Supplementary Material

for

Absence of Spin Frustration in the Kagomé Layers of Cu2+ Ions in Volborthite $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ and Observation of the Suppression and Re-Entrance of Specific Heat Anomalies in Volborthite under an External Magnetic Field

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Spin exchanges of the *I*2/*a* and *P*2$_1$/*a* phases of volborthite by energy mapping analysis

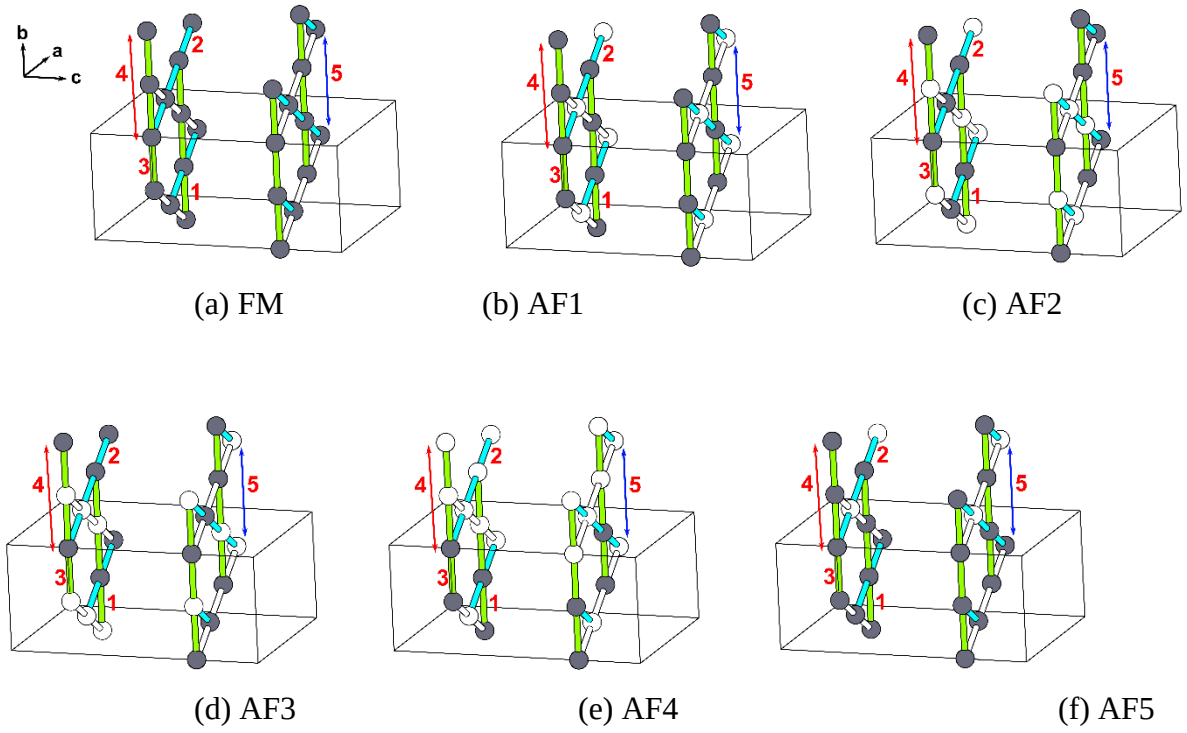
To extract the values of the spin exchanges for the *I*2/*a* and *P*2$_1$/*a* phases of volborthite, we carry out DFT calculations encoded in the VASP[1,2] using the augmented plane wave method[3,4] and the PBE exchange-correlation functional.[5] To take into account the effect of electron correlation of the Cu 3d states, we use the DFT plus on site repulsion (DFT+U) method[6] with U_{eff} = U – J = 4 and 5 eV.

A. *I*2/*a* phase

To determine the five spin exchanges $J_1 – J_5$ of the *I*2/*a* phase, we consider six ordered spin states FM, AF(i) (i = 1 to 5) shown in Figure S1. Then, the total spin exchange energies of these states can be written as

$$E = \sum_{i=1}^{5} n_i J_i S^2 \qquad \text{(S1)}$$

where S refers to the spin of the Cu^{2+} ion (i.e., S = 1/2). The values of n_i(i = 1 to 5) found for the six spin states are listed in Table S1. The relative energies (meV/FU) obtained for the FM, and AFi (i = 1 – 5) states by DFT+U calculations are listed in Table S2. By mapping the relative energies of the ordered magnetic states determined by DFT+U calculations to those determined by the spin exchange energies, we obtain the values of the spin exchanges $J_1 – J_5$ listed in Table S3 and Table 1 of the text.



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

(d) AF3 (e) AF4 (f) AF5

Figure S1. Six ordered spin states, i.e., the FM and AF(i) (i = 1 to 5) states, of the *I*2/*a* phase employed for the energy-mapping analysis, where the gray and white circles represent the up and down spin sites of Cu^{2+} ions.

Table S1. Values of n_i for the six ordered spin states

	n_1	n_2	n_3	n_4	n_5
E_{FM}	-16	-16	-16	-16	-8
E_{AF1}	16	16	-16	-16	-8
E_{AF2}	-16	16	16	-16	-8
E_{AF3}	16	-16	16	-16	-8
E_{AF4}	0	0	0	16	-8
E_{AF5}	0	0	-16	-16	8

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

	U_{eff} = 4 eV	U_{eff} = 5 eV
FM	47.87	37.85
AF1	0.69	0
AF2	0	0.65
AF3	46.24	38.49
AF4	16.94	13.61
AF5	23.95	18.63

Table S3. Values of the spin exchanges $J_1 - J_5$ (in K) calculated for the *I*2/a phase

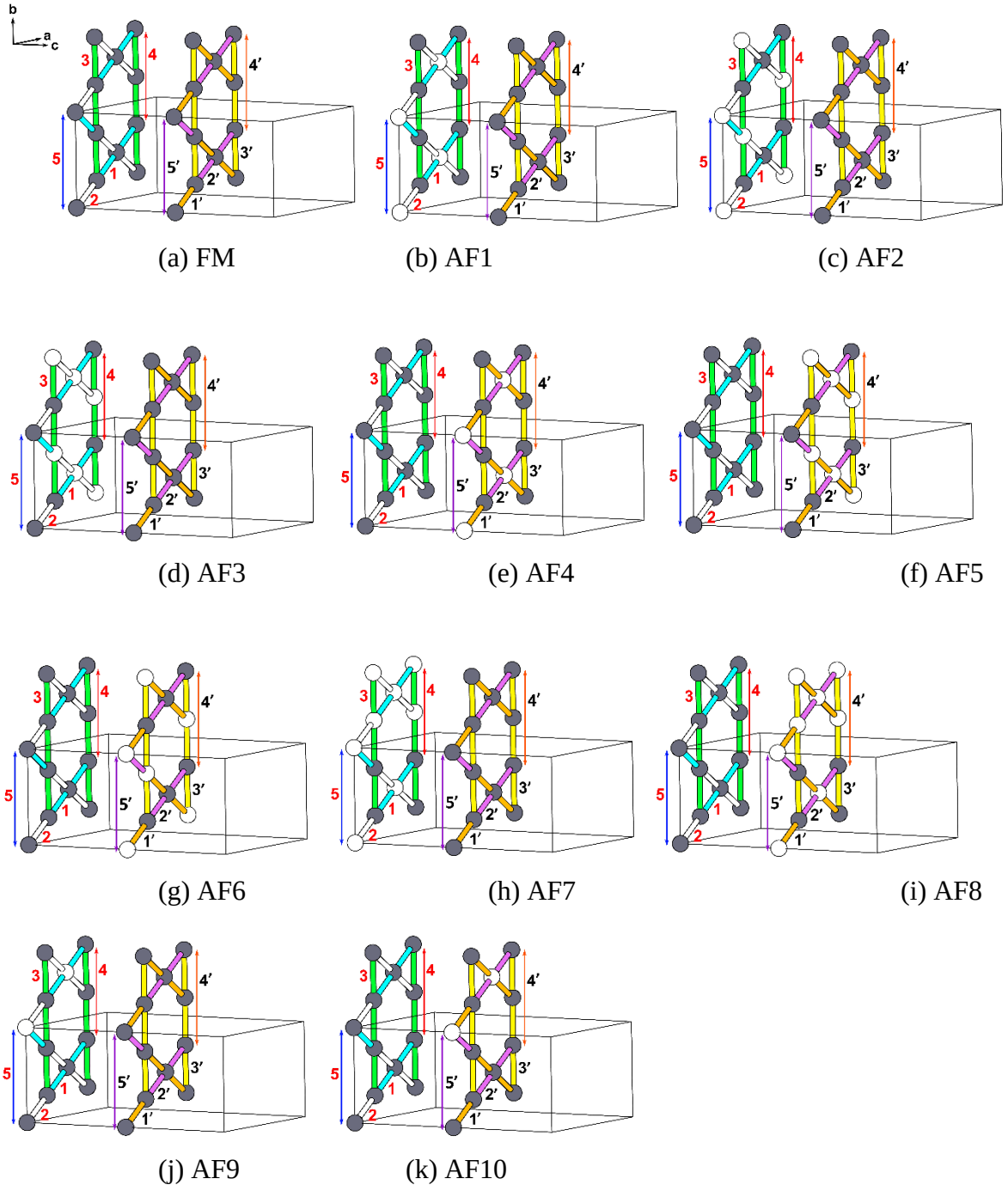
	U_{eff} = 4 eV	U_{eff} = 5 eV
J_1/J_2	0.010	0
J_3/J_2	0.025	-0.017
J_4/J_2	0.145	0.149
J_5/J_2	0.014	0.016
J_2	542 K	439 K

B. $P2_1/a$ phase

To determine the 10 spin exchanges of the $P2_1/a$ phase, namely, $J_1 – J_5$ for the layer 1 and $J'_1 – J'_5$ for the layer 2, we consider 11 ordered spin states FM, AF(i) (i = 1 to 10) shown in Figure S2. Then, the total spin exchange energies of these states can be written as

$$E = \sum_{i=1}^{5} \mathrm{n_i} J_\mathrm{i} \mathrm{S}^2 + \sum_{i=1}^{5} n'_i J'_i \mathrm{S}^2 \qquad \text{(S2)}$$

where S = 1/2. The values of n_i (i = 1 to 5) and n_i' (i = 1 to 5) found for the 11 spin states are listed in Table S4. The relative energies (meV/FU) obtained for the FM, and AFi (i = 1 – 10) states by DFT+U calculations are listed in Table S5. By mapping the relative energies of the ordered magnetic states determined by DFT+U calculations to those determined by the spin exchange energies, we obtain the values of the spin exchanges listed in Table S6 and Table 1 of the text.



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

(d) AF3 (e) AF4 (f) AF5

(g) AF6 (h) AF7 (i) AF8

(j) AF9 (k) AF10

Figure S2. 11 ordered spin states, i.e., the FM and AF(i) (i = 1 to 10) states, of the $P2_1/a$ phase employed for the energy-mapping analysis, where the gray and white circles represent the up and down spin sites of Cu^{2+} ions.

Table S4. Values of n_i and n_i' for the 11 ordered spin states

	n_1	n_2	n_3	n_4	n_5	n_1'	n_2'	n_3'	n_4'	n_5'
E_{FM}	-8	-8	-8	-8	-4	-8	-8	-8	-8	-4
E_{AF1}	8	8	-8	-8	-4	-8	-8	-8	-8	-4
E_{AF2}	-8	8	8	-8	-4	-8	-8	-8	-8	-4
E_{AF3}	8	-8	8	-8	-4	-8	-8	-8	-8	-4
E_{AF4}	-8	-8	-8	-8	-4	8	8	-8	-8	-4
E_{AF5}	-8	-8	-8	-8	-4	-8	8	8	-8	-4
E_{AF6}	-8	-8	-8	-8	-4	8	-8	8	-8	-4
E_{AF7}	0	0	0	8	-4	-8	-8	-8	-8	-4
E_{AF8}	-8	-8	-8	-8	-4	0	0	0	8	-4
E_{AF9}	0	0	-8	-8	4	-8	-8	-8	-8	-4
E_{AF10}	-8	-8	-8	-8	-4	0	0	-8	-8	4

Table S5. Relative energies (meV/FU) obtained from DFT+U calculations

	U_{eff} = 4 eV	U_{eff} = 5 eV
FM	25.87	20.25
AF1	2.18	1.21
AF2	1.42	1.21
AF3	25.14	20.61
AF4	1.41	0.58
AF5	0	0
AF6	25.72	21.08
AF7	10.31	8.03
AF8	9.86	7.65
AF9	13.86	10.59
AF10	13.49	10.27

Table S6. Values of the spin exchanges $J_1 - J_5$ (in K) calculated for the $P2_1/a$ phase

	U_{eff} = 4 eV		U_{eff} = 5 eV	
	Layer 1	Layer 2	Layer 1	Layer 2
J_1/J_2	-0.001	-0.025	-0.009	-0.035
J_3/J_2	0.031	0.031	-0.009	-0.006
J_4/J_2	0.141	0.135	0.145	0.138
J_5/J_2	0.014	0.013	0.015	0.014
J_2	550 K	582 K	446 K	473 K

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