A DFT+*U* study of point defects in spinel ferrites

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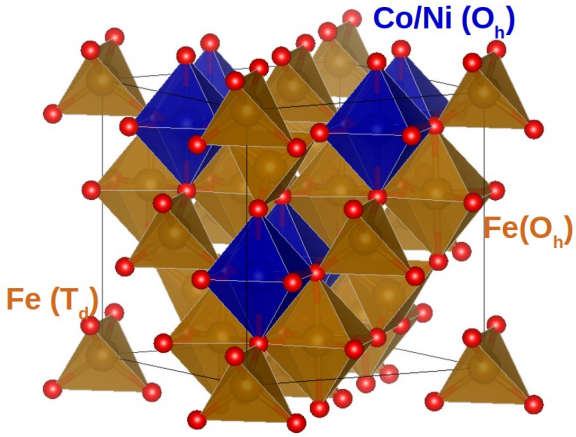
Spinel ferrites: $CoFe_2O_4$ (CFO) and $NiFe_2O_4$ (NFO)

- Distorted *fcc* lattice of oxygen atoms with cations (Co^{2+}/Ni^{2+}, Fe^{3+}) in tetrahedral (T_d) or octahedral (O_h) sites

- Partially inverse cation distribution

  = Co^{2+} or Ni^{2+} mostly in O_h atomic sites



General formula: $[Co_{1-\lambda}Fe_{\lambda}]_{Td}[Co_{\lambda}Fe_{2-\lambda}]_{Oh}O_4$

λ = inversion parameter

λ = 1 for inverse; λ = 0 for normal spinel

Interests in electronic and spintronic applications

- Insulating and ferrimagnetic with high T_C
- May be ferroelectric (intrinsic multiferroic)
- Tunable electronic and magnetic properties through cation ordering and defects engineering

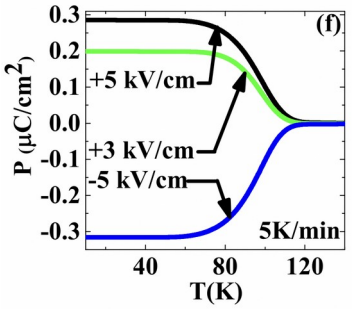
  Goal: **Understanding the role of defects by *ab initio* calculations**

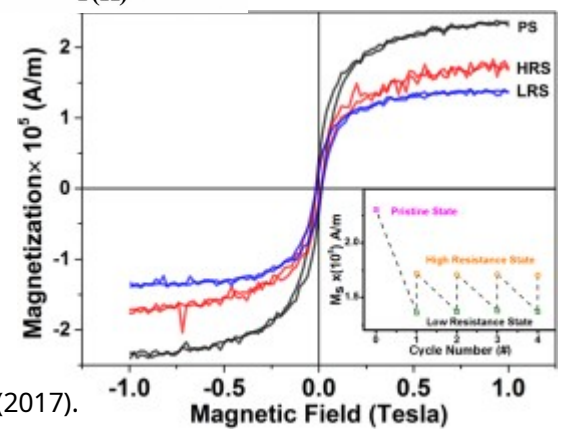
Outline:

- Cation ordering in O_h sites
- Cation ordering between O_h and T_d sites (inversion)
- Vacancies (off-stoichiometric structures)

NFO

Dey, *et al.*, Phys. Rev. B **99** 144412 (2019).





Al/CFO/FTO

Munjar & Khare, Sci. Rep. **7**, 12427 (2017).

Calculation methods

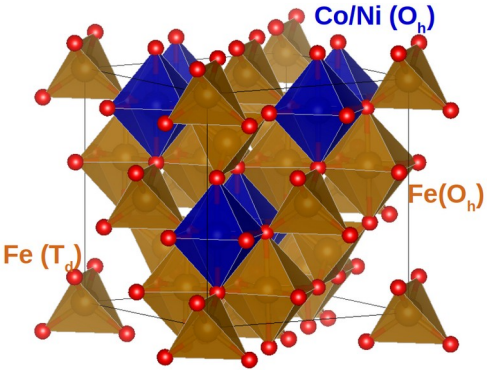
- *Ab initio* DFT calculations: VASP code
- E_{xc} functional: GGA-PBEsol
- Hubbard *U* (on site interaction):

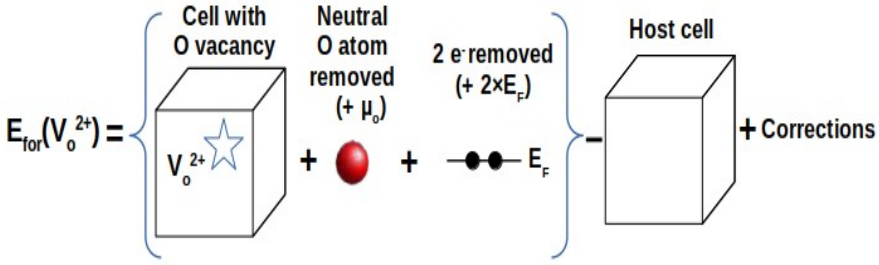
  $U_{Fe} = U_{Co} = 4$ eV, and $U_{Ni} = 2.5$ eV

- Supercell approach, using a cubic conventional cell of 8 f.u. (56 atoms)
- Formation energy of vacancy M with charge state q :

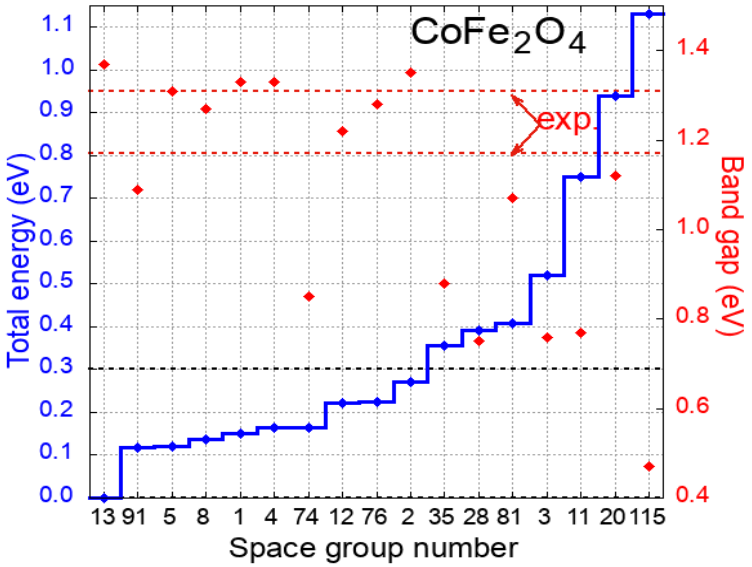
$$E_f(V_M^q) = E_{tot}(V_M^q) - E_{tot}(\text{bulk}) + \Sigma n_M \mu_M + qE_F + E_{\text{corrections}}$$

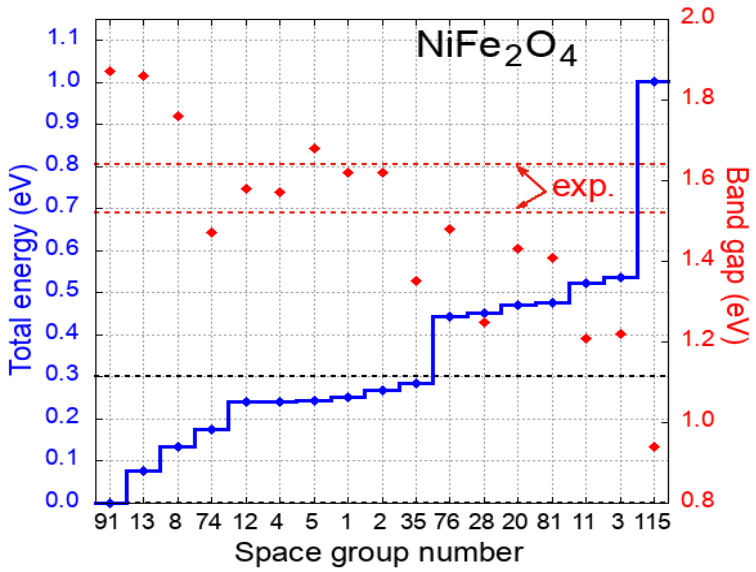
$E_{\text{corrections}}$ calculated with PyDEF2





Cation ordering at O_h sites (inverse spinels)

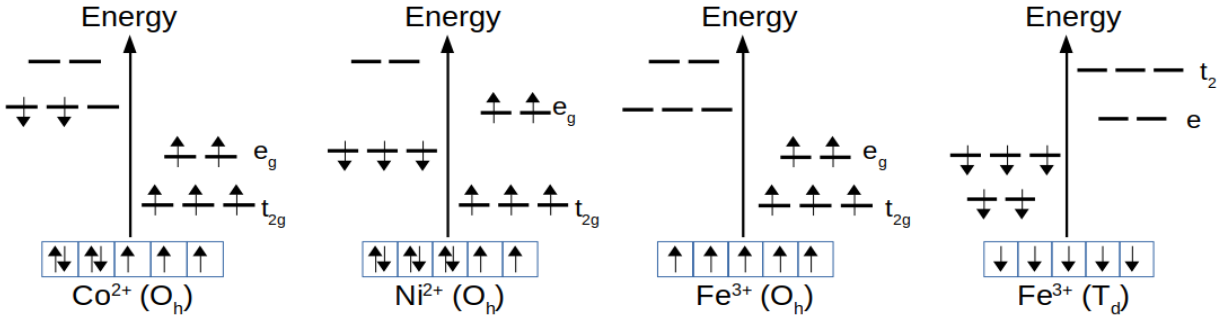




- For most stable structures (ΔE < 0.3 eV), band gap variation < 0.5 eV
- Band gap ↘ when stability ↘
- Most stable space group: 13-*P2/c* for CFO and **91-*P4$_1$22*** for NFO (in agreement with Ref. Ivanov, *et al.*, Phys. Rev. B **82**, 024104 (2010).)

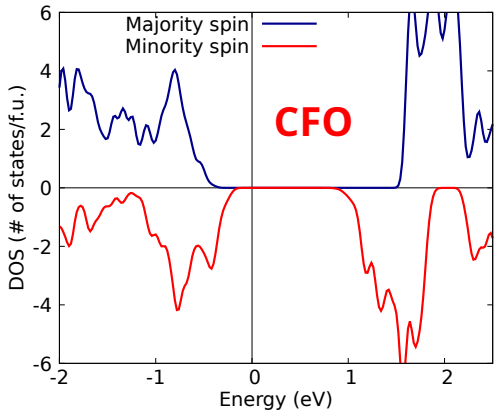
Electronic and magnetic properties of perfect inverse spinels ($P4_122$)

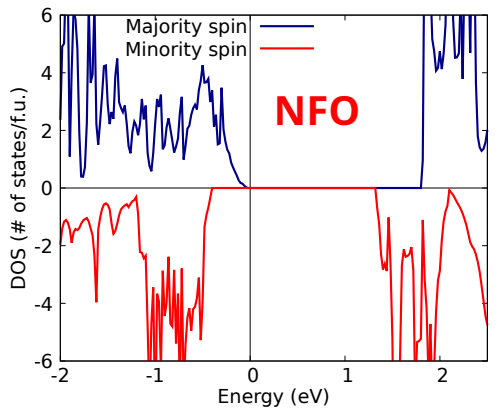
- Calculated band gap: 1.09 eV (CFO) and 1.73 eV (NFO)
- Ferrimagnetic with an antiferromagnetic coupling between cations in O_h and T_d sites.
- Spin magnetic moments:



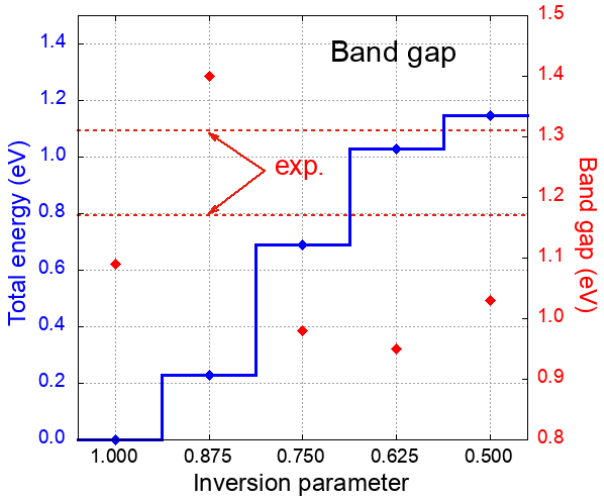
	Co^{2+} (O_h)	Ni^{2+} (O_h)	Fe^{3+} (O_h)	Fe^{3+} (T_d)
Theoretical	3 μ_B	2 μ_B	5 μ_B	-5 μ_B
Calculated	**2.60 μ_B**	**1.54 μ_B**	**4.04 μ_B**	**-3.90 μ_B**

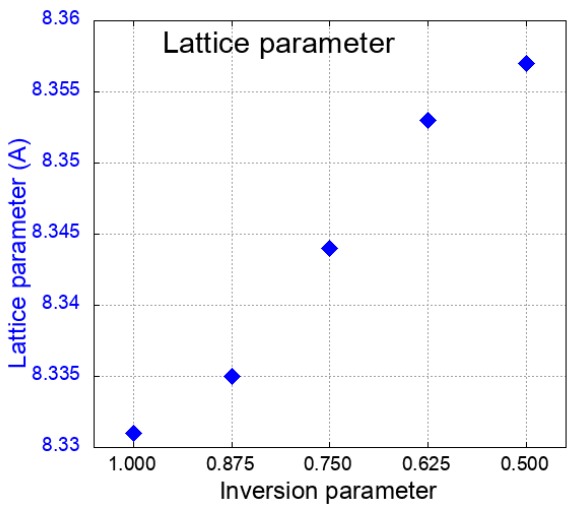
Total magnetic moments (/ f.u.): M_S(CFO) = **3 μ_B**, M_S(NFO) = **2 μ_B**

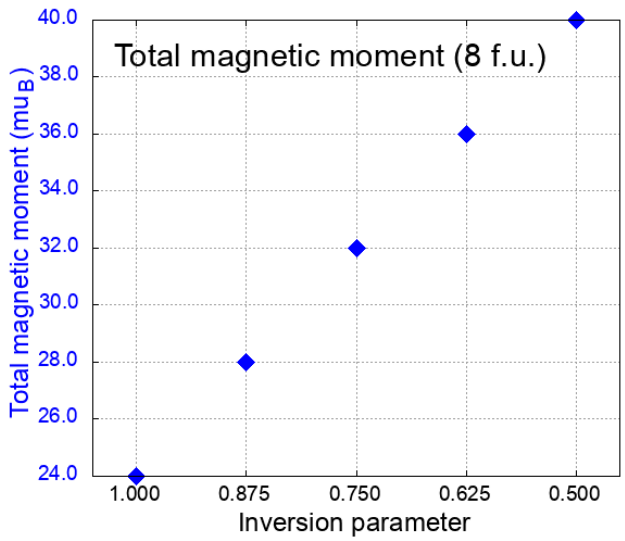




Partial inversion in CFO: $[Co_{1-\lambda}Fe_{\lambda}]_{Td}[Co_{\lambda}Fe_{2-\lambda}]_{Oh}O_4$







- Magnetic moment increases with decreasing λ: +4 μ_B per atom inversion ($\Delta\lambda = 0.125$)
- Higher λ ↔ Higher stability.
- Inverse distribution more stable for NFO than CFO

Co or O vacancy in CFO

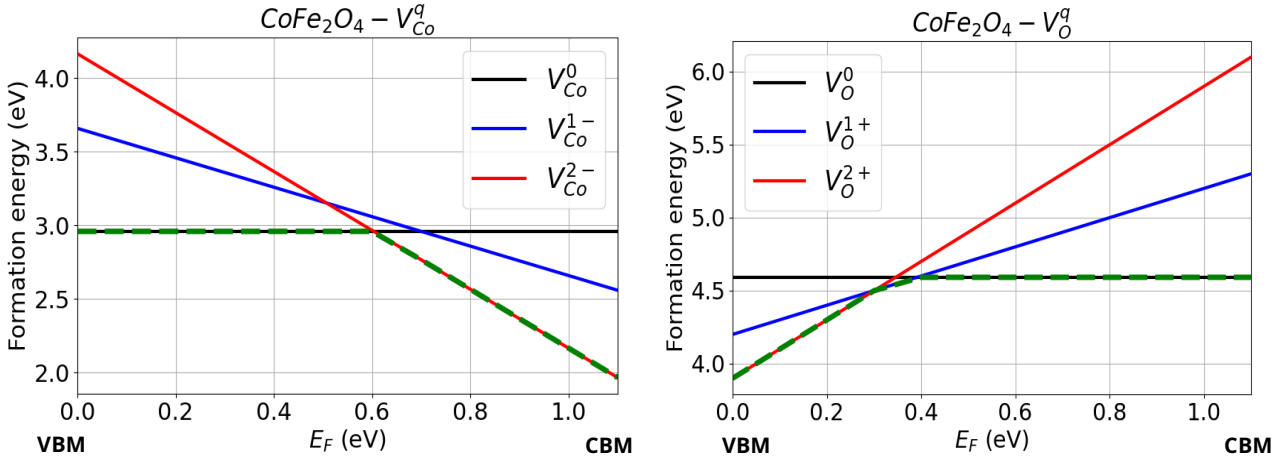
- V_M^q: vacancy of atom M with charge state q:

  V_M^q ↔ remove of 1 M atom + q electrons, e.g.:

  V_O^0 ↔ removal of 1 neutral O atom

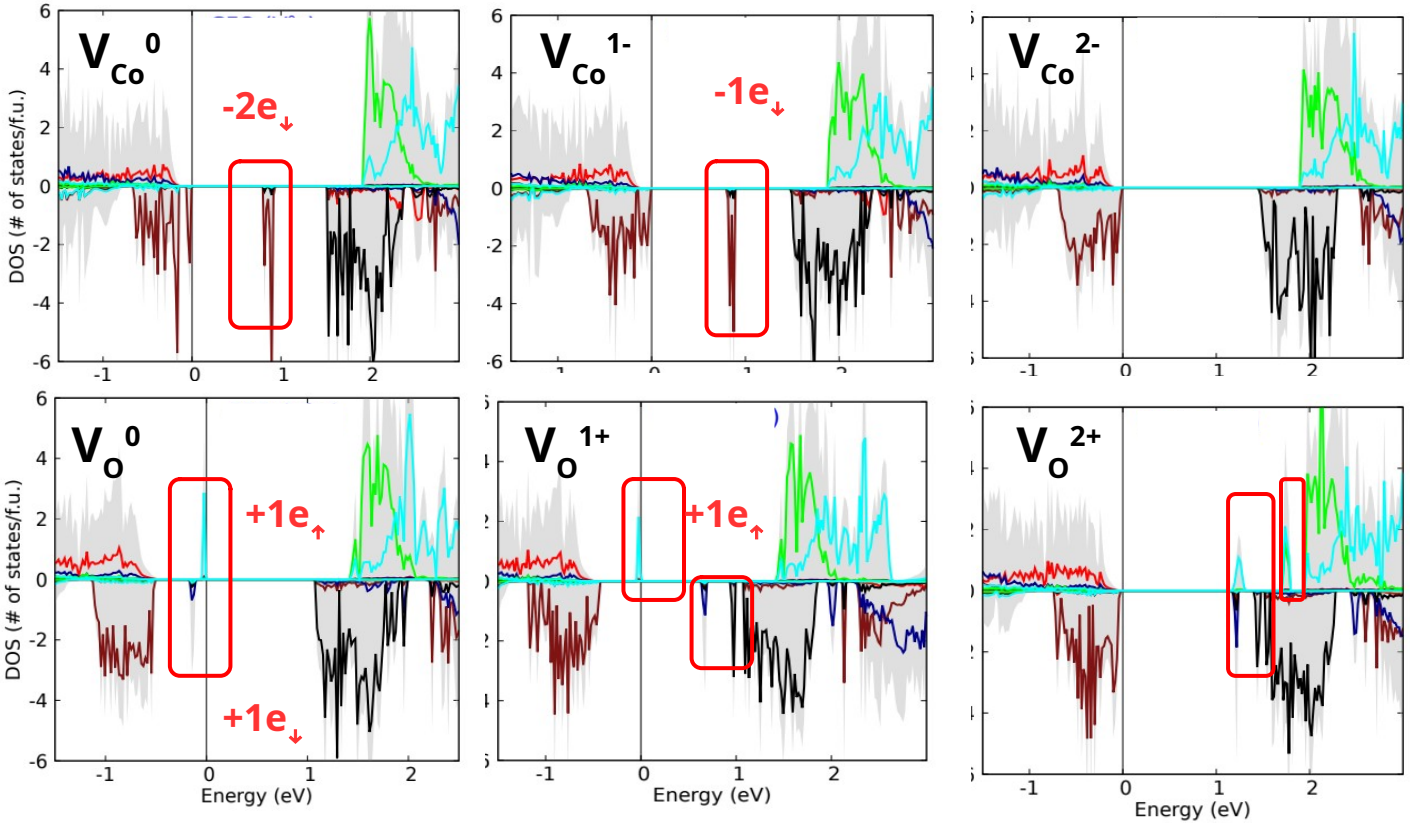
  V_O^{2+} ↔ removal of 1 O^{2-} anion

Defect formation energy w.r.t. Fermi level E_F



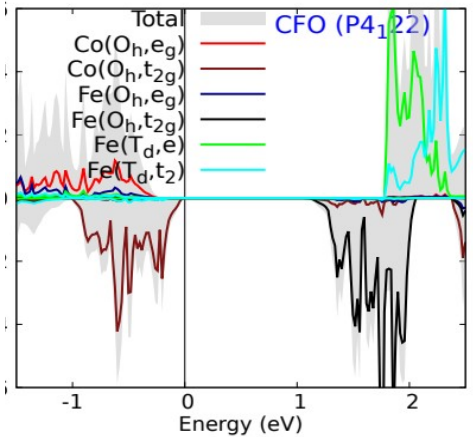
- If E_F near VBM: V_{Co}^0 or V_O^{2+}
  near CBM: V_{Co}^{2-} or V_O^0
- **Effect of vacancy: defect states on neighboring cations → induce the change of spin magnetic moments of these cations**

Co or O vacancy in CFO



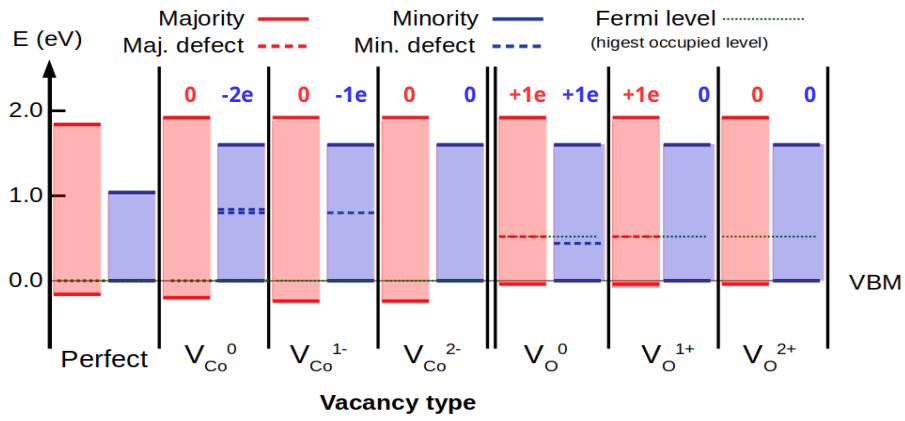
Majority Spin ↑

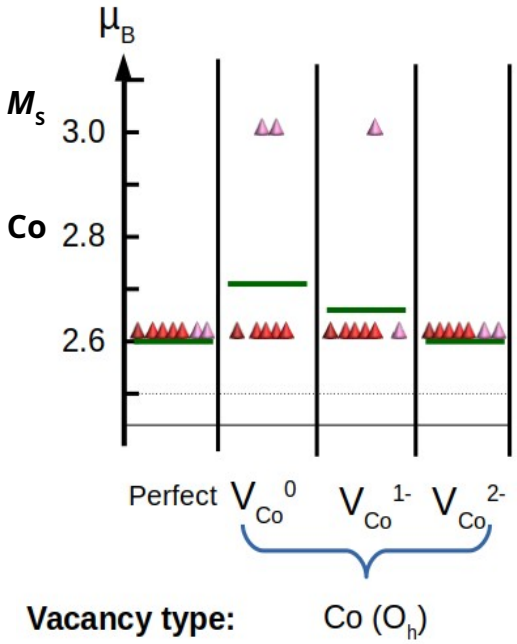
Minority Spin ↓

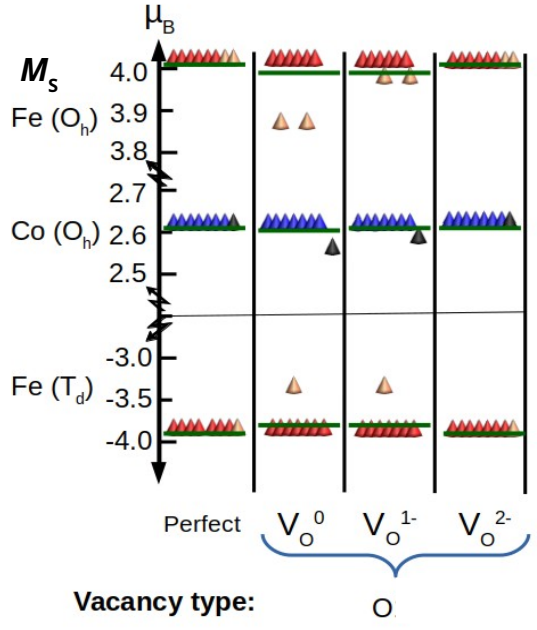


- Cation vacancy: Co minority-spin defect states
- Oxygen vacancy: Co, Fe (O_h and T_d) defect states for both spins

Co or O vacancy in CFO







Defect states associated with changes of spin magnetic moments of first-neighbor cations

If V_O: no change of magnetization

If V_{Co}: change of magnetization

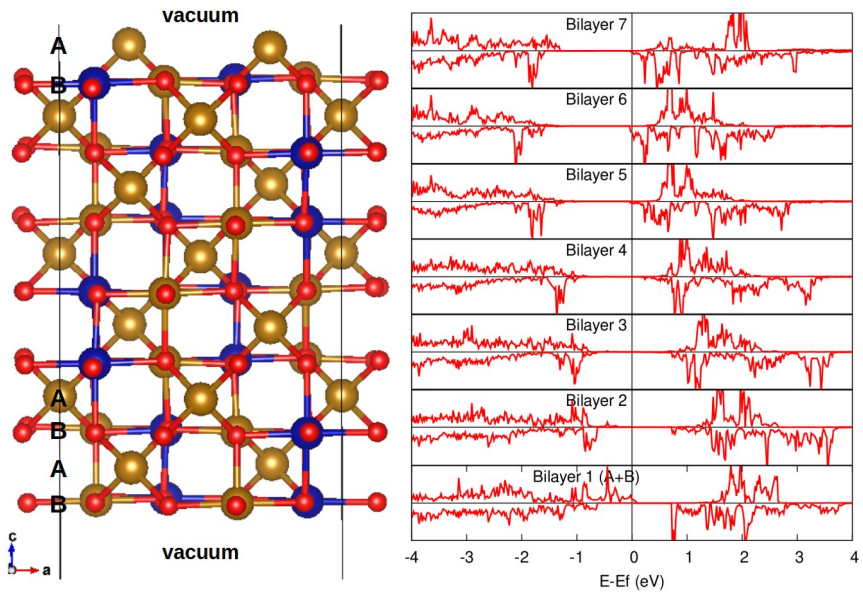
Conclusion and perspectives

- CFO is more likely to show partial inversion than NFO.
- Total spin magnetic moment:
  - Increases when the inversion parameter decreases.
  - Decreases with V(cation), but not affected by V(O)
- Creation of defect states

Perspectives:

From bulk to thin films to include interface and surface effects

Electronic vs atomic reconstructions



Acknowledgements

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