First-Principles Study of Iron Oxide Polytypes: Comparison of GGA+*U* and Hybrid Functional Method (Supporting Information)

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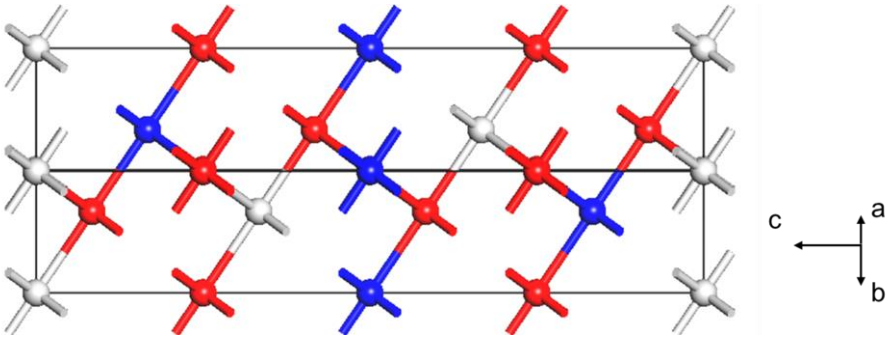

Figure S1. During DFT calculations, the cell parameters of the B1 structure are redefined from a cubic to hexagonal structure to properly assign the antiferromagnetic configuration of the atomic spins in the iron atoms. This causes the simulated cell of the B1 phase to consist of six Fe and six O atoms. Iron atoms with up spins are shown in blue, and those with down spins are shown in white, and oxygen atoms are shown in red.

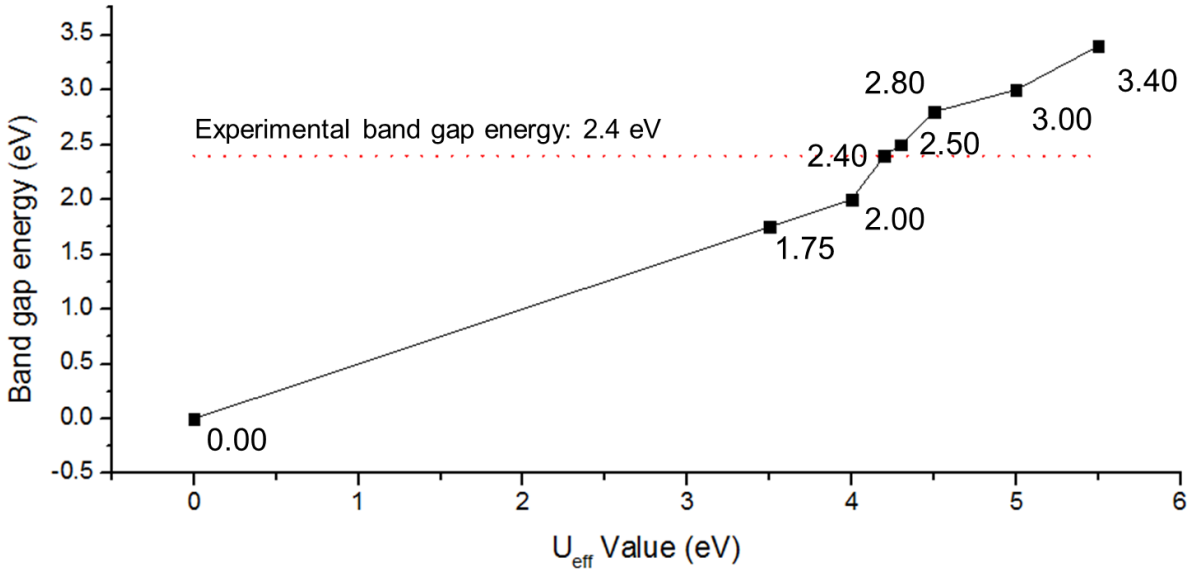

Figure S2. Change in the band gap of the B1 phase as a function of the Hubbard correction parameter (U_{eff}). We chose U_{eff} = 4.2 eV, which reproduces the experimental band gap of 2.4 eV.

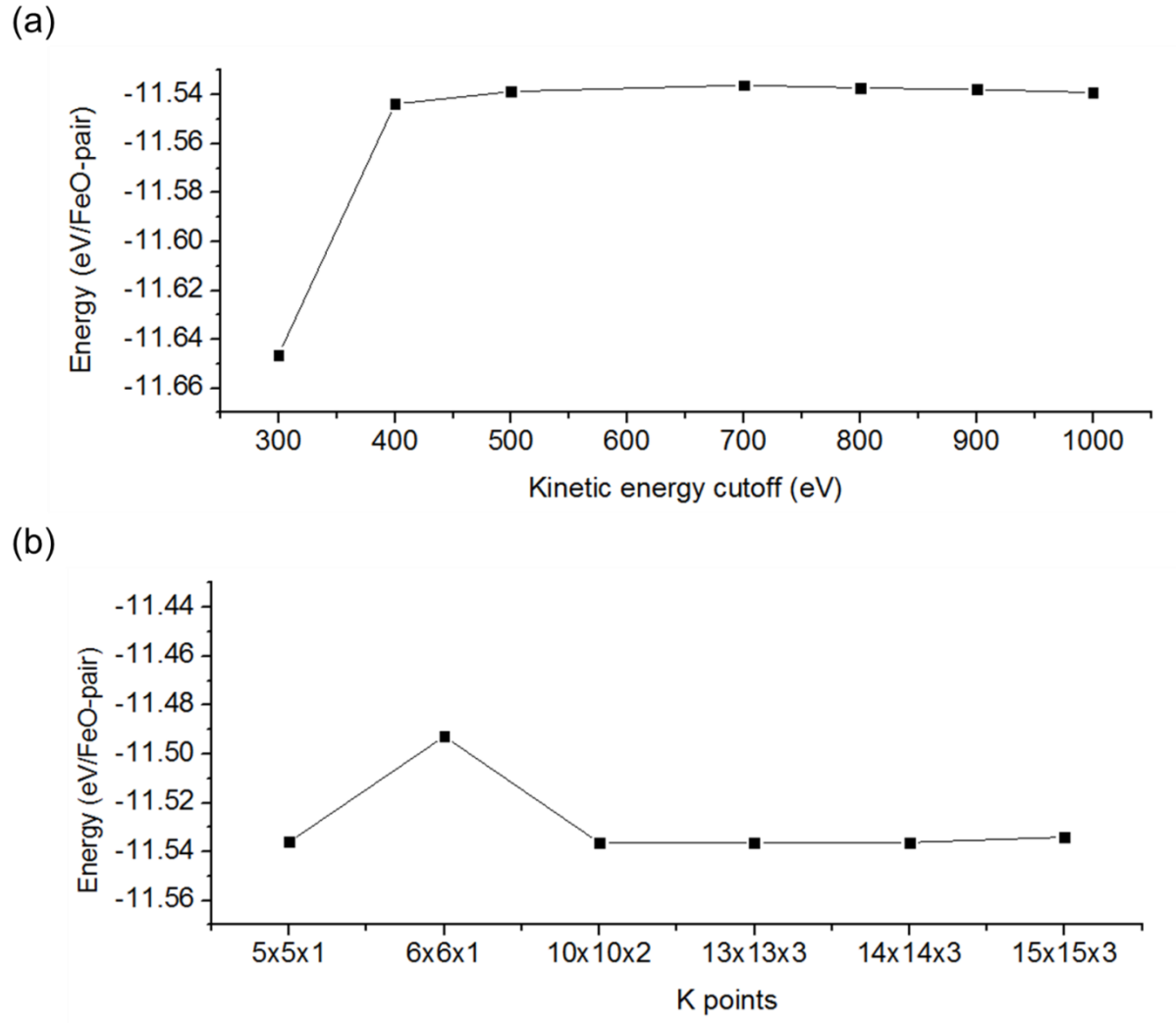

Figure S3. Dependence of the self-consistent field energies of the B1 phase on the choice of (a) the kinetic energy cutoff (E_{cut}) and (b) the mesh size for the reciprocal space integration (k-point grid). Considering the convergence, we finally chose 700 eV for the kinetic energy cutoff for all of the other calculations using a planewave basis and a 15×15×3 k-point grid set for the calculation of the B1 phase.

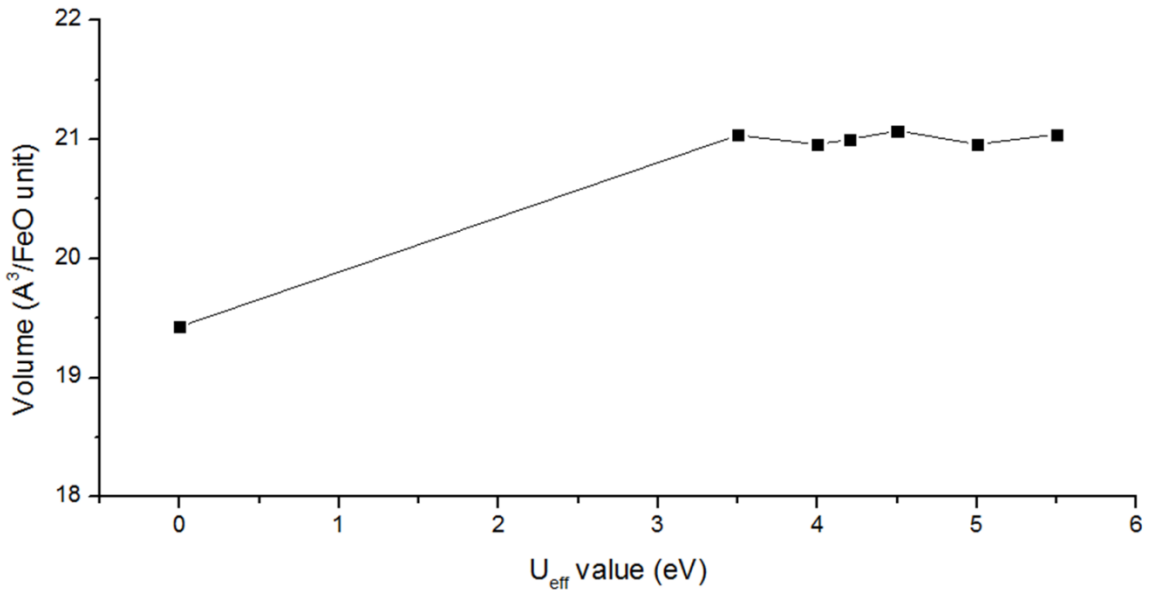

Figure S4. Optimized volumes of the B1 phase from the PBE+*U* method while varying the Hubbard correction parameter (U_{eff}) from 0 to 5.5 eV. This shows that the application of the Hubbard correction significantly expands the volume.

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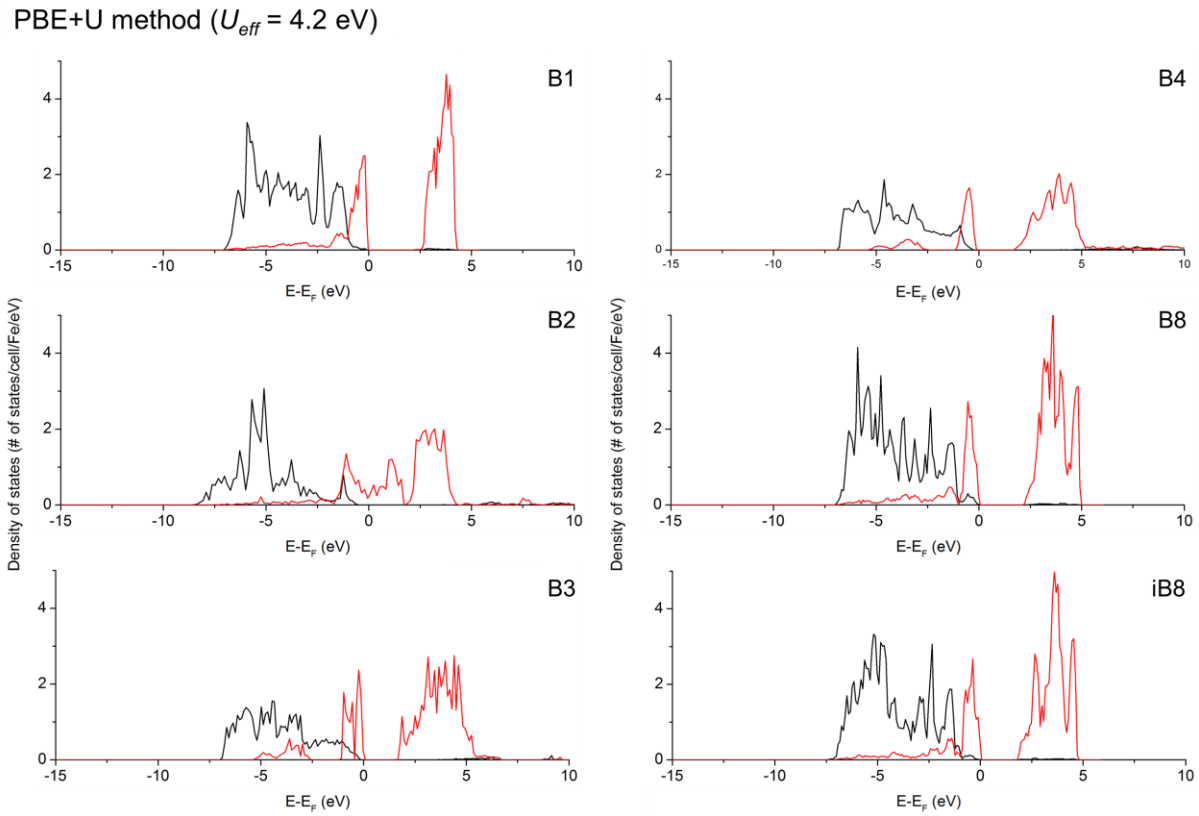

Figure S5. Calculated partial density of states (PDOS) of each phase using PBE+*U* method (U_{eff} = 4.2 eV). Calculated band gaps are 2.4 eV for B1, 1.6 eV for B3 and B4, 2.4 eV for B8, and 1.8 eV for iB8, while no band gap exists for B2 near Fermi level. Red and black lines represent down spin and up spin electrons.

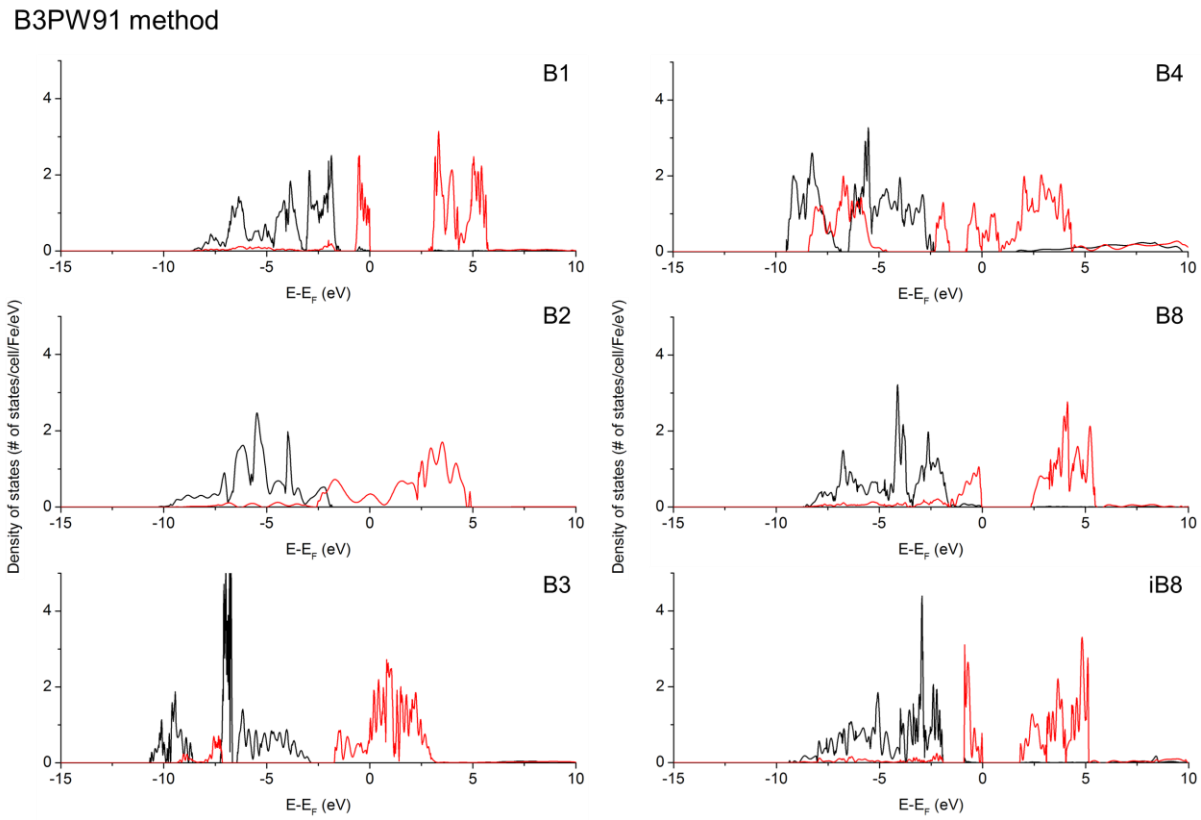

Figure S6. Calculated partial density of states (PDOS) of each phase using B3PW91 method. Calculated band gaps are 2.7 eV for B1, 2.2 eV for B8, and 1.8 eV for iB8, while no band gap exists for B2, B3, and B4 near Fermi level. Red and black lines represent down spin and up spin electrons.

Table S1. Equation of state parameter of each structure with PBE, PBE+*U* (U_{eff} = 4.2 eV), and B3PW91 methods. E_0 is relative value which is energy difference between B1 and each structure.

Structures	Methods	Relative E_0 (eV/FeO-pair)	V_0 (Å^3/FeO-pair)	B_0 (GPa)	B_0'
B1	PBE	0.00	19.44	169.41	2.82
	PBE+U	0.00	21.07	138.80	4.81
	B3PW91	0.00	19.80	167.48	3.70
	Exp.[a)]	0.00	20.25	175.00	4.00
B2	PBE	0.596	18.63	190.80	6.01
	PBE+U	1.140	18.75	189.97	4.28
	B3PW91	1.037	17.92	264.24	0.00
B3	PBE	0.008	24.41	146.25	7.29
	PBE+U	0.229	26.51	99.72	0.00
	B3PW91	1.034	23.29	183.54	7.73
B4	PBE	0.016	23.88	114.35	2.24
	PBE+U	0.088	25.73	140.68	0.15
	B3PW91	1.069	23.96	152.12	0.00
B8	PBE	-0.005	19.30	166.34	6.06
	PBE+U	0.162	21.09	144.39	7.04
	B3PW91	0.234	20.25	142.38	0.47
iB8	PBE	-0.177	19.01	196.09	2.01
	PBE+U	0.311	20.82	149.40	5.06
	B3PW91	0.270	19.37	196.09	2.01

a) Zhang, J. Z., Effect of Defects on the Elastic Properties of Wustite. *Phys Rev Lett* **2000**, *84*, 507-510.

Table S2. Computed *d*-orbital occupancy and the local spin of Fe depending on various structure and DFT methods of PBE, PBE+*U* (U_{eff} = 4.2 eV), and B3PW91. All results indicate that the electronic structures are converged into d^6 electronic configuration of Fe^{2+}.

Method	PBE	
Structure	*d*-orbital occupancy (e/Fe)	Local spin (e/Fe)
B1	6.14	3.40
B2	6.10	3.54
B3	6.07	3.59
B4	6.07	3.58
B8	6.16	3.32
iB8	6.14	3.36
Method	PBE+*U* (U_{eff} = 4.2 eV)	
Structure	*d*-orbital occupancy (e/Fe)	Local spin (e/Fe)
B1	6.11	3.70
B2	6.08	3.73
B3	6.02	3.86
B4	6.09	3.76
B8	6.11	3.69
iB8	6.09	3.69
Method	B3PW91	
Structure	*d*-orbital occupancy (e/Fe)	Local spin (e/Fe)
B1	6.27	3.70
B2	6.31	3.68
B3	6.25	3.73
B4	6.22	3.76
B8	6.31	3.67
iB8	6.29	3.67