Unraveling structure and bonding evolution of newly discovered iron oxide FeO_2

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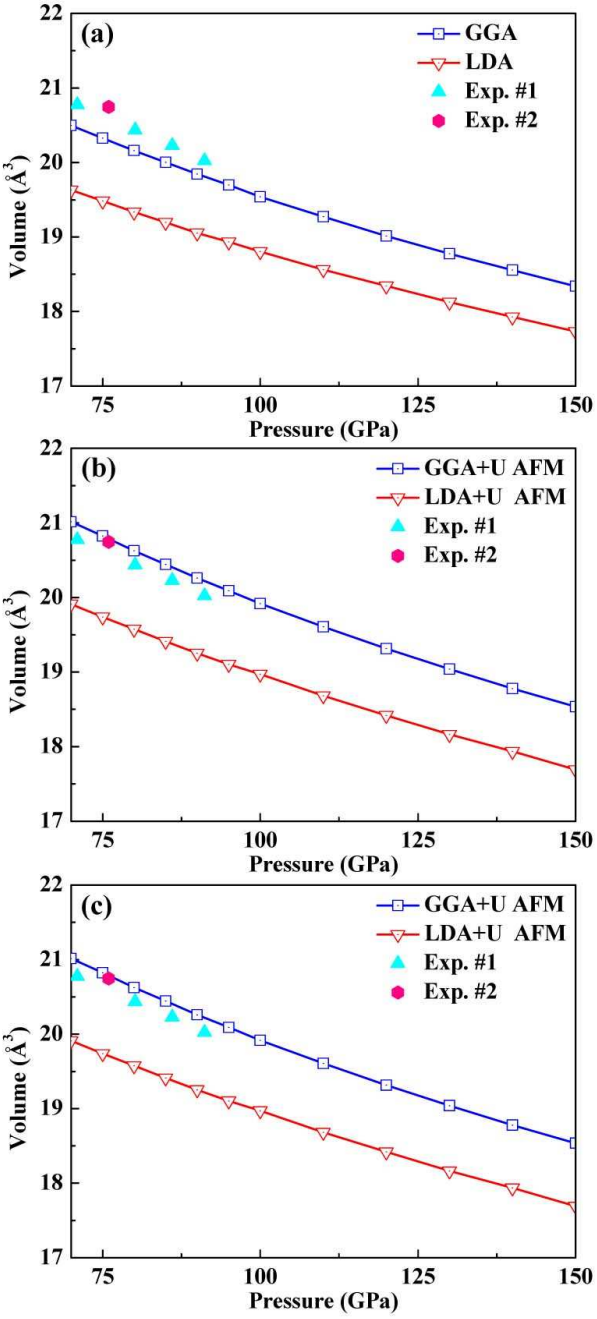

FIG. S1: Calculated pressure-volume relations of P-phase FeO_2 compared with experimental data (Exp. #1 [1] and Exp. #2 [2]). (a) Results obtained using the GGA and LDA functionals; (b) results obtained using the GGA+U and LDA+U functionals; (c) results obtained using the GGA+U and LDA+U functionals by small core (hard) potential.

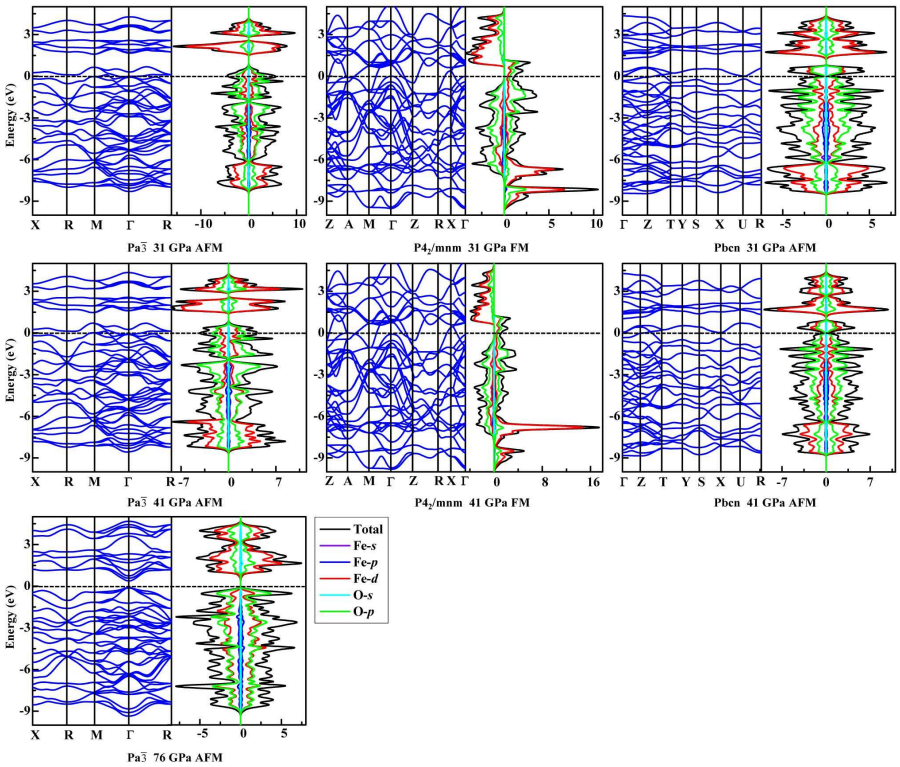

FIG. S2: The electronic band structure and density of states of stable P-phase, and two metastable $P4_2/mnm$ and $Pbcn$ phases of FeO_2 at select high-pressure points.

TABLE S1: Calculated structural data of $P4_2/mnm$, $P2/m$, $Pbcn$ and P-phases of FeO_2 obtained using the GGA+U functional spin polarization and antiferromagnetic configuration.

Phase	Pressure	State	Lattice Parameters	Atomic Coordinates			
				Atom	x	y	z
$P4_2/mnm$	31 GPa	FM	a=b=4.3252 Å, c=2.8607 Å	Fe(2a)	0.5000	0.5000	0.5000
			α=β=γ=90°	O(4g)	0.1952	0.1952	0.5000
	41 GPa	FM	a=b=4.2697 Å, c=2.8450 Å	Fe(2a)	0.5000	0.5000	0.5000
			α=β=γ=90°	O(4g)	0.1959	0.1959	0.5000
	76 GPa	AFM	a=b=4.0321 Å, c=2.8477 Å	Fe(2b)	0.5000	0.5000	0.0000
			α=β=γ=90°	O(4f)	0.2000	0.2000	0.0000
$P2/m$	31 GPa	AFM	a=4.3313 Å, b=2.8466 Å	Fe(1c)	0.0000	0.0000	0.5000
			c=4.0722 Å, α=γ=90°	Fe(1e)	0.5000	0.5000	0.0000
			β=89.5938°	O(2n)	0.8300	0.5000	0.2588
				O(2m)	0.6573	0.0000	0.7665
	41 GPa	AFM	a=4.3003 Å, b=2.8187 Å	Fe(1c)	0.0000	0.0000	0.5000
			c=4.0100 Å, α=γ=90°	Fe(1e)	0.5000	0.5000	0.000
			β=89.4253°	O(2n)	0.8334	0.5000	0.2540
				O(2m)	0.6547	0.0000	0.7610
	76 GPa	AFM	a=4.2353 Å, b=2.7374 Å	Fe(1c)	0.0000	0.0000	0.5000
			c=3.8344 Å, α=γ=90°	Fe(1e)	0.5000	0.5000	0.0000
			β=89.1379°	O(2n)	0.8398	0.5000	0.2439
				O(2m)	0.6502	0.0000	0.7489
$Pbcn$	31 GPa	AFM	a=4.1350 Å,b=5.4008 Å	Fe(4c)	0.5000	0.6488	1.2500
			c=4.6432 Å, α=β=γ=90°	O(8d)	0.7570	0.8884	1.4277
	41 GPa	AFM	a=4.0635 Å,b=5.3799 Å	Fe(4c)	0.5000	0.6478	1.2500
			c=4.5809 Å, α=β=γ=90°	O(8d)	0.7537	0.8886	1.4306
	76 GPa	AFM	a=3.8665 Å,b=5.2878 Å	Fe(4c)	-0.5000	0.6445	0.7500
			c=4.4543 Å, α=β=γ=90°	O(8d)	-0.2545	0.8899	0.9320
$Pa\bar{3}$	31 GPa	AFM	a=b=c=4.6333 Å	Fe(4a)	0.0000	0.0000	0.0000
			α=β=γ=90°	O(8c)	0.6513	0.6513	0.6513
	41 GPa	AFM	a=b=c=4.5837 Å	Fe(4a)	0.0000	0.0000	0.0000
			α=β=γ=90°	O(8c)	0.6504	0.6504	0.6504
	76 GPa	AFM	a=b=c=4.3639 Å	Fe(4a)	0.0000	0.0000	0.0000
			α=β=γ=90°	O(8c)	0.3523	0.3523	0.3523
	81 GPa	AFM	a=b=c=4.3511 Å	Fe(4a)	0.0000	0.0000	0.0000
			α=β=γ=90°	O(8c)	0.3526	0.3526	0.3526

TABLE S2: Calculated lattice parameters of P-phase FeO_2 at 76GPa under different potentials, with or without spin polarization, and in various magnetic states. The results obtained using the PBE+U potential with spin polarization in the AFM state find the best overall match with the experimental data (the two data sets at the top and bottom of the table, respectively, are highlighted in bold).

PAW potentials	Methods	Structural Parameters			
		Volume (Å^3)	Lattice constant (Å)	O-O bond length(Å)	Fe-O bond length(Å)
Standard potential	PBE+U with spin polarization-AFM	**83.104**	**4.3639**	**2.2322**	**1.7873**
	PBE+U with spin polarization-FM	82.213	4.3658	2.1826	1.7903
	PBE+U without spin polarization	80.487	4.3176	1.8756	1.7895
	PBE	81.155	4.3295	2.0655	1.7808
	PBE with spin polarization	81.160	4.3296	2.0695	1.7808
	LDA	77.805	4.2691	2.0257	1.7566
	LDA+U with spin polarization	78.805	4.2691	2.0257	1.7566
Both Fe and O are small core (hard) potential	PBE+U with spin polarization-AFM	82.216	4.3483	2.2141	1.7814
	PBE+U with spin polarization-FM	82.387	4.3513	2.1861	1.7839
	PBE+U without spin polarization	79.851	4.3062	1.9045	1.7819
	PBE	80.046	4.3097	2.0658	1.7721
	PBE with spin polarization	80.052	4.3098	2.0669	1.9045
Experiment [2]		**83.115**	**4.3640**	**1.9371**	**1.7925**

TABLE S3: Calculated Bader's charge of typical iron oxides, peroxides, monoxides and dioxides, where N_e is the number of electron and in unit of e.

System	Pressure	Fe		O	
		N_e	Bader's charge	N_e	Bader's charge
FeO	0GPa	6.68	+1.32	7.32	−1.32
	76GPa	6.73	+1.27	7.27	−1.27
Fe_2O_3	0GPa	6.25	+1.75	7.17	−1.17
	76GPa	6.28	+1.72	7.14	−1.14
Fe_3O_4	0GPa	6.33/6.41	+1.67/+1.59	7.21	−1.21
	76GPa	6.28/6.53	+1.72/+1.47	7.15/7.18	−1.15/−1.18
FeO_2	31GPa	6.25	+1.75	6.875	−0.875
	41GPa	6.26	+1.74	6.87	−0.87
	76GPa	6.40	+1.60	6.80	−0.80
System	Pressure	Na/Ca/Mn/Mg/Cr		O	
		N_e	Bader's charge	N_e	Bader's charge
Na_2O_2	0GPa	0.21	+0.79	6.77/6.79	0.79
	76GPa	0.32/0.30	+0.68/+0.70	6.68/6.70	−0.68/0.70
CaO_2	0GPa	6.44	+1.56	6.78	−0.78
	76GPa	6.54	+1.44	6.71/6.74	−0.71/−0.74
MnO	0GPa	5.61	+1.39	7.39	−1.39
	76GPa	5.67	+1.33	7.33	−1.33
MgO	0GPa	0.345	+1.655	7.655	−1.655
	76GPa	0.395	+1.605	7.605	−1.605
MnO_2	0GPa	5.156	+1.844	6.922	−0.922
	76GPa	5.175	+1.825	6.9125	−0.9125
CrO_2	0GPa	4.12	+1.88	6.94	−0.94
	76GPa	4.14	+1.86	6.93	−0.93

TABLE S4: Calculated and experimental sound velocities of P-phase FeO_2 at high pressure, where pressure and elastic constant are in unit of GPa, and sound velocities are in unit of km/s.

	Pressure	C_{11}	C_{12}	C_{44}	V_P	V_S	ν
Theoretical	76	834.72	308.57	235.52	10.76	5.92	0.282
	81	855.94	321.10	240.65	10.85	5.95	0.285
Experimental [3]	81(±2.00)				9.57(±0.20)	4.09(±0.06)	0.39

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[1] Q. Y. Hu, D. Y. Kim, J. Liu, Y. Meng, L. X. Yang, D. Z. Zhang, W. L. Mao, and H. K. Mao, Proc. Natl. Acad. Sci. U. S. A **114**, 1498 (2017).
[2] Q. Y. Hu, D. Y. Kim, W. G. Yang, L. X. Yang, Y. Meng, L. Zhang, and H. K. Mao, Nature **534**, 241 (2016).
[3] J. Liu, Q. Y. Hu, D. Y. Kim, Z. Q. Wu, W. Z. Wang, Y. M. Xiao, P. Chow, Y. Meng, V. B. Prakapenka, H. K. Mao, and W. L. Mao, Nature **551**, 494 (2017).