Supporting Information

Band Gap in Magnetite above Verwey Temperature Induced by Symmetry Breaking

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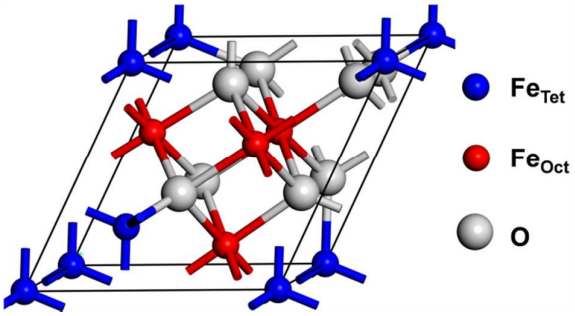

Figure S1. Optimized geometry of magnetite in the high temperature phase. The small blue balls represent the iron ions at tetrahedral sites (Fe_{Tet}), the small red balls represent the iron ions at octahedral sites (Fe_{Oct}) and the big grey balls represent the oxygen ions arranged in a slightly disordered face centered cubic lattice.

The geometry of Fe_3O_4 was fully relaxed at the PBE+U and the hybrid functional (HSE06 and B3LYP) level with the symmetry of $Fd\bar{3}m$ kept during the geometry relaxation. The optimized geometry of the unit cell is shown in Figure S1. The lattice parameters for the conventional cell obtained by different methods are listed in Tabel S1 and Table S2. PBE based on plane wave basis set and PAW pseudopotential gives a lattice parameter of 8.380 Å for the conventional cell which agrees well with the previous PBE result (3.87 Å)[1] and is slightly smaller than the experimental value of 8.394 Å[2]. PBE based on all-electron basis sets by CRYSTAL14 results in a much smaller lattice parameter of 8.354 Å. Generally, PBE+U and B3LYP slightly overestimate the lattice parameter and HSE06 always gives a value very close to the experimental one. For HSE06 and B3LYP the lattice parameter is not sensitive to the percent of exact exchange. While the lattice parameter decreases slowly with the decreasing of U value. Besides the lattice parameter, another important structure parameter is the oxygen ion coordinate, x, which specifies the Wyckoff position in the $Fd\bar{3}m$ space group. B3LYP, HSE06 and PBE+U give the x value from

0.25457 to 0.25492 in good accordance with the experimental value of 0.25490 [2].

Table S1. Lattice parameters (a) for the conventional cell and oxygen ion coordinates (x) for experimental and optimized Fe_3O_4 by HSE and B3LYP with different percent of exact exchange.

	HSE (25%)	HSE (20%)	HSE (15%)	B3LYP (20%)	B3LYP (15%)	PBE	Exp[2]
a (Å)	8.389	8.393	8.395	8.448	8.448	8.354	8.394
x	0.25470	0.25472	0.25476	0.25457	0.25461	0.25549	0.25490

Table S2. Lattice parameters (a) for the conventional cell and oxygen ion coordinates (x) for optimized Fe_3O_4 obtained from GGA+U with different U values in unit of eV.

	U = 4	U = 3.5	U = 3	U = 2.5	U = 2	U = 1.5	U = 1	U = 0
a (Å)	8.505	8.491	8.477	8.463	8.448	8.433	8.418	8.380
x	0.25492	0.25481	0.25477	0.25471	0.25482	0.25471	0.25466	0.25458

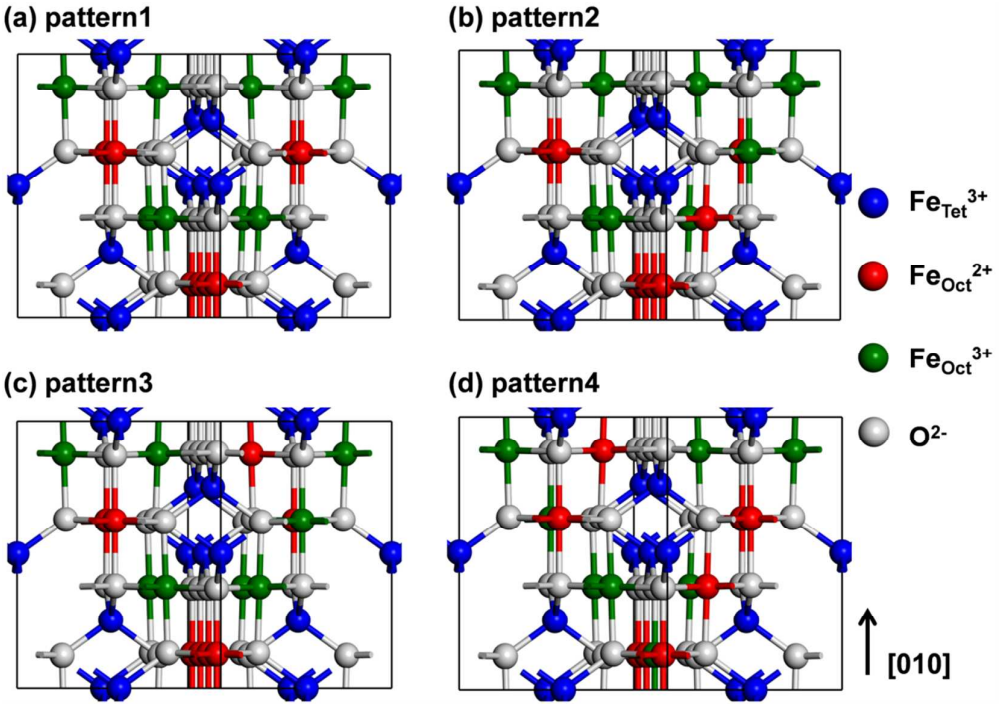

Figure S2. Different charge ordering patterns from conventional cell calculations.

Table S3. Magnetic moment and net charge of Fe ions at tetrahedral and octahedral sites labeled as m_{Tet}, m_{Oct}, Q_{Tet} and Q_{Oct}, energy difference per Fe_3O_4 formula (ΔE) between symmetric (E_{sy}) and asymmetric (E_{asy}) ground states ($\Delta E = E_{asy} - E_{sy}$) and band gap ($E_g$) derived from PBE+U with different U values.

	m_A (μ_B)	m_B (μ_B)	Q_A (e)	Q_B (e)	ΔE (eV)	E_g (eV)
U = 4 eV	-3.988	4.087 4.087 3.635 3.634	+1.670	+1.753 +1.748 +1.459 +1.458	-0.579	0.474
U = 3 eV	-3.925	4.011 4.009 3.635 3.634	+1.642	+1.708 +1.707 +1.482 +1.480	-0.283	0.0
U = 2.5 eV	-3.897	3.784 3.916 3.768 3.777	+1.634	+1.571 +1.659 +1.563 +1.568	-0.189	--
U = 2 eV	-3.857	3.759 3.848 3.759 3.766	+1.619	+1.568 +1.624 +1.569 +1.573	-0.113	--
U = 1.5 eV	-3.808	3.735 3.776 3.741 3.747	+1.604	+1.565 +1.593 +1.569 +1.572	-0.048	--
U = 1 eV	-3.747	3.697 3.705 3.713 3.714	+1.589	+1.558 +1.564 +1.567 +1.567	0.002	--
U = 0 eV	-3.584	3.626	+1.553	+1.540	0	--

Table S4. Magnetic moment and net charge of Fe ions at tetrahedral and octahedral sites labeled as m_{Tet}, m_{Oct}, Q_{Tet} and Q_{Oct}, energy difference per Fe_3O_4 formula (ΔE) between symmetric (E_{sy}) and asymmetric (E_{asy}) ground states ($\Delta E = E_{asy} - E_{sy}$) and band gap ($E_g$) derived from HSE and B3LYP with reduced percent of exact exchange.

	m_{Tet} (μ_B)	m_{Oct} (μ_B)	Q_{Tet} (e)	Q_{Oct} (e)	ΔE (eV)	E_g (eV)
HSE 20%	-4.164	4.120 4.119 3.908 3.916	+2.158	+2.119 +2.121 +1.990 +1.991	-0.111	0.032
HSE 15%	-4.096	4.020 4.036 3.916 3.918	+2.117	+2.062 +2.071 +1.998 +2.001	-0.095	--
B3LYP 15%	-4.080	4.021 3.846 4.091 3.853	+2.098	+2.047 +1.944 +2.094 +1.947	-0.100	--

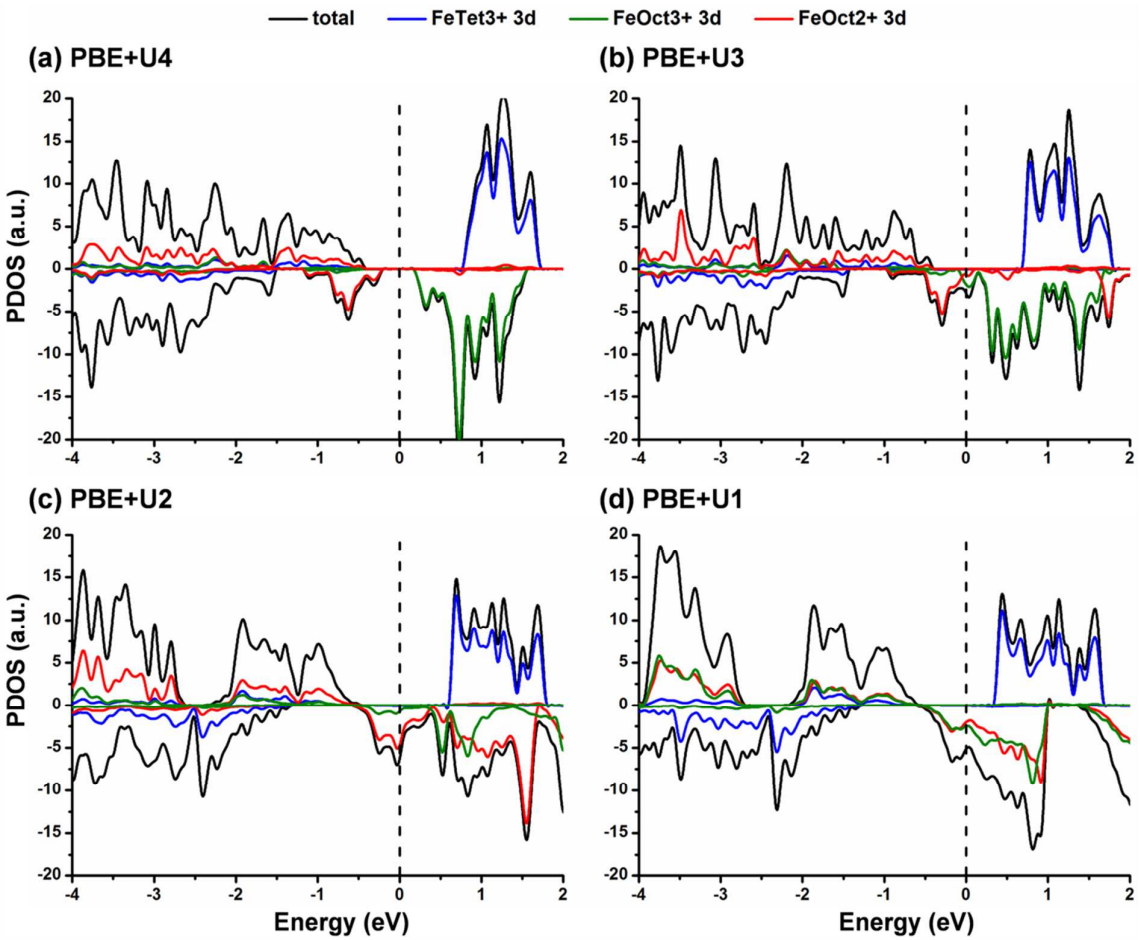

Figure S3. PDOS calculated by PBE+U without symmetry with different U values. (a) U = 4 eV, (b) U = 3 eV, (c) U = 2 eV, (d) U = 1 eV.

When U equal to 3 eV, some states from Fe_{Oct}^{3+} and Fe_{Oct}^{2+} overlap at the Fermi level quenching the band gap (see Figure S3b). When U goes down to 2 eV, states from Fe_{Oct}^{3+} and Fe_{Oct}^{2+} show similar character and the overlap at the Fermi level becomes more prominent (see Figure S3c). When the U value is as small as 1 eV, the states from Fe_{Oct}^{3+} and Fe_{Oct}^{2+} are nearly the same and the DOS thus exhibits the same character as that from PBE calculation, i.e. a half-metal character (see Figure S3d). Thus the band gap is led by the symmetry breaking among Fe_{Oct} ions.

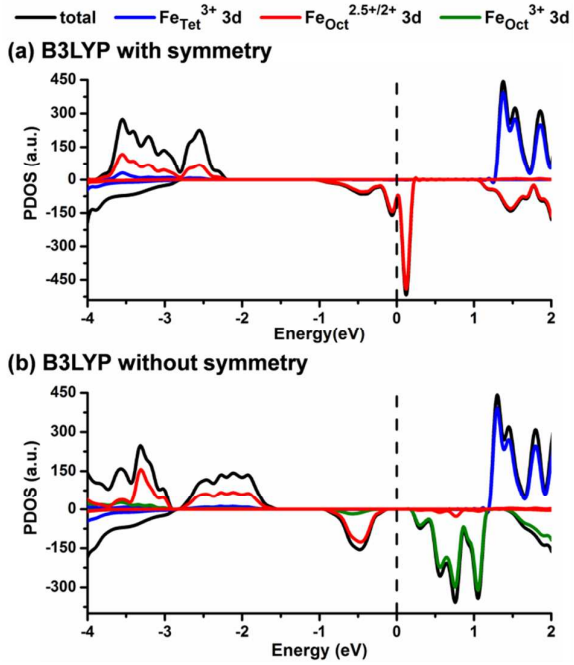

Figure S4. PDOS from B3LYP calculations with and without symmetry.

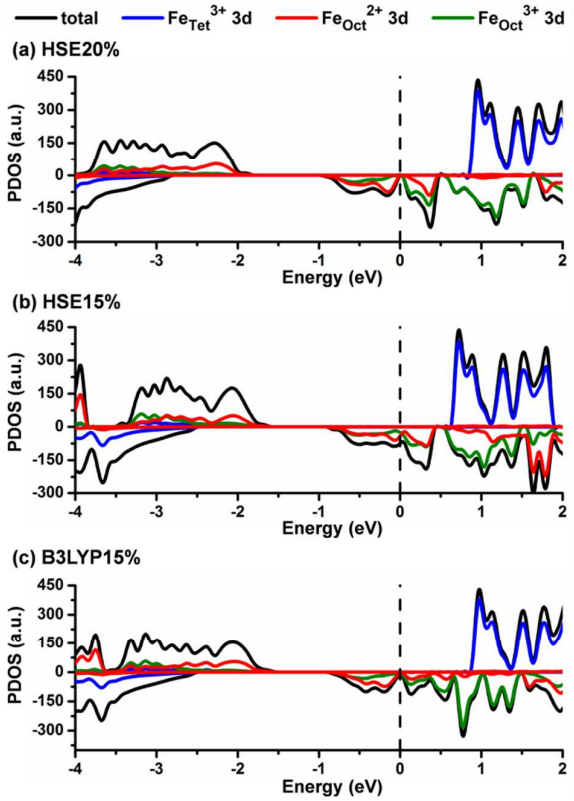

Figure S5. PDOS from HSE06 and B3LYP without symmetry with reduced percent of exact exchange.

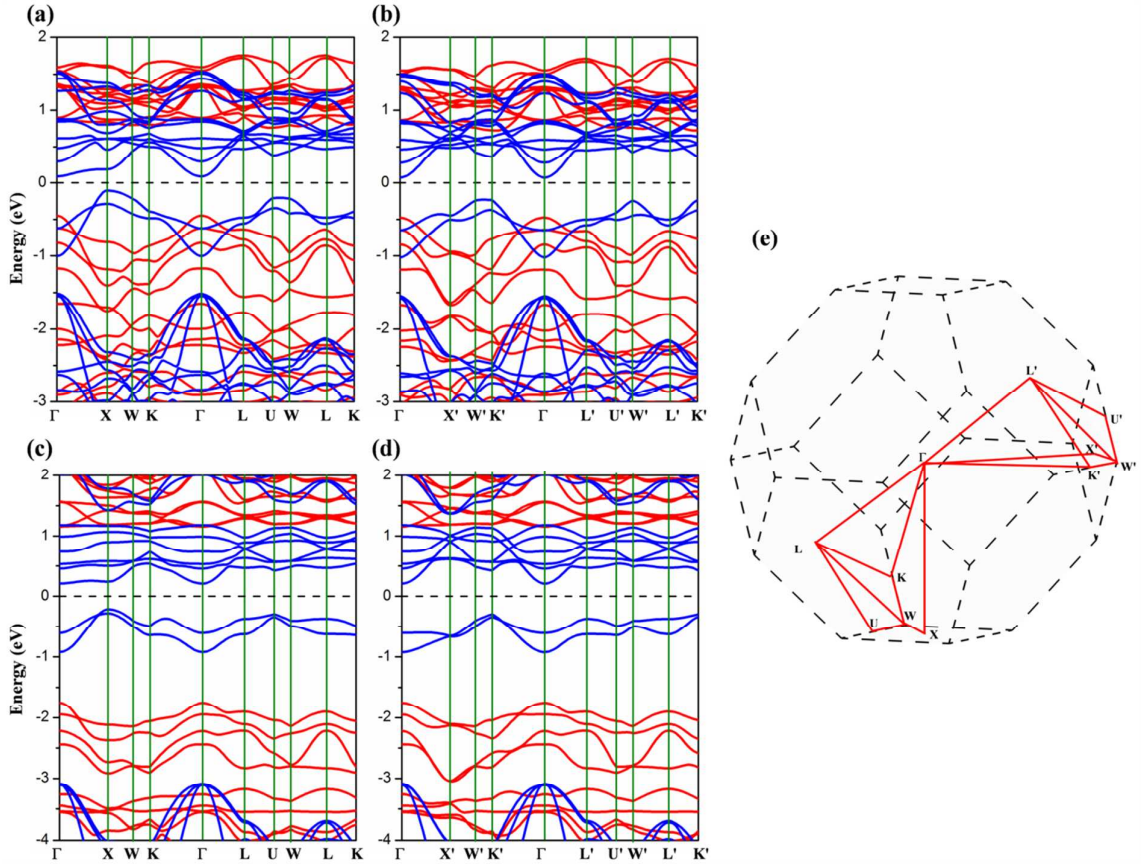

Figure S6. Electronic band structures of magnetite with different k-point paths calculated with (a)~(b) PBE+U (U = 3.5 eV) and (c)~(d) HSE06. (e) Different k-point paths in the first Brillouin zone.

The electronic band structure of magnetite is calculated with both PBE+U (U = 3.5 eV) and HSE methods as shown in Figure S6. Note that due to the symmetry breaking by charge ordering, the original equivalent high symmetric k points may be different. For example, the band structures obtained from PBE+U (Figure S6a, b) and HSE (Figure S6c, d) with two different paths shown in Figure S6e are different. This is because the high symmetric k points X, K and U are different from the k points X', K' and U' due to the symmetry breaking. Anyway, the valence band maximum is at one of the six X points in the Brillouin zone and the conduction band minimum is always at the Γ point indicating that magnetite is an indirect semiconductor.

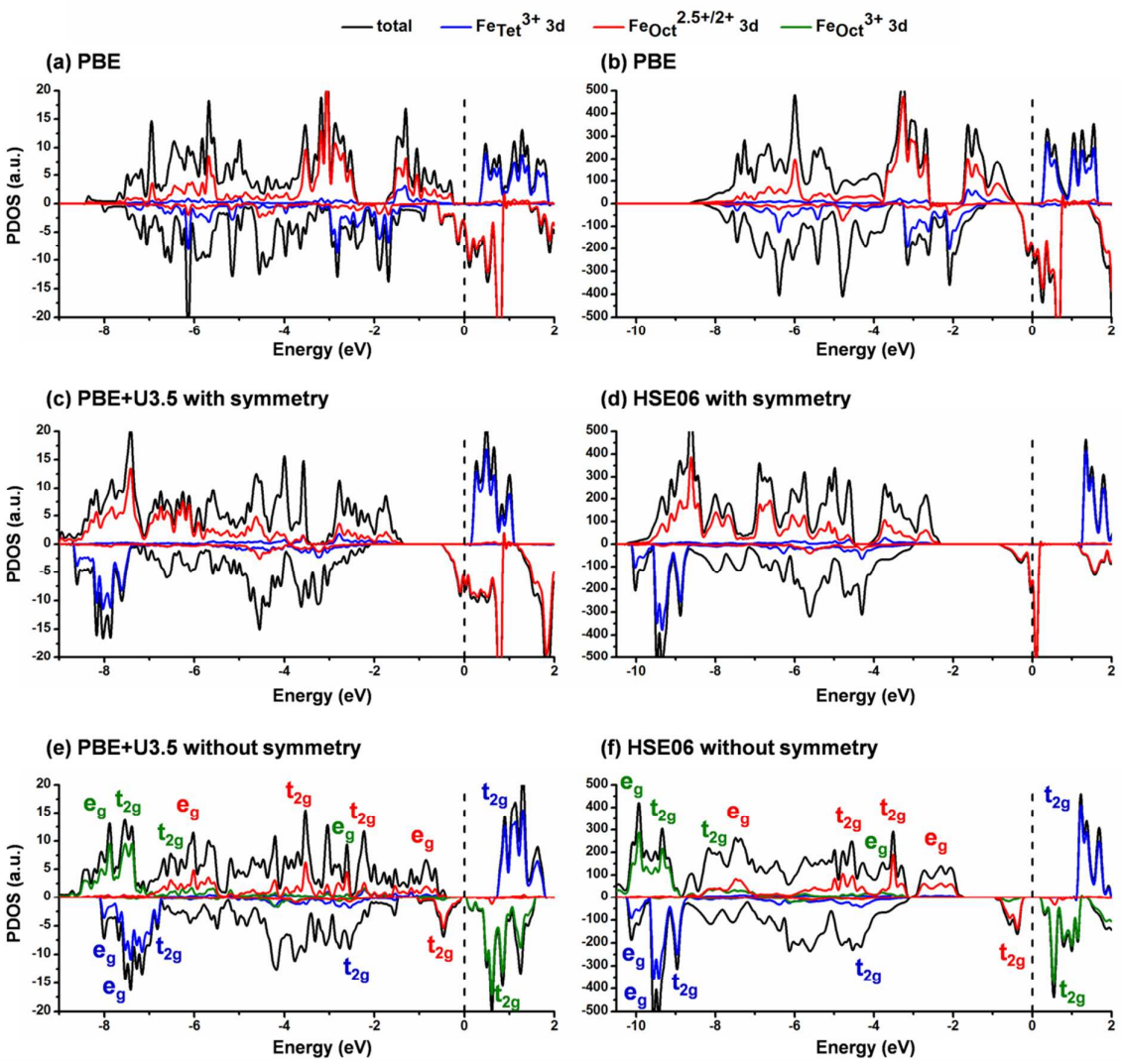

Figure S7. Large range projected density of states (PDOS) of magnetite calculated with different methods with d electron states marked by t_{2g} and e_g. The left part (a), (c) and (e) are from Quantum Espresso code and the right part (b), (d) and (f) are from CRYSTAL14 code. The U value used in (c) and (e) is 3.5 eV.

Reference

(1) Noh, J.; Osman, O. I.; Aziz, S. G.; Winget, P.; Bredas, J. L. A Density Functional Theory Investigation of the Electronic Structure and Spin Moments of Magnetite. *Sci. Technol. Adv. Mater* **2014**, *15*, 044202.

(2) Wright, J. P.; Attfield, J. P.; Radaelli, P. G. Charge Ordered Structure of Magnetite Fe_3O_4 Below the Verwey Transition. *Phys. Rev. B* **2002**, *66*, 214422.