Atomic and Electronic Structure of the $YFeO_3$ Surface with Oxygen Vacancies

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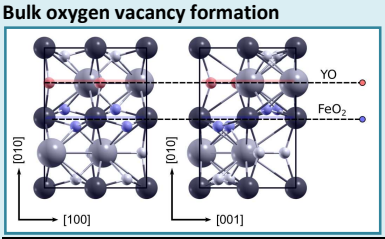
Introduction

The field of application of the complex oxides with a perovskite structure (ABO_3) is very wide: sensors and detectors, solar cells, photocatalysts and solid oxide fuel cells. It was found that the defect formation in the crystal lattice of ABO_3 leads to a significant increase in catalytic activity, so perovskite compounds can be used as alternative multifunctional catalysts for the neutralizing of diesel gases.
The atomic and electronic structure of $YFeO_3$ at the formation of oxygen vacancies on the surface was studied using modern computer simulation methods.

Methods and calculation parameters

- Quantum Espresso software package (DFT+ pseudopotential)
- PBE functional
- 6×4×6 k-point grid for orthorhombic $YFeO_3$ cell
- Cutoff energy – 60 Ry
- Ultrasoft PP for Y, Fe, O from QE database
- Hubbard correction (*DFT + U*) with the U_{eff} = 4 eV
- Spin-polarization (*G-type* anti-ferromagnetic order for Fe)

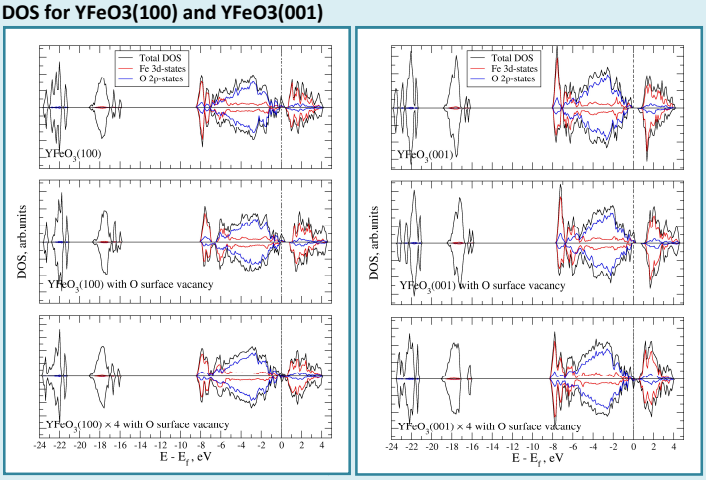
Bulk oxygen vacancy formation



$$E_{form} = E_{vac} - E_{ideal} + \frac{1}{2}E_{O2}$$

Configuration	E_{form}, eV	Difference, eV
$YFeO_{3-\delta}$ (δ = 0.25) – O1	3.69	
$YFeO_{3-\delta}$ (δ = 0.25) – O2	3.79	0.10
$YFeO_{3-\delta}$ (δ = 0.0625) – O1	3.13	
$YFeO_{3-\delta}$ (δ = 0.0625) – O2	3.42	0.29

DOS for YFeO3(100) and YFeO3(001)



Formation of an oxygen vacancy leads to the appearance of levels in the band gap, as well as to a partial delocalization of the *3d* states of Fe. At the vacancy formation on the $YFeO_3$(010) surface there are distributed states corresponding to the surface Fe atoms
In the case of the (001) and (100) surfaces there is a partial splitting of the peak corresponding to the bulk states, this occurs due to the formation of the Fe-Fe bond when oxygen is removed from the surface and the surface layers are included in the atomic relaxation process.

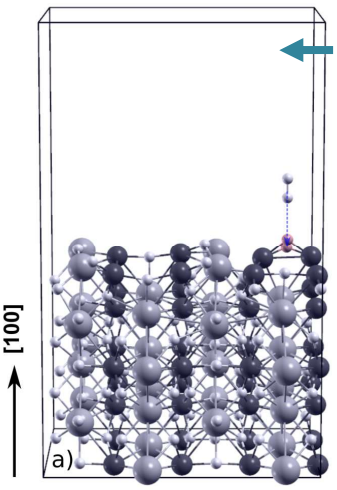
$YFeO_3$ surfaces: (001), (010) and (100). The formation energies

Surface	Area, m^2	Slab characteristics	Surface energy, J/m^2
(001)	$4.36 \cdot 10^{-19}$	5 layers	0.92
		7 layers	0.91
		5 layers, the lower layers are fixed	0.97
(010)	$4.11 \cdot 10^{-19}$	9 layers (FeO_2)	1.03
		9 layers (YO)	1.31
		9 layers (FeO_2), the lower layers are fixed	1.05
(100)	$3.01 \cdot 10^{-19}$	5 layers	1.06
		5 layers, the lower layers are fixed	1.11

- All simplification and number of atomic layers insignificantly influence on the values of surface energy.
- (010)-(FeO_2) surface is more favorable

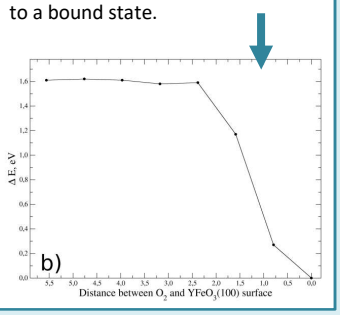
$$E_{surf} = \frac{E_{unrel.slab} - E_{rel.slab}}{2S}$$

Formation of an oxygen complex on the YFeO3(100) surface

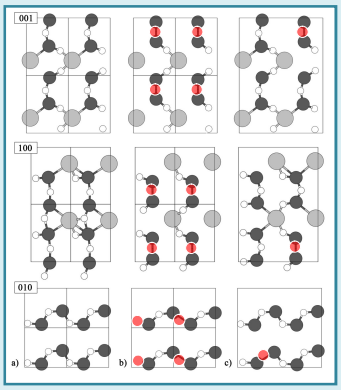


An oxygen molecule barrier-free movement to a vacancy

The change in total energy at transition from a non-interacting O_2 molecule and a $YFeO_3$(100) surface with an oxygen vacancy to a bound state.



Formation of O vacancies on the surface



Surface	Area, m^2	E_{form}, eV
(001)	$4.36 \cdot 10^{-19}$	2.40
	$17.45 \cdot 10^{-19}$	1.74
(100)	$4.11 \cdot 10^{-19}$	1.79
	$16.44 \cdot 10^{-19}$	**0.81**
(010)	$3.01 \cdot 10^{-19}$	3.51
	$12.03 \cdot 10^{-19}$	3.33

$$E_{form} = E_{slab+vac} - E_{slab} + \frac{1}{2}E_{O2}$$

Atoms of $YFeO_3$ surface layers: a) without oxygen vacancy; b) one vacancy per unit cell cross-section; c) one vacancy per cell area increased by 4 times

Conclusion

- There is a tendency to a decrease in the formation energy with an increase in the surface area, which corresponds to a decrease in the vacancy concentration.
- The smallest value of 0.81 eV was obtained for the (100) surface, which is approximately four times less than the formation energy of a bulk oxygen vacancy.
- An analysis of the electronic structure showed a partial delocalization of the 3d states of Fe atoms at the surface formation process, formation of an oxygen vacancy, due to the appearance of Fe-Fe bond, enhances delocalization effect.
- An oxygen molecule moves to a surface vacancy without barrier. For $YFeO_3$(100) energy gain of this process is 1.6 eV

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