DFT exploration of the family of 2D metal organic frameworks $M(C_4N_2H_4)Cl_2$

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Introduction

This ab initio computational research focuses on developing a new class of Metal Organic Frameworks (MOFs) with the potential of revolutionizing the IT world by offering a new class of easy-to-design and more flexible materials exhibiting switchable and stimuli-responsive characteristics.

To achieve this new class of MOFs, it is essential to gain a clear understanding of the role of the magnetic and structural local correlations, to investigate the electronic band-structure and to carry out successful predictions of dopant locations.

Background Research

Kreno et al.[1] has shown great potential in MOFs as these modular materials enable the organic component to be functionalised while preserving the overall framework topology. Recent computational advances in this field focused on ab initio random structure searching by implementing the Wyckoff Alignment of Molecules (WAM)[2] approach in order to find topologically diverse MOFs, to predict the nature and locations of dopants and to overcome the limitations of the widely used reverse topological approach.[3]

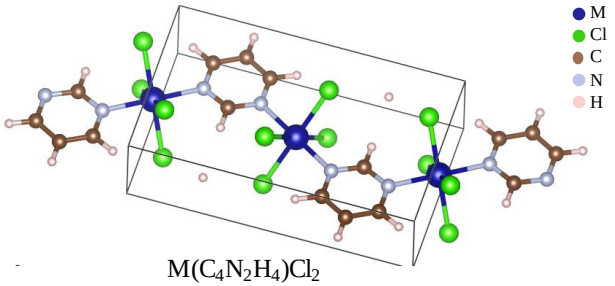
References

[1] L. E. Kreno et al. Analytical Chemistry, 82:8042–8046 (2010)
[2] J. Darby et al. Chem. Mater., 32:5835–5844 (2020)
[3] J. Keupp. Faraday Discuss., 211:79–101 (2018)
[4] M. L. Evans et al. Journal of Open Source Software, 5: 2563 (2020)
[5] A J. Morris et al. Comp. Phys Communications, 185:1477–1485 (2014)

Research Overview & Methodology

- This computational exploration has investigated the structure and properties of a new family of 2D metal organic frameworks, $M(C_4N_2H_4)Cl_2$, where M = transition metals V to Cu

Structure from XRD
Symmetry breaking
→ Hamiltonian
DFT (PBE) + MBD*
→ Geometry Optimization
CASTEP
→ Hamiltonian
DFT + U
→ Band-structure & DOS
Matador[4] + OptaDOS[5]



$M(C_4N_2H_4)Cl_2$

Results & Conclusions

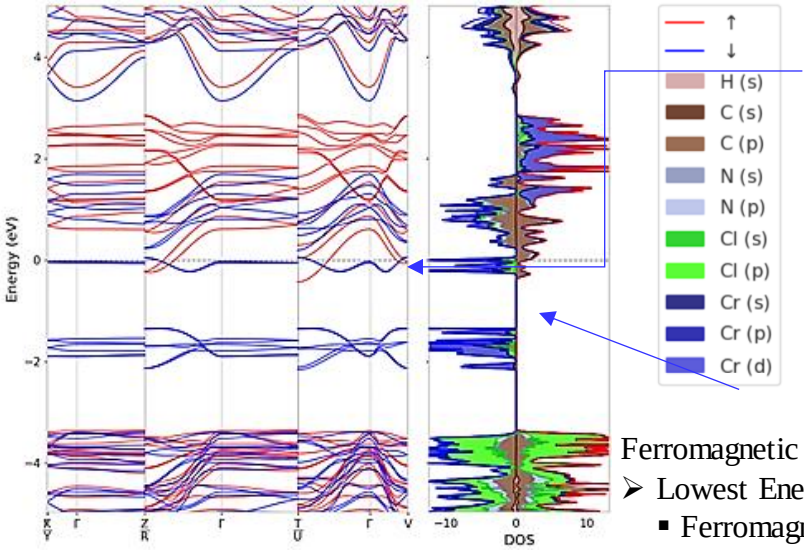
- HOMOs showed low levels of dispersion

Hubbard U correction opened the band gap around the Fermi Level

- For M = Cr: Spin difference of 3.9 electrons between up and down d-states occupancies
  ⇨ *SPIN = 2 for Cr*

Exchange Interaction $[E_{FM}-E_{AFM}]$

M:		
	Chromium	0.72 meV
	Nickel	6.51 meV
	Cobalt	-0.06 meV
	Iron	1.41 meV
	Vanadium	-4.00 meV



Band-structure & DOS of $Cr(C_4N_2H_4)Cl_2$

- Band crossing around the Fermi level found with Cr & Fe
- Larger band-gap around the Fermi level found with V & Co

Ferromagnetic Configuration for Cr

- Lowest Energy Configurations:
  - Ferromagnetic: Cr, V, Co
  - Anti-ferromagnetic: Fe, Ni