# The evolution of materials modelling and structure prediction

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# It all started with a post on LinkedIn!

- Research fields and methods evolve, of course. But what I have experienced is this evolution coinciding with my retirement and appointment to emeritus status. Since my PhD, my research field has been Computational Solid State Chemistry. I have modelled the structures and properties of many materials, particularly those with applications in optics and energetics. This has included modelling defects and dopants in such important and diverse materials as uranium dioxide and lithium niobate. Throughout, my preferred approach has been the use of interatomic potentials, although I have collaborators who use density functional theory (DFT), and we have published joint studies. However, this approach has now evolved considerably. Empirical fitting of interatomic potentials, which I carried out for many materials, can now be replaced by Machine Learning based methods, although how the potentials are tested and validated is an interesting issue. AI can generate possible starting structures, where we based structures on related materials, or in some cases used Genetic Algorithm based methods. And finally, DFT software has become easier to use, and seems to be viewed (by some) as the only method that should be used for almost any material. Earlier this year I had a review article rejected because it wasn't 'DFT enough' even though, as a review, it would surely be expected to include a range of different approaches! I believe that potentials based methods are still relevant, especially for complex materials, and I know that I am not alone in this belief. I recently published a paper with collaborators on ion migration in LaAlO3, which demonstrates that these methods still have their uses. I will be watching the further evolution of my field with interest.

# Plan of talk

- Previously employed methods – examples and issues
  - Empirical fitting of potentials
  - Structure prediction
- A comparative case study using ML potentials
- Structure prediction then and now
- Closing thoughts and conclusions

# Previously employed methods – examples and issues (1)

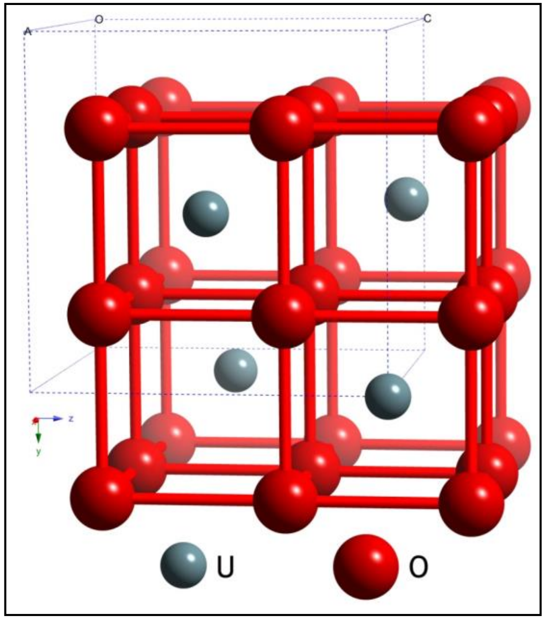
- Empirical fitting of potentials
  - Examples of ideal scenarios – $UO_2$ and $LiNbO_3$
  - Less ideal situations – where only the structure is available – $LiCaAlF_6$

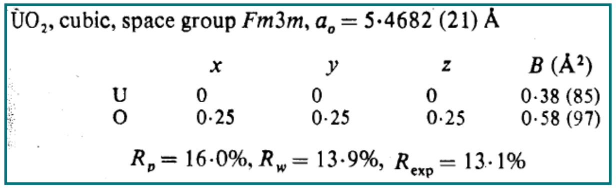
# Modelling $UO_2$

My first postdoc position involved modelling fission gas in $UO_2$ (in Richard's group at UCL), but I returned to nuclear fuels in 2010 in a collaboration with **Mark Read** (AWE/Birmingham).

M S D Read and R A Jackson, *Journal of Nuclear Materials,* **406**, 293-303 (2010)

# Experimental Data for Empirical Fitting: $UO_2$





$UO_2$, cubic, space group $Fm3m$, $a_o = 5{\cdot}4682\ (21)$ Å

| | $x$ | $y$ | $z$ | $B$ (Å²) |
|---|---|---|---|---|
| U | 0 | 0 | 0 | 0·38 (85) |
| O | 0·25 | 0·25 | 0·25 | 0·58 (97) |

$R_p = 16{\cdot}0\%$, $R_w = 13{\cdot}9\%$, $R_{\text{exp}} = 13{\cdot}1\%$

S. A. Barrett, A. J. Jacobson, B. C. Tofield, B. E. F. Fender, The Preparation and Structure of Barium Uranium Oxide $BaUO_{3+x}$, Acta Cryst. **38** (Nov) (1982) 2775–2781.

**Elastic Constants / GPa**

| Reference | $C_{11}$ | $C_{12}$ | $C_{44}$ |
|---|---|---|---|
| Dolling *et al.* [1] | 401 ± 9 | 108 ± 20 | 67 ± 6 |
| Wachtman *et al.* [2] | 396 ± 1.8 | 121 ± 1.9 | 64.1 ± 0.17 |
| Fritz [3] | 389.3 ± 1.7 | 118.7 ± 1.7 | 59.7 ± 0.3 |

**Dielectric Constants / GPa**

| Reference | Static $\varepsilon_0$ | High Frequency $\varepsilon_\infty$ |
|---|---|---|
| Dolling *et al.* [1] | 24 | 5.3 |

[1] G. Dolling, R. A. Cowley, A. D. B. Woods, Crystal Dynamics of Uranium Dioxide, Canad. J. Phys. 43 (8) (1965) 1397–1413.
[2] J. B. Wachtman, M. L. Wheat, H. J. Anderson, J. L. Bates, Elastic Constants of Single Crystal $UO_2$ at 25°C, J. Nucl. Mater. 16 (1) (1965) 39–41.
[3] I. J. Fritz, Elastic Properties of $UO_2$ at High-Pressure, J. Appl. Phys. 47 (10) (1976) 4353–4358.

# How good is the final fit?

| Parameter | Calc. | Obs. | Δ% | Parameter | Calc. | Obs. | Δ % |
|---|---|---|---|---|---|---|---|
| **Lattice Constant [Å]** | 5.4682 | 5.4682 | 0.0 | **$C_{11}$ [GPa]** | 391.4 | 389.3 | 0.5 |
| **$U^{4+}$ – $U^{4+}$ Separation [Å]** | 3.8666 | 3.8666 | 0.0 | **$C_{12}$ [GPa]** | 116.7 | 118.7 | -1.7 |
| **$U^{4+}$ – $O^{2-}$ Separation [Å]** | 2.3678 | 2.3678 | 0.0 | **$C_{44}$ [GPa]** | 58.1 | 59.7 | -2.7 |
| **$O^{2-}$ – $O^{2-}$ Separation [Å]** | 2.7341 | 2.7341 | 0.0 | **Bulk Modulus [GPa]** | 208.3 | 204.0 | 2.1 |
| **Static Dielectric Constant** | 24.8 | 24.0 | 3.3 | **High Frequency Dielectric Constant** | 5.0 | 5.3 | 5.7 |

**Very good agreement with structure and lattice properties**

# $LiNbO_3$: a long-time obsession in defects chemistry!

Background: a potential for $LiNbO_3$ was originally developed in Richard’s group:
H Donnerberg, S M Tomlinson, C R A Catlow and O F Schirmer, *Phys. Rev. B,* **40,** 11909 (1989)

Revisited in my collaboration with Mario Valerio, mainly to be able to fit both the ferroelectric and paraelectric phases of the material:
R A Jackson and M E G Valerio, *Journal of Physics: Condensed Matter*, **17**, 837-843 (2005)

# $LiNbO_3$: structural agreement

| | **Ferroelectric phase** | | | | |
|---|---|---|---|---|---|
| | Exp. [1] | This work | | Donnerberg potential | |
| | | 0 K | 295 K | 0 K | 295 K |
| **a=b** | 5.1474 | 5.1559 | 5.1868 | 5.2271 | 5.2631 |
| **c** | 13.8561 | 13.6834 | 13.7103 | 14.2730 | 14.2167 |
| | **Paraelectric phase** | | | | |
| | Exp. [2] | This work | | Donnerberg potential | |
| | | 0 K | 293 K | 0 K | 293 K |
| **a=b** | 5.2924 | 5.1530 | 5.0919 | 2.3030 | 2.3042 |
| **c** | 13.8462 | 13.8418 | 13.2111 | 5.6412 | 5.6402 |

[1] S C Abrahams, P Marsh, *Acta Cryst. B,* **42**, 61 (1986)

[2] H Boysen, F Altorfer, *Acta Cryst. B,* **50,** 405 (1994)

# When only structural data is available: $LiCaAlF_6$

J B Amaral, D F Plant, M E G Valerio and R A Jackson
*J. Phys. Condensed Matter*, **15**, 2523-2533 (2003)

$LiCaAlF_6$ is of interest as a host material for rare earth ions with applications in solid state lasers.
A good modelling project is to determine where the dopant ions are located!

| Parameter | Experimental | Calculated | % difference |
|---|---|---|---|
| $a = b$ (Å) | 5.01 | 5.03 | 0.42 |
| $c$ (Å) | 9.64 | 9.62 | -0.24 |
| $\gamma$ (deg) | 120.0 | 120.0 | 0.0 |

Predictions from the modelling guided experimental work and helped interpret data.

# Previously employed methods – examples and issues (2)

- **Structure prediction**

➢ This hasn't been an issue for me as I have mainly worked with known structures

➢ Work from Richard's group by **Tim Bush** and **Scott Woodley** developed Genetic Algorithms for structure prediction:

# Use of Genetic Algorithms – example publications

*Evolutionary programming techniques for predicting inorganic crystal structures* (TS Bush, CRA Catlow and PD Battle) - *J. Mater. Chem.*, **5**, 1269-1272 (1995)

*The prediction of inorganic crystal structures using a genetic algorithm and energy minimisation* (SM Woodley, PD Battle, JD Gale and CRA Catlow) - *PCCP*, **1**, 2535-2542 (1999)

# Genetic Algorithms – principles

**Crystal Structure Prediction**: The primary application was solving complex crystal structures that were previously unknown or difficult to determine through experimental methods.

- **Cost Function**: based on Pauling's rules, recently extended and quantified as the bond valence model
- **Energy Minimisation**: The candidate structures identified by the genetic algorithm were then optimised using standard lattice energy methods.

# Comparative study: ML, DFT and IP in silica modelling

- I'm grateful to Richard, who sent me a copy of:

*Modelling silica using MACE-MP machine learnt interatomic potentials* (Nasir et al, *PCCP,* **27**, 19784, 2025)

- In comparison with:

*Interatomic potentials for* $SiO_2$ (Sanders et al, J. Chem. Soc., Chem. Commun.,1271–1273, 1984).

# Comparative study - details

- The paper used the MACE architecture ML-IP framework designed for atomistic simulations.
- MACE-MP-0 was trained on a database which consists of approximately **1.5 million** DFT-relaxed configurations derived from **~150 000** unique crystal structures in the Materials Project database.
- The point is made that the MP method used is not restricted to a particular coordination environment, so it can model phase changes where appropriate.

# Comparative study - results

The paper considers zeolites and silica phases, and includes a comparison of calculated cohesive energies with those calculated by interatomic potentials and DFT, and with experimental values.

My favourite zeolite, zeolite A, wasn't included, so I have chosen ZSM-5 as an example.

Energies are in kJ $\text{mol}^{-1}$ per T site relative to $\alpha$-quartz

| | **IP** | **DFT** | **MACE-mp0** | **Exp.** |
|---|---|---|---|---|
| ZSM-5 | 9.7 | 8.3 | 8.5 | 6.8 |

# ML potentials – some general observations

- The paper shows that ML potentials can be used very successfully in modelling silica structures.
- One point made is that since the potentials are trained on DFT results, the particular DFT approach used is important.
- In order to include long range interactions (dispersion) the training dataset needs to include these effects, and where empirical dispersion corrections have been included, the resulting ML potentials have shown improved prediction of cohesive energies.

# AI and structure prediction – how does it work?

- **Learning from data** – analysing structures and learning the ‘language’ of how atoms are arranged in crystals’.
- **Generative models** develop new crystal structures based on user-defined properties like composition and pressure.
- **Hybrid approaches**: AI is combined with traditional methods. AI generates possible structures which can then be tested using potentials or DFT.

# Generative AI for crystal structures

See for example:
*Generative AI for crystal structures: a review* (de Breuk et al, *npj Computational Materials* **11**, 370 (2025))

- This presents a comprehensive review of the field, and includes a range of predicted crystal structures generated using different generative models.
- Examples given include $V_5O_8$ which may not yet be synthesised, so the method seems ideal in this case.

# Closing thoughts and conclusions

- ML potentials are very useful when empirical fitting isn’t an option, and can be quicker and more efficient. Looking back, many of the complex structures I have worked on would benefit from this methodology.
- However, they are only as good as the training dataset (note the earlier point about inclusion of dispersion interactions)
- AI structure prediction is useful for structures where there is no experimental information, but again, it is necessary to be aware of limitations of training, particularly in relation to the ‘language’ of atomic arrangement in crystal structures.

# Acknowledgements

- Thanks to the organisers for accepting this!
  - It’s a while since I last gave a talk at a Christmas SSCG meeting, and the opportunity was appreciated. It’s also nice to be back in Leeds.
- I’ve (hopefully) kept the talk short to give time for discussion.
- I’ll make the slides available after the meeting (links will be put on LinkedIn and BlueSky), so hopefully the discussions will continue.

# Some contrasting views of work locations (particularly $LiNbO_3$)

# (Not) my office