Supplementary Information

DFT analysis of the role of the number of layers: accounting for the multiple energy gaps in iron oxychloride

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Text S1:

Identification of ground state spin of FeOCl.

Due to the presence of unpaired electron in Fe^{3+}, the spin of the system is considered for calculation. The electronic configuration of Fe^{3+} is $[Ar]3d^5$. For d orbitals, the electron arrangement in accordance with Pauli's exclusion principle results in two possibilities: (i) all the five electrons can be unpaired, resulting in a high spin state (5) or (ii) four electrons get paired up, leading to one unpaired electron, resulting in a low spin state (1). In addition to this, the unpaired electrons can have either up or down directions. When both spin state and directions are considered, this leads to seven possible arrangements. These are as follows:

1) Spin undefined- The spin state and direction are not specified.
2) High up- All Fe^{3+} are in high spin, up state (+5)
3) High down- All Fe^{3+} are in high spin, down state(-5)
4) Low up- All Fe^{3+} are in low spin, up state (+1)
5) Low down- All Fe^{3+} are in low spin down state (-1)
6) High up down- One of the Fe^{3+} is in high-up and the other in high-down state
7) Low up down- One of the Fe^{3+} is in low-up and the other in low-down state

Table S1: Identification of the ground state spin configuration of FeOCl

Spin and direction	**Energy gap (eV)**	**a (Å)**	**b(Å)**	**c(Å)**	**Enthalpy (eV)**
undefined	1.480	3.9122	8.1078	3.3276	-8453.11
High up	1.479	3.9115	8.1085	3.3275	-8453.11
High down	1.486	3.9097	8.1428	3.3279	-8453.11
Low up	0.307	3.8729	7.6654	3.1169	-8450.18
Low down	-	3.7701	7.8247	3.3756	-8452.37
High up-down	**1.903**	**3.8429**	**8.1005**	**3.3382**	**-8453.21**
Low up-down	-	3.8897	7.9698	3.3281	-8452.65

Table S2: Variation of energy gap of bulk FeOCl with variation in U parameter

U (eV)	**Energy gap (eV)**
0	0.805
1	1.082
2	1.392
3	1.741
4	1.948
5	1.913
5.2	1.909
5.3	1.903
5.4	1.898
5.6	1.887
5.8	1.874
6	1.861

Table S3: Variation of energy gap of monolayer FeOCl with variation in U parameter

U (eV)	**Energy gap (eV)**
5.2	2.108
5.3	2.129
5.4	2.151
5.6	2.189
5.8	2.227
6	2.255

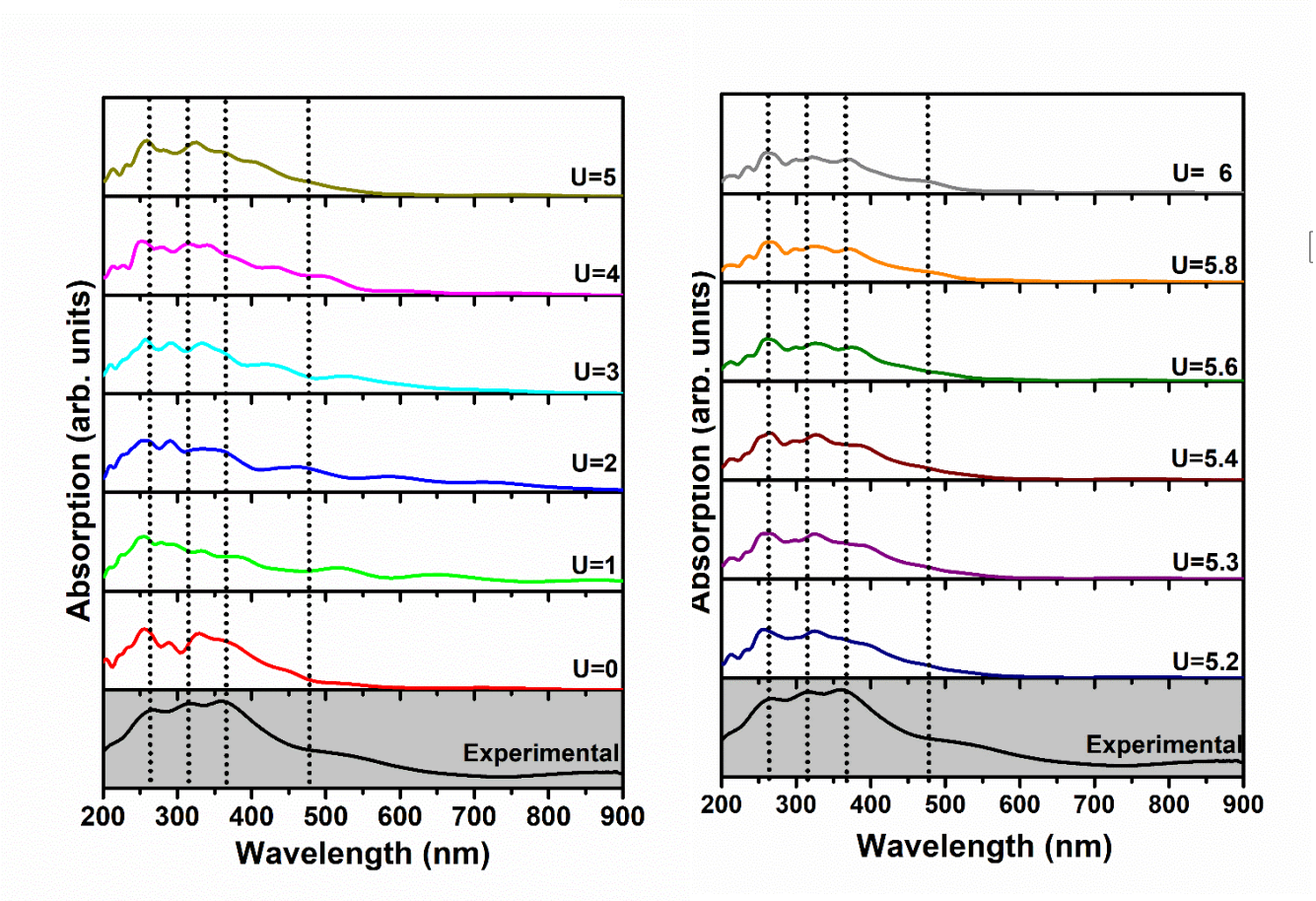

Fig. S1: Comparison of absorption spectra obtained corresponding to different U values with that obtained experimentally

Table S4: Variation of bond length and magnetic moment with variation in U parameter

U (eV)	Bond lengths (Å)		Magnetic moment (μ_B)
0	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	1.93857 1.93857 2.15598 2.15599 2.36555 2.36556	4.25
1	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	1.95353 1.95353 2.14349 2.14349 2.37135 2.37135	4.09
2	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	1.96661 1.96661 2.13844 2.13844 2.37856 2.37856	4.15
3	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	1.98073 1.98073 2.13262 2.13262 2.38514 2.38514	4.19
4	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	1.99046 1.99046 2.13387 2.13387 2.38957 2.38957	4.23
5	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	2.00503 2.00503 2.12691 2.12691 2.39544 2.39544	4.27
5.2	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	2.00523 2.00523 2.12920 2.12920 2.39573 2.39573	4.27
5.3	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	2.00630 2.00630 2.12893 2.12893 2.39626 2.39626	4.27

5.4	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	2.00746 2.00746 2.12854 2.12854 2.39686 2.39686	4.28
5.6	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	2.00993 2.00993 2.12802 2.12802 2.39789 2.39789	4.28
5.8	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	2.01240 2.01240 2.12772 2.12772 2.39895 2.39895	4.29
6	O 1 -- Fe 2 O 2 -- Fe 1 O 2 -- Fe 2 O 1 -- Fe 1 Cl 1 -- Fe 1 Cl 2 -- Fe 2	2.01480 2.01480 2.12686 2.12686 2.40011 2.40010	4.29

Table S5: Bond lengths in the optimized structures of bulk and monolayer (Fe 1 and Fe 2 are down and up spin, respectively)

Bond	**Bond length(Å)**	
	Bulk	**Monolayer**
O 1 - Fe 2	2.0148	2.0161
O 2 - Fe 1	2.0148	2.0164
O 2 - Fe 2	2.1269	2.1262
O 1 - Fe 1	2.1269	2.1265
Cl 2 - Fe 2	2.4001	2.4002
Cl 1 - Fe 1	2.4001	2.4016

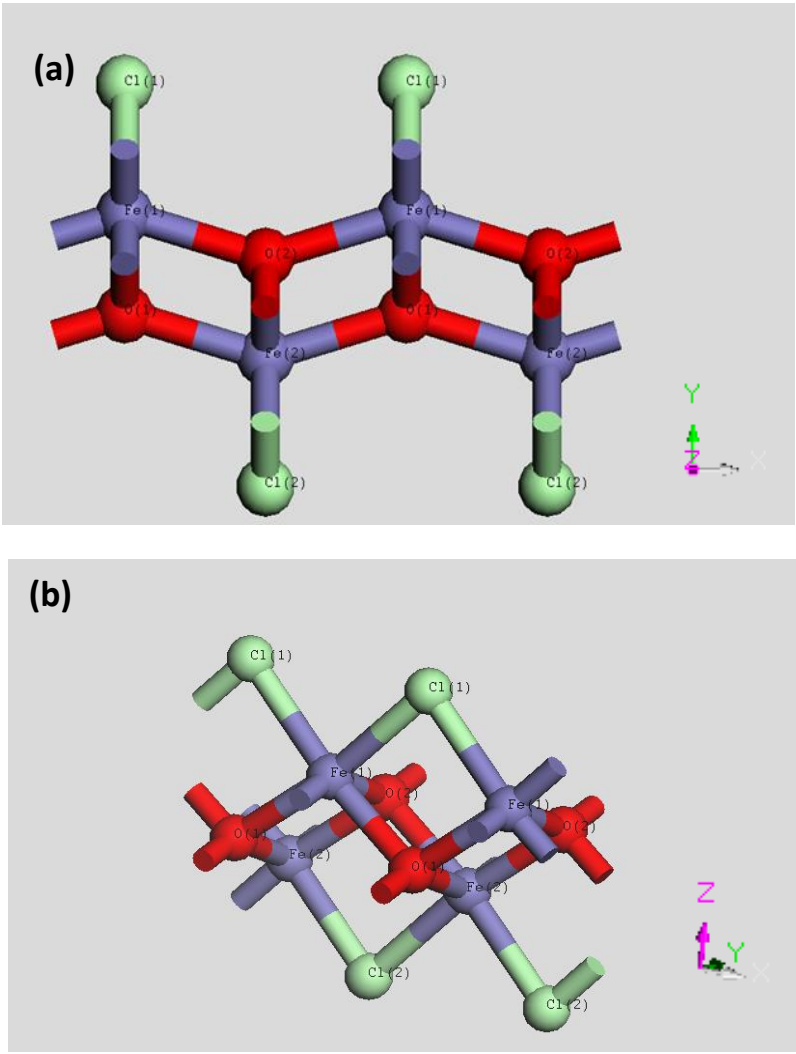

Fig. S2: A portion of the lattice for (a) Bulk and (b) monolayer FeOCl showing the indexing of each atom. Images are in different angles in order to ensure visibility

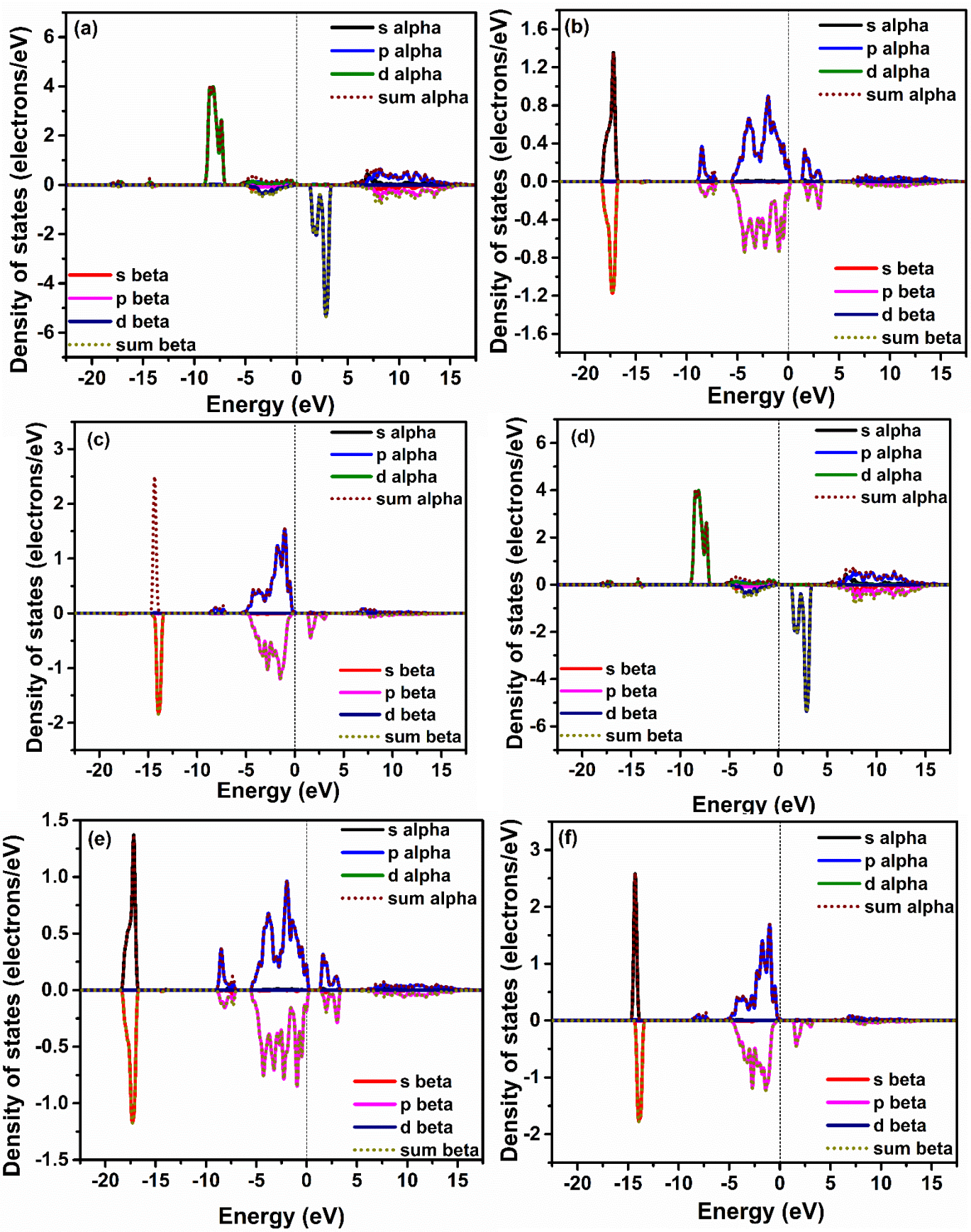

Fig. S3: PDOS corresponding to individual atoms for: bulk FeOCl (a) Fe, (b) O and (c) Cl and monolayer FeOCl (d) Fe, (e) O and (f) Cl

Text S2 : Finding the AFM ground state in a supercell

From calculations using unit cell, it was identified that FeOCl exists in an antiferromagnetic configuration in the ground state. This implies that there are equal number of up and down spins. When a supercell is considered, there can be different possible arrangements from which the preferred ground state is to be identified. To reduce computational cost, a 2x1x1 supercell is considered first (Fig S4). The four possible spin arrangements are considered and the details of the calculations are included in Table S6 . The lowest energy configuration corresponds to the arrangement 2 listed in the table. This indicates that nearby Fe atoms are having opposite spins. When a 2 x 1 x 2 supercell is considered, this leads to two possible arrangements as shown in Fig. S5. The enthalpy for AFM1 is -3.3802 x 10^4 eV whereas it is -3.3813 x 10^4 eV for AFM2. The corresponding energy gaps are 1.19 and 1.86 eV, respectively. The AFM2 configuration results in the lower energy and the energy gap matches with the experimental results. Further, the configuration is in accordance with the previous reports. Hence, this spin arrangement is used for analysing the role of oxygen vacancies (OVs)

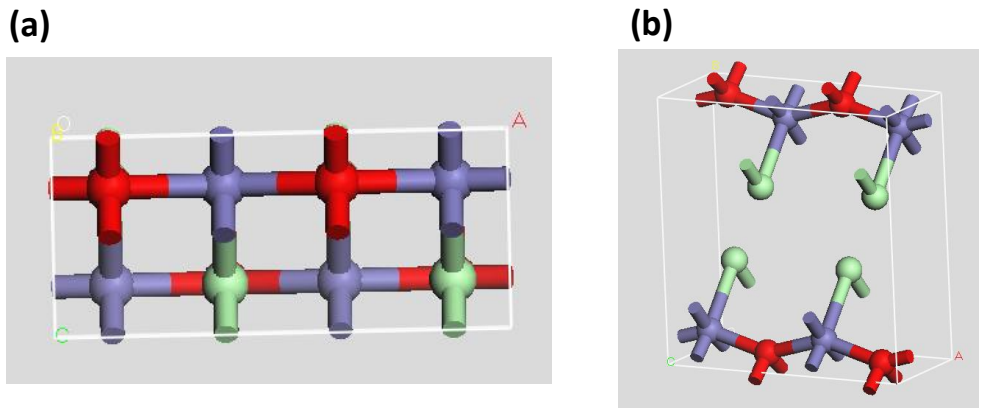

Fig. S4: The 2 x1x1 supercell used to analyse the spin configuration. Images are in different angles in order to ensure visibility

Table S6: Energy gap and enthalpy values obtained corresponding to different possible spin configuration in a 2x1x1 supercell

No.	Spin Configuration	Energy gap (eV)	Enthalpy (x10^4 eV)
1	++/↑↑ --/↓↓	1.388	-1.690641
2	-+/↓↑ +-/↑↓	1.898	**-1.690686**
3	+-/↑↓ +-/↑↓	1.888	-1.690668
4	--/↓↓ ++/↑↑	1.388	-1.690641

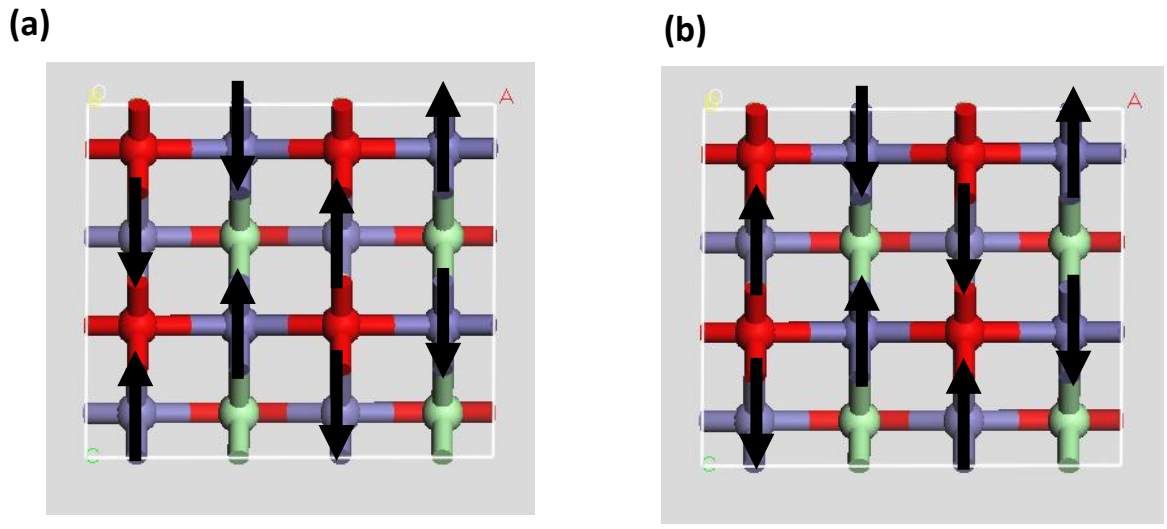

Fig. S5: The 2 x1x2 supercell used to analyse the spin configuration (a) AFM1 (b) AFM2. The arrows indicate the spin directions

Text S3: Analysing the charge state of oxygen vacancies

When an oxygen atom is missing from the lattice, it leads to vacancy with a +2 charge (V_O^{++}), when one electron is trapped in this OV, it has a charge state of +1 (V_O^{+}). When two electrons are trapped, it results in a neutral OV (V_O). These three possible states are analysed by deleting an oxygen atom from the supercell and assigning the required charge to the system. For the calculations, U=5.3 eV is used. The structure used for the study of OVs is given in Fig. S6. The structures are geometry optimized for the different charge states and the lowest energy is obtained for V_O^{++}. The band structures and DOS obtained for the structures are given in Fig. S6. The V_O^{++} ground state is in accordance with the ESR spectrum reported in our previous work wherein any OV signal was not detected due to the absence of unpaired electron. Hence, this charge state is used for further analysis.

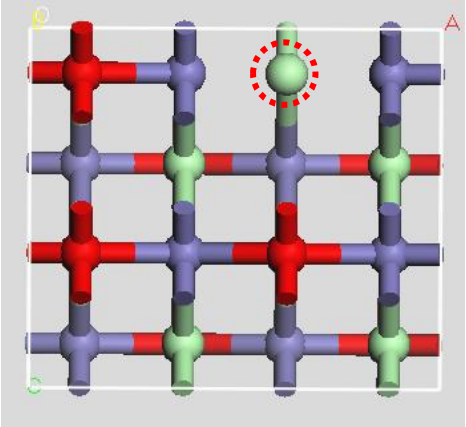

Fig. S6: The 2 x1x2 supercell in AFM2 spin configuration used to analyse the effect of OVs. The red circle corresponds to the missing oxygen in the lattice.

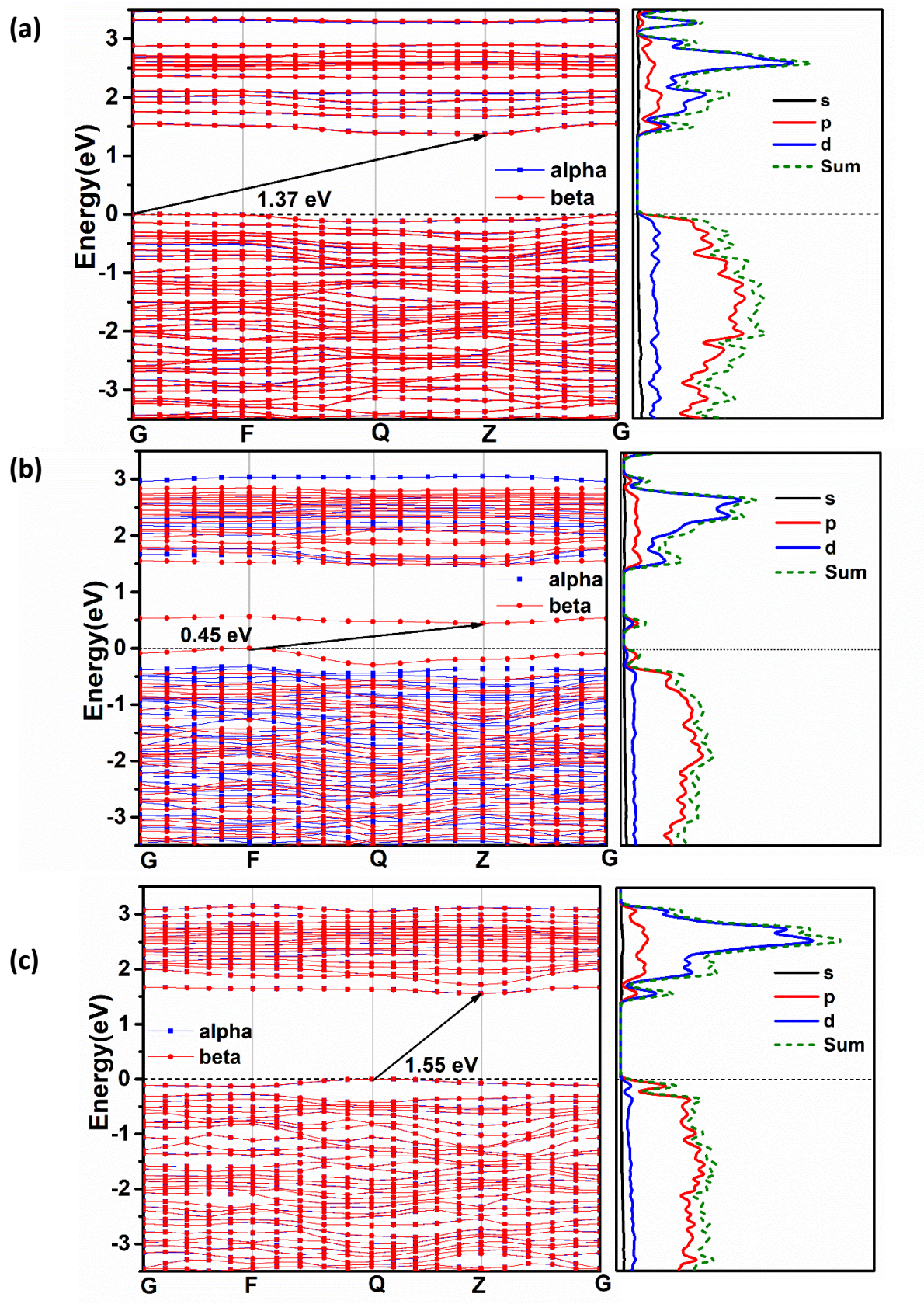

Fig. S7: Band structure and DOS obtained for different charge states of OVs (a) V_O (b) V_O^{+} (c) V_O^{++}