# TUTORIAL EXPO: SPACE GROUP DETERMINATION

The **Space group determination** folder contains:

- **DEFAULT_SPG** folder
- **NO_DEFAULT_SPG** folder

- **DEFAULT_SPG** folder

It contains: **dapsone.exp** [the input file for the space group determination step by EXPO in case of Dapsone ($C_{12}H_{12}N_2O_2S$), once the unit cell has been determined]; **pd_0005.xye** (the file containing the experimental profile counts); **dapsone.fra** (the file of the fractional coordinates of the true model, hydrogen atoms excluded), **dapsone.pdf** (the file containing the structure information published in **paper.pdf**).
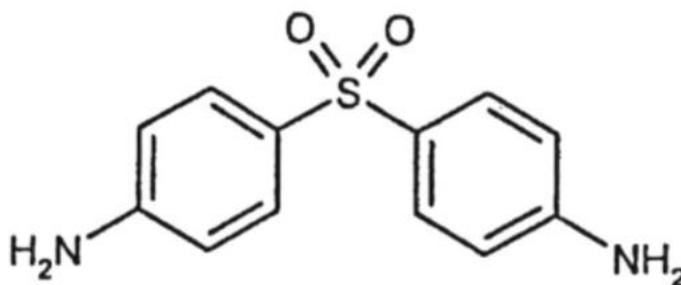
The input file 'dapsone.exp' consists of the following lines:

```
%Structure dapsone
%Job Dapsone (C12H12N2O2S)
%Data
Cell  25.538 8.061 5.762 90 90 90
Content (C12H12N2O2S)4
Pattern    pd_0005.xye
Wavelength 1.54056
findspace
%continue
```

The directive `findspace` of the command `%data` is introduced to activate the space group determination procedure by EXPO. It is based on a statistical analysis of the integrated intensity extracted by assuming the Laue largest symmetry compatible with the identified crystal system and no extinction conditions (in the case of **dapsone** the assumed space group is *Pmmm*).

At the end of the automatic procedure all the possible extinction symbols corresponding to the crystal system [and for each extinction symbol, the corresponding space group(s)] are ranked in function of decreasing values of a figure of merit (FoM).

In case of **dapsone**, the most probable space group suggested by EXPO is the correct one.

To run EXPO on **dapsone**, in order to determine the space group by EXPO:
- o Click on EXPO icon

- o **File** in the upper Menu
- o **Load and Go**
- o Use 'dapsone.exp' as Input File and give the Output Filename you like (dapsone.out is the default output file name)
- o **Go**

  The powder pattern and the vertical bars associated to the calculated reflection positions (generated by assuming the symmetry of the space group *Pmmm*) are visualized.
- o Click on **Next** button to go on continuously until the automatic space group determination procedure is carried out; at the end of this process the following window, showing the extinction symbols listed according to the calculated probability (FoM), will appear:

Space Group	Extinction symbol	FoM	Nabs	Nasym	No. in CSD	% of CSD	Rank	Chiral
P 21 21 21	P 21 21 21	0.168	6	17	58438	7.24	4	yes
P 21 21 2	P 21 21 -	0.072	5	17	3293	0.41	19	yes
P 21 2 21	P 21 - 21	0.054	4	17	3293	0.41	19	yes
P 21 2 2	P 21 - -	0.023	3	17	79	0.01	136	yes
P n m 21	P n - -	0.020	5	17	499	0.06	56	no
P n 21 m	P n - -	0.020	5	17	499	0.06	56	no
P n m m	P n - -	0.020	5	9	247	0.03	73	no
P n m n	P n - n	0.020	16	9	568	0.07	48	no
P n 2 n	P n - n	0.020	16	17	251	0.03	72	no

List   OK   Cancel

- o Click on **OK** to select the Space Group 'P 21 21 21' first ranked in the list (the file 'dapsone1.exp' is created);
- o Click on **OK**

The space group automatically selected by EXPO is the correct one, it can be verified by carrying out the rest of the steps of the structure solution process, by

- o Clicking on **Next** button to go on continuously until the end of the run.

The structure model obtained at the end of Direct Methods procedure, executed on the first set of phases (default choice), is partially correct, it could be improved by the Structure model optimization tools of EXPO (*e.g.*, *via* the COVMAP procedure, for more details see the 'Readme structure model optimization.docx' file available at the 'Structure model optimization' folder); the solution could be searched also by exploring the rest of the stored sets of phases (for more details, see the 'Readme solution by Direct Methods.docx' available at the 'Solution by Direct Methods' folder); in this last case:

- o Select **Solve** > **Explore Trials** in the main Menu;
- o Select by check button the option '**Explore trials not processed yet**'.

At the end of the procedure the twenty available structure models are ranked according to increasing RF values and the first ranked model, except for some labelling errors, is the correct one (it can be verified by comparing the structure model with the published one stored in the **dapsone.fra** file).

- • **NO_DEFAULT_SPG** folder

It contains: **nickel.exp** [the input file for the space group determination step by EXPO in case of trans-Dichloro-bis(triphenylphosphine)nickel(II) - $(C_{36}H_{30}Cl_2NiP_2)$]; **pd_0013.pow** (the file containing the experimental profile counts); **nickel.fra** (the file of the fractional coordinates and isotropic thermal factors of the true model, hydrogen atoms excluded); **nickel.pdf** (the file containing the structure information published in **paper.pdf**).
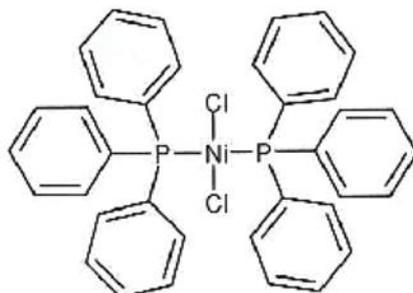
The input file 'nickel.exp' consists of the following lines:

```
%Structure nickel
%Job trans-Dichloro-bis(triphenylphosphine)- nickel(II) - (C36H30Cl2NiP2)
%Data
Cell      11.638  8.197  17.388  90  107.03  90
Content    (C36H30Cl2NiP2)2
Pattern    pd_0013.pow
Wavelength 1.54056
findspace
%Continue
```

The asymmetric unit is one half of the molecule.

The directive `findspace` of the `%data` command activates the space group determination procedure.

In case of **nickel** the automatic procedure for the space group identification by EXPO fails: the correct space group is 'P 2/c' (whose extinction symbol is 'P 1 c 1'), while the largest probability value extinction symbol supplied by EXPO at the end of the space group determination step is 'P 1 21/c 1' (the corresponding space group is 'P 21/c'). The correct extinction symbol 'P 1 c 1' is the second one in the list of the extinction symbols ranked according to the probability value (FoM). In order to recognize the correct extinction symbol a visual inspection by graphic interface is strongly suggested by verifying if the extinction conditions, stated by the most probable extinction symbol, agree with the experimental pattern.

To run EXPO on **nickel**, in order to determine the space group by EXPO and, at the end to the automatic space group determination procedure, to identify the correct extinction symbol by visual inspection, the following pathway should be carried out:

- Click on EXPO icon
- **File** in the upper Menu
- **Load and Go**;
- Use 'nickel.exp' as Input File and give the Output Filename you like (nickel.out is the default output file name)
- **Go**
  The powder pattern and the vertical bars associated to the calculated reflection positions (generated by assuming the symmetry of the space group *P2/m*) are visualized.

o Click on **Next** button to go on continuously until the automatic space group determination procedure is carried out; at the end of the procedure the following window, showing the extinction symbols listed according to the calculated probability (FoM), will appear:

Find space group

| Space Group	Extinction symbol	FoM	Nabs	Nasym	No. in CSD	% of CSD	Rank	Chiral
P 21/c	P 1 21/c 1	0.446	19	21	279041	34.57	1	no
P 2/c	P 1 c 1	0.325	19	21	5232	0.65	14	no
P c	P 1 c 1	0.325	19	41	3447	0.43	18	no
P 21	P 1 21 1	0.132	0	41	41791	5.18	5	yes
P 21/m	P 1 21 1	0.132	0	21	4023	0.50	17	no
P 2	P 1 - 1	0.096	0	41	142	0.02	96	yes
P 2/m	P 1 - 1	0.096	0	21	110	0.01	111	no
P m	P 1 - 1	0.096	0	41	21	0.00	202	no
P 21/n	P 1 21/n 1	0.008	18	21	279041	34.57	1	no

List   OK   Cancel

o Click on the 'List' button located on the bottom left corner of the window, to have access to the list of systematically absent reflections in case of the most probable extinction symbol (*i.e.*, 'P 1 21/c 1');
o Click on 'Num' column in order to sort the absent reflections in terms of increasing sequential numbers, corresponding to increasing 2θ values:

List of systematically absent reflections

Num	h	k	l	Extinction condition	Probability for extinction	Type
1	0	0	1	c (h 0 l : l)	1.000	Single
3	1	0	-1	c (h 0 l : l)	0.998	Single
5	1	0	1	c (h 0 l : l)	0.601	Overlapped
6	0	1	0	21 (0 k 0 : k)	0.542	Overlapped
13	2	0	-1	c (h 0 l : l)	0.948	Overlapped
16	1	0	-3	c (h 0 l : l)	0.906	Overlapped
18	0	0	3	c (h 0 l : l)	0.998	Single
20	2	0	1	c (h 0 l : l)	0.831	Single
23	2	0	-3	c (h 0 l : l)	0.917	Overlapped

Close

o Zoom the pattern in the low 2θ region 10°-11° (*i.e.*, by using the 'Zoom' button from the main window) and check if some reflections belonging to this region are also in the list of absent reflections (by marking the reflection in the list it is shown in the pattern). The overlapping reflections n. 5 (101) and n. 6 (010) are systematically absent due to the presence of the *c* glide and of the 2_1 axis, respectively; but their absence does not agree with the experimental pattern, due to the presence of a corresponding evident observed peak, as shown in the following figure:

List of systematically absent reflections

Num	h	k	l	Extinction condition	Probability for extinction	Type
1	0	0	1	c (h 0 1 : 1)	1.000	Single
3	1	0	-1	c (h 0 1 : 1)	0.998	Single
5	1	0	1	c (h 0 1 : 1)	0.601	Overlapped
6	0	1	0	21 (0 k 0 : k)	0.542	Overlapped
13	2	0	-1	c (h 0 1 : 1)	0.948	Overlapped
16	1	0	-3	c (h 0 1 : 1)	0.906	Overlapped
18	0	0	3	c (h 0 1 : 1)	0.998	Single
20	2	0	1	c (h 0 1 : 1)	0.831	Single
23	2	0	-3	c (h 0 1 : 1)	0.917	Overlapped
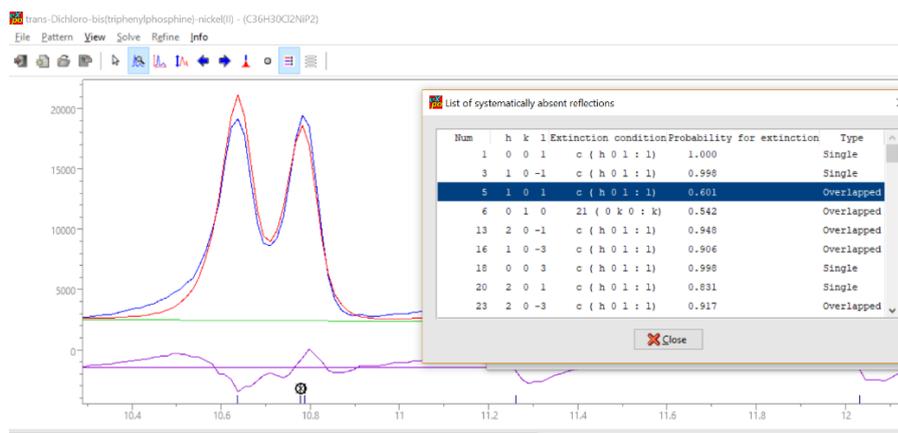
Close

- o Click on 'Close' in order to check the second extinction symbol in the list;
- o Select by mouse the second extinction symbol (*i.e.*, 'P 1 c 1') and click on the 'List' button repeating all the steps carried out in case of 'P 1 21/c 1'.
  It is easily seen that only the reflection n. 5 (101) is now absent (due to the *c* glide presence) while the reflection n. 6 (010) is present, in agreement with the experimental pattern, as shown in the following figure:

List of systematically absent reflections

Num	h	k	l	Extinction condition	Probability for extinction	Type
1	0	0	1	c (h 0 1 : 1)	1.000	Single
3	1	0	-1	c (h 0 1 : 1)	0.998	Single
5	1	0	1	c (h 0 1 : 1)	0.601	Overlapped
13	2	0	-1	c (h 0 1 : 1)	0.948	Overlapped
16	1	0	-3	c (h 0 1 : 1)	0.906	Overlapped
18	0	0	3	c (h 0 1 : 1)	0.998	Single
20	2	0	1	c (h 0 1 : 1)	0.831	Single
23	2	0	-3	c (h 0 1 : 1)	0.917	Overlapped
28	1	0	3	c (h 0 1 : 1)	0.718	Single

Close
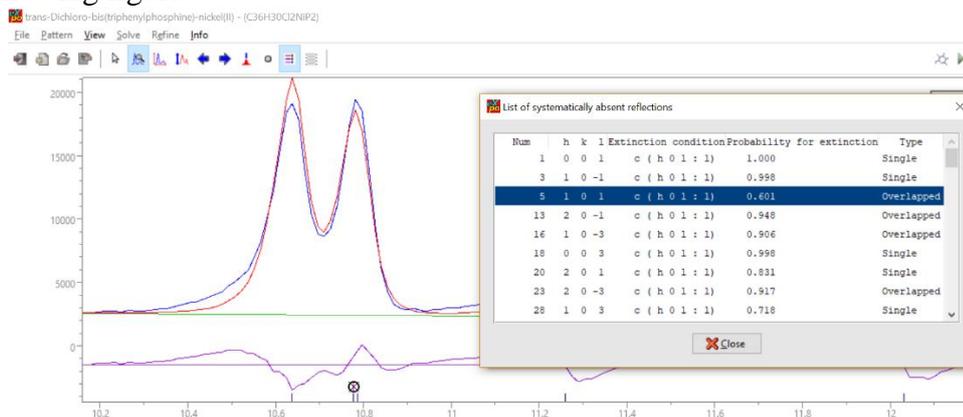
Assuming that the pattern does not contain peaks due to an impurity, this visual inspection suggests that the correct extinction symbol is not the first one in the list but the second one. Two space groups are compatible with the P 1 c 1 extinction symbol: P 2/c and P c;

- o Select the space group P 2/c, having the largest frequency in the Cambridge Structural Database (CSD);
- o Click on **OK** (the file 'nickel1.exp' is created);
- o Click on **OK**
- o Click on **Next** button to go on continuously until the end of the run.

The structure model obtained at the end of Direct Methods procedure, executed on the first set of phases (default choice), is not interpretable, the rest of stored sets of phases can be explored in order to find the correct structure model (for more details, see the 'Readme solution by Direct Methods.docx' file available at the 'Solution by Direct Methods' folder):

- o Select **Solve** > **Explore Trials** in the main Menu;
- o Select by check button the option '**Explore trials not processed yet**'.

At the end of the procedure the twenty available structure models are ranked according to increasing RF values and the first ranked model is the correct one (all the 21 non-H atoms are rightly located and labelled, it can be verified by comparing the structure model with the published one stored in the **nickel.fra** file).