

**(f) Additional calculations using ordered spin states not considered above**

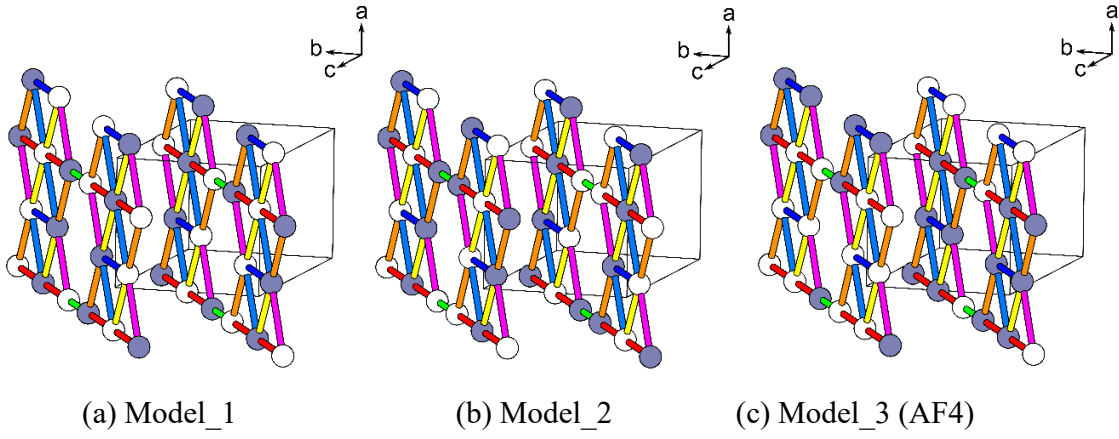


Table S4. Coefficients  $n_i$  of  $E_i = \sum_{i=1}^8 n_i J_i S^2$  of Model\_1, Model\_2 and Model\_3 (AF4) state

(2a, 2b, 2c)	$J_1$	$J_2$	$J_3$	$J_4$	$J_5$	$J_6$	$J_7$	$J_8$
Model_1	32	16	-32	32	32	-32	16	16
Model_2	32	16	-32	32	32	-32	-16	16
Model_3 (AF4)	0	-16	0	0	32	-32	16	16

Table S5. Relative energies of (meV/FUs) associated with the J-values obtained from DFT+U calculations for the Model\_1 and Model\_2 (AF4) state

$\Delta E(\text{meV/FUs})$	U = 3 eV	U = 4 eV	U = 5 eV
Model_1	0	0	0
Model_2	8.91	8.33	7.65
Model_3 (AF4)	17.16	14.15	11.54

