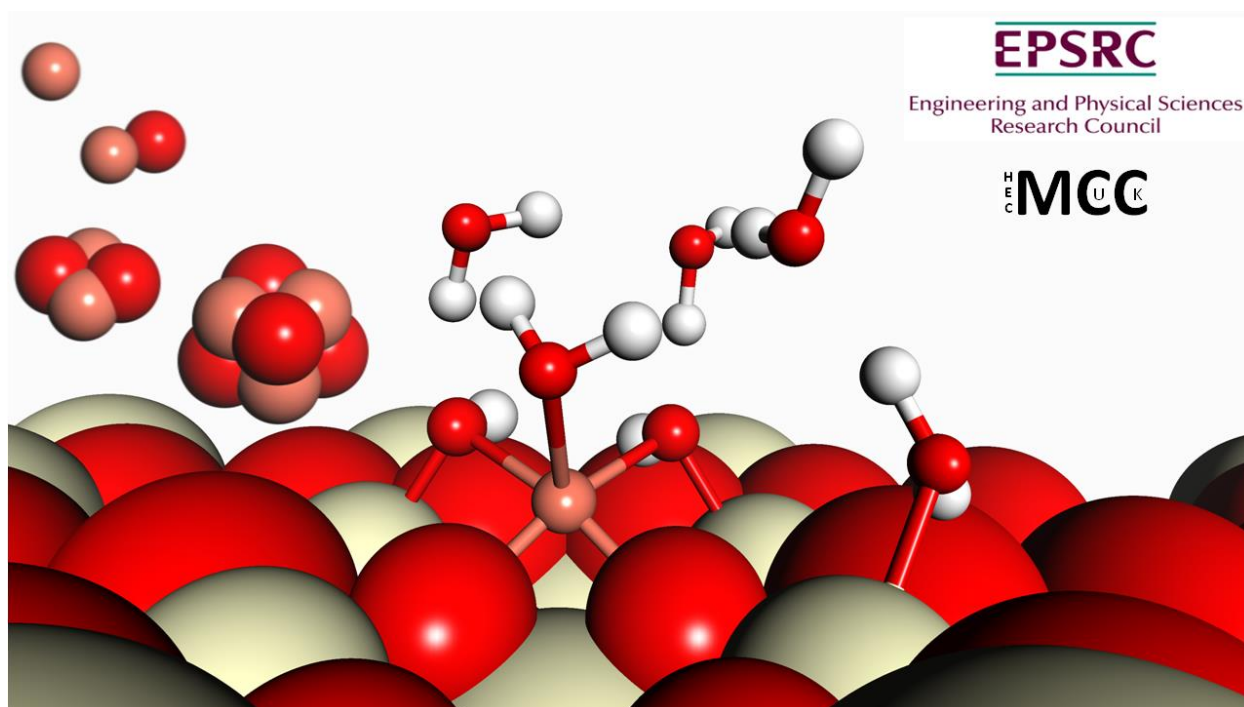


# MCC 4<sup>th</sup> Conference



**Daresbury Laboratory**

Wednesday 6<sup>th</sup> – Friday 8<sup>th</sup> July 2022

## Sponsors

The MCC is very grateful for funding from EPSRC.

We are grateful that this event is also sponsored by:

STFC, Daresbury Laboratory

QC-CCP

## Organising Committee

Georgia Lomas, Alin-Marin Elena, Thomas Keal, Alexey Sokols, and Scott Woodley

We also would like to thank all members, particularly colleagues who have helped us complete our recent outline for an EPSRC proposal, our theme leaders and all of you, including our invited guests, who have joined us in Daresbury in-person or online.



12:30	<b>Registration Desk Open</b>	<b>Daresbury Laboratory</b>
12:30	<b>Lunch</b>	<b>14:00 Start – Welcome Address</b>
Session 1:	<b>Biomaterials &amp; Soft Matter</b>	<b>Theme Leaders J Christie, C Lorenz</b>
14:05	<b>Invited: TBA</b>	Sarah Harris CCPBioSim, Leeds
14:35	Temperature Dependence of Charge Mobility in Rubrene from Fragment Orbital-Based Surface Hopping	<b>Jan Elsner</b> UCL (blu)
14:55	Effect of polymer topology on the self-assembly of micelles	Chris Lorenz KCL (lor)
15:15	Overview of CoSeC support for MCC	Tom Keal CoSeC
15:35	<b>Tea</b>	
Session 2:	<b>Environment &amp; Smart Mater.</b>	<b>Theme Leaders J Harding, N Harrison</b>
16:00	<b>Invited:</b> From Gomberg to graphene and beyond: new multifunctional 2D materials based on persistent radicals	Stefan Bromley Barcelona
16:30	Thermodynamics up to the melting point in a TaVCrW high entropy alloy: Systematic ab initio study aided by machine learning potentials	Ying Zhou Loughborough (bulk-pan)
16:50	Thermal conductivity of radiation damaged tritium breeder materials	Megha Sanjeev Lancaster (mur)
17:10	An <i>ab initio</i> investigation of the impact of intrinsic defects on the thermal properties of CeO <sub>2</sub>	Thomas Smith Huddersfield (bulk-mol)
17:30	<b>Poster Session</b> Starting with lightning presentations (1 slide per poster)	
20:00	Session ends	

Thursday 7 <sup>th</sup> July		
Session 3:	<b>Fund. of Low Dim. Materials</b>	<b>Theme Leaders M Molinari, S Woodley</b>
9:10	<b>Invited:</b> Predicting structure formation and transformation in low-dimensional systems via studying their energy landscapes	Christian Schön MPI, Stuttgart
9:40	BN doped PAHs – Towards 2D molecular recognition	Jack Warren Cardiff (rol)
10:00	Chlorine Activated Stacking Fault Removal Mechanism in thin Film CdTe Solar Cells: the missing Piece	Pooja Goddard Loughborough (pan)
10:20	Understanding nucleation of Co and Mn nanoclusters on anatase (101) surface	Pavel Stishenko Cardiff (log)
10:40	Chiral valley phonons and flat phonon bands in moiré materials	Indrajit Maity Imperial (lis)
11:00	<b>Coffee</b>	

Session 4:	Fund of Surfaces & Interfaces	<b>Theme Leader</b> B Slater, M Watkins
11:20	Phosphate adsorption on {111}, {110}, and {100} surfaces of ceria: A DFT study	Khoa Minh Ta Huddersfield (mol)
11:40	The thermoelectric properties of Polyaniline-SrTiO <sub>3</sub> composites	Nathan Wood Huddersfield (mol/coo)
12:00	Obtaining Interfacial Free Energies from Atomistic Simulations using an Einstein Crystal Reference State	John Harding Sheffield (har)
12:20	Towards Modelling Realistic WS <sub>2</sub> /H <sub>2</sub> O/SiO <sub>2</sub> Interfaces	<b>Katherine Milton</b> UCL (shl)
12:40	<b>Lunch</b>	
Session 5:	Fund. of Bulk Materials	<b>Theme Leaders</b> A Shluger, K McKenna
13:50	Approximating Many-Electron Wave Functions using Neural Networks	Matthew Foulkes Imperial (fou)
14:10	Anharmonicity and entropic stabilisation in zirconia from first principles	Kasper Tolborg Imperial (wal)
14:30	Exploring the Nanoparticle Exsolution Process in Perovskite Oxide	Ji Wu/ Steve Parker Bath (par)
14:50	The Impact of E Field on Defect Generation and Migration Processes in Dielectrics	Jack Strand UCL (shl)
15:10	<b>Coffee</b>	
Session 6:	Materials Discovery	<b>Theme Leaders</b> G Day, K Jelfs
15:50	<b>Invited:</b> Computational Chemistry: An Industrial Perspective	Misbah Sarwar Johnson Matthey
16:20	Investigating the structure and stability of PdZn bi-metallic alloys by coupling density functional theory and cluster expansions	Lara Kaban Cardiff (log)
16:40	Computational design of green ternary semiconductors for optoelectronic applications	<b>Santanu Saha</b> Oxford (fil)
17:00	Crystal structure predictions of organic halide salts	Joseph Glover Southampton (day)
17:20	<b>Invited:</b> Quantum computing for strongly correlated materials (QC-CCP, QEVEC)	François Jamet National Physical Laboratory
17:50	session ends	
18:00 – 21:00	<b>Conference BBQ</b>	

Friday 8 <sup>th</sup> July		
Session 7:	Reactivity & Catalysis	<b>Theme Leader</b> D Willock, R Catlow
9:10	Ab initio study of the Para-xylene Oxidation Redox Cascade	H Thomas Cardiff (log)
9:30	Interatomic-potential-based Computational Approaches for Modelling Defect Chemistry and Surface Oxidation of Solid Materials	Xingfan Zhang UCL (sok)
9:50	A mechanism for the CO <sub>2</sub> -to-CO conversion catalysed by carbon monoxide dehydrogenase	<b>Umberto Terranova</b> Buckingham (ter)
10:10	Localised thermal levering events drive spontaneous kinetic oscillations in catalysis	Matt Quesne Cardiff (cat)
10:30	Coffee	
Session 8:	Energy Gen, Storage & Trans	<b>Theme Leaders</b> S Islam, A Walsh
11:00	<b>Invited:</b> Exploring Battery Materials with Atomistic Simulations: Electrodes, Electrolytes, and Interfaces Thereof	René Windiks Materials Design
11:30	The Wadsley-Roth Materials Family as Functional Energy Materials	Adrien Richard UCL (cor)
11:50	Molecular Dynamics Simulations of Radiation Damage in High Temperature Superconductors	<b>S Murphy</b> Lancaster (mur)
12:10	Surprising improvement of SnS <sub>2</sub> properties through superlattice formation for battery applications	Conor Price Exeter (hep)
12:30	Intrinsic Defect Study on High-voltage Spinel LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub> as Cathode Material for Li-ion Batteries	Jiayi Cen UCL (dos)
12:50	Final Remarks and Close	

Standby Talk	The hydrogen and water interactions with the pristine surfaces of monoclinic and orthorhombic FeNbO <sub>4</sub>	Xingyu Wang Leeds (lee)
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# *Invited Talks*

## *From MCC Advisory Panel*

*Misbah Sarwar  
Christian Schön  
Stefan Bromley*

*Johnson Matthey  
MPI, Stuttgart  
Barcelona*

## *From UK's CCPs*

*Sarah Harris  
François Jamet*

*Leeds; CCP Bio Sim  
National Physical Laboratory;  
CCP QC*

## *From Industry*

*René Windiks*

*Materials Design*

# Exploring Battery Materials With Atomistic Simulations: Electrodes, Electrolytes, and Interfaces Thereof

René Windiks

Materials Design S.A.R.L.  
42, Avenue Verdier, 92120 Montrouge, France

*Invited Talk*

The design of next generation batteries with high performance and long lifetimes requires a profound understanding of the constituent materials, essentially to predict their properties and interactions with each other. This talk shows how atomic-scale modeling with Materials Design's MedeA® environment [1,2] is complementary to experimental techniques to synthesize compounds and examine battery cells during cycling. Based on computational thermodynamics and molecular dynamics simulations we determined the structural stability, voltage profiles, electrical conductivity trends, and lithium transport mechanism of an anode material that is based on a Wadsley-Roth phase. Analogue computational techniques are used to predict the electrochemical stability window of solid electrolytes and the decomposition products that are formed in redox reactions with charge carriers. With density functional methods (VASP) and forcefield simulations (LAMMPS) we assessed the electrical conductivity and the ionic conductivity of the solid electrolyte interface. The phase-dependent open-current voltages of lithium nickel oxide are calculated with a cluster expansion technique (UNCLE) and post-density functional method.



## REFERENCES

[1] M. Christensen et al. Software Platforms for Electronic/Atomistic/Mesosopic Modeling: Status and Perspectives. Integrating Materials and Manufacturing Innovation (2017), DOI:10.1007/s40192-017-0087-2.

[2] MedeA®, Materials Design, Inc., San Diego, CA, USA, 2021, <http://www.materialsdesign.com>



## Quantum Computing for Strongly Correlated Materials

Francois Jamet

National Physical Laboratory, Hampton Road, Teddington,  
Middlesex, UK, TW11 0LW

*Invited Talk*

Quantum embedding approaches for materials simulations, such as the dynamical mean-field theory (DMFT), provide corrections to first-principles calculations for strongly correlated electrons, which are poorly described at lower levels of theory. These embedding methods are computationally demanding on classical computing architectures, and hence remain restricted to small systems, limiting the scope of their applicability. Quantum computers have the potential to overcome this limitation.

In this talk, I will first give an introduction to quantum computing and then I will give an example of a quantum algorithm for materials simulation: the Quantum subspace expansion algorithm for Green's functions (arxiv:2205.00094).



## Computational Chemistry: An Industrial Perspective

Misbah Sarwar

Johnson Matthey Technology Centre, Blounts Court, Sonning  
Common, Reading, RG4 7QE

*Invited Talk*

The talk will give an overview of how multi-scale modelling combined with advanced characterization techniques are being used in industry to understand the structure and activity of catalytic materials in industry. Examples of insight gained from modelling Pt nanoparticles for PEM Fuel cells combined with electron microscopy will be presented. A case study of how combining Molecular Dynamics and QENS provides insight into the diffusion mechanism of molecules in zeolites used as SCR catalysts will also be presented.



# Predicting structure formation and transformation in low-dimensional systems via studying their energy landscapes

J. Christian Schön

\* *MPI for Solid State Research, D-70569 Stuttgart, Germany*  
*e-mail: C.Schoen@fkf.mpg.de*

***Invited Talk***

New chemical materials and compounds serve as the foundation for the modern technology of our civilization, being environmentally friendly, with stable and controllable properties, and at the same time energy efficient in their synthesis. Such materials are nowadays often grown in a bottom-up approach on a substrate, and in the extreme we are dealing with and aiming for low-dimensional systems with bespoke properties, where the stability of such materials often becomes an issue of concern. Among these systems, we find monolayers on surfaces or inside layered compounds, ultrathin films, nanotubes and nanowires, just to name a few, which are becoming increasingly important from a technological point of view.

The ability to predict such kinetically stable and/or thermodynamically (meta)stable nanomaterials, followed by a computation of their properties and evaluation of their kinetic and thermodynamic stability and possible structural transformations, is clearly of great value in their design and synthesis.[1] For the past three decades, the prediction of feasible structures and transformations of three-dimensional bulk crystalline compounds[1,2] on the one hand, and of single atom clusters[3] and (bio)molecules[4] on the other hand, has shown great progress, and the computational approaches used are expected to be also applicable to low-dimensional systems.[5,6] In this presentation, we will discuss examples of predictions of structures and their transformations using global energy landscape explorations and molecular dynamics simulations, such as quasi-zero-dimensional (e.g., compact clusters),[7,8] one-dimensional (e.g., atom chains),[9] quasi-one-dimensional (e.g., nanotubes),[9] two-dimensional (e.g., monolayers),[5,10] quasi-two-dimensional (e.g., layer-like building blocks for layered compounds),[11] and composite (e.g., multi-molecule patterns on substrates)[12,13] systems.



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[1] J. C. Schön, M. Jansen, *Angew. Chem. Int. Ed.*, 35:1286 (1996); [2] S. M. Woodley, C.R.A. Catlow, *Nature Mater.*, 7:937 (2008); [3] D. J. Wales, H. Scheraga, *Science*, 285:1368 (1999); [4] G. M. Day et al., *Acta Cryst. B*, 61:511 (2005); [5] J. C. Schön, *Process. Appl. Ceram.*, 9:157 (2015); [6] S. M. Woodley, G. M. Day, C. R. A. Catlow, *Phil. Trans. Royal. Soc. A*, 378:20190600 (2020); [7] M. Rapacioli, J. C. Schön, N. Tarrat, *Theor. Chem. Acc.*, 140:85 (2021); [8] O. A. Sanders-Gutierrez, et al., *Comp. Mater. Sci.*, 201:110908 (2022); [9] J. C. Schön, in: *Energy landscapes of nanoscale systems*, Ed: D. J. Wales, chapter 12 (Elsevier, Amsterdam, 2022); [10] R. Gutzler, J. C. Schön, *Z. Anorg. Allg. Chem.*, 643:1368 (2017); [11] A. Mahmoodabadi, M. Modarresi, J. C. Schön, in preparation; [12] S. Abb, et al., *Angew. Chem. Int. Ed.*, 58:8336 (2019) ; [13] P. Alexa, et al., *ChemPhysChem*, 20:2340 (2019)

# *MCC Member Talks*

## Temperature Dependence of Charge Mobility in Rubrene from Fragment Orbital-Based Surface Hopping

Jan Elsner\*, Jochen Blumberger

\**Department of Physics and Astronomy, UCL*

*e05-biosoft-blu*

Charge transport in high-mobility organic semiconductors (OS) operates in a difficult regime between the limits of band transport and small polaron hopping. In previous work we developed fragment orbital-based surface hopping (FOB-SH), a non-adiabatic molecular dynamics technique for propagation of charge carriers coupled to lattice vibrations in nanoscale materials. Here we apply FOB-SH to calculate the temperature dependence of the hole mobility in the representative OS rubrene and obtain an inverse power law in excellent agreement with experiment. Our simulations show that this is a consequence of increasing non-local electron-phonon coupling with increasing temperature, resulting in a steady decrease in quantum delocalization of the hole and thus mobility. We also present first extensions of FOB-SH to study the non-equilibrium dynamics of charge carriers in response to a temperature gradient giving us access to the Seebeck coefficient and to a better understanding of the thermoelectric physics of OS.

## Effect of polymer topology on the self-assembly of micelles

Raquel Lopez-Rios De Castro, Robert M. Ziolek, and Christian D. Lorenz\*

\*Department of Physics, KCL

e05-biosoft-lor

The structure of molecules has often been shown to play an important role in the function and properties of the materials that they form at various lengths and time scales. In polymer science, the choice of macromolecular structures historically has been linear and randomly branched. More recently, more controlled polymer topologies have been formulated because of the development of increasingly advanced synthetic techniques. As a result, there has been an increased interest in the role that topology plays in a variety of systems, ranging from thin films [1] to elastomers [2,3] to micelles [4,5]. While in all these investigations there are differences observed as a result of the changing topologies, very little is known as to how the molecular scale interactions of these polymers which have the same composition but just different topology result in these differences.

In this presentation, I will show our latest results of large-scale molecular dynamics simulations in which we investigate the self-assembly of a range of different polymer topologies (linear diblock, linear triblock, branched and cyclic) of poly(methyl acrylate)-poly(ethylene oxide) block polymers. In doing so, we combine graph theory and machine learning (dimension reduction and clustering) techniques to gain a unique insight into the self-assembly process of these different topology polymer molecules. Also, we provide a detailed description of how the conformations of each of these different topologies vary within the self-assembled micellar structures. With this detailed description of the structure of these micelles, one can better assess how drugs could be incorporated into nanoparticles formed by the different polymers. Additionally, with the detailed description provided by our study, we have the foundations for topology-based rational design of self-assembled polymeric nanoparticles.

**References:** [1] A. Giuntoli, A. Chremos & J. F. Douglas. (2020) *J. Chem. Phys.* **152**, 044501. [2] J. Wang, T. C. O'Connor, G. S. Grest & T. Ge. (2022) *arXiv* 2201.10498. [3] R. Jiang, Y. Chen, S. Yao, T. Liu, Z. Xu, C. B. Park & L. Zhao (2019) *Polymer* **179**, 121628. [4] S. Honda, T. Yamamoto & Y. Tezuka. (2010) *J. Am. Chem. Soc.* **132**, 10251-10253. [5] S. Honda, T. Yamamoto & Y. Tezuka. (2013) *Nat. Comm.* **4**, 1574.

## **Thermodynamics up to the melting point in a TaVCrW high entropy alloy: Systematic *ab initio* study aided by machine learning potentials**

Ying Zhou\*, Prashanth Srinivasan, Fritz Körmann, Blazej Grabowski, Roger Smith, Pooja Goddard, Andrew Ian Duff

\**Department of Mathematical Sciences, Loughborough University*

*e05-bulk-pan*

Multi-principal-component alloys have attracted great interest as a novel paradigm in alloy design, with often unique properties and a vast compositional space auspicious for materials discovery. High entropy alloys (HEAs) belong to this class and are being investigated for prospective nuclear applications with reported superior mechanical properties including high temperature strength and stability compared to conventional alloys.

Here we calculate high temperature properties of the multicomponent body-centered low-activation HEA TaVCrW with DFT accuracy using a modified version of the two-stage up-sampled thermodynamic integration using Langevin dynamics (TU-TILD) approach. The proposed approach is based on density-functional theory (DFT) and thermodynamic integration combined with machine-learning based interatomic models, and in the present work improves the computational efficiency of the standard TU-TILD method by a factor of 4. The described methodology is also relevant to potential applications of HEAs in nuclear energy, and our modified formalism is well positioned for thermodynamic property prediction and high-throughput screening of multi-principal component alloys more generally. The machine learning potentials that were fitted using *ab initio* MD are now being tested for their applicability in radiation damage studies of HEAs. The outcome of this research will be reported at the meeting.

## Thermal conductivity of radiation damaged tritium breeder materials

Megha Sanjeev\*, Mark R. Gilbert, Samuel T. Murphy

\**Engineering Department, Lancaster University*

*e05-power-mur*

In a fusion reactor, the breeder blanket is the means by which the tritium fuel required for the fusion reaction is bred. Breeder materials are subjected to irradiation by high-energy neutrons leading to the formation of defects, such as vacancies and interstitials. The presence of these defects changes the efficiency of heat transfer through the breeder blanket to the coolant, directly affecting the overall efficiency of electricity generation of the reactor. The effect of these defects on overall heat transfer depends on how they modify the underlying thermal conductivity of the materials themselves. Measuring the impact of specific types of defects on the thermal conductivity of materials is experimentally difficult to achieve. Therefore, in this study we employ atomistic simulation, principally non-equilibrium molecular dynamics (NEMD), to study the evolution of the thermal conductivity in a leading ceramic breeder blanket candidate,  $\text{Li}_2\text{TiO}_3$ .

In the first instance, we examine the perfect crystal, where the simulations indicate a high degree of anisotropy in the thermal conductivity of in the different Cartesian directions, which is attributed to the material's complex layered structure. Following this, we examine point defects that may arise due to lithium burn-up and radiation damage. We show the relationship between the stoichiometry of  $\text{Li}_2\text{TiO}_3$  and the thermal conductivity by examining both Li-rich and Li-poor cases, which respectively represent the expected beginning and end states of the ceramic breeder material. We also investigate larger defects such as voids and helium bubbles, the effects of which are studied as a function of porosity and bubble size. By examining how these defects in the material affect the thermal conductivity, we can discuss how this may impact reactor efficiency as the blanket material ages.



## **An ab initio investigation of the impact of intrinsic defects on the thermal properties of CeO<sub>2</sub>**

Thomas Smith\*, Samuel Moxon, Joshua S. Tse, Jonathan Skelton, David J. Cooke, Lisa J. Gillie and Marco Molinari

*\*Department of Chemistry, University of Huddersfield*

*e05-bulk-mol*

Cerium dioxide is commonly used as a simulant material for PuO<sub>2</sub>. This is beneficial not only experimentally as PuO<sub>2</sub> is toxic, radioactive and has high costs of post-processing, but also computationally as ceria does not require spin-orbit coupling and non-collinear magnetism, thus requiring significantly less resources. Ceria's use as a proxy is supported by both systems crystallising in the fluorite (Fm-3m) structure across a wide temperature range, and Ce and Pu both having oxidation states of 3+ and 4+. The thermal conductivity of the materials is an important property as it is associated with the performance of the nuclear fuel. Only a small difference of less than  $\sim 1 - 2 \text{ W m}^{-1} \text{ K}^{-1}$  is present across a wide temperature range of 300 - 2000 K between ceria and plutonia. As the harsh conditions imposed on nuclear fuels result in the formation of defects such as point defects and more complex Frenkel and Schottky defects, here we focus on the latter two as they will have an impact on the thermal conductivity of the material. We employ a DFT+U approach to investigate the thermophysical properties of defective ceria systems, to evaluate their phonon dispersions using a band unfolding methodology, and finally to calculate the thermal properties using the constant relaxation time approximation.

## BN doped PAHs – Towards 2D molecular recognition

Jack Warren\*, Andrew Logsdail, Alberto Roldan, Davide Bonifazi

\*Cardiff Catalysis Institute, Cardiff University

e05-nano-rol

Boron-nitride is isoelectronic to  $sp^2$  bonded carbon, as a BN and CC bonds contain the same number of electrons; furthermore, monolayer hexagonal BN (h-BN) is isostructural to graphene, both consisting of a uniform hexagonal lattice. h-BN is a wide-gap semiconductor, with an electronic bandgap in the UV region of 4.0-5.8 eV<sup>1</sup> with applications as a dielectric substrate material, an insulator, or as a thermal conductor<sup>2</sup>. Introducing BN sub-units to polyaromatic carbon molecules and extended graphene sheets is thus relatively accessible and can change the band gap and creates an electron poor hole in the surface of the graphene that could be complimentary for the adsorption of electronegative aromatic moieties.

2-8-14-trixylyl-hexaphenyl borazinocoronene was synthesized by our collaborators and was found to crystallise in the presence of aromatic species such as halogenated benzenes. The halo-benzene molecules within these crystals were found by x-ray crystallography to possess multiple common orientations. Should these orientations be separated by a suitable energy barrier then these crystals could be the foundation of a data storage device. Additionally, should a change in orientation change the bandgap of the coronene then perhaps these materials could also be used as molecular sensors.

In this study, we explore the interactions occurring in the co-crystal of 2-8-14-trixylyl-hexaphenyl borazinocoronene +  $C_6H_5X$  to determine the viability of BN-doped PAHs to be used for 2-D molecular recognition. We study the analogous non-doped coronene to determine the properties introduced by the borazine and then model the interactions occurring in both crystal systems. We also model the rotations of the halogenated benzenes to study the PES inside the crystal and evaluate the barriers of rotation. We find potential energy minima in our system that corresponds to the different occupancies in the crystal structures and evaluate the thermodynamic stability of those orientations. With this knowledge we will gain critical insight into the suitability of these materials as possible data storage material.

1 Y. N. Xu and W. Y. Ching, *Phys. Rev. B*, 1991, **44**, 7787–7798.

2 H. Wang, T. Taychatanapat, A. Hsu, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero and T. Palacios, *IEEE Electron Device Lett.*, 2011, **32**, 1209–1211.

## Chlorine Activated Stacking Fault Removal Mechanism in thin Film CdTe Solar Cells: the missing Piece

Pooja Goddard\*, Peter Hatton, Michael J. Watts, John M. Walls, Ali Abbas, Roger Smith

\*Department of Chemistry, Loughborough University

e05-surfin-pan

The conversion efficiency of as-deposited, CdTe solar cells is poor and typically less than 5%. A CdCl<sub>2</sub> activation treatment increases this to up to 22%. Studies have shown that stacking faults (SFs) are removed and the grain boundaries (GBs) are decorated with chlorine. Thus, SF removal and device efficiency are strongly correlated but whether this is direct or indirect has not been established. Here we explain[1] the passivation responsible for the increase in efficiency but also crucially elucidate the associated SF removal mechanism. The effect of chlorine on a model system containing a SF and two GBs is investigated using density functional theory. The proposed SF removal mechanisms are feasible at the 400°C treatment temperature. It is concluded that the efficiency increase is due to electronic effects in the GBs while SF removal is a by-product of the saturation of the GB with chlorine but is a key signal that sufficient chlorine is present for passivation to occur.

[1] Hatton et al, *Nature Communications*, 2021, 12(1), 4938

## Understanding nucleation of Co and Mn nanoclusters on anatase (101) surface

Pavel V. Stishenko\*, Andrew J. Logsdail

\*School of Chemistry, Cardiff University

e05-surfin-log

Cobalt-base catalysts on anatase support are widely used for Fischer-Tropsch synthesis. Knowing and controlling the size of Co nanoparticles is crucial for selectivity of the synthesis process. Recently, the addition of Mn as a promoter has been demonstrated to change the catalyst's selectivity, although the mechanism of this effect is still unclear. Characterisation studies have revealed that the presence of Mn during catalyst production significantly reduces the average size of metal nanoparticles, drawing a conclusion that the particle nucleation process is probably affected by Mn.

To examine the interactions of Co and Mn adatoms on the TiO<sub>2</sub> anatase surface, we have explored energy landscape of single-atom and two-atom clusters on the prominent (101) facet. The meta-GGA approximation of the density functional theory was employed, as implemented in the FHI-aims software. Comprehensive enumeration of probable adsorption sites was performed with subsequent geometry and spin optimisation. Pairs of adatoms placed in adjacent adsorption sites were enumerated with the SuSMoST code, and subsequently energetic quantities studied with FHI-aims. The calculations revealed that Co and Mn adatoms energetically prefer to form heterogeneous two-atom clusters., and that Mn adatoms seem to be less mobile than Co ones. Therefore, we conclude that the introduction of Mn adatoms results in reduced diffusion of Co adatoms, which hinders ripening and coalescence of catalyst's nanoparticles; the reduced coalescence results in smaller nanoparticle size and higher dispersion.

### References:

1. V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Computer Physics Communications*, 2009, 180, 2175–2196.
2. S. S. Akimenko, G. D. Anisimova, A. I. Fadeeva, V. F. Fefelov, V. A. Gorbunov, T. R. Kayumova, A. V. Myshlyavtsev, M. D. Myshlyavtseva and P. V. Stishenko, *J Comput Chem*, 2020, 41, 2084–2097.

## Chiral valley phonons and flat phonon bands in moiré materials

Indrajit Maity\*, Arash A. Mostofi, Johannes Lischner

*\*Department of Materials, Imperial College London, UK.*

*e05-surfin-lis*

A chiral object is not the same as its mirror image. The chirality of quasiparticles is a critical concept behind many modern developments in condensed matter physics. Some recent examples include Klein tunnelling and the chiral magnetic effect due to chiral Fermions. Using detailed atomistic simulations, we show that multiple phonon modes in twisted bilayers of WSe<sub>2</sub> can be chiral [1]. We demonstrate distinct chiral behavior of the K/K' valley phonons for twist angles near 0 and 60 degrees. Furthermore, we observe the flattening of bands near the phononic bandgap edges in this system. We find that a finite phonon angular momentum can be generated by applying a temperature gradient in this system [2]. We discuss the possibility of using different optical spectroscopy techniques to probe these chiral phonons. Our findings, which are more generally applicable to moiré systems created from 2D materials that break inversion symmetry, have important implications for understanding electron-phonon and exciton-phonon scattering and for designing phononic crystals.

[1] I. Maity, Arash A. Mostofi, J. Lischner, Phys. Rev. B Letters, 105 L04140 (2022).

[2] S. Mandal, Arash A. Mostofi, J. Lischner, M. Jain, I. Maity, under preparation.

## Phosphate adsorption on {111}, {110}, and {100} surfaces of ceria: A DFT study

Khoa Minh Ta\*, Samuel Moxon, Marco Molinari

*\*Department of Chemistry, University of Huddersfield*

*e05-surfin-mol*

Ceria nanoparticles (CeNPs) are nanozyme that exhibit enzyme mimetic activities (e.g. superoxide dismutase, catalase, phosphatase). Such activities are hindered by the adsorption of bodily electrolytes at the surfaces of CeNPs when in contact with biological media. A strong bodily electrolyte is the phosphate ion and here we study its interaction with the three most stable {111}, {110}, and {100} surfaces of ceria using Density functional theory (DFT) calculations. We found that the preferential facet for phosphate adsorption follows {100} > {110} > {111}. An adsorbed 5-fold coordinated P species is also seen and calculated as a stable intermediate, suggesting that this species could be responsible for the early stages of the scavenging of ceria surfaces, a process known experimentally that sees the transformation of ceria into cerium phosphate. The IR and Raman spectra are evaluated for all the most stable adsorption configurations showing that the main vibrational fingerprint for the ceria-phosphate interaction is between 500 and 1100  $\text{cm}^{-1}$ .

## The thermoelectric properties of Polyaniline-SrTiO<sub>3</sub> composites

Nathan D. Wood<sup>\*1</sup>, Joshua S. Tse<sup>1</sup>, Jonathan M. Skelton<sup>2</sup>, David J. Cooke<sup>1</sup>, Lisa J. Gillie<sup>1</sup> and Marco Molinari<sup>1</sup>

*\*Department of Chemistry, University of Huddersfield*

*e05-surfin-coo*

Oxides are well-explored materials for thermoelectric (TE) applications. However, they are currently limited to higher temperature applications (> 700 K) in part due to their high thermal conductivity ( $\sim 1 - 10 \text{ W m}^{-1} \text{ K}^{-1}$ ) at lower temperatures. TE devices allow the direct conversion of heat into electricity and as such will play a critical role in the sustainable and green energy generation. The performance of a TE materials is gauged using the figure of merit,  $ZT = S^2\sigma T/\kappa$ , which includes the Seebeck coefficient  $S$ , the electrical conductivity  $\sigma$ , and the thermal conductivity  $\kappa$ . An oxide of great promise is SrTiO<sub>3</sub> but its applicability as low temperate hinders its applications ( $\kappa = 9\text{--}12 \text{ W m}^{-1} \text{ K}^{-1}$  at room temperature). Decreasing  $\kappa$  can be achieved through several methods: doping, nanostructuring and nanocompositing. Doping SrTiO<sub>3</sub> has been shown to lead to improvements in both  $\sigma$  and  $\kappa$ , whilst nanostructuring has been shown to be a less effective strategy for reducing  $\kappa$  compared to other oxides. Therefore, recent work has moved towards nanocompositing, i.e. generating composites of SrTiO<sub>3</sub> using conductive polymers or graphene. The introduction of these materials creates an interface that can scatter phonons and/or induce quantum effects, which lead to an enhancement of the thermal and electrical TE properties. Our research explores the structural and TE properties of the interface between the most stable surface {100} of SrTiO<sub>3</sub> and polyaniline in its various oxidation states using a DFT+U methodology and energy minimisation techniques.

## Obtaining Interfacial Free Energies from Atomistic Simulations using an Einstein Crystal Reference State

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*e05-surfin-har*

We present a general method for computing interfacial free energies from atomistic simulations which is particularly useful for solid/liquid interfaces. Our method uses an Einstein crystal as a universal reference state and is more flexible than previous approaches [1]. Surfaces with dipoles, complex reconstructions, and partially dissolved species are all easily accommodated within the framework. It may also be extended to calculating the relative free energy of different phases and other types of defect. We tested our method by calculating the interfacial free energy of NaCl with water and obtained a value of 0.13 J/m<sup>2</sup>, in line with previous work. We have applied our method to interfaces of bassanite and gypsum with water and predicted equilibrium morphologies for bassanite and gypsum that compare well with experiments and previous calculations. Results for calcium carbonate and potassium nitrate will also be presented.

[1] Stephen Yeandel, Colin Freeman and John Harding; J. Chem. Phys. (in press) (2022); <https://doi.org/10.1063/5.0095130>



## Towards Modelling Realistic WS<sub>2</sub>/H<sub>2</sub>O/SiO<sub>2</sub> Interfaces

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e05-surf-in-shl

Transition Metal Dichalcogenides (TMDs) are widely studied 2D materials with applications in photovoltaics and transistors [1]. These thin materials are transferred onto insulating substrates such as SiO<sub>2</sub> for use in electronic devices. However, the transfer method is known to affect the optical properties of TMDs, with mechanical exfoliation methods increasing the band offsets between the TMD and SiO<sub>2</sub> substrate [2]. Mechanical exfoliation occurs in ambient conditions thus, the SiO<sub>2</sub> substrate will have water adsorbed to the surface. Therefore, we explore the effect of confined water trapped between the SiO<sub>2</sub> substrate and WS<sub>2</sub>. Three interfaces were built and optimized explicitly with 1, 2, and 3 water layers present using molecular dynamics (MD), density functional theory (DFT), and ab-initio MD (AIMD). AIMD allowed us to sample more configurations at 400 K to avoid over-structuring water. The electronic properties of the interface, such as band gaps and band alignment, were investigated using DFT. Overall, we show there is a change in band offset depending on the amount of water present. Understanding the effect of water will be critical in understanding the functioning of 2D materials in electronic devices and understanding experimental results.

[1] Choi, W. et al. *Materials Today* 20, 116–130 (2017)

[2][ Afanas'ev, V. v. et al. *Nanotechnology* 30, (2019)

## Approximating Many-Electron Wave Functions using Neural Networks

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*e05-bulk-fou*

Given access to accurate solutions of the many-electron Schrödinger equation, most of condensed matter physics, chemistry and materials physics could be derived from first principles. Exact wave functions of systems with more than a few electrons are out of reach because they are NP-hard to compute in general, but approximations can be found using polynomially scaling algorithms. The key challenge for many of these algorithms is the choice of an approximate parameterized wave function, which must trade accuracy for efficiency. Neural networks have shown impressive power as practical function approximators and promise as a way of representing wave functions for spin systems, but electronic wave functions have to obey Fermi-Dirac statistics. This talk introduces a deep learning architecture, the Fermionic neural network, which is capable of approximating many-electron wavefunctions and greatly outperforms conventional approximations. The use of FermiNet wave functions boosts the accuracy of the simple and appealing variational quantum Monte Carlo method until it rivals the very best conventional quantum chemical approaches.

# Anharmonicity and entropic stabilisation in zirconia from first principles

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*e05-bulk-wal*

Stability of high temperature phases is of continuous importance in solid state chemistry with many materials exhibiting exciting properties in their high temperature polymorphs. However, their discovery is largely serendipitous due to a lack of computational methods to predict high temperature stabilities.

Here, we investigate the high temperature stability and properties of zirconia, which is one of the most studied oxide ceramics, using anharmonic phonon theory and ab initio molecular dynamics simulations.

Applying self-consistent phonon theory including quasi-particle corrections, we show how the soft-mode cubic-to-tetragonal phase transition develops. However, anharmonic free energies at the current level of theory are unable to predict the reverse transition upon heating.

Based on molecular dynamics simulations, we show that the cubic polymorph is likely to be stabilised due to spontaneous defect formation, which is also the driving force for the well-known ionic conductivity at high temperatures.

## Exploring the Nanoparticle Exsolution Process in Perovskite Oxide

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*e05-bulk-par*

The creation of socketed metal nano-particle through dopant exsolution from complex perovskite oxides has attracted significant interests over the past few years in the field of solid state ionics. Compared to deposited metal nano-particles, these exsolved nano-particles retain good catalysis performances but are more resilient towards coking and delamination/agglomeration during cycling. Thus, these durable exsolved nano-particles have many promising applications, like in chemical looping devices and anodes of solid oxide fuel/electrolyser cells (SOCs).

Despite its great application potential, the mechanism behind the nano-particle exsolution process is not yet clear. Earlier theoretical efforts have shown that the migration of the transition metal dopants towards the perovskite surface are thermodynamically favourable. However, these findings cannot explain the highly reducing condition (5% H<sub>2</sub>/Ar mixed gas) and high temperature (above 950°C) required to activate the exsolution process in experiments. In this work, atomistic simulation methods were applied to two typical perovskite systems, (La, Sr)<sub>1-x</sub>(Ni, Ti)O<sub>3-d</sub> and (La, Ca)<sub>1-x</sub>(Ni, Ti)O<sub>3-d</sub>, to study the kinetics of the metal cation migration during exsolution. We have shown that the introduction of A-site deficiency greatly reduces this barrier and makes cation migration viable under reported experimental conditions. Furthermore, we have evaluated a number of factors possible to affect the diffusion kinetic and identified what might be effective to ease the exsolution condition, and provide insights for future optimisation to utilize this exsolution process better.

## The Impact of E Field on Defect Generation and Migration Processes in Dielectrics

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*e05-bulk-shl*

The interaction between electric fields and metal oxides is of fundamental importance to develop accurate models of dielectric breakdown. In this talk, we demonstrate the use of hybrid density functional theory, implemented in CP2K<sup>[1]</sup>, to calculate how an applied electric field<sup>[2]</sup> affects the generation of oxygen Frenkel pairs in monoclinic (m-) HfO<sub>2</sub>. We find that, within a linear regime, the electric field modulates the barrier height by a simple dot product between the electric field intensity and the zero-field electric dipole at the transition state, similar to previous results for MgO<sup>[3]</sup>. Even at breakdown fields, barriers for Frenkel pairs generation exceed 6 eV in the perfect m-HfO<sub>2</sub> lattice. Injection of extra electrons from electrodes significantly lowers the barriers for creation of defect pairs (DPs), which are further reduced by the field to around 2 eV. We find the existence of electrons in a trap state not only reduces the activate energy of the generation process, but also opens up new reaction pathways which have even lower (1.5 eV, 0.8 eV) activation energies, making vacancy generation at room temperature physically feasible. Our calculation therefore show that electron injection is a vital part of the oxygen vacancy generation mechanism in m-HfO<sub>2</sub>. While bias application facilitates the injection of electrons into the oxide, these extra electrons facilitate the creation of O vacancies and the energy barrier for this process is, in turn, also lowered by the field. The field also affects the rates of electron transfer through O vacancies and diffusion of O vacancies and interstitial ions. The investigation of the diffusion of O interstitial ions through multiple migration pathways demonstrates that the rapid diffusion of O ions in pristine m-HfO<sub>2</sub> is only possible within the 3C oxygen lattice.

[1] VandeVondele, Joost, et al. *Computer Physics Communications* 167.2 (2005): 103-128.

[2] Souza, Ivo, Jorge Íñiguez, and David Vanderbilt. *Physical review letters* 89.11 (2002): 117602.

[3] El-Sayed, Al-Moatasem, et al. *Physical Review B* 98.6 (2018): 064102.

## Investigating the Structure and Stability of PdZn Bi-Metallic Alloys by Coupling Density Functional Theory and Cluster Expansions

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*e05-surfin-log*

Metals alloys are known to improve the performance of heterogenous catalysts for many different reactions, such as CO<sub>2</sub> hydrogenation [1,2]. Predicting an effective and novel catalyst, by computing combinations of elements and compositions using Density Functional Theory (DFT), is expensive and highly time-consuming. To accelerate the discovery process, one can couple DFT with cluster expansion (CE), which we demonstrate here in the identification of an effective and novel catalyst for CO<sub>2</sub> hydrogenation. We focus on the PdZn (101) and (110) facets, which are most stable for binary alloys, and CE models for both of facets were tested in the concentration range where the body-centred tetragonal (BCT) phase exists, which is from 40 to 50 % Zn concentration. Our results show that higher Pd concentrations are predicted for both facets in the sub-surface while the top layers remain chemically ordered in a 1:1 alloy; the behavior changes outside the stable BCT range, where segregation of Zn on the top surface is predicted for Zn concentrations above 50 %. The outcomes highlight the critical importance of CE approach for determining structure–property relationships and accelerating the discovery and design of surfaces and nanostructured materials.

[1] G. A. Olah, *Angew. Chem., Int. Ed.* (2005), 44, 2636.

[2] F. Brix et al., *The Journal of Physical Chemistry Letters* 2020 11 (18), 7672-7678

# Computational design of *green* ternary semiconductors for optoelectronic applications

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*e05-discov-fil*

Perovskites based on lead halide are one of the most promising contenders for different optoelectronic applications. Despite rapid progress, their inherent toxicity and stability issues still remain to be resolved. To mitigate these problems, different approaches such as cation mixing, anion mixing, or doping have been investigated. These studies have generated a parallel interest in the design and discovery of green materials made of abundant, inexpensive and environmentally friendly chemical elements. We pursue this search by identifying recurrent structural templates other than perovskites.

Through combination of high-throughput methodology and DFT studies, we identified several new structural templates. A further analysis on few selected templates based on Cu and Zn led to several promising candidates. There has been a recent report on the synthesis of  $\text{RbCu}_2\text{Cl}_3$  [1].

We acknowledge funding support from EPSRC (EP/V010840/1) and ARCHER2 Supercomputing Service.

[1] E. N. Kovalenko *et al.* *Low Temp. Phys.* 47(427), 2021

## Crystal structure predictions of organic halide salts

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e05-discov-day

The ability to predict the crystal structures of a given material from its chemical composition has been a long-standing goal of the computational community. With the help of the blind test studies hosted by the CCDC, significant developments in crystal structure prediction (CSP) methodologies of organic molecular materials have been made which typically involve a form of global search of the lattice energy surface. It is now possible to generate accurate crystal structure landscapes for quite complex and (often) polymorphic systems, including pharmaceutical molecules, multi-component crystals and even solvates. However, despite these achievements there is still significantly less progress in the prediction of salt structures.

As part of an on-going collaboration aimed at the discovery of porous molecular crystals, we will demonstrate a workflow that we have used in our research group for performing CSP studies on a series of organic halide salts. We will show that in many cases, we are able to predict the experimental crystal structure of different polymorphs and have been successful in elucidating the crystal structures of some salts for which only an experimental powder x-ray diffraction pattern could be obtained.



## Ab initio study of the Para-xylene Oxidation Redox Cascade

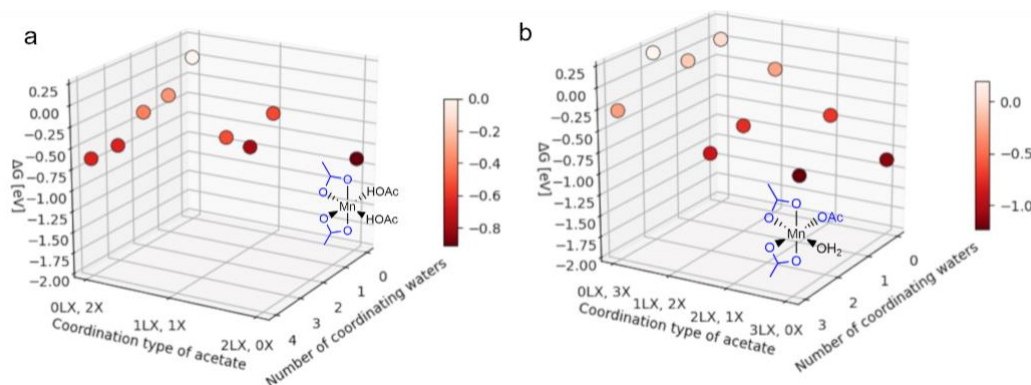
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e05-react-log

The industrial oxidation of para-xylene to terephthalic acid uses a homogenous Co/Mn/Br catalyst in aqueous acetic acid solvent under elevated temperatures and pressures. [1] The oxidation process is of significant commercial value as terephthalic acid is an intermediate used in the production of polyethylene terephthalate (PET), which meets 7% of the global plastic demand, including 62% of plastic bottles. [1] The process engineering and kinetics aspect of the para-xylene oxidation process is well understood, and there is a strong correlation between the structure of the catalyst and its activity; [2] however, there is little knowledge of the actual catalyst structure under operating conditions. To aid in elucidating the catalyst structure, computational modelling has been used here to assess the thermodynamic stability of possible manganese and cobalt complexes; redox potentials are also calculated, in an aim to relate the structure of the catalyst to its activity.

To derive the thermodynamic stability of the catalysts, changes in Gibbs' Free Energy ( $\Delta G$ ) for substituting inner-sphere ligands were evaluated using density functional theory (DFT). [3] The Mn(II) and Mn(III) species with the lowest  $\Delta G$  coordinate zero and one waters, respectively, as shown in Figure 1. The low number of waters coordinating to Mn(III) facilitates inner-sphere bromide coordination, allowing for efficient electron transfer. [2] The analogous results for the Co(II) and Co(III) species suggest both coordinate zero water ligands, which implies reduced thermodynamic driving force for ligand rearrangement when compared to the Mn complexes. Coupling the results with calculated Mn(II/III) reduction potentials aids in understanding the active form of bromide involved in the catalysis. Figure 1:  $\Delta G$  landscape for the speciation of the (a.) Mn(II) and (b.) Mn(III) catalysts, with the schematics of the most thermodynamically stable structures shown.  $\Delta G$  are calculated assuming a solvent environment of 34.6 mol% water in acetic acid and industrial operating conditions of  $T = 473$  K and  $P = 2.25$  MPa.  $\Delta G$  are normalized against the values for the neutral acetates, giving  $\Delta G = 0$  for these species.



[1] R. Zhang, X. Ma, X. Shen, *Journal of Environmental Management*, 2020, **260**, 110062

[2] R. Taylor, D. Housley, M. Barter, A. Porch, K. Whiston, A. Folli and D. Murphy, *Catalysis Science and Technology*, 2022.

[3] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Computer Physics Communications*, 2009, **180**, 2175–2196.

## Interatomic-potential-based Computational Approaches for Modelling Defect Chemistry and Surface Oxidation of Solid Materials

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e05-react-sok

Atomistic simulations using interatomic potentials (IPs) have long been playing an active role in disentangling the mysteries in materials science, especially for understanding complex materials and interfaces that are computationally too demanding for electronic-structure calculations. We presented several recent advances in modelling defects and surface oxidation dynamics using IP-based approaches. Polarisable shell-model IPs are widely used for modelling charged defects at the dilute limit in solids using the Mott-Littleton approach and hybrid QM/MM embedded-cluster techniques. Recently, we proposed a novel IP development scheme assisted by the QM/MM approach that, for the first time, unifies the predictions of different charged states of intrinsic defects in CeO<sub>2</sub> between the Mott-Littleton approach and QM/MM calculations using hybrid DFT functionals. The new IP accurately reproduces a wide range of physical, chemical, and thermodynamical properties of CeO<sub>2</sub>, showing excellent agreement with experimental and DFT references. These findings offer opportunities for accurate large-scale modelling of the partial reduction behaviour and nonstoichiometry in CeO<sub>2</sub>, as well as a prototype for developing robust shell-model IPs for other imperfect crystals.<sup>1</sup> Besides, the reactive force-field (ReaxFF) provides a cost-effective framework for modelling the dynamics of chemical reactions in a wide range of systems. Using ReaxFF-based molecular dynamics (MD) simulations, we elucidated the distinct oxidation mechanisms of nanomaterials, including nanoparticles, nanowires, and two-dimensional materials, which can be significantly different from their bulk counterparts and result in various novel oxide nanostructures with unique properties.<sup>2-4</sup> These results demonstrate the critical role of IP-based techniques in extending the modelling time- and length-scales towards a more realistic description of defect chemistry and surface reactions.

1. X. Zhang, C. Richard A. Catlow, Alexey A. Sokol *et al.*, *in preparation*.
2. X. Zhang, *et al.*, *Materials & Design*, 2022, 110605.
3. X. Zhang, *et al.*, *ACS Nano*, 2019, 13, 3005-3014.
4. X. Zhang, *et al.*, *Applied Surface Science*, 2020, 504, 144437.

## A mechanism for the CO<sub>2</sub>-to-CO conversion catalysed by carbon monoxide dehydrogenase

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e05-react-**ter**

The carbon monoxide dehydrogenase enzyme efficiently converts CO<sub>2</sub> to CO and, therefore, could enable an affordable CO<sub>2</sub> recycling strategy. The reduction of CO<sub>2</sub> occurs at a peculiar nickel-iron-sulfur cluster, following a mechanism that remains little understood. In this study, we have used ab initio molecular dynamics simulations to explore the free energy landscape of the reaction. We predict the existence of a COOH ligand that strongly interacts with the surrounding protein residues and favours a mechanism where a H<sub>2</sub>O molecule is eliminated before CO. We have taken advantages of the insights offered by our simulations to revisit the catalytic mechanism and, in particular, the role of the residues surrounding the active centre, thus assisting in the design of inorganic catalysts that mimic the enzyme.

## Localised thermal levering events drive spontaneous kinetic oscillations in catalysis

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e05-react-cat

A combination of computational and experimental techniques have been used to rationalise the origins of oscillations in CO oxidation products over Rh/Al<sub>2</sub>O<sub>3</sub> catalysts, under *in-operando* conditions. *State-of-the-art* spectroscopy techniques have allowed for temporal and spatial fine scale resolution of CO oxidation, with both DRIFTS and XANES analysis pinpointing the relative changes in absorbed species during time “on-line”. When combined with *in-situ* mass spectrometry a highly resolved picture of coupled oscillations in CO oxidation and CO<sub>2</sub> production emerged. Periodic DFT techniques were then applied to rationalize these experimental observations, with the use of both the PBE and SCAN functionals in combination with plane-wave basis sets. Surface mediated reaction profiles were calculated for each of the low-index surfaces of Rh for the following reactions: (1) carbon oxidation, (2) CO oxidation and (3) Boudouard reaction. It was found that with a high barrier of >2.5 eV, the Boudouard reaction was kinetically inaccessible under reaction conditions; however, the CO oxidation barriers of between 0.63-1.35 eV could be accessed at around 300K. Additionally, the localised release of ~2.9 eV for CO oxidation may enable a coupled subsequent Boudouard reaction step that would regenerate surface binding sites for CO through a highly exothermic carbon oxidation step. Therefore, our combined experimental/computational results are consistent with our proposed localised leveling phenomenon, whereby CO oxidation is a precursor to coupled Boudouard and carbon oxidation steps. This work offers an important proof of concept, where turning of thermally coupled reaction mechanisms at the nanoscale is possible and may be harnessed toward novel chemical routes.

# The Wadsley-Roth Materials Family as Functional Energy Materials

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*e05-power-cor*

The Wadsley-Roth (W-R) family of materials is made up of transition metal oxides mainly composed of Tungsten, Titanium and Niobium and are thought to be highly disordered. Members of the W-R family are defined by their structure based on  $\text{ReO}_3$  – type blocks, which stack to form blocks of corner-sharing octahedra of size  $(m \times n)$  delimited by crystallographic shear planes (CS) and are connected to each other via edge-sharing. Block units connect infinitely in directions perpendicular to the  $(m \times n)$  plane. Tetrahedral sites can also be present in the same plane as the blocks to fill voids. An index was created to classify these materials depending on their type of block structure.

Over recent years, these materials have gained much interest from the scientific community. However, publications almost systematically study these materials individually (i.e. interest in a particular composition) rather than as a family of materials. This has led to the properties of the W-R family remaining unknown, for the most part, especially in terms of how the block structure can influence electronic and insertion properties, for example. Typically, one would dope such materials in an aliovalent fashion to bolster their electronic properties such as electronic conduction and charge carrier migration, for example. However, with the difference in Oxygen to Metal (O/M) ratio between structures of the W-R family being quite small, it proves to be an arduous task to identify which compound is synthesised. Furthermore, it is not clear whether doping through traditional methods for these materials (annealing to include oxygen vacancies etc.) would be effective here as a phase transition from a doped compound to a defect-free block structure is possible thanks to the proximity in O/M ratio values between different W-R members.

With no current or past studies on the relationship between structure and electronic properties in W-R compounds, it is impossible to predict which methods will be more effective than others to better these promising materials and thus leaves researchers to the time-consuming method of trial and error. For this reason, I have endeavoured throughout my PhD research to be able to present the first comprehensive computational prediction study on the W-R materials as energy materials and, more importantly, on the relationship between structure and electronic performance and how these are transferrable across the entire W-R family. This research was carried using HF-DFT methods and the GTO-based code CRYSTAL17, thus also rendering it a higher precision study than all the few computational studies concerning W-R materials in the materials' community literature.

## **Molecular Dynamics Simulations of Radiation Damage in High Temperature Superconductors**

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*e05-power-mur*

The advent of high-temperature superconductors (HTS) with high field strengths offers the possibility of building smaller, cheaper magnetically confined fusion reactors. However, bombardment by high energy neutrons ejected from the fusion reaction may damage the HTS tapes and impair their operation. Recreating the conditions present in an operational fusion reactor is experimentally challenging, therefore, this work uses molecular dynamics simulations to understand how radiation modifies the underlying crystal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . To facilitate the simulations a new potential was developed that allowed exchange of Cu ions between the two symmetrically distinct sites without modifying the structure. Radiation damage cascades predict the formation of amorphous regions surrounded by regions decorated with Cu and O defects found in the CuO-chains. The simulations suggest that the level of recombination that occurs is relatively low, resulting in a large number of remnant defects and that there is a no substantial temperature effect

## Surprising improvement of SnS<sub>2</sub> properties through superlattice formation for battery applications

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*e05-power-hep*

In order to address the ever-increasing demand for better battery materials, we present a study exploring the potential of multi-layered superlattice made from 2D materials to understand the benefits and drawbacks such layered materials could have as potential electrodes.

Layered materials have demonstrated promise as electrode materials due to their interlayer spacing allowing for easy lithium intercalation and diffusion, and SnS<sub>2</sub> has in particular shown promise as an electrode material. Unfortunately, whilst this material has exhibited fast rates and high capacities, this results in the consumption of the layered SnS<sub>2</sub> structure. However, recent techniques have allowed the development of novel materials formed by superlatticing with other layered materials.

Using first-principles density functional theory, we show the properties of SnS<sub>2</sub> can be enhanced through combination with other layered materials in a superlattice structure. In particular, we explain how the properties vital to a successful working electrode (such as the open-circuit voltage, electrical conductivity and volumetric expansion) can be predicted from those of the components, offering improvements over those of SnS<sub>2</sub> itself. Using thermodynamic arguments, we are able to comment on the stability of these materials during cycling and ultimately predict the final lithium capacities, something that is vital for maximising the overall energy density of a battery. With these, we also identify a further improvement in the thermodynamic stability arising from superlattice formation, where the resultant lithium storage capacity is dramatically higher than that possible with either of the component materials.

## Intrinsic Defect Study on High-voltage Spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as Cathode Material for Li-ion Batteries

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*e05-power-dos*

High-voltage spinel  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  (LMNO) is a promising cobalt-free cathode material which can deliver high energy density ( $650 \text{ W h kg}^{-1}$ ) due to its high operating voltage  $\sim 4.7 \text{ V}$  (vs  $\text{Li}^+/\text{Li}$ ) arising from the  $\text{Ni}^{2+}/\text{Ni}^{4+}$  couple. The material can be synthesized with varying degree of cation disorder, and they have different electrochemical performance. Cation disordering is usually accompanied by the formation of oxygen vacancies and  $\text{Mn}^{3+}$  species, making it challenging to rationalise the most significant factors towards designing LMNO with optimum electrochemical performance.

This presentation will share the latest scientific findings on the defect chemistry of the ordered phase  $P4_332$  LMNO where we used density functional theory to predict the defect formation energy of all possible intrinsic defects under various synthesis conditions. We find that most defects are deep and small polarons are formed, generating  $\text{Mn}^{3+}$ ,  $\text{Mn}^{2+}$  (*n*-type) and  $\text{Ni}^{3+}$  (*p*-type) species. The cation disordering behaviour can be explained by the low formation energy of antisite defects. Our work provides explanations for experimental observations and guidelines for defect-controlled synthesis.



# *Posters*

## The development of ab-initio and force-field models to analyze colorants in cultural heritage

Ian Shuttleworth

*School of Science and Technology  
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*e05-surfin-shu*

Theoretical and computational investigations can productively contribute to the understanding of how the materials in cultural heritage age. Within this field, force-field and molecular dynamics techniques are set to establish themselves as powerful complementary approaches to the experimental analysis of the structure-property relationships of colorant materials i.e. dyes, lakes and pigments, where large computational unit cells are required to realistically describe the experimental system.

The current work uses a combination of first-principles and molecular dynamic approaches to formulate accurate, predictive models of these systems. The investigations have initially focused on developing a reliable and robust force-field description of key compounds including red lead ( $\text{Pb}_3\text{O}_4$ ), mercury (II) sulphide  $\alpha\text{-HgS}$  (vermillion) and arsenic sulphide  $\alpha\text{-As}_4\text{S}_4$  (realgar). The predictions of the force field descriptions of these systems have then been benchmarked against ab-initio un-defected and the far more intricate - though much more realistic - defected trial sets.

The dilemma in this development is the trade-off between transferability and accuracy. Large-scale model screening is a powerful tool to analyse experimental data but can involve significant compromises or approximations. The doubt caused by these factors will be discussed together with strategies that have been developed to quantify and minimize this error. Some discussion of the predictive and interpretive power of these models and to explain the aging and wearing phenomena sadly seen in painted art will be presented.

## Accurate modelling of defective TiO<sub>2</sub> surfaces

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\*Department of Chemistry, Cardiff University

e05-surfin-log

As part of an EPSRC-funded Prosperity Partnership titled “Sustainable Catalysis for Clean Growth”, which focuses on catalytic solutions to reaching Net-Zero 2050, the properties of transition metal oxides (TMO) are important knowledge for applications as catalyst supports. TMOs, such as TiO<sub>2</sub>, are widely used to support metal nanoparticles due to a range of metal-support interactions that can be tuned to optimise catalytic performance; examples include charge transfer, geometric reconstruction and defect formation <sup>1</sup>. The tunability creates a multifunctional catalyst with possible active sites on the support, at the metal-support interface and on the metal sites <sup>2</sup>. Consideration of all the active sites is crucial in the design of materials that will enable the transition to Net-Zero 2050, particularly in the conversion of CO<sub>2</sub> to useful products such as methanol, ethanol, formic acid and formaldehyde.

TMO catalysts have been widely studied using computational approaches, such as Hubbard-corrected Density Functional Theory (DFT+U), where the choice of the exchange correlation functional and the magnitude of Hubbard correction are crucial contributors in ensuring an accurate representation of the material’s geometry, electronic structure and energetics. However, a thorough justification of the DFT parameters is often overlooked and so calibration of relevant DFT parameters is presented here with respect to bulk rutile and anatase TiO<sub>2</sub>, and surface anatase TiO<sub>2</sub> models with (101) and (001) crystallographic planes. After establishing the optimal parameters, defects, particularly oxygen vacancies, are considered in bulk and at surfaces to ascertain whether the DFT+U methodology is required and what magnitude of U value is suitable. Comparison of DFT-computed structural and electronic properties with experimental literature allows optimisation of the U parameter, which we discuss further. The results are a foundation for future computational work regarding the reactivity of TiO<sub>2</sub>-supported catalysts.

### References

1. X. Du, Y. Huang, X. Pan, B. Han, Y. Su, Q. Jiang, M. Li, H. Tang, G. Li and B. Qiao, *Nat. Commun*, 2020, 11, 5811.
2. S. Kattel, P. Liu and J. G. Chen, *J. Am. Chem. Soc.*, 2017, 139, 9739-9754.

## A First Principles Study of the $\Sigma 3$ {111} Twin Boundary in BaTiO<sub>3</sub>

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e05-surfin-mck

Ferroelectric materials have become an essential part of the modern world, found in capacitors for microelectronics, actuators, ultrasonic medical devices, and power storage devices. The behaviours and properties of these materials however are impacted by complicated extended defects such as grain boundaries. Using the VASP code, as well as PBEsol and HSE06 functionals, we present a density functional theory investigation into the  $\Sigma 3$  {111} twin boundary in cubic and tetragonal barium titanate (BaTiO<sub>3</sub>). We model the stability of the pristine twin boundary as well as its effects on the electronic properties and polarisation of BaTiO<sub>3</sub>. We also examine the interaction between the extended defect and both neutral and double positively charged oxygen vacancy point defects in the material. The pristine twin boundary has a low formation energy and is benign in terms of its impact on the electronic properties of BaTiO<sub>3</sub>. Oxygen vacancies segregate favourably to the twin boundary.

## Simulating Hydrogenation in Magnesium through the Application of Machine Learning Models

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*e05-surfin-lin*

In this contribution, we simulate magnesium hydride systems through the application of machine learning (ML) models, with the goal of identifying the rate limiting steps of the hydrogenation process. If metal hydride systems are to reach their full potential, it is vital that we develop a detailed fundamental understanding of how these systems evolve. Experimentally, it is difficult to pinpoint the factors that contribute to the differences between metal hydride systems, e.g differences in the speed of hydrogenation. Accurate molecular dynamics simulations of metal hydride systems could shed light on the rate limiting steps of the hydrogenation and dehydrogenation reactions, but traditional approaches to approximating the potential energy surface, such as classical force fields and density functional theory (DFT), are either lacking in accuracy or computational efficiency. Large size, long-timescale simulations are therefore infeasible via these methods. ML has been applied to an abundance of problems, to assign simple functions to complicated patterns. A generic many-parameter model is designed, and parameter values are tuned to fit the model to specific examples. We apply the same concepts to produce a model that approximates the potential energy surface, mimicking the predictions of DFT with a less complicated, less computationally intensive model. This enables the simulation of large-scale atomic systems for longer time scales. The nature of ML incurs the risk of transferability issues; the model may extrapolate from our examples incorrectly when it encounters a particularly unfamiliar atomic structure. In such an event, we perform DFT on these structures and add them to set of examples used to train the model. Through repeated improvement of the ML model, we hope to identify the rate limiting steps of the hydrogenation process in magnesium, and consequently, potential improvements to the development of new catalysts to accelerate the reaction kinetics of metal hydride systems.

## Combining Monte Carlo simulation and HPC to yield new insights into grain boundary structure and surface stability

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e05-surfin-par

In Monte Carlo (MC) simulation the dynamics are *unphysical*, something which can be exploited to overcome certain issues which commonly bedevil atomistic simulation, e.g. the system getting trapped in a local free energy minimum. Here we showcase two novel applications of MC simulation which, in conjunction with state-of-the-art HPC resources and recent improvements to the community MC simulation program DL\_MONTE, enable key properties of interfaces in crystalline materials to be calculated with improved accuracy:

Grain boundary structure and stability in doped metal oxides. Using a MC simulation method which involves *transforming* atoms' elements during the simulation (e.g. a Ce atom becomes a Zr atom), we calculated the equilibrium structures and formation energies of 6 different tilt-grain boundaries (GBs) in Zr-doped ceria, for a wide range of Zr concentrations. Interestingly, while varying Zr concentration we observed sudden transitions in GB structure akin to first-order bulk phase transitions. Moreover, we found that the doped-GB formation energies were often *negative*. Our methodology paves the way to a more accurate evaluation of the role of dopants on GB properties, e.g. microstructure and cation diffusivity, in metal oxide solid solutions.

Surface free energies of metal oxides and pharmaceutical crystals. While it is routine to calculate the *energy* associated with a given crystal surface, calculating the *free energy* is significantly more challenging. We have developed a MC method which involves transforming a slab system into a bulk system, in order to calculate the free energy of a given surface. We have applied the method to various surfaces of ceria and paracetamol. The method elucidates that with increasing temperature the *free energies* of the surfaces decrease, while the *energies* of the surfaces continue to increase. This reflects the fact that energy is increasingly inaccurate as a measure of surface stability as temperature is increased. Hence our method promises to provide an accurate measure of surface stability at high temperatures, something which should lead to an improved understanding of, e.g. wetting and reactivity, in many materials.

## DFT + $U$ study of $\text{UO}_2$ and $\text{PuO}_2$ with Occupation Matrix Control

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*e05-bulk-nik*

In the actinide series of elements, many of the chemical and physical properties display a turning point at plutonium. The actinide dioxides, which are the subject of this work, change from Mott-Hubbard insulators to charge transfer insulators at  $\text{PuO}_2$ .<sup>1-2</sup>  $\text{UO}_2$  and  $\text{NpO}_2$  have antiferromagnetic (AFM) ground states,<sup>3-4</sup> while a nonmagnetic (NM) ground state, which has been established by various experiments over a wide temperature range (4 - 1000K),<sup>5-8</sup> is found for  $\text{PuO}_2$ . However, previous DFT +  $U$  simulations have predicted an AFM ground state for  $\text{PuO}_2$ .<sup>9</sup> The inconsistency between experiment and DFT +  $U$  simulation over the correct magnetic ground state of  $\text{PuO}_2$  needs to be clarified. As  $\text{PuO}_2$  is a product of the recycling of spent  $\text{UO}_2$  nuclear fuel, detailed understanding of  $\text{PuO}_2$  is clearly essential not just at a fundamental level, but also to inform its safe current and long-term storage.

There are typically many different ways in which the actinide  $f$  orbitals may be populated, and use of the Hubbard  $U$  parameter in DFT calculations can lead to the location of meta-stable states arising from those electronic configurations.<sup>10</sup> The occupation matrix control (OMC) method in VASP, developed by Allen and Watson, is able to impose initial occupation matrices (OMs) on the orbitals of interest.<sup>11</sup> By considering all possible occupations of the actinide  $5f$  orbitals, the true ground state is the OM state with lowest energy. There are  $C_7^2=21$  OMs for FM and 1k colinear AFM  $\text{UO}_2$ ,  $C_7^1=7$  OMs for NM  $\text{UO}_2$ ,  $C_7^4=35$  OMs for FM and 1k colinear AFM  $\text{PuO}_2$ , and  $C_7^2=21$  OMs for NM  $\text{PuO}_2$ .

We initially tested the OMC on  $\text{UO}_2$  bulk, as  $\text{UO}_2$  is much better studied than  $\text{PuO}_2$ , with a wide range of  $U$  values (0.0 – 7.0 eV in 1.0 eV steps). When the  $U$  value not too small ( $> 2$  eV), the [0000101], [00000101] and [0000200] OMs are always found to be the lowest energy state of AFM, FM and NM  $\text{UO}_2$ , while the AFM ground state is found for  $\text{UO}_2$  with  $U \geq 3.0$  eV. After locating the ground state of  $\text{UO}_2$ , various properties (lattice parameter, magnetic moment, band gap and densities of states) have been compared over a wide range of  $U$ . We conclude that  $4.0 \text{ eV} \leq U \leq 5.0 \text{ eV}$ , with  $U = 4.0 \text{ eV}$  is the best, gives a good overall balance of agreement with experiments. Similar to  $\text{UO}_2$ , when  $U$  is not too small ( $> 2.0 \text{ eV}$ ), the same OM states of  $\text{PuO}_2$  are found to have the lowest energy for the AFM, FM and NM states, these are [1010101], [1010101] and [0000202],

respectively. The NM ground state is found for PuO<sub>2</sub> with  $U > 2$  eV for the first time, in agreement with experimental results.  $4.0 \text{ eV} \leq U \leq 4.5 \text{ eV}$ , with  $U = 4.5 \text{ eV}$  is the best, is a good compromise for the simulation of the studied NM PuO<sub>2</sub> bulk properties, i.e. lattice parameter, magnetic moment, band gap and densities of states.

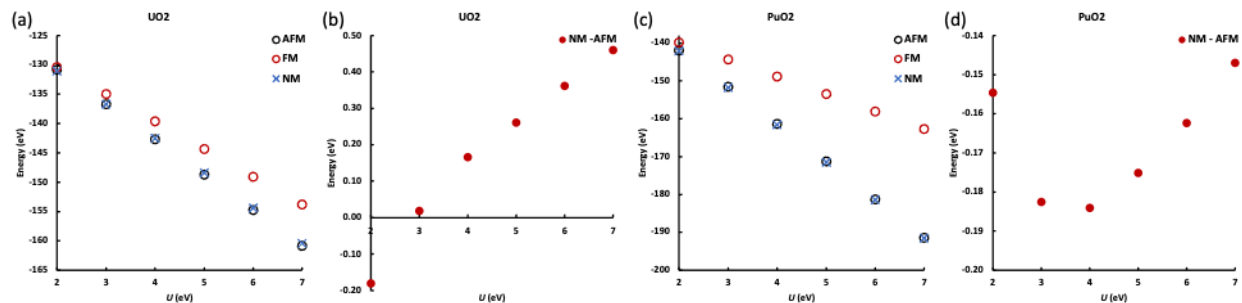


Figure 1 (a) energy of the most stable AFM, FM and NM OM state of UO<sub>2</sub> (b) energy difference between the most stable AFM and NM state of UO<sub>2</sub> (c) energy of the most stable AFM, FM and NM OM state of PuO<sub>2</sub> and (d) energy difference between the most stable AFM and NM state of PuO<sub>2</sub>.

## References

1. Chen, J.-L.; Kaltsoyannis, N. *The Journal of Physical Chemistry C* 2019, 123, 15540-15550.
2. Chen, J.-L.; Kaltsoyannis, N. *Journal of Nuclear Materials* 2022, 560, 153490.
3. Osborn, R.; Taylor, A. *Journal of Physics C: Solid State Physics* 1988, 21, L931.
4. Kern, S.; Morris, J. *Journal of Applied Physics* 1988, 63, 3598-3600.
5. Raphael, G.; Lallement, R. *Solid State Communications* 1968, 6, 383-385.
6. Kern, S.; Loong, C. K. *Journal of Physics: Condensed Matter* 1990, 2, 1933-1940.
7. Kern, S.; Robinson, R. *Physical Review B* 1999, 59, 104.
8. Yasuoka, H.; Koutroulakis, G. *Science* 2012, 336, 901-904.
9. Sun, B.; Zhang, P. *The Journal of chemical physics* 2008, 128, 084705.
10. Larson, P.; Lambrecht, W. R. *Physical Review B* 2007, 75, 045114.
11. Allen, J. P.; Watson, G. W. *Physical Chemistry Chemical Physics* 2014, 16, 21016-21031.



## **Incorporation and diffusion of krypton and xenon in uranium mononitride; a density functional theory study**

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*e05-bulk-nik*

Nitride fuels such as UN are considered as ideal candidates for Generation IV nuclear reactors, especially lead-cooled fast reactors, due to their high metal density and melting temperature, excellent thermal conductivity, and good compatibility with lead coolant. During irradiation of nuclear fuel, the fission of uranium generates a large number of fission noble gases (Ng). These Ng atoms have low solubility in the fuel matrix and may migrate in the fuel, form bubbles inside and on the boundary of the grains, or escape to the fuel-clad gap, leading to fuel swelling and reduction in the thermal conductivity of the fuel rods. Thus, for the safe and efficient use of nitride fuels, it is important to have a comprehensive understanding of the generation and migration of Ng atoms in the fuel matrix. Given the difficulty of experimentally studying radioactive materials, computational simulation is particularly valuable.

Based on the above considerations, we systemically studied the incorporation and diffusion behaviour of Kr and Xe in UN by density functional theory (DFT). We first calculated the solution energies of Kr and Xe in the UN interstitial site, U vacancy ( $V_U$ ), N vacancy ( $V_N$ ), and the bound Schottky defect (SD) sites, and found high stoichiometric dependence. Under U-rich and N-rich conditions, Kr and Xe have the lowest solution energy at SD and  $V_U$ , respectively, while under near-stoichiometric conditions, Kr and Xe behave differently with the former preferring a  $V_U$  and the latter preferring the SD.

Then, we calculated the diffusion coefficients of Kr and Xe in UN via the  $V_U$ -assisted and interstitial mechanisms. We found that the two mechanisms show opposite stoichiometric dependence, with the former increasing from U-rich to N-rich conditions and the latter decreasing. The reasonable agreement between our calculated  $V_U$ -assisted diffusion coefficient with experiment – similar or better than existing theoretical and empirical models – indicates that the  $V_U$ -assisted mechanism governs Xe diffusion in UN. We believe our work provides a good theoretical basis to predict the diffusivity of Ng in UN grains, and that it will contribute to fission gas release models in UN.

## Efficient Extraction of Crystalline Force Constants via the Derivative of a Gaussian Process

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*e05-bulk-fro*

Machine learning (ML) a surrogate model is increasingly demonstrated as a useful tool for exploring potential energy surfaces (PESs). One of the ML models is a Gaussian process (GP) model [1, 2, 3], which is particularly well suited to Bayesian (probabilistic) model construction. To efficiently compute PESs with a minimal number of electronic structure calculations (i.e. DFT), the GP model can be differentiated [4, 5], and conditioned (trained) directly on the available forces (energy derivative) [6]. This exact transformation requires differentiating the GP kernel for the problem at hand. This could lead to the decrease in the number of data points (from expensive electronic structure calculations) required for a given accuracy (at the cost of an increasing complexity of a GP model). By obtaining a standard GP model, the second and the third force constants can be calculated by taking the derivatives (from the first until the sixth order) of the GP kernel and performing linear operation among the derivative kernels with arbitrary order. This construction can yield another GP model which links the information of energies and forces to the second and the third force constants. We apply this cutting-edge technique to deducing the anharmonic properties of crystals and compare them to the more standard approach such as a finite different approach.

[1] Sugisawa, T. Ida et al., *The Journal of Chemical Physics* 153 (2020) 114101.

[2] J. Dai et al, *Journal of Chemical Theory and Computation* 16 (2020) 1386.

[3] J. Broad et al, *The Journal of Chemical Physics* 155 (2021) 144106.

[4] E. Solak et al, *NIPS'02: Proceedings of the 15th International Conference on Neural Information Processing Systems* (2002) 8.

[5] A. McHutchon, *Differentiating Gaussian Processes*.

[6] E. Garijo del Río et al, *Physical Review B* 100 (2019) 104103.1

## P-type impurities and doping in 4H-SiC

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*e05-bulk-shl*

To create a p-type 4H-SiC MOSFET device, 4H-SiC is generally bombarded with high energy ions of either Al<sup>+</sup> or B<sup>+</sup> during ion implantation. Out of these two dopant species, Al is most preferred. However, several recent experimental studies have discovered the occurrence of a drop in device channel mobility caused by the formation of a trap band of similar activation energy to Al's ionization energy ( $E_v + 0.201$  eV). This appears to be a direct consequence of the implantation of high Al implantation dosages into 4H-SiC.

The most practical way forward for industry at present would be to use an alternative p-dopant species in the creation of p-type 4H-SiC MOSFET devices. However, no alternative dopants, which possess similar dopant levels to Al, are currently known.

We have conducted investigations, via the use of DFT calculations, into substitutional point defects produced as a result of insertion of trivalent (B, Ga, In, Tl, Sc) and divalent (Be, Mg, Ca, Ba, Zn, Cu) impurities, as well as F, in the aim to find a suitable p-dopant alternative. Substitutional defects,  $X_{Si}$  and  $X_C$  (where X=impurity), have been evaluated via calculation of incorporation energies and dopant levels to establish the favourability of formation and thermal activation of each. Given the shallowness of Al's dopant level, accurate doping levels have been verified via assessment of Kohn-Sham (KS) single electron eigenvalue defect levels and thermal ionization energies. Electronic structures have also been examined for confirmation that holes produced by insertion of these impurities are able to be fully mobilized. This has led to the widening of the KS defect level, in which the defect's VBM is taken to be the HOMO-1 state, for  $Al_{Si}$ ,  $Ga_{Si}$ , and  $In_{Si}$ .

For trivalent impurities at  $X_{Si}$  sites, we find that incorporation energy is directly proportional to the impurity's atomic radius, except for Al, and that thermal ionization energy is affected by the impurity atom's position related to Si within the periodic table. Al is found to have both the smallest incorporation and ionization energies. Divalent  $X_{Si}$  defects do not appear to be more favourable than Al, but exploration of their energy landscapes is taking place due to the presence of their double hole states. Currently all investigated  $X_C$  defects are unfavourable. Therefore, our results so far indicate Al is the best and still the only industrially viable p-dopant for 4H-SiC.

## Modeling of Intrinsic Hole Trapping in Crystalline and Amorphous Ga<sub>2</sub>O<sub>3</sub>

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*e05-bulk-shl*

Ga<sub>2</sub>O<sub>3</sub> is a transparent semiconductor possessing ultrawide bandgap (~5 eV), a high breakdown electric field, which is a potential candidate for the power electronics. It has been found that holes can be trapped spontaneously in crystalline Ga<sub>2</sub>O<sub>3</sub>, however there are no clear evidence about holes trapping in amorphous Ga<sub>2</sub>O<sub>3</sub>. In this work, we studied geometry relaxation and hole trapping in crystalline and amorphous Ga<sub>2</sub>O<sub>3</sub> using the density functional theory (DFT) with optimized PBE0-TC-LRC nonlocal functional satisfying the Koopmans' theorem. Twenty structures were produced initially using ab initio molecular dynamics (MD) melt and quench (MQ) methods, then initial amorphous Ga<sub>2</sub>O<sub>3</sub> were calculated using DFT. We found that the average bandgap of amorphous Ga<sub>2</sub>O<sub>3</sub> is 4.2 eV, which decrease from crystalline structure. The dominant coordination number of Oxygen (90%) is three, which is same as β-crystalline β-Ga<sub>2</sub>O<sub>3</sub> containing ~60%. The self-trapped hole energy in amorphous structure is deeper than that of crystalline structure ~0.7 eV. We found that holes trend to localize around lower (two or three) coordinated Oxygen in amorphous structure, which is the same as found in crystalline structure, where holes can be trapped only three coordinated Oxygen.

## **A QM/MM Study of Native Point Defects in AlN: Donor-acceptor Behaviour, and Optical Transitions**

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*e05-bulk-sok*

Understanding the donor and acceptor behaviour of aluminium nitride is still a challenging task for both experimentalist and computational scientists. For the first-principle research of charge defects in AlN, one of the key challenges is that the electron ionisation process is not well described in the periodic boundary condition based DFT techniques. Here we present an embedded cluster method, which is able to describe the ionization process without any ambiguity from the origin of the problem to the vacuum level. By using the Chemshell code, embedded defective AlN clusters in the QM/MM environment are treated with DFT methods with the PBE0, B97-2 and BB1K hybrid exchange functionals to obtain the formation energies of native vacancy, interstitial, and anti-site point defects. We are able to present a full picture of the donor and acceptor behaviour of all defects. These new results allow us to draw the coordinate-configuration diagrams to show many possible optical transitions related to the intrinsic defects, which gives new insight to the experimental observations and other previous calculations.

# Investigating structurally distortive Néel transitions in 3d transition metal monoxides using atomistic approaches

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*e05-bulk-smw*

The 3d transition metal monoxides (TMOs), despite their structural simplicity, have complex ground state magnetic properties which today still pose a challenge to model. MnO is a classic example of this class of material, in the paramagnetic (PM) phase it has the cubic NaCl structure. Below the Néel temperature (118° K) the antiferromagnetic (AFM) phase is stable and the onset of magnetic order is coupled with a rhombohedral lattice distortion ( $\Delta a = 0.62^\circ$ ,  $\Delta a = 0.08 \text{ \AA}$ ) [1]. Spins on the  $\text{Mn}^{2+}$  ions are coupled antiferromagnetically between every Mn-O-Mn 180° bridge via super-exchange (next nearest neighbour,  $J_2$ ), a competing, weaker AFM super-exchange also acts between nearest neighbour  $\text{Mn}^{2+}$  cations ( $J_1$ ), mediated via Mn-O-Mn 90° bridges. The stronger  $J_2$  interaction drives the observed long-range AFM ordering but also results in FM ordered planes stacked along the [111] axis, which opposes the spin orientation favoured by the  $J_1$  exchange, resulting in frustrated interactions in the (111) planes. Below the ordering temperature, the rhombohedral distortion is believed to alleviate the magnetic frustration [2].

In this work we propose an approach to model the cooperative lattice distortion in MnO by including parametrizable interatomic potentials to model spin-spin super-exchange interactions within the lattice. We aim to model the rhombohedral lattice distortion by including the effects of super-exchange in the vibrational dynamics of the MnO lattice, utilising functionality from the simulation codes VAMPIRE [3] and GULP [4]. Quantitative predictions will be made by averaging ensembles of states over a temperature range, crossing  $T_N$ .

[1] A.J. Logsdail, C.A. Downing, C.R.A. Catlow, A. A. Sokol, Chem. Phys Lett. 690 (2017) 47-53.

[2] J.A.M. Paddison, M.J. Gutmann, J.R. Stewart, M.G. Tucker, M.T. Dove, D.A. Keen, A.L. Goodwin, Phys. Rev. B 97 (2018) 1–5.

[3] R. Evans, W. Fan, P. Chureemart et al., J. Phys. Cond. Mat., 26 (2014)

## **Weak anisotropy of band gap modulation using uniaxial strain in MoS<sub>2</sub>**

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*e05-nano-mck*

Strain in nanomaterials is often a useful parameter to examine, especially for light emitting materials due to its potential to modify band gap and photoluminescence efficiency. Although strain is known to reduce the band gap in monolayer transition metal dichalcogenides such as MoS<sub>2</sub>, the effect of strain direction has not yet been fully investigated. The variation of band gap with strain in few-layer systems is also yet to be systematically studied. Here, density functional theory is used to investigate the effects of uniaxial strain on monolayer MoS<sub>2</sub> as well as the effect of biaxial strain in monolayer and few-layer systems. For monolayer MoS<sub>2</sub> the linear band gap variation is found to only weakly depend on the direction of applied strain. The direct band gap gradient with respect to strain varies by only 4.6 meV/% (from  $-52.7 \pm 0.6$  meV/% to  $-57.3 \pm 0.1$  meV/%) for strain applied along the armchair and zigzag directions respectively. These gradients are also shown to decrease when biaxial strain is applied to an increasing number of layers. These findings should be directly applicable to the other hexagonal-shaped Van der Waals-bonded transition metal dichalcogenides

## Predicting and Modelling Clusters

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*e05-nano-smw*

We are interested in modelling clusters isolated in vacuum<sup>1-3</sup> and on surfaces, <sup>4,5</sup> and one of the developers of a cluster database of predicted nanoclusters: <http://hive.chem.ucl.ac.uk>. Our focus in this area is that of predicting the atomic structures of clusters, using a global optimization scheme, as implemented as part of the KLMC code<sup>6</sup>, that first searches for local minima (LM) on the energy landscape defined using interatomic potentials (IP), which are subsequently refined using a DFT approach\*. To calculate the IP and DFT energies and perform the local optimizations, we use the GULP and FHI-aims software, respectively. This approach relies on the success of the global optimization procedure for finding LM and the availability and quality of the interatomic potentials to reproduce both the DFT LM and the DFT energy ranking of the LM. Thus, we develop and test the suitability of interatomic potentials for this approach to structure prediction. Here we will present results from our investigation of different functions employed as IPs, show the match between IP and DFT landscapes for example inorganic clusters, including a metal fluoride, oxide, and nitride, and present analysis of a selection of the predicted atomic structures. \* We acknowledge the support of EPSRC, The MMM Hub and the MCC for computer resources (grant references EP/R029431 and EP/T022213).

References: [1] Structure and properties of nanosilicates with Olivine ( $\text{Mg}_2\text{SiO}_4$ )<sub>N</sub> and Pyroxene ( $\text{MgSiO}_3$ )<sub>N</sub> compositions; DOI: 10.1021/acsearthspacechem.9b00139 [2] Are octahedral clusters missing on the carbon energy landscape? DOI: 10.1039/C8NA00013A [3] Synthesis target structures for alkaline earth oxide clusters DOI: 10.3390/inorganics6010029 [4] Development of interatomic potentials for supported nanoparticles: The Cu/ZnO case; DOI: 10.1021/acs.jpcc.7b04502 [5] Morphology of Cu clusters supported on reconstructed polar ZnO (0001) and (000 $\bar{1}$ ) surfaces; DOI: 10.1039/D0TA08351H [6] An efficient genetic algorithm for structure prediction at the nanoscale; DOI:10.1039/c6nr09072



## Growth and reactivity of Hexagonal Boron Nitride

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*e05-react-msa*

The properties of epitaxially grown 2D materials such as hexagonal boron nitride (hBN) and graphene are highly dependent on the growth mechanism and on the presence of defects in the epitaxial layer. In our study we employ density functional theory (DFT) to investigate the epitaxial growth of hBN on a Ru(0001) surface and develop a detailed understanding of the formation of hBN from borazine ( $B_3H_6N_3$ ). Our results predict the formation of a  $(3 \times 3)$  meta-stable structure, consistent with results from helium atom scattering experiments. Our findings may have implications for CVD processes, the creation of defect sites and the design of new nanomaterials based on exploiting the growth phases of hBN.

We have also investigated the effect of defects on the catalytic activities of hBN. hBN has many advantages for heterogeneous catalysis, including high surface area, high thermal stability, and high durability whilst being more sustainable than the ubiquitously employed precious and transition metal-based catalysts. Through DFT simulations, we have explored metal-free hBN as a valid alternative to precious metal catalysts for producing  $H_2$  via the reaction of ammonia with a hBN divacancy (VBN). Ammonia decomposition proceeds with an activation barrier of 0.52 eV. Furthermore, the reaction of ammonia with epitaxially grown hBN on a Ru(0001) substrate was investigated, and we observed similar  $NH_3$  decomposition energy barriers (0.61 eV), but a much more facile  $H_2$  desorption barrier (0.69 eV vs 5.89 eV).

## Computational investigation of CO<sub>2</sub> hydrogenation over low index Rh surfaces

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e05-react-cat

The alleviation of CO<sub>2</sub> emissions has become an urgent issue, requiring the development of technology for carbon dioxide capture, utilization and storage. Particularly, attractive is the energy-efficient catalytic CO<sub>2</sub> conversion using renewable energy, which has attracted great attention worldwide and which could potentially mitigate CO<sub>2</sub> emissions and produce commodity fuels and chemicals. It is thermodynamically feasible to convert CO<sub>2</sub> conversion by introducing H<sub>2</sub> to produce oxygenates (alcohols and dimethyl ether) and hydrocarbons (olefins, liquid hydrocarbons, and aromatics). However, the mechanistic routes of CO<sub>2</sub> hydrogenation even to C1 molecules (CO, CH<sub>3</sub>OH and CH<sub>4</sub>) are multiple and complex. A powerful tool for exploring the reaction mechanisms under realistic conditions is provided by the combination of Density Functional Theory (DFT) and dynamics simulations which can complement *operando* experimental techniques and identify descriptors of activity and selectivity for CO<sub>2</sub> hydrogenation.

It has been noted that metal Rh catalyst can perform with better selectivity for CO, CH<sub>4</sub> or CH<sub>3</sub>OH when interacting with various oxide supports. First of all, the reaction mechanisms of Rh catalyst which shows high CH<sub>4</sub> selectivity need to be studied and compared with the later calculations. When calculating the initial steps of CO<sub>2</sub> hydrogenation over Rh(111), (100), and (110) surfaces, it has been found that CO<sub>2</sub> dissociation is more favorable when compared with the formation of HCOO\* and COOH\*. Bidentate HCOO\* adsorbed with both O atoms located between two surface Rh atoms transforms into the most stable state (with both O atoms positioned on top of surface Rh atoms) by barrierless rotation. In addition, H<sub>2</sub> adsorption at the top site results in considerable H<sub>2</sub> bond elongation, suggesting that Rh readily facilitates H<sub>2</sub> dissociation. With the electronic analysis by the means of density of states (DOS) and crystal orbital Hamilton population (COHP), H<sub>2</sub> adsorption at the top site is more stable when compared with the physical adsorption – corresponds to s-s and s-d interactions between Rh and H atoms. Meanwhile, the s-s interaction contributes more to the Rh-H bond strength when elongated H<sub>2</sub> adsorbed at the Rh top site.

## Photocatalytic Degradation of Organic Pollutants in Wastewater: the Effect of Dissolved Chloride Anions over TiO<sub>2</sub> Activity

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e05-react-cat

Dissolved organic compounds are one of the main responsible for environment pollution caused by wastewater.<sup>1</sup> Despite the promising performance of TiO<sub>2</sub> towards the photodegradation of such pollutants, its activity can decrease drastically in the presence of dissolved anions.<sup>2,3</sup> Recently, experimental investigation at Cardiff University has observed that phenol degradation catalysed by TiO<sub>2</sub> is drastically modified in brine. Anatase presented a drop of activity in brine, whilst enhancement of rutile activity was observed under the same reaction conditions. In this work, the effect of chlorides over the photocatalytic degradation of phenol by titania polymorphs (anatase and rutile) is investigated by periodic DFT methods. After the generation of charge separation in the modelled titania systems, adsorbed chlorides were the preferential site for partial hole localisation, although small energy differences are computed between partially localised hole densities over adsorbed chloride or hydroxyl. Moreover, chlorides can reduce or inhibit the ability of r-TiO<sub>2</sub> (110) and a-TiO<sub>2</sub> (101) systems to localise polarons in the slab structure. These results indicate that both mechanisms – hole scavenging and the inhibition of hole localisation - can be the origin of the effect of chlorides on photocatalytic activity of both titania polymorphs. Interestingly, whilst such effects result in a depletion of hydroxyl radical formation over anatase, an increase of rutile activity in brine is observed due to high energy barriers for formation of hydroxyl radicals over this system, more facile formation of chlorine radicals, and potential phenol degradation by chlorine radicals. Despite the slight endothermicity of the reaction between chlorine radicals and phenol, such an energy cost can be surmounted by the exothermicity of the overall phenol degradation process. These results provide fundamental insight into the photocatalytic properties of titania polymorphs and elucidate the effect of adsorbed anions over radical formation and oxidative decomposition of organic pollutants.

<sup>1</sup>Q. Guo *et al.*, Chem. Rev., **2019**, 119, 11020. <sup>2</sup>E. Bouleghimat *et al.*, Chemosphere, **2020**, 251, 126469. <sup>3</sup>M. Krivec *et al.*, Phys. Chem. Chem. Phys., **2014**, 16, 14867.

## The hydrogen and water interactions with the pristine surfaces of monoclinic and orthorhombic FeNbO<sub>4</sub>

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*e05-react-abc*

The FeNbO<sub>4</sub> materials has shown the potential of being used as the catalytic electrode to the hydrogen evolution/oxidation reaction. Unlike other Fe-based materials, such as the FeVO<sub>4</sub> and LaFeO<sub>3</sub> material, the orthorhombic FeNbO<sub>4</sub> shows a unique structure where the Fe<sup>3+</sup> and Nb<sup>5+</sup> cations distribute randomly in the 4f site of the structure. In this way, it was believed to reduce the loss of oxygen and reduction of Fe<sup>3+</sup> under the hydrogen atmosphere.

In this study, we have employed the Density Functional Theory (DFT) to study the pristine surfaces and the related dissociation reactions of H<sub>2</sub> and H<sub>2</sub>O respectively. The simulation results show that there are three pristine surfaces, namely (010), (110), and (111), and those three surfaces in both the monoclinic and orthorhombic FeNbO<sub>4</sub> showed a similar configuration, even if the distribution of the cations are totally different. We have also found that the oxygen within the water molecule prefers to get coordinated with the surface cations, forming the chemisorption, while the adsorption reaction between the H<sub>2</sub> and surface atoms is so weak that only physisorption was formed here. In addition, out of those three surfaces, we have studied the hydrogen dissociation at the (010) surfaces and found that in the heterolytic dissociation pathway (Fe-O site), there exit a low energy barrier around 0.46 eV, which we thinks is worth of doing further research.

## First-principles calculations on $AB_2$ alloy for hydrogen storage

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*e05-discov-lin*

$AB_2$  Laves phase alloys as promising materials for solid state hydrogen storage have been studied in this work by ab initio density functional theory calculations. The formation energies of  $AB_2$  alloys and the hydrogenation enthalpies (differences between total energies of the hydride and alloy/ $H_2$ ) of  $AB_2$  hydrides were shown to relate to the electronegativity, atomic and covalent radii of atoms in the unit cell. In an  $Ti_{1-x}A'_xB_2$  alloy with fixed  $B$  atom, the formation energy of the alloy generally increases as the atomic radius of  $A'$  atom increases or decreases as the electronegativity of  $A'$  atom increases. The enthalpy of an  $Ti_{1-x}A'_xB_2$  hydride (where  $0.125 \leq x \leq 0.375$ ) generally decreases as the average atomic/covalent radius of atoms in the unit cell increases or increases as the average electronegativity of atoms in the unit cell increases. The effects of electronegativity and atomic/covalent radius in formation energies of  $Ti_{1-x}A'_xB_2$  alloys and enthalpies of  $Ti_{1-x}A'_xB_2$  hydrides are in reverse. In general, the stabilities of  $AB_2$  alloys or  $AB_2$  hydrides after hydrogenation are inversely proportional to the volume change of the unit cell. If an atomic substitution leads to the increase of formation energy, the alloy becomes less stable when the substitution concentration increases, and vice versa. The relation between enthalpy of an  $Ti_{1-x}A'_xB_2$  hydride and average covalent radius or volume change of unit cell is nearly linear ( $R^2 > 0.9$ ) when the substitution concentration  $x$  is smaller than 0.13. This study will benefit experimentalists when choosing an appropriate  $AB_2$  alloy composition for hydrogen storage at specified conditions (e.g. temperature and plateau pressure of hydrogen absorption/desorption).

## A Computational Re-evaluation of Se as a Solar Absorber

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e05-power-dos

Trigonal selenium (c-Se) was the first material to display the photovoltaic (PV) effect and has recently regained interest due to its suitable direct band gap, high earth abundance, non-toxicity, simple composition and low melting point.<sup>1</sup> It was used by Charles Fritts to make the world's first PV solar cell but the cell's low power conversion efficiency (PCE) of <1% made it commercially unfeasible. Starting with silicon in 1954, many other materials and technologies reached much higher PCEs and effectively rendered c-Se obsolete.<sup>2,3</sup> However, c-Se solar cells have improved considerably in the last 40 years with a current record PCE of 6.5%.<sup>4</sup>

In this work, the Vienna Ab initio Simulation Package (VASP) was used to perform hybrid density functional theory calculations on crystalline selenium's 5 known polymorphs (c-Se, rhombohedral,  $\beta$ -monoclinic,  $\gamma$ -monoclinic,  $\delta$ -monoclinic) to determine the ideal phase for solar cell operation. Band structure calculations revealed that all polymorphs except  $\gamma$ -monoclinic have an indirect fundamental band gap with a slightly higher direct band gap. C-Se was found to have the lowest direct band gap (1.904 eV with spin-orbit coupling) and highest charge carrier mobilities, allowing it to reach the highest efficiencies in single junction cells. The band gap is still quite high which allows tandem applications with low band gap absorbers like silicon.<sup>5</sup> Analysis of the material's optical response showed that it can reach PCEs up to 23% with a thickness of 2  $\mu\text{m}$ , making it a promising cheap alternative to commonly used high efficiency solar absorbers.

### References:

- 1 M. Zhu, G. Niu and J. Tang, *J. Mater. Chem. C*, 2019, **7**, 2199–2206.
- 2 D. M. Chapin, C. S. Fuller and G. L. Pearson, *J. Appl. Phys.*, 1954, **25**, 676–677.
- 3 A. Goetzberger, J. Luther and G. Willeke, *Sol. Energy Mater.*, 2002, 11.
- 4 T. K. Todorov, S. Singh, D. M. Bishop, O. Gunawan, Y. S. Lee, T. S. Gershon, K. W. Brew, P. D. Antunez and R. Haight, *Nat. Commun.*, 2017, **8**, 682.
- 5 T. H. Youngman, R. Nielsen, A. Crovetto, B. Seger, O. Hansen, I. Chorkendorff and P. C. K. Vesborg, *Sol. RRL*, 2021, **5**, 2100111.

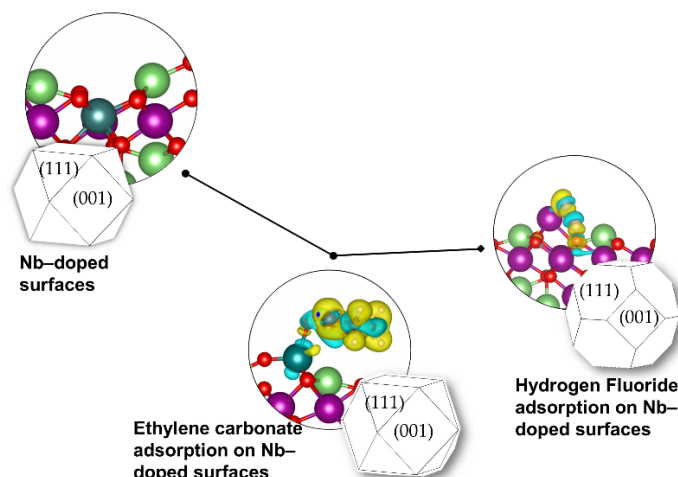
## Lithium manganese oxide Nb<sup>5+</sup> surface doping and the effect of ethylene carbonate and hydrogen fluoride adsorptions

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e05-react-lee

Cation doping is recommended as an effective method of reducing trivalent manganese (Mn<sup>3+</sup>) ions which undergo disproportionation reaction in lithium manganese oxide-based (LiMn<sub>2</sub>O<sub>4</sub>) lithium-ion batteries. Despite the intense studies on LiMn<sub>2</sub>O<sub>4</sub> doping, the surface interaction between the modified spinel and the electrolyte components is not fully understood. Here, we discuss the adsorption of ethylene carbonate (EC) and hydrogen fluoride (HF) onto the major pure and Nb-doped LiMn<sub>2</sub>O<sub>4</sub> surfaces using the density functional theory. The constructed morphologies of the pristine surfaces indicated the dominance of the (001) surface, which was in agreement with the reported literature. However, upon Nb doping on the second layers, the (111) surface stability improved, resulting in an enhanced (111) plane on the morphology. Moreover, the adsorption of EC further improves the dominance of the (111) surface, while a minimal charge transfer was recorded which was mainly due to the electronic rearrangement within the molecule. Similarly, the HF adsorptions further enhanced the (111) surface plane, where the molecule dissociates to form Mn/Nb-F and O-F bonds. These are interesting findings, since exposing the (111) surface plane on the particle morphologies promotes the formation of a stable solid electrolyte interface (SEI), which significantly reduces Mn dissolution.





























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