Introduction to the FAULTS program

Montse Casas Cabanas

perfect hcp

intrinsic I1 (growth)

intrinsic I2 (deformation)

extrinsic E

twin-like T2
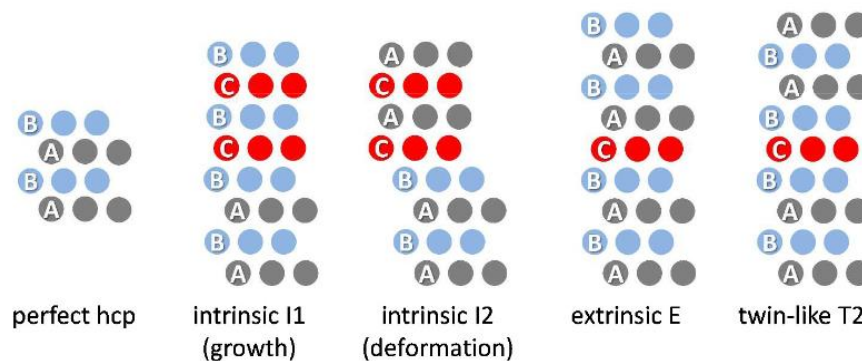
Defects in crystalline materials

REAL materials can be complex…
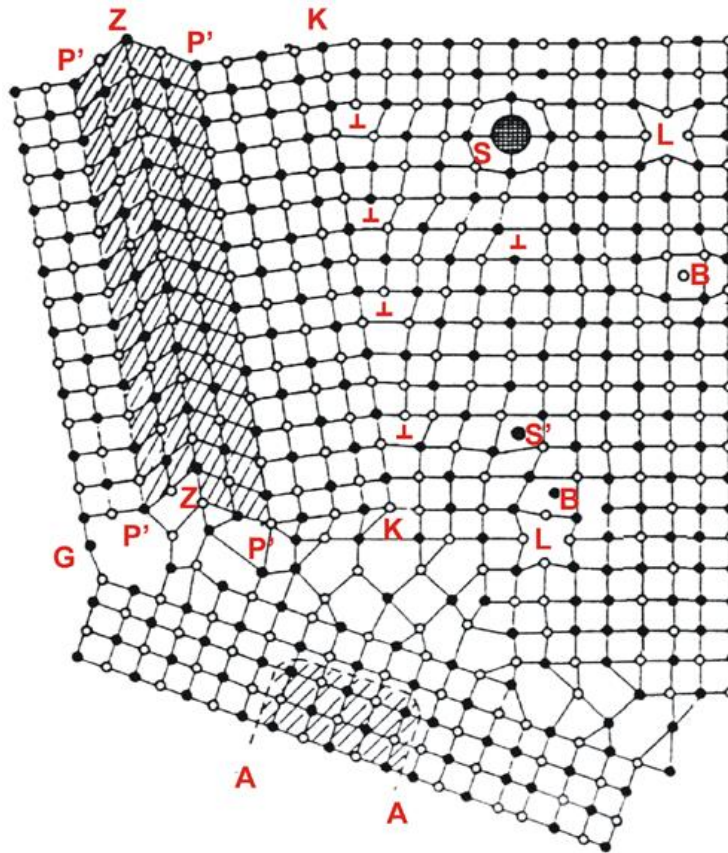
A   antiphase domain
B   interstitial atom
G, K   grain boundary
L   vacancy
S   substitutional impurity
S'   interstitial impurity
P, Z   stacking faults
⊥   dislocations
                   intergrowths

Hornbogen E. and Petzow G. Z. Metallk., 61:81-94, 1970

FAULTS program

Rietveld softwares (FullProf, GSAS, etc.) include advanced models for anisotropic size and strains and antiphase domains BUT cannot model non-averaged structures
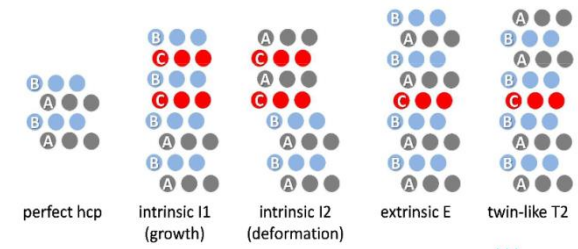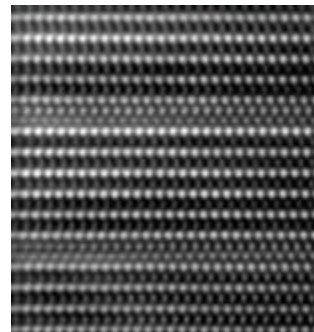
Ni(OH)$_2$

Casas-Cabanas *et al. Journal of Power Sources* **2007**, *174*, 414.

Li$_2$MnO$_3$
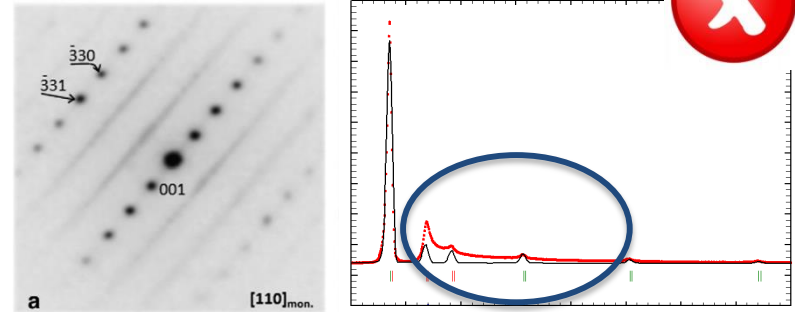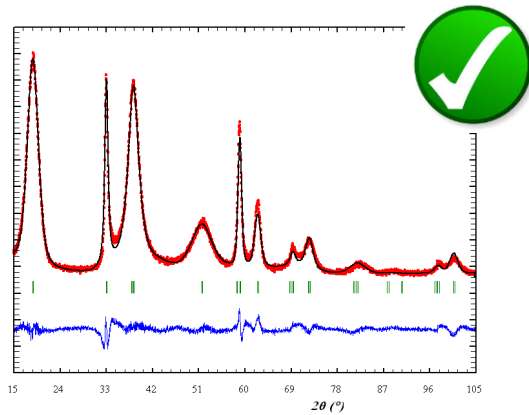
Boulineau *et al. Solid State Ionics* **2010**, *180*, 1652.

FAULTS

✓ **Fast**

✓ **Robust**

✓ **User friendly**

✓ **DiFFaX2FAULTS convertor**

✓ **Secondary phases**

✓ **Background refinement**

…

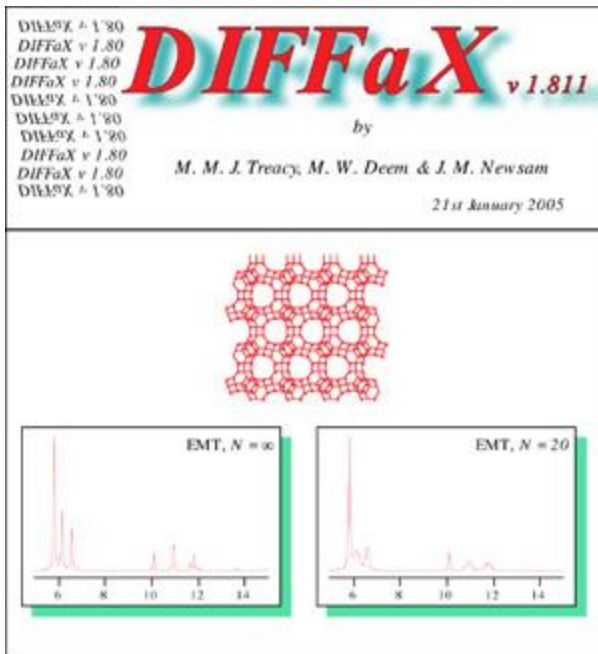perfect hcp | intrinsic I1 (growth) | intrinsic I2 (deformation) | extrinsic E | twin-like T2
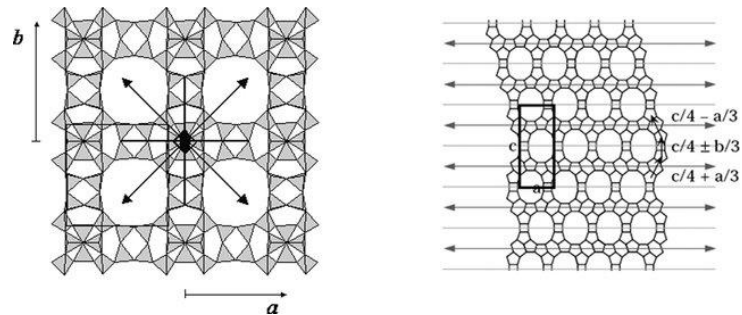
FAULTS program

History

1991 **DIFFaX**: recursion algorithm for computing diffraction from faulted crystals with coherent planar defects. Simulation code in Fortan 77.

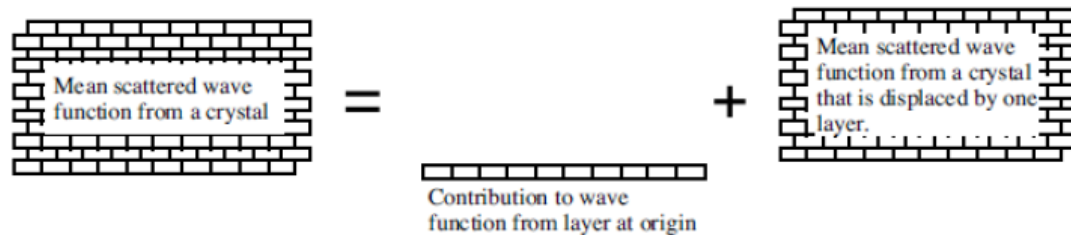Developed by M.M. Treacy and J.M. Newsam to study zeolite-type materials

Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating diracted intensities from crystals containing planar faults. Proc. R. Soc. Lond. A, 433:499-520, 1991.
http://www.public.asu.edu/~mtreacy/DIFFaX_manual.pdf

FAULTS program

DIFFaX recursion algorithm

DIFFaX exploits the recurring patterns found in randomized stacking sequences to compute the average interference wavefunction scattered from each layer type occurring in a faulted crystal.

$$\Psi(\mathbf{u}) = F(\mathbf{u}) + \exp(-2\pi i \mathbf{u} \cdot \mathbf{R}) \ \Psi(\mathbf{u}) \qquad \Longleftrightarrow \qquad \Psi(\mathbf{u}) = \frac{F(\mathbf{u})}{1 - \exp(-2\pi i \mathbf{u} \cdot \mathbf{R})}$$
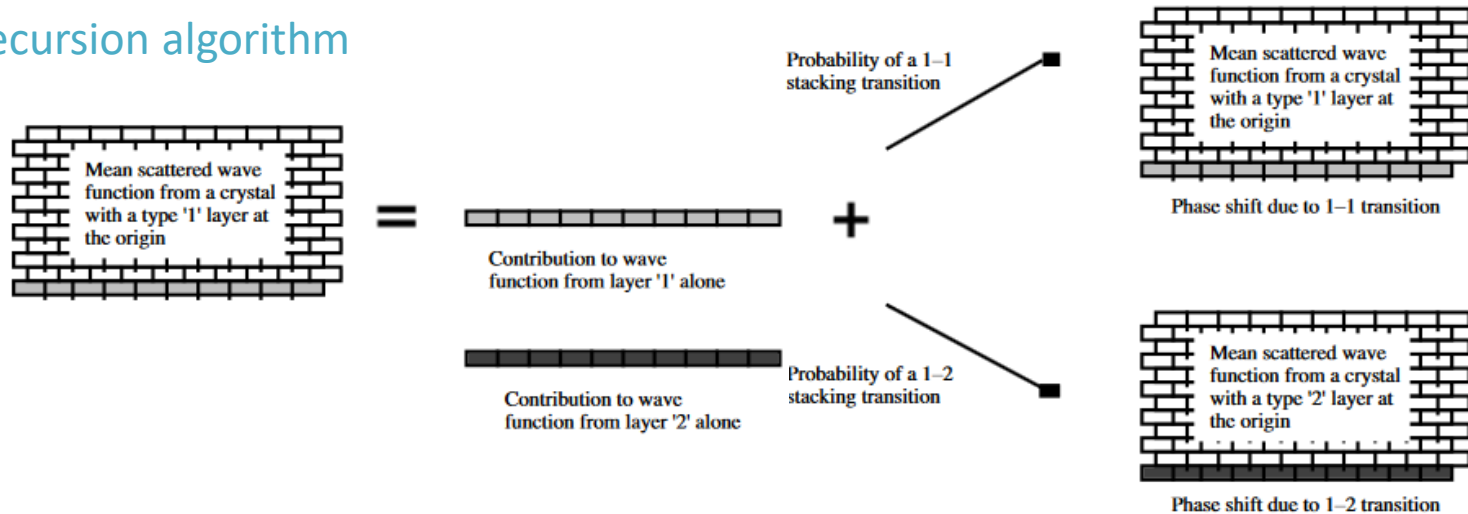
The scattered wave function from a crystal centered on any layer, is equivalent to the scattering contribution from that layer plus the scattered wavefunction from the displaced crystal centered at the next layer.

Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating diracted intensities from crystals containing planar faults. Proc. R. Soc. Lond. A, 433:499-520, 1991.
http://www.public.asu.edu/~mtreacy/DIFFaX_manual.pdf

FAULTS program

DIFFaX recursion algorithm

Mean scattered wave function from a crystal with a type '1' layer at the origin

Probability of a 1–1 stacking transition

Mean scattered wave function from a crystal with a type '1' layer at the origin

Phase shift due to 1–1 transition

Mean scattered wave function from a crystal with a type '1' layer at the origin

=

Contribution to wave function from layer '1' alone

+

Contribution to wave function from layer '2' alone

Probability of a 1–2 stacking transition

Mean scattered wave function from a crystal with a type '2' layer at the origin

Phase shift due to 1–2 transition

$$\Psi_i(\mathbf{u}) = F_i(\mathbf{u}) + \sum_{j=1,2} \alpha_{ij} \exp(-2\pi i \mathbf{u} \cdot \mathbf{R}_{ij})\,\Psi_j(\mathbf{u})$$

The intensity of a statistical ensemble of crystallites is given by the incoherent sum :

$$\frac{I(\mathbf{u})}{N} = \sum_{i=1,2} g_i \left(F^*(\mathbf{u})\Psi(\mathbf{u}) + F(\mathbf{u})\Psi^*(\mathbf{u}) - |F_i(\mathbf{u})|^2 \right)$$

where the layer existence probability factors gi are given by:

$$g_i = \sum_{j=1}^{N} g_j \alpha_{ji} \qquad \sum_{i=1}^{N} g_i = 1$$

Treacy M.M.J., Newsam J.M. and Deem M.W. A general recursion method for calculating diracted intensities from crystals containing planar faults. Proc. R. Soc. Lond. A, 433:499-520, 1991.
http://www.public.asu.edu/~mtreacy/DIFFaX_manual.pdf

The FAULTS program

Simulation → Refinement

START

Read **Input** control file
Layer description, refinable parameters

Refinement?

No (Simulation)

Yes

Read **Intensity** data file
Many formats (depending on the diffractometer)

Read **Background** file
Several background types + account for 2^{ary} phases

Call **optimization** routine
Levenberg-Marquard optimization

Get **calculated intensities**

Get **agreement factors**

Get **calculated intensities**

Max calc. Functions, Convergence criterion ?

Yes

No

Get **new parameter values**

Write **Output** file

END

M Casas-Cabanas, J Rodríguez-Carvajal, MR Palacín *Zeitschrift für Kristallographie*, Suppl 23, 243-248, 2006
M. Casas-Cabanas, M. Reynaud, J. Rikarte, P. Horbach, J. Rodríguez-Carvajal *J. Appl. Cryst. 2016*

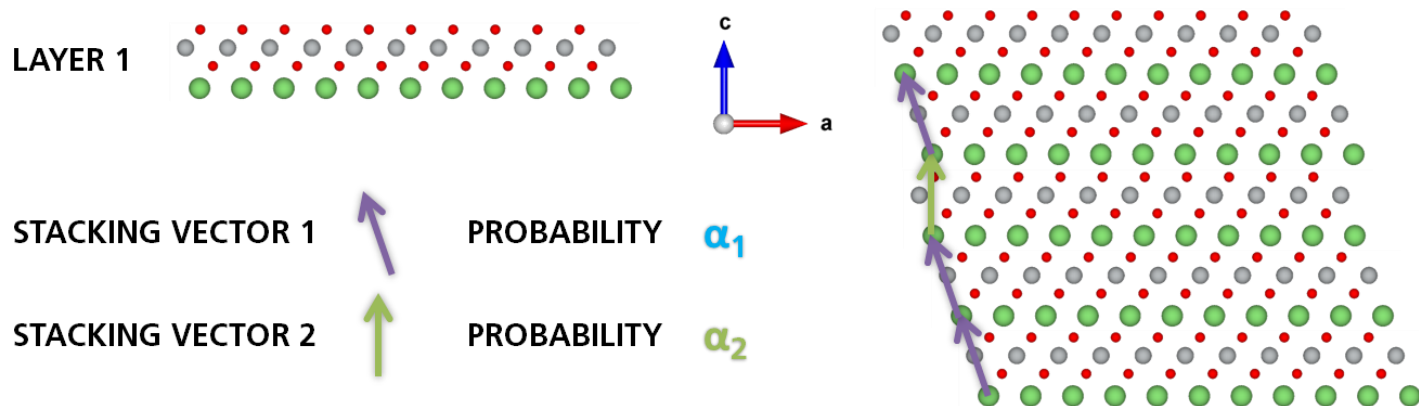# The FAULTS program

Included in FullProf Suite

The FAULTS program

Building your structural model

no crystallographic unit cell
no space group
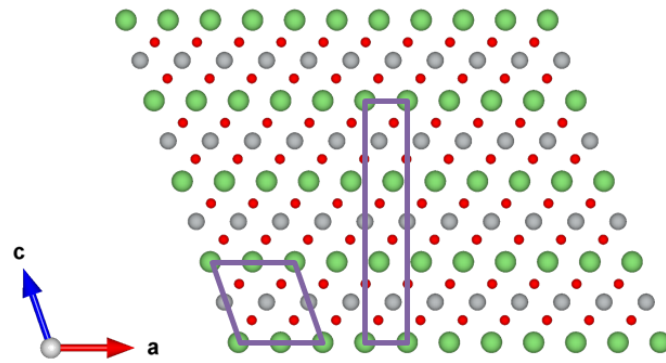
but **layers** interconnected via **stacking vectors** that occur with certain **probabilities**

LAYER 1

STACKING VECTOR 1   PROBABILITY α_1

STACKING VECTOR 2   PROBABILITY α_2

Treacy *et al. Proc. R. Soc. Lond. A* **1991**, *433*, 499 ; Casas-Cabanas et al. *Z. Kristllogr. Suppl*. **2006**, *23*, 243.
Rodriguez-Carvajal and Gonzalez-Platas, CrysFML repository, at https://forge.epn-campus.eu/projects/show/crysfml

The FAULTS program

Building your structural model

4 layers are required to describe fault clustering in diamond
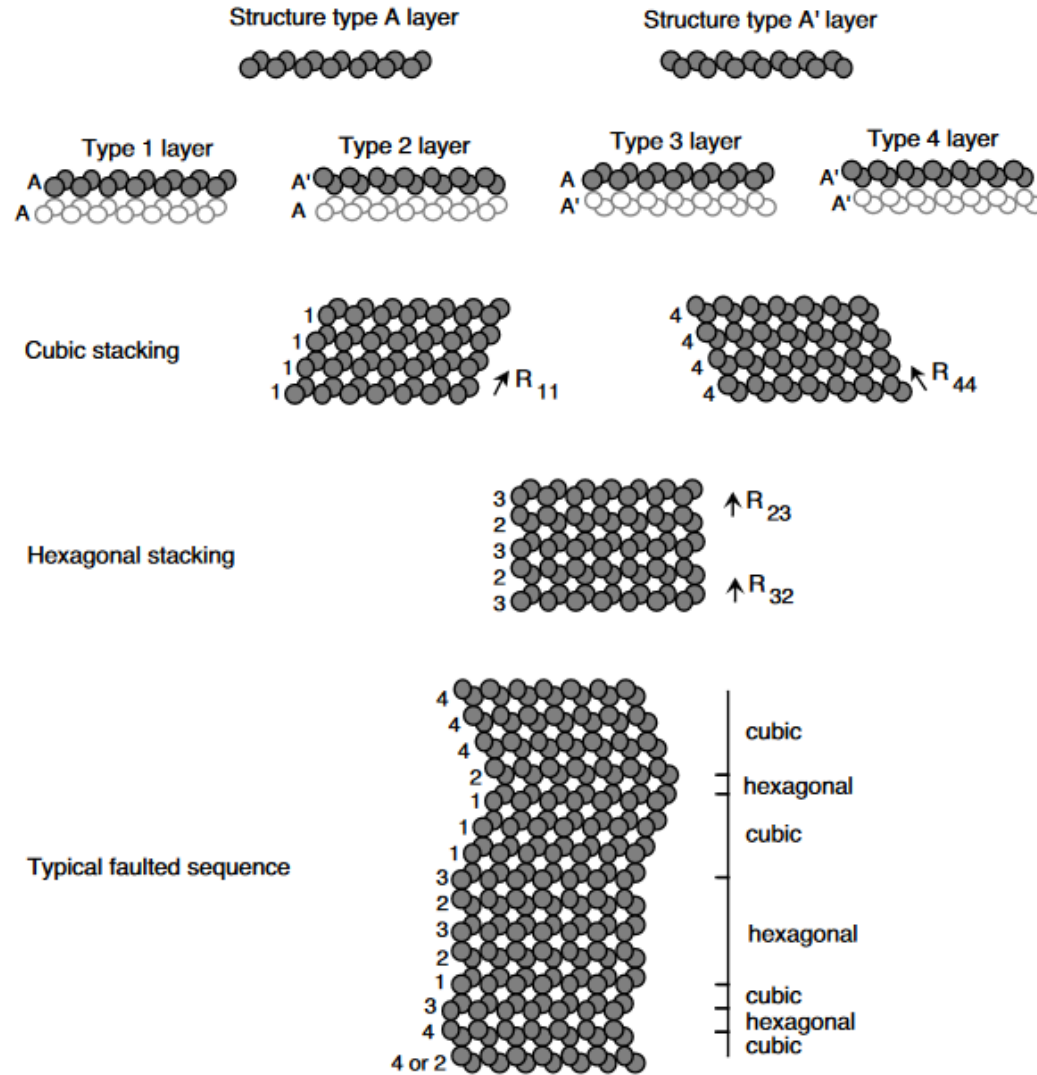
Figure 7: [1$\bar{1}$0] view showing fault clustering in diamond/lonsdaleite.

The FAULTS program

The *.flts input file

The FAULTS program

Output files

Final report	Contains refined values for refinable parameters. Same structure as input file, can be used as input file for further iterations.	LiNiO2_refine_new.flts
Crystallographic structure files	Contains structural model to be read with visualization programs.	LiNiO2_refine1.fst LiNiO2_refine1_flts.cif LiNiO2_refine1_flts.vesta
Progress report	contains information about the different steps of the calculation.	LiNiO2_refine1.out
Observed and calculated profile	Contains experimental pattern, calculated one with the best fit, their difference plot and Bragg reflections.	LiNiO2_refine1.prf

The FAULTS program

Some important information:

- Profile parameters

$$H_G^2 = U tan^2\theta + V tan\theta + W + \frac{4ln2\lambda^2}{\pi D_G^2 cos^2\theta}(\frac{180}{\pi})^2$$

$$H_L = X tan\theta + \frac{2\lambda}{\pi D_L cos\theta}(\frac{180}{\pi})$$

The combination of profile parameters should not lead to a profile function with negative values!

- Tabs are not allowed in the input files of FAULTS (use Notepad++ or similar)

- A missing refinement code will not be considered as zero but will produce an error

- All the non-optional sections and keywords have to be present in the *.flts input file

The FAULTS program

Some important information:

- Filename extension is limited

- DIFFaX2FAULTS permits to convert DIFFaX input files into FAULTS input files

- Check output files and message errors from the commander window

- Read the manual! It contains valuable information

FAULTS manual

Montse Casas Cabanas (CIC energiGUNE), Marine Reynaud (CIC energiGUNE)
Jokin Rikarte Ormazabal (CIC energiGUNE), Pavel Horbach (ILL)
and Juan Rodriguez Carvajal (ILL)

September 2018

The FAULTS program

Building your structural model

- the creation of error-free files is surprisingly difficult

- Frequently, the plane of the layers will not coincide conveniently with any of the unit cell faces of the parent crystal

- There can be different equivalent structure descriptions

- Check your model with vesta or FPStudio!

Example 1	Example 2	Example 3
Graphite	$LiNiO_2$	Li_2MnO_3
Building structural model	Building structural model of a layered material (ideal vs defects)	Building structural model of a monoclinic cell
Layer description different from unit cell (3R)	Simulation and refinement	Simulations of XRD and ED patterns
Simulation	Use of secondary phases	
	Generation of the Bragg positions of the average cell	

FAULTS program

Energy storage
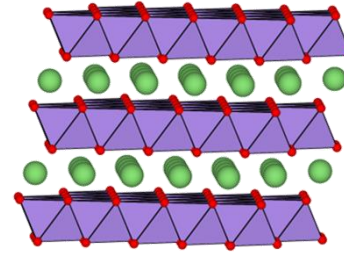
Graphite
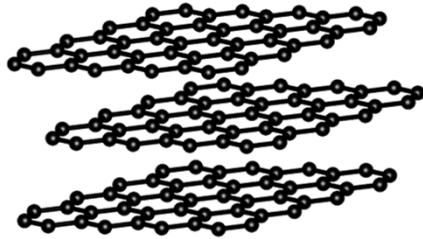
γ-MnO$_2$
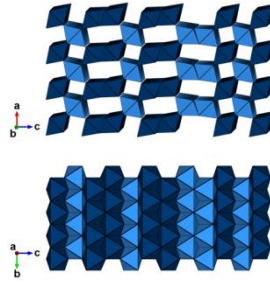
Layered transition metal oxides

PHYSICAL-CHEMICAL PROPERTIES
⇕
STRUCTURAL FEATURES

Catalysis

Drug delivery

Superconductors
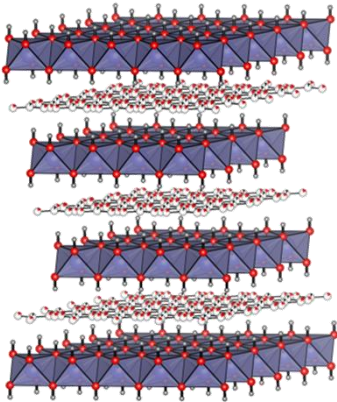
Magnetism

Layered double hydroxides (LDHs)
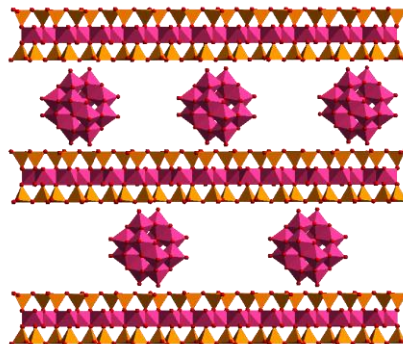
Pillared Clays (PILCS)
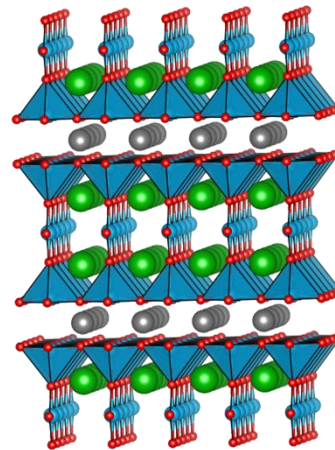
Cuprates
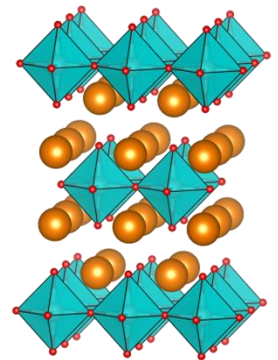
Layered perovskites

The FAULTS program

Example 2   LiNiO$_2$