Supplementary Material (ESI) for PCCP

The Magnetic and Electronic Structure of Vanadyl Pyrophosphate from Density Functional Theory

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Table S1. DFT optimized VOPO. The cell parameters *a*, *b*, and *c* are calculated to be 7.669, 9.617, and 8.453 Å, respectively. The space group is *Pnab* (No. 60).

	Fractional atomic coordinates		
Atom	*x*	*y*	*z*
V	0.0380	0.0040	0.3074
P	0.0455	0.2029	-0.0013
O1	0.2551	0.0276	-0.3145
O2	0.2500	0.1713	0.0000
O3	-0.0299	0.1443	-0.1499
O4	-0.4715	0.1421	-0.1476
O5	-0.0241	0.1348	0.4986

Table S2. Additional nine spin configurations for least-squares fitting (ΔE in K).

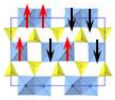
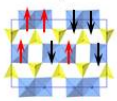
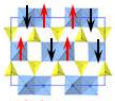
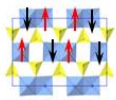
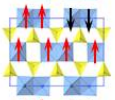
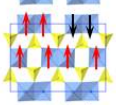
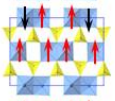
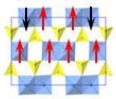
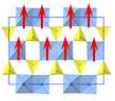
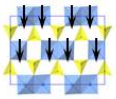
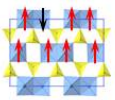
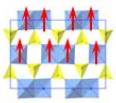
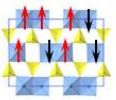
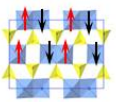
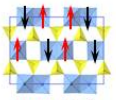
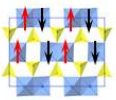
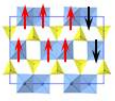
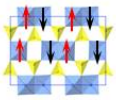
	Configuration		Energy Component	ΔE
	1st layer	2nd layer		
7			$4J_O + 8J_{OPO} + 8J_{chain}$	294.7
8			$8J_O + 4J_{OPO} + 8J_{chain}$	647.6
9			$4J_{OPO} + 8J_{chain}$	1233.7
10			$4J_O + 8J_{chain}$	1586.8
11			$16J_{layer}$	2089.7
12			$J_O + J_{OPO} + 2J_{chain} + 2J_{layer}$	1629.4
13			$7J_O + 7J_{OPO} + 2J_{chain} + 2J_{layer}$	273.3
14			$8J_O + 6J_{OPO} + 8J_{chain} + 4J_{layer}$	406.3
15			$6J_O + 6J_{OPO} + 4J_{layer}$	526.3

Table S3. Six spin configurations used for calculating spin exhcnage couplings at different *a*'s.

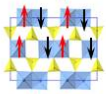
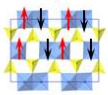
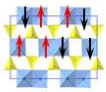
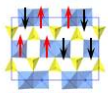
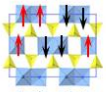
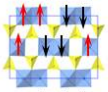
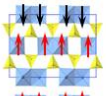
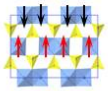
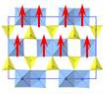
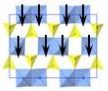
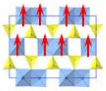
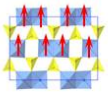
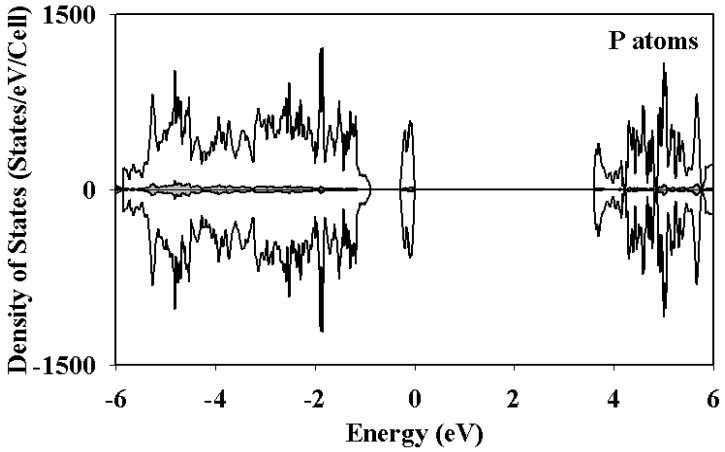
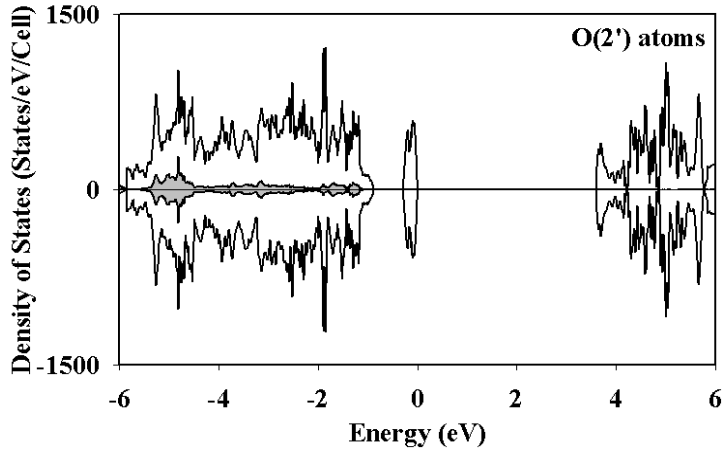
Configuration			Energy Component
	1st layer	2nd layer	
1			$8J_O + 8J_{OPO}$
2			$8J_O + 8J_{chain}$
3			$8J_{OPO} + 8J_{chain}$
4			$16J_{chain}$
5			$16J_{layer}$
6			*0*

Figure S1. The projected density of states (shaded) for P, O(2'), and O(3) atoms superimposed on the total density of states (unshaded) for VOPO. The energy zero is placed at the top of the valence bands.

(a) P atoms



(b) O(2') atoms



(c) O(3) atoms

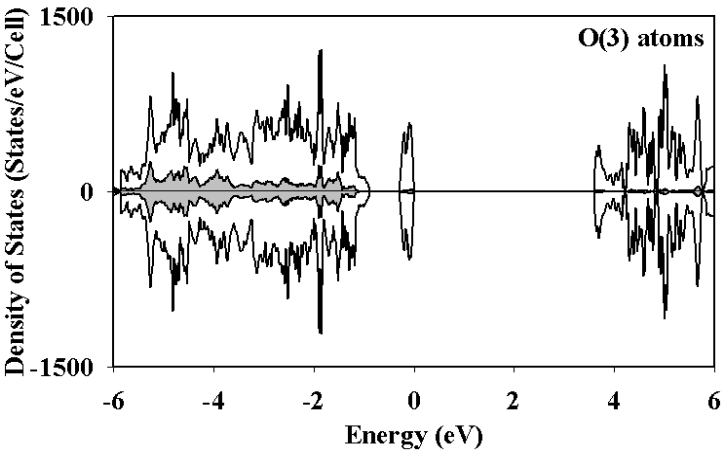
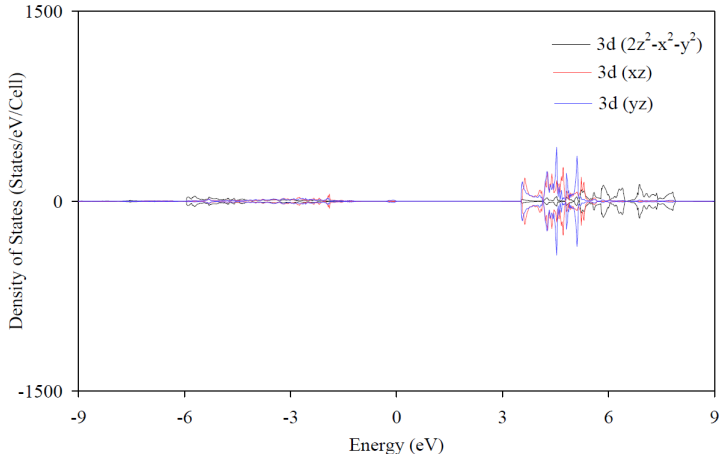
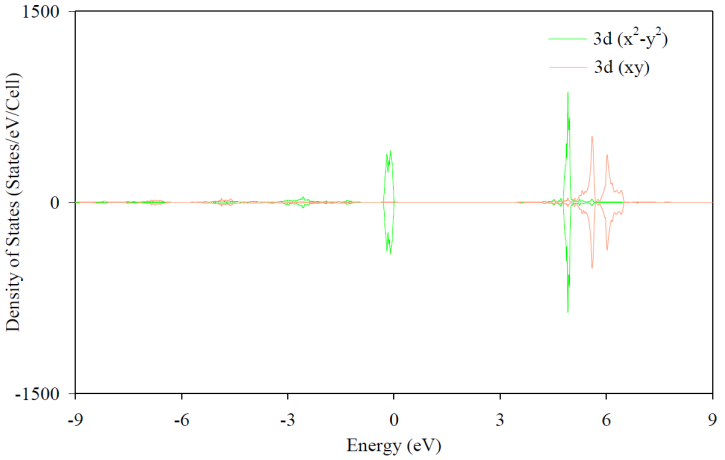


Figure S2. Orbital-resolved density of states of V, O(1), and O(2).

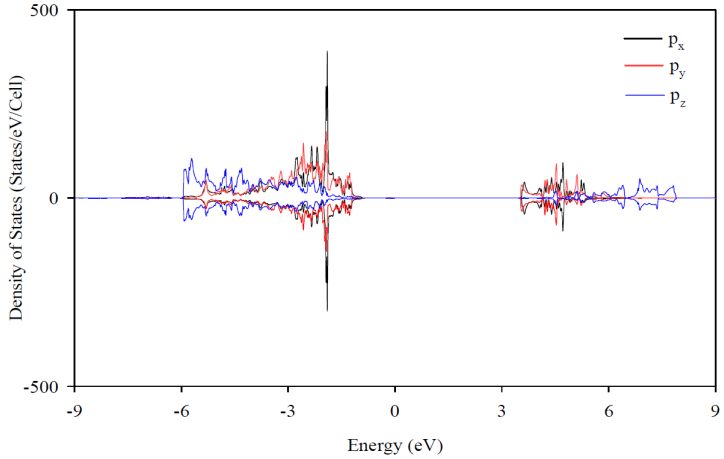
(a) V (part1)



(b) V (part2)



(c) O(1)



(d) O(2)

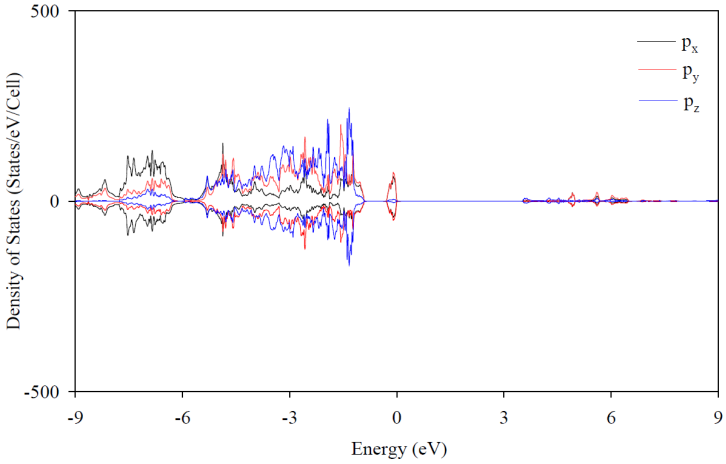


Figure S3. The dependence of the unit cell relative energies to the lattice parameter *a*.