Electronic Supplementary Information

A complete ab initio thermodynamic and kinetic catalogue of the defect chemistry of hematite α-Fe₂O₃, its cation diffusion, and sample donor dopants

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1. Choosing U values

In this section, we present the criteria we applied to choose the U values. The determination of the value of U is not straight forward and could introduce some empiricism to ab initio calculations. For example, it is common to vary U values to find the ones that match a certain experimental such as the band gap or lattice constant. As shown in Figure 1, for hematite and since we consider two U values (on oxygen p-states and iron d-stated), this empirical approach does not result in a unique set of U values. Thus, in this work, when choosing U values, the first goal is to achieve the expected behavior of the total energy of the exact (but unknown) density functional which should be a linear dependence on the electronic occupation as concluded by Perdew et. al[1]. The second goal is to allow localization of small polarons which play an important role in hematite as suggested from experiments[2,3]. Based on these criteria, The values (U(Fe) = 3 eV and U(O) = 7 eV) were able to localize small electron and hole polarons and achieve linear response of the partial occupancy of charges as shown in Figure 2. A consequence that was not intended is that these values did not yield s significant departure from experimental values for both the lattice constant and electronic band gap as shown in Figure 1.



Figure 1 (a) Band gap values as function of U(Fe) and U(O). (b) Hematite unit cell volume as function of U(Fe) and U(O). Dashed horizontal lines represent the experimental values [10,11].



Figure 2 Linear reponse of adding or removing fractional charge at selected values for Hubbard U term. U(Fe) = 3 eV and U(0) = 7 eV. Energies for charged cells were corrected using Freysoldt-Neugebauer-Van de Walle [4] (FNV) correction scheme.

2. Charge states of point defects

In this section we list the point defects we considered in hematite with their charge states and Kröger-Vink notation.

Table 1 List of point defects considered in this work and their charge states

Native Point Defects		Dopants	Dopants		
Defect	charge	Symbol	Defect	Charge	Symbol
Oxygen vacancy	0	V [×] ₀		-3	$Ti_{Fe}^{///}, Sn_{Fe}^{///}$
	+1	V ₀ [■]	Titanium or	-2	$Ti_{Fe}^{\prime\prime}, Sn_{Fe}^{\prime\prime}$
	+2	$V_0^{\bullet\bullet}$	Tin substitutional	-1	$Ti_{Fe_{,}}^{/} Sn_{Fe}^{/}$
Iron vacancy	0	V_{Fe}^{\times}		0	$Ti_{Fe_{,}}^{\times} Sn_{Fe}^{\times}$
	-1	V/ _{Fe}		1	Ti_{Fe} , Sn_{Fe}
	-2	$V_{Fe}^{//}$		2	Ti_{Fe} , Sn_{Fe}
	-3	$V_{Fe}^{///}$		3	Ti_{Fe} , Sn_{Fe}
Oxygen Interstitial	0	0 ×		4	Ti_{Fe} , Sn_{Fe}
	-1	O_I^{\prime}		0	$Ti_{I}^{\times}, Sn_{I}^{\times}$
	-2	0'/	Titanium or Tin	1	$Ti_{I,}^{\bullet} Sn_{I}^{\bullet}$
Iron Interstitial	0	Fe_{I}^{\times}	interstitial	2	$Ti_{I} Sn_{I}$
	+1	Fe_I^{\blacksquare}		3	Ti^{\bullet}_{I} , Sn^{\bullet}_{I}
	+2	Fe ^I		4	Ti^{I} , Sn^{I}
	+3	Fe ^{•••}			

3. FNV correction

Here, we report the finite size correction we applied in our calculations. In this work, we adopt Freysoldt-Neugebauer-Van de Walle [4] (FNV) correction scheme implemented using COFFEE code[5]. In this method, the charge induced by the defect is modeled as a Gaussian distribution. The interaction strength of this Gaussian model charge is calculated for different cell sizes and extrapolated to an infinite supercell to estimate the error due to this interaction energy in small supercells. For the potential alignment term, the electrostatic potentials of the model system and the DFT calculation are compared far from the defect to calculate the value of this term

The (FNV) correction scheme[4,5] was applied to the final (DFT+U) calculations only. For standard DFT, we found that FNV correction overestimates the interaction energy between periodic images of charges. This is because of the delocalization of charge all over the defective supercell in standard DFT calculations for most defects. So, we only added the potential alignment term to pure DFT calculations. However, for DFT+U, we applied the full scheme (both electrostatic correction term ($E_{electrostatic}^{correction}(q)$) and potential alignment term ($q\Delta V$)).

 $E_{i}^{correction}(q) = E_{electrostatic}^{correction}(q) + q\Delta V$

Values of electrostatic correction term $({}^{E_{electrostatic}^{correction}(q)})$ in hematite are shown in Table 2 for each charge state. While values of ΔV are listed in Table 3 for each native point defect. Each ΔV is multiplied by the corresponding charge (q) to get the potential alignment term. The procedure of these calculations can be found in the documentation of COFFEE code[5].

q	± 1	± 2	± 3	± 4
Correction energy (eV)	0.06	0.23	0.52	0.93

Table 2 Values of electrostatic correction term $(E_{electrostatic}^{e_{orrection}}(q))$ using FNV scheme

Table 3 Values of ΔV in potential alignment term using FNV scheme for hematite

Point Defect	V ₀	V _{Fe}	01	Fe _I
ΔV (eV)	-0.01	-0.025	0.005	0.02

4. O₂ molecule correction

Oxygen molecule overbinding is a common problem in DFT. It is well known that the binding energy of the O_2 molecule exhibits large errors when local density approximation

(LDA) or generalized gradient approximation (GGA) is used. The binding energy of oxygen molecule is overestimated when calculated using these functionals. The PBE [6] functional used in this work is a version of GGA approximation. We employed Wang et al [7] approach to calculate this correction by comparing formation energies of non-transition metal oxides to experimental values as shown in Figure 3. We reproduced the same value of -1.36 eV obtained by Wang et al [7] as in Figure 3(a).



Figure 3 DFT (in panel a) and DFT+U (in panel b) calculated formation energies of non-transition metal oxides are plotted versus their corresponding experimental values. In panel (a) the orange line is the best fit and a -1.36 eV shift is needed for this line to be equal to the experimental values (blue line). While, in panel (b) a shift of 2.796 is needed for the orange line to be equal to the experimental values (blue line).

We assessed the necessity of this correction by comparing the results of our defect model to the experimentally measured off-stoichiometry by Dieckmann[8]. It is clear from Figure 4 that overbinding correction is essential in pure DFT to obtain an accurate defect model that agrees with experimental results. Panel (b) in Figure 4 shows that some disagreement still exist which may be attributed to self-interaction and to delocalization of 3d orbitals caused by pure GGA. The results of DFT+U without O_2 correction are included in the main manuscript and have a good agreement with experiments.



Figure 4 The deviation from stoichiometry (δ) in hematite Fe_2O_3 is plotted vs pO₂ at three different temeperatures (1373 K, 1473 K, and 1573 K). In panel (a), pure DFT results (solid) are presented without adding the O₂ overbinding correction. While in panel (b), O₂ overbinding correction of -1.36 eV is included. Scattered markers in both panels are experimental data from literature [8].

5. Bulk properties

In the table below, we summarize the computed bulk properties of hematite using pure DFT and DFT+U compared to prior theoretical calculations [9] and experimental measurements[10,11]. The partial density of states in *Figure 5* shows that hematite is a charge transfer insulator. Valence band is composed of a mixture of Fe d-states and O p-states.

	Lattice constant (A°)	Inter-axial angle (°)	μ _{Fe} (Bohr-magneton)	$E_g(eV)$
DFT (this work)	5.46	54.7	3.34	0.7
DFT+U (this work) (U(Fe) = 3 eV, U(O) = 7 eV)	5.44	55.3	3.92	2.4
DFT+ U (U(Fe) = 4 eV, U(O) =0) [9]	5.496	55.19	4.16	2.12
HSE06 [9]	5.416	55.91	4.21	2.95
Experiment [10,11]	5.43	55.23	4.9	2-2.2



Figure 5 Partial Density of states for a unit formula in the perfect crystal of Fe_2O_3 using DFT+U calculation. Density of up spin states are given positive values while down spin states are given negative values.

6. Defect formation energies

Defect formation energies as function of Fermi level are plotted in Figure 6. Only oxygen rich condition resultse are shown.

Vacancy formation energies in hematite had been calculated before in literature. Here we compare our results with the most recent calculations performed by Banerjee et al. [9] in Figure 7.



Figure 6 (a) Vacancy formation energies at oxygen rich condition (b) Interstitial formation energies at oxygen rich condition. Both are based on our DFT+U calculations.



Figure 7 The calculated formation energies for the oxygen vacancies and iron vacancies using our DFT+U parameters are shown in panel (a) and panel (b), respectively, at oxygen rich condition. Only, the charge states with lowest formation energies are plotted to facilitate comparison with HSE06 results adapted from Ref. [9]. DFT+U label in the figures denotes results from this work. While HSE06 label denotes results from reference [9]. The dashed line represents the band gap as calculated by our DFT+U parameters which is 2.4 eV. However, the band gap for the HSE06 is 2.95 eV as calculated in Ref. [9].

7. Electronic Structure of point defects

The electronic structure of defective supercells was analyzed using Löwdin charges, magnetic moments and by plotting the density of states and integrated local density of states (ILDOS). we present this analysis for each defect type separately.

Oxygen Vacancies

The neutral oxygen vacancy is accompanied by 2 excess electrons in the crystal. Löwdin charges show that the extra charge is localized on the 2 close neighboring Fe ions and to a lesser extent on the 2 far neighboring Fe ions. This observation is also supported by examining magnetic moments of those four Fe ions. For a more quantitative analysis we plot the density of states to investigate the effect of the introduced defect. It is clear in Figure 8 panel (a) that the presence of a neutral oxygen vacancy perturbs both valence and conduction bands. The three distinct states in the gap are as follows: the first state after valence band is occupied by 2 electrons distributed over Fe and O atoms as shown in panel (a) in Figure 9. While the second state is occupied by the 2 extra electrons in the crystal as the ILDOS for this state in Figure 9 panel (b) shows strong localization over the 2 neighboring Fe atoms confirming Löwdin charges and magnetic moments observations. Finally, the third state is due to perturbation in conduction band and they are Fe unoccupied states as shown in Figure 9 panel.

Analysis of (1+) O vacancy in Figure 8 panel (b) shows similar electronic structure to the neutral vacancy. However, the perturbed valence state is now occupied by only 1 electron instead of 2 in the case of neutral vacancy. Also, the last occupied state is occupied by the extra electron and it is localized on one of the close Fe atoms. This is also confirmed by Löwdin charge and magnetic moment of this Fe atom. While the (2+) O vacancy only causes perturbation of Fe states in the conduction band and there are no occupied gap states due to absence of excess electrons.



Figure 8 The density of states (DOS) for defective crystals with a neutral oxygen vacancy in (a) and with (1+) and (2+) charge in (b and c), respectively. The positive and negative values for DOS represent up and down spins, respectively. The black solid vertical line at zero energy denotes the energy of the last occupied state.



Figure 9 Integrated local density of states (ILDOS) for gap states in hematite (2x2x2) supercell with a neutral oxygen vacancy. The lowest energy state in the gap is shown in panel (a) where 2 electrons distributed over Fe and 0 ions. These are perturbed valence band states. In panel (b) the two extra electrons in the supercell are localized over 2 Fe ions. While in panel (c) the perturbed states from conduction band are Fe unoccupied d-states. Fe ions are shown in blue while oxygen ions are red.

Iron Vacancies

Neutral Fe vacancies introduce 3 holes in the supercell. These 3 holes are clearly localized on 3 of the neighboring oxygen ions according to Löwdin charges and magnetic moments of those ions. Similarly, we find that 2 holes are localized on 2 oxygen atoms in the case of (1-) Fe vacancy and 1 hole is localized on 1 oxygen atom in the case of (2-) Fe vacancy. Finally, no significant excess magnetic moments or reduced charges are found in the case of (3-) Fe vacancy due to the absence of holes.



Figure 10 The density of state (DOS) for defective crystals with a neutral iron vacancy in (a) and with (1-), (2-) and (3-) charge in (b, c and d), respectively. The positive and negative values for DOS represent up and down spins respectively. The black solid vertical line at zero energy denotes the energy of the last occupied state.

However, when we plot the density of states in *Figure 10* for the four charge states, we find an empty gap in the four defective cells. In contrast to oxygen vacancies, the existence of Fe vacancies doesn't introduce deep levels in the gap. Surprisingly, the hole states on oxygen atoms were found to be within the conduction band when plotting the partial density of states *Figure 11* for each of the 3 neighboring oxygen atoms.



Figure 11 Partial Density of states for one of the nearest neighbor oxygen atoms to a neutral iron vacancy

Oxygen Interstitials

According to point defects energetics, oxygen interstitials are of the least importance compared to other point defects as shown in section 3.1 in the main text. However, neutral oxygen interstitials in split-dumbbell orientation (as shown in Figure 12) appear with low concentrations at high PO₂ regime. Analysis of the electronic structure of this defect shows that no deep states exist in the supercell with a neutral oxygen interstitial as shown in *Figure 13*, panel a. While for the very low concentration charge states (1-) and (2-), many deep states arise in band gap in addition to perturbation to valence band.



Figure 12 Configuration of oxygen interstitials in split-dumbbell structure. The two 0 atoms forming the dumbbell are shown in black color



Figure 13 The density of state (DOS) for defective crystals with a neutral oxygen interstitial in (a) and with (1-) and (2-) charge in (b and c), respectively. All O interstitials here are in split-dumbbell configuration. The positive and negative values for DOS represent up and down spins respectively. The black solid vertical line at zero energy denotes the energy of the last occupied state.

Iron Interstitials

The density of states for the 4 charge states of iron interstitials are plotted in Figure 13. However, the thermodynamics of point defects show that (2+) Fe interstitial is a dominant defect in low pO₂ regime. So, it is necessary to understand the electronic structure of this defect. As seen in Figure 13c, the occupied state in the band gap has 3 electrons localized on the interstitial atom and the six oxygen atoms forming the octahedron containing this Fe ion. (See also Figure 14a). This means that only 3 electrons out of 6 in the d-subshell of the Fe interstitial ion are trapped in the bandgap. While the remaining 3 electrons are in the valence band. Also, this defect perturbs the conduction band states in neighboring Fe atoms. The ILDOS in Figure 14, panel (b) shows that unoccupied state close to the conduction band localized on the nearest neighboring Fe ions along the <111> direction in the trigonal supercell.



Figure 14 The density of state (DOS) for defective crystals with a neutral iron interstitial in (a) and with (1+), (2+) and (3+) charge in (b, c and d), respectively. All Fe interstitials here are in octahedral positions. The positive and negative values for DOS represent up and down spins respectively. The black solid vertical line at zero energy denotes the energy of the last occupied state.



Figure 15 Integrated local density of states (ILDOS) for gap states in hematite (2x2x2) supercell with a (2+) Fe interstitial. The last occupied states are shown in panel (a) having 3 electrons localized on the interstitial in the middle of the supercell and the neighboring oxygen ions. While the first unoccupied state is shown in panel (b) having 1 electronic state localized on the closest Fe ions to the

interstitial along <111> direction. Fe ions are shown in blue while oxygen ions are red.

8. Standard DFT

Here we present the Kröger-Vink diagrams based on pure DFT energetics at 1100 K and 700 K in Figure 15 and Figure 16, respectively.



Figure 16 Concentration of native point defects in hematite at T = 1100 K using standard DFT (U=0)



Figure 17 Concentration of native point defects in hematite at T = 700 K using standard DFT (U=0)

9. Isobaric self-diffusion coefficients



Figure 18 Self diffusion coefficients of Fe ions along <111> direction in hematite are plotted versus temperature. 21 isobars are shown starting from p02= 1 atm to p02 = 10^{-20} atm. These were fitted to Arrhenius law to extract effective diffusivities and diffusion barriers.

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