

## Supplementary information for:

# “A DFT study of the structures, stabilities and redox behaviour of the major surfaces of magnetite $\text{Fe}_3\text{O}_4$ ”

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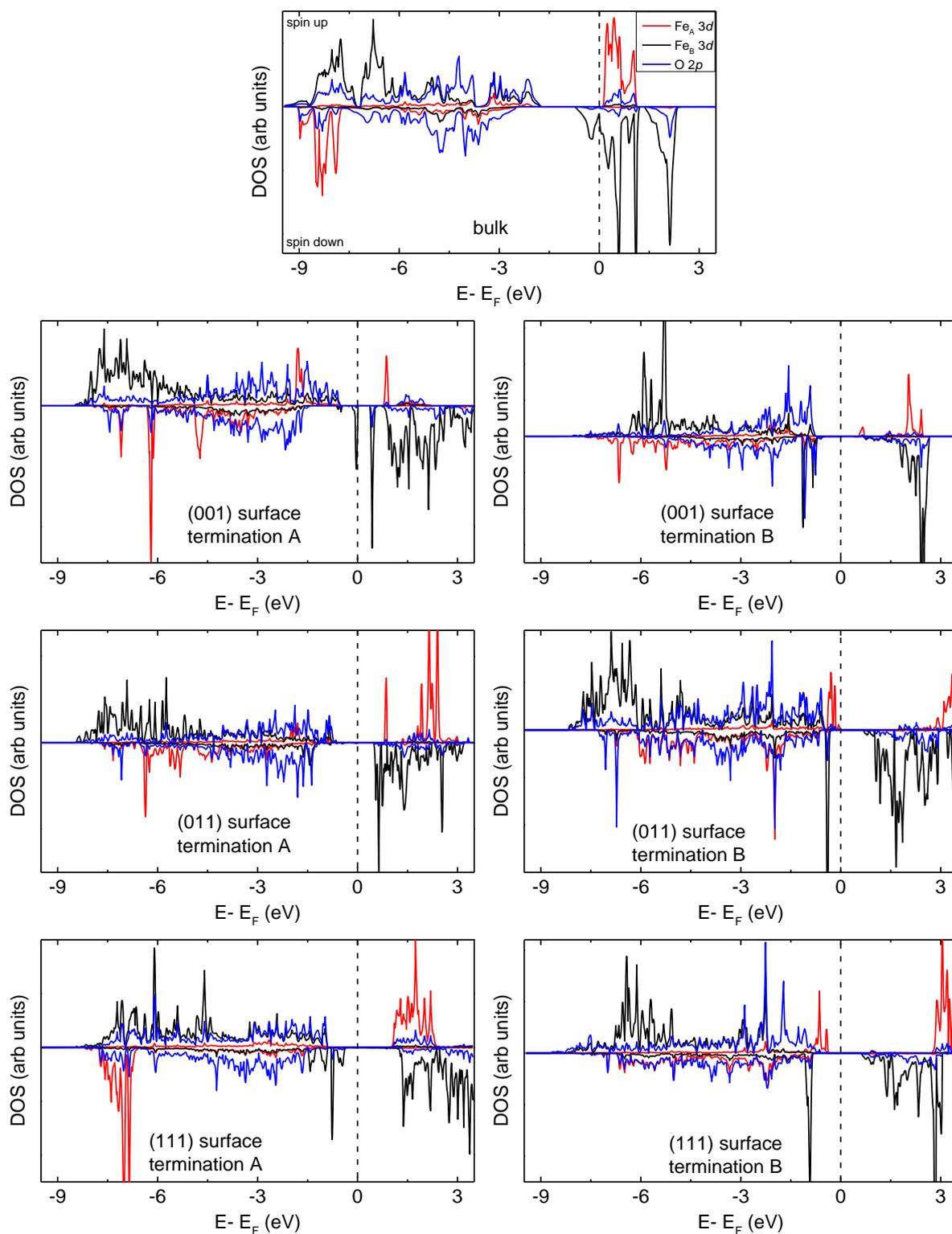
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Supplementary information contains:

- figures showing the density of states of  $\text{Fe}_3\text{O}_4$  bulk phase and surfaces,
- table with the corrected and uncorrected energy values for the reduction and oxidation of the (001) and (111) surfaces,
- graphs showing the corrected and uncorrected surface free energies as a function of the oxygen chemical potential and
- description of the uncorrected results in the above graph.

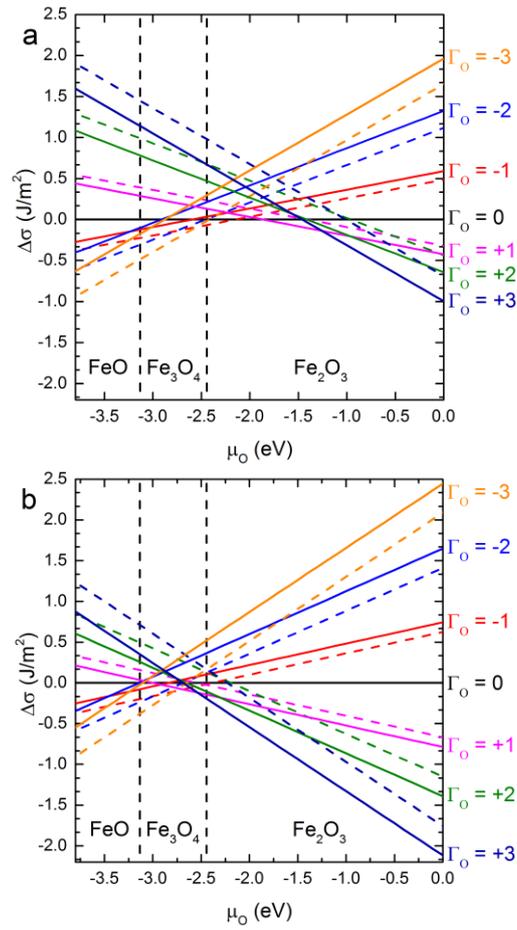
**Figure S1.** Density of states of one formula unit of  $\text{Fe}_3\text{O}_4$  bulk phase and the terminations of various surfaces. For the surfaces, the density of states is shown for all the surface layers with dangling bonds.



**Table S1.** Vacancy formation energy ( $E_{\text{vac}}$ ) and adsorption energy per adatom ( $E_{\text{ads}}$ ) corrected and uncorrected for the two most likely conformations of the first ( $\Gamma = \pm 1$ ) and second ( $\Gamma = \pm 2$ ) defect. All energies are in eV.

Surface	$ \Gamma $	$E_{\text{vac}}$		$E_{\text{ads}}$	
		corrected	uncorrected	corrected	uncorrected
(001)	1	2.60	2.14	-1.87	-1.41
		3.28	2.82	-1.14	-0.68
	2	3.23	2.77	-0.96	-0.50
		3.31	2.85	-0.80	-0.35
(111)	1	2.84	2.38	-3.00	-2.54
		3.56	3.10	-2.04	-1.59
	2	3.45	2.99	-2.30	-1.85
		3.64	3.18	0.43	0.89

**Figure S2.** Relative surface free energies ( $\Delta\sigma$ ) for the  $\text{Fe}_3\text{O}_4$  (a) (001) and (b) (111) surfaces as a function of the oxygen chemical potential ( $\mu_{\text{O}}$ ). The areas corresponding to  $\mu_{\text{O}}$  smaller than  $-3.13$  eV, bigger than  $-2.44$  eV and between these two values represent the conditions under which bulk  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  respectively are the stable oxides. Solid and dashed lines represent corrected and uncorrected results respectively.



## Temperature and pressure effects on the uncorrected surface free energies

The correction of the O<sub>2</sub> energy does not affect the slope of the lines plotted in **Figure S2**, but it changes the relative positions of the satellite correction lines. The analysis of the uncorrected surface free energies above complements the one in the main text of this publication. For the (001), although at ambient conditions ( $\mu_{\text{O}} = -0.3$  eV) the ( $\Gamma = +3$ ) oxidised surface is the most likely situation, at lower values of oxygen chemical potential ( $\mu_{\text{O}} = -1.0$  eV) a lower degree of oxidation ( $\Gamma = +1$ ) can be expected. Further reducing conditions (from  $\mu_{\text{O}} = -1.5$  up to  $-2.0$  eV), make the stoichiometric surface the most stable one. From this point until just the chemical potential conditions in which bulk Fe<sub>3</sub>O<sub>4</sub> starts being the most stable iron oxide phase, the reduced surface that has lost one oxygen atom becomes the most thermodynamically stable. For most of the conditions in which Fe<sub>3</sub>O<sub>4</sub> is the most stable phase, the ( $\Gamma = -3$ ) reduced surface is the most stable in this range and until the lowest potential considered in this study. For the (111), the surface ( $\Gamma = +3$ ) oxidized is the most stable at ambient conditions (from  $\mu_{\text{O}} = -0.30$  eV) and until  $-2.10$  eV. From this value of  $\mu_{\text{O}}$  and until  $-2.44$  eV, the ( $\Gamma = +1$ ) surface becomes the most stable one, while for a very short range of  $\mu_{\text{O}}$  (of approximately 0.30 eV), the ( $\Gamma = -1$ ) surface is the thermodynamically most stable one. Finally, for the rest of the conditions in which bulk Fe<sub>3</sub>O<sub>4</sub> is the most stable iron oxide phase, and until the lowest potential considered in this study, the most stable surface is the ( $\Gamma = -3$ ) reduced one.

For the (001) and (111), the ( $\Gamma = +3$ ) oxidized surface is the most likely situation at ambient conditions. However, for the conditions in which bulk Fe<sub>3</sub>O<sub>4</sub> is the most stable oxide, the ( $\Gamma = -1$  and  $-3$ ) reduced are the most stable states of the (001) and (111) surfaces.