EXPO&more International Workshop
30 September – 3 October 2019

CNR Istituto di Cristallografia

Space group determination

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Outline

- Some basic concepts (symmetry operations, symmetry in direct space, space groups, symmetry in reciprocal space..);

- The space group determination method in ***EXPO***;

- Space group determination by ***EXPO***: some applications and suggestions in case of failures of a default run;

- Final remarks.

Space group determination

Second step in the pathway of the solution process:

- INDEXING
- **SPACE GROUP DETERMINATION**
- PROFILE DECOMPOSITION AND INTENSITY EXTRACTION
- STRUCTURE SOLUTION AND MODEL OPTIMIZATION
- RIETVELD REFINEMENT

Some basic concepts: symmetry operations

Symmetry in direct space

A crystal can be described by a regular repetition of a unit cell.
In addition to the lattice periodicity, it can show other types of symmetries.

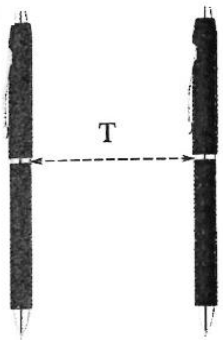
A symmetry operation is an operation that leaves unchanged all the properties of the space after its application.

Symmetry elements: points, axes or planes with respect to which the symmetry operations are carried out.

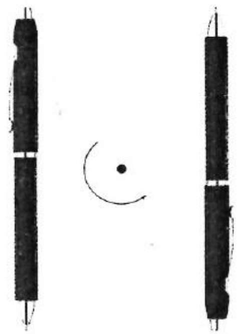
Symmetry in direct space

Examples of symmetry operations:*

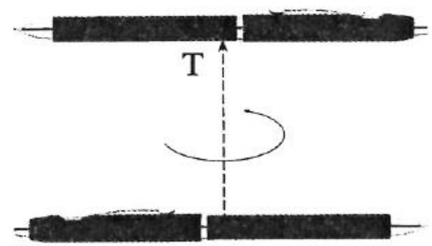
Translation



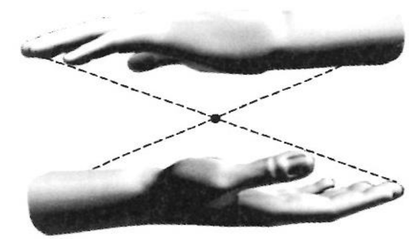
Rotation



Rototranslation



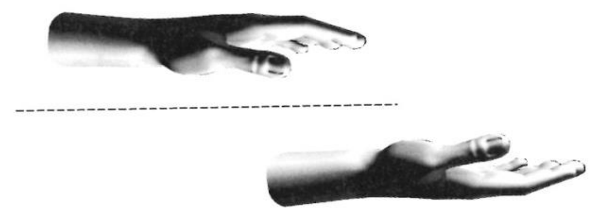
Inversion with respect to a point



Reflection with respect to a plane

Rotoinversion or rotoreflection

Glide plane



*Altomare, A., Cuocci, C., Moliterni, A. & Rizzi, R. (2013). *Single crystal and powder XRD techniques: An overview*. In *Inorganic Micro- and Nanomaterials,* edited by A. Dibenedetto & M. Aresta, pp. 57-91. Berlin: De Gruyter.

Point groups and Laue classes

The point groups are combinations of symmetry operators that do not imply translations (*i.e.*, simple rotation or inversion axis). Their number is 32.

The eleven centrosymmetric crystallographic point groups are known as *Laue classes* (or *Laue groups*):

Crystal System	Laue Classes	
Triclinic	$\bar{1}$	
Monoclinic	$2/m$	
Orthorhombic	mmm	
Tetragonal	$4/m$	$4/mmm$
Trigonal	$\bar{3}$	$\bar{3}m$
Hexagonal	$6/m$	$6/mmm$
Cubic	$m\bar{3}$	$m\bar{3}m$

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Space groups

A crystallographic space group is the set of geometrical symmetry operations that take a three-dimensional periodic object (*i.*e., a crystal) into itself.

If all the combinations of symmetry operations, together with the possible cells (primitive or centred), are taken into account, the total number of space groups is 230.

Symmetry equivalents in direct and reciprocal space

If m symmetry operators are present:

$$C_s=(R_s, T_s)\ , \qquad\qquad s=1,\dots,m$$

where R_s is a matrix, the rotational component of the symmetry operation and T_s is the translational component of the symmetry operation,

in direct space, if C_s is applied to r_j (*i.e.*, a generic positional vector in the unit cell):

$$r_{js} = R_s\, r_j + T_s, \qquad\qquad s=1,\dots,m$$

are **symmetry equivalent positions**;

in reciprocal space, the reflections

$$hR_s, \qquad\qquad s=1,\dots,m$$

are **symmetry equivalent reflections**.

Systematically absent reflections

The presence of some symmetry operators has consequences on reciprocal space: *it is responsible for the absence of some classes of reflections that have $I_{\mathbf{h}} = 0$ and are called* ***systematically absent reflections.***

Let us consider the symmetry equivalent reflections

$\mathbf{hR}_s$, $\quad s = 1,\ldots, m \quad$ *and*

$$\boxed{F_{\mathbf{hR}_s} \, exp(2\pi i \mathbf{hT}_s)} = \sum_{j=1}^{N} f_j \, exp(2\pi i \mathbf{hR}_s \boldsymbol{r}_j) \, exp(2\pi i \mathbf{hT}_s) = \sum_{j=1}^{N} f_j \, exp(2\pi i \mathbf{h}\boldsymbol{r}_{js}) = \boxed{F_{\mathbf{h}}}$$

$$\boldsymbol{r}_{js} = \mathbf{R}_s \boldsymbol{r}_j + \mathbf{T}_s$$

$$F_{\mathbf{hR}_s} = F_{\mathbf{h}} \, exp(-2\pi i \mathbf{hT}_s) \qquad (1)$$

$$|F_{\mathbf{hR}_s}| = |F_{\mathbf{h}}| \quad \text{and} \quad \varphi_{\mathbf{hR}_s} = \varphi_{\mathbf{h}} - 2\pi \, \mathbf{hT}_s$$

For each reflections **h** for which

$\mathbf{hR}_s = \mathbf{h}$ and $\mathbf{hT}_s \neq n$, $\quad n$ integer

(1) is violated unless the reflection has $|F_{\mathbf{h}}| = 0$ (and, therefore, $I_{\mathbf{h}} = 0$, because $I_{\mathbf{h}} \propto |F_{\mathbf{h}}|^2$), *i. e.*, unless **the reflection is sistematically absent or extinct.**

Space group determination

The presence of symmetry operators has consequences on reciprocal space.

For example, in case of $P2_1/c$

- **Reflections** (0 *k* 0), with $k = 2n + 1$

and

- **Reflections** (*h* 0 *l*), with $l = 2n + 1$

are absent (*i.e.*, their intensities are zero), due to the presence of

- 2_1 axis || ***b*** , $\mathbf{R} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$, $\mathbf{T} = \begin{pmatrix} 0 \\ 1/2 \\ 0 \end{pmatrix}$ [affecting reflections (0 *k* 0)), with $k = 2n + 1$]
- *c* glide ⊥ ***b***, $\mathbf{R} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, $\mathbf{T} = \begin{pmatrix} 0 \\ 0 \\ 1/2 \end{pmatrix}$ [affecting reflections (*h* 0 *l*)), with $l = 2n + 1$]

The analysis of the diffraction intensities provides information on the systematically absent reflections.

Symmetry in reciprocal space

From systematic absences it is possible to recognize:

- *the centring type of the unit cell (e.g., in case of A-, B-, C-, F-, I-, R-centred cell);*

- *the presence of a screw axis;*

- *The presence of a glide plane.*

Space group determination

The combination of the information on Laue group and systematically absent reflections → The determination of the Extinction Symbol (ES).

For example, in case of cubic system, one of the ES is:

F - - -

The first character of the ES is the symbol of the centring type of the cell

The next characters represent the reflections conditions for the symmetry directions.
Symmetry directions without conditions are represented by a 'dash'.

A symmetry direction with reflection conditions is represented by the symbol of the corresponding screw axis or glide plane.

Space group determination

The combination of the information on Laue group and systematically absent reflections → The determination of the Extinction Symbol (ES).

The determination of the ES is based on the integrated intensities of each individual reflection, that,

in case of single crystal data, can be accurately estimated.

The space group determination is usually a trivial task.

in case of powder data, are affected by unavoidable errors due to multiple causes (*e.g.*, overlap of reflections, wrong background definition, preferred orientation effects,…).

The space group determination can be not straightforward.

The space group determination method in EXPO

The space group determination method (Altomare *et al*. 2004, 2005, 2007, 2008) implemented in *EXPO* (Altomare *et al*., 2013) is a probabilistic approach based on statistical analysis of integrated intensities of reflections.

Space group determination method in EXPO

The space group determination step exploits the full pattern decomposition results obtained in the space group with the Laue largest symmetry compatible with the geometry of the cell and no extinction conditions (*e.g.*, *P*2/*m*, *Pmmm* and *P*4/*mmm* in case of monoclinic, orthorhombic and tetragonal systems, respectively).

Full pattern decomposition (Laue symmetry)

Probability of each possible extinction symbol *via* a statistical analysis of the reflection intensities

List of the extinction symbols ranked according to the calculated probability

Space group determination method in EXPO

*The probabilistic approach**

- The intensities are extracted from the experimental pattern *via* the Le Bail algorithm, by considering the Laue largest symmetry corresponding to the identified crystal system.
- All the extinction symbols corresponding to the crystal system are considered [*i.e.*, 14 for the monoclinic system, 111 for the orthorhombic, 31 for the tetragonal, 12 for the trigonal-hexagonal systems (only hexagonal axes considered), 18 for the cubic system**].
- The extracted intensities are normalized according to the Wilson plot method and submitted to statistical analysis for the space group determination.

* Altomare, Giacovazzo & Moliterni (2008). *Indexing and Space Group determination* in *Powder Diffraction Theory and Practice*, pp. 206-226, RCSPublishing, Cambridge.

** *International Tables for Crystallography* (2006). Vol. A, Chapter 3.1, pp-44.54, ed. Th. Hahn. Springer, Dordrecht.

Space group determination by EXPO

The probabilistic approach

The probability P of each extinction symbol is calculated by taking into account the probability p of each symmetry element regarding the symbol.

For example:

$$P(P\text{- - -})=p(P)p(2_{[100]})p(m\perp \mathbf{a})p(2_{[010]})p(m\perp \mathbf{b})p(2_{[001]})p(m\perp \mathbf{c})$$

where p is calculated by using the extracted normalized intensities.

For example:

$$p(2_{[010]})=1 - p(2_{1[010]}),$$

where $$p(2_{1[010]})=1 - \langle z_{0k0}\rangle_{k=2n+1},$$

and $\langle z_{0k0}\rangle_{k=2n+1}$ is the average of the normalized intensities (suitably weighted) of the reflections of type (0 k 0), with k=2n+1.

Space group determination by EXPO

The probabilistic approach

$$\langle z \rangle = \left(\Sigma\, w_j z_j\right)/\Sigma\, w_j,$$

where

$$\begin{cases} w_j = 1 \text{ for single reflection,} \\ 0 < w_i < 1 \text{ depending on the overlapping degree.} \end{cases}$$

The smallest the $\langle z \rangle$ value of a class of reflections, the closest to 1 is the probability of the symmetry element corresponding to the extinction of that class.

Space group determination by EXPO

The graphical selection of an extinction symbol provides:

- the list of space group(s) compatible with the extinction symbol;
- useful tools for checking if the most probable ES suggested by the automatic procedure is fully reliable and, eventually, for making a different choice.

If more than one space group is compatible with the same ES, the ES cannot unambiguously define the space group, like, for example, in the following cases:

Crystal system	Extinction Symbol	Space groups
Monoclinic	*P* 1-1	*P2, Pm, P2/m*
Orthorhombic	*P- - -*	*P222, Pm2m, P2mm, Pmm2, Pmmm*
Orthorhombic	*P - -a*	*Pm2a*, $P2_1ma$, *Pmma*
Tetragonal	*P- - -*	*P4, P-4, P4/m, P422, P4mm, P-42m, P-4m2, P4/mmm*
Hexagonal	$P6_1$ - -	$P6_1$, $P6_5$, $P6_122$, $P6_522$
Cubic	*P- -n*	*P-43n, Pm-3n*

In these cases, the choice of the correct space group is made by carrying out the solution process for each possible space group or, by selecting one of them by taking into account additional information coming from structures already solved.

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How to carry out the space group determination step by EXPO:

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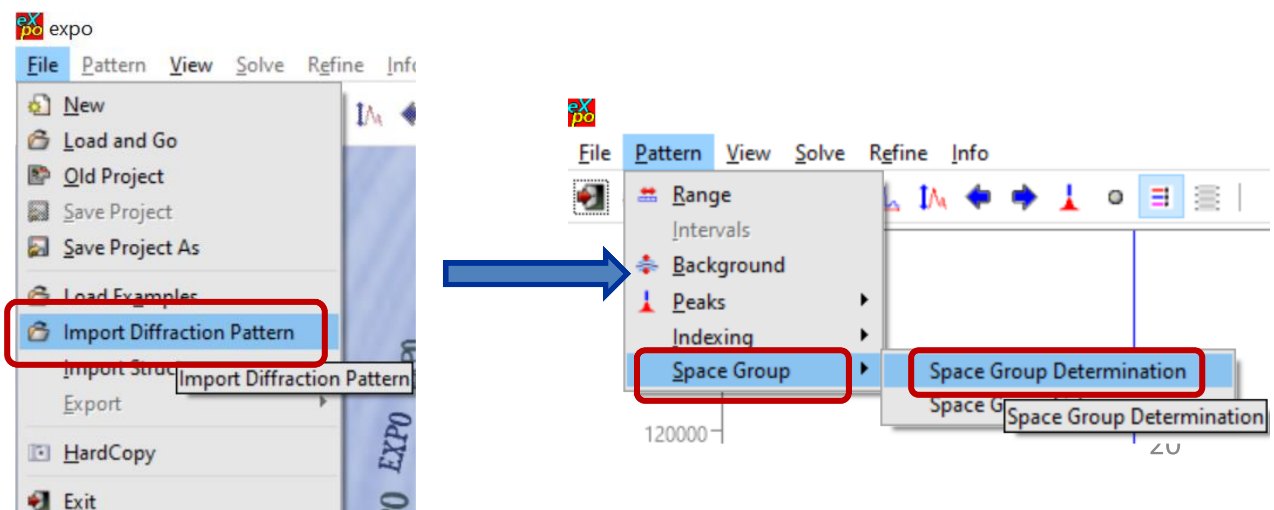
- By loading an external input file, once the unit cell has been determined, requiring minimal information and consisting of commands (the first character in the line must be '%') and directives (sub-commands following the related command):

%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

Minimal information

- By graphic interface:



An example of space group determination by *EXPO*:

Cerium dioxide- Conventional X-ray data

Published cell: a= 5.40972 Å – Space group: F m -3 m

(CIF file No. 4343161 of COD database).

If the cell parameters and cell content are provided:

Missing Information

Cell Parameters

a: 5.412165 b: 5.412165 c: 5.412165 α: 90.0000 β: 90.0000 γ: 90.0000

Volume: 158.531

Space Group

☑ Find Space Group

Space Group Symbol: P m -3 m

Cell Content: Ce 4 O 8

Content Volume: 307.120 Volume per Atom: 13.211 Density: 7.211

OK

Find space group

Space Group	Extinction symbol	FoM	Nabs	Nasym	No. in CSD	% of CSD	Rank	Chiral
F m -3 m	F - - -	0.709	12	1	532	0.07	53	no
F 2 3	F - - -	0.709	12	1	77	0.01	139	yes
F -4 3 m	F - - -	0.709	12	1	50	0.01	163	no
F m -3	F - - -	0.709	12	1	39	0.00	172	no
F 4 3 2	F - - -	0.709	12	1	31	0.00	183	yes
F 41 3 2	F 41 - -	0.381	13	1	37	0.00	174	yes
F d -3 m	F d - -	0.092	14	1	127	0.02	104	no
F d -3	F d - -	0.092	14	1	88	0.01	126	no
F -4 3 c	F - - c	0.074	16	1	87	0.01	128	no
F m -3 c	F - - c	0.074	16	1	48	0.01	167	no
P n -3	P n - -	0.066	4	1	31	0.00	181	no
P n -3 m	P n - -	0.066	4	1	25	0.00	192	no
P a -3	P a - -	0.064	3	1	732	0.09	42	no
F d -3 c	F d - c	0.010	18	1	116	0.01	107	no
P n -3 n	P n - n	0.007	8	1	103	0.01	115	no
P 21 3	P - - -	0.007	1	1	499	0.06	55	yes

List OK Cancel

EXPO provides the list of extinction symbols ranked according to a suitable Figure of Merit (FoM).
The most probable extinction symbol (*F*- - -) does not unambiguously define the space group.

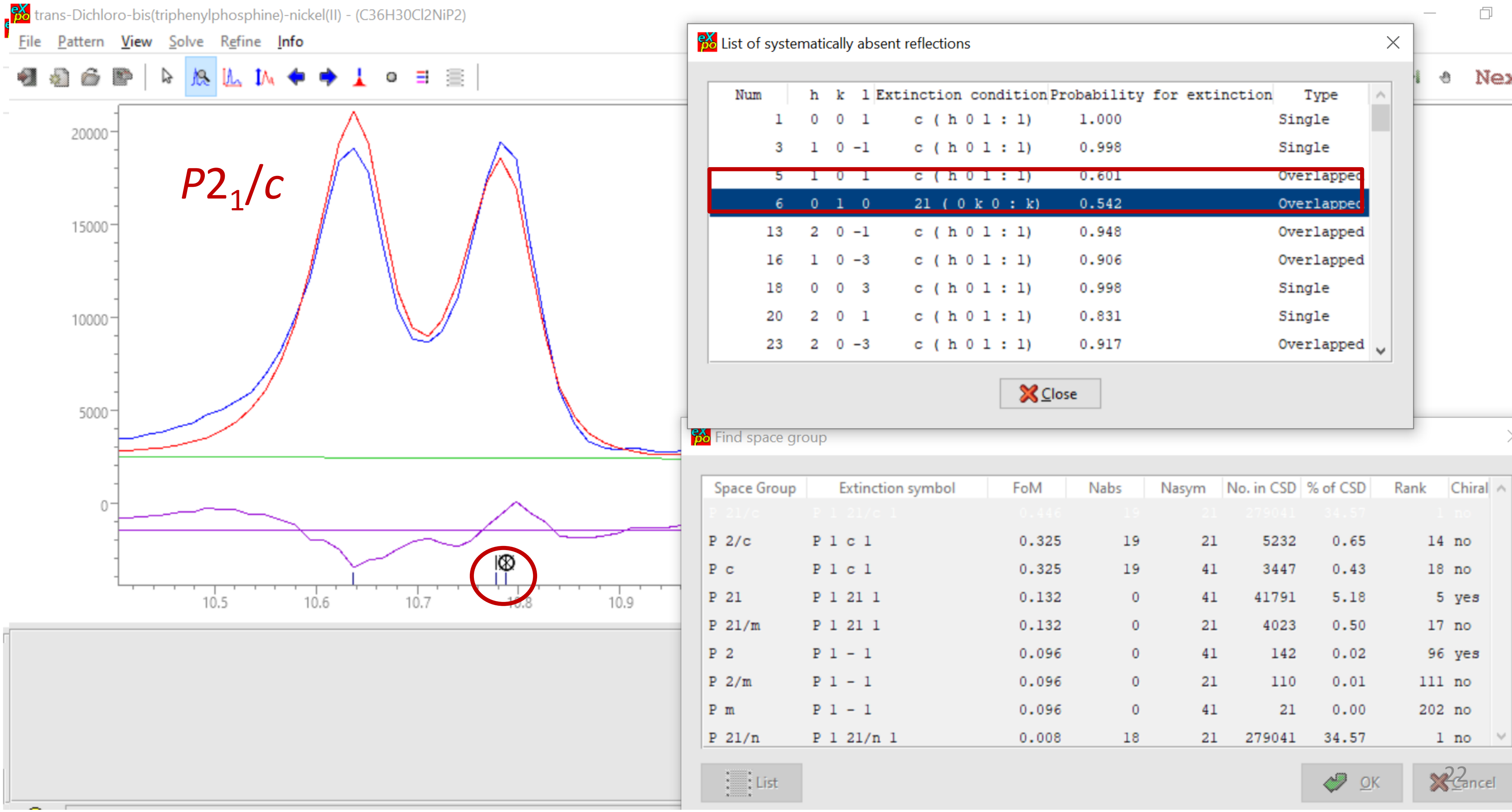
If more space groups are compatible with the same ES, they are ranked according to decreasing values of the number of their occurrences in the CSD database (No in CSD).

Space group determination by EXPO:

NICKEL: Dichlorobis(triphenylphosphine)nickel(II) - ($C_{36}H_{30}Cl_2NiP_2$)

X-ray laboratory data - Published space group: $\boxed{P2/c}$

Florence, A. J., Shankland, N., Shankland, K., David, W. I. F., Pidcock, E., Xu, X., Johnston, A. Kennedy, A. R., Cox, P. J., Evans, J. S. O. Steele, G. Cosgrove, S. D. & Frampton, C. (2005). *J. Appl. Cryst.* **38**, 249-259.



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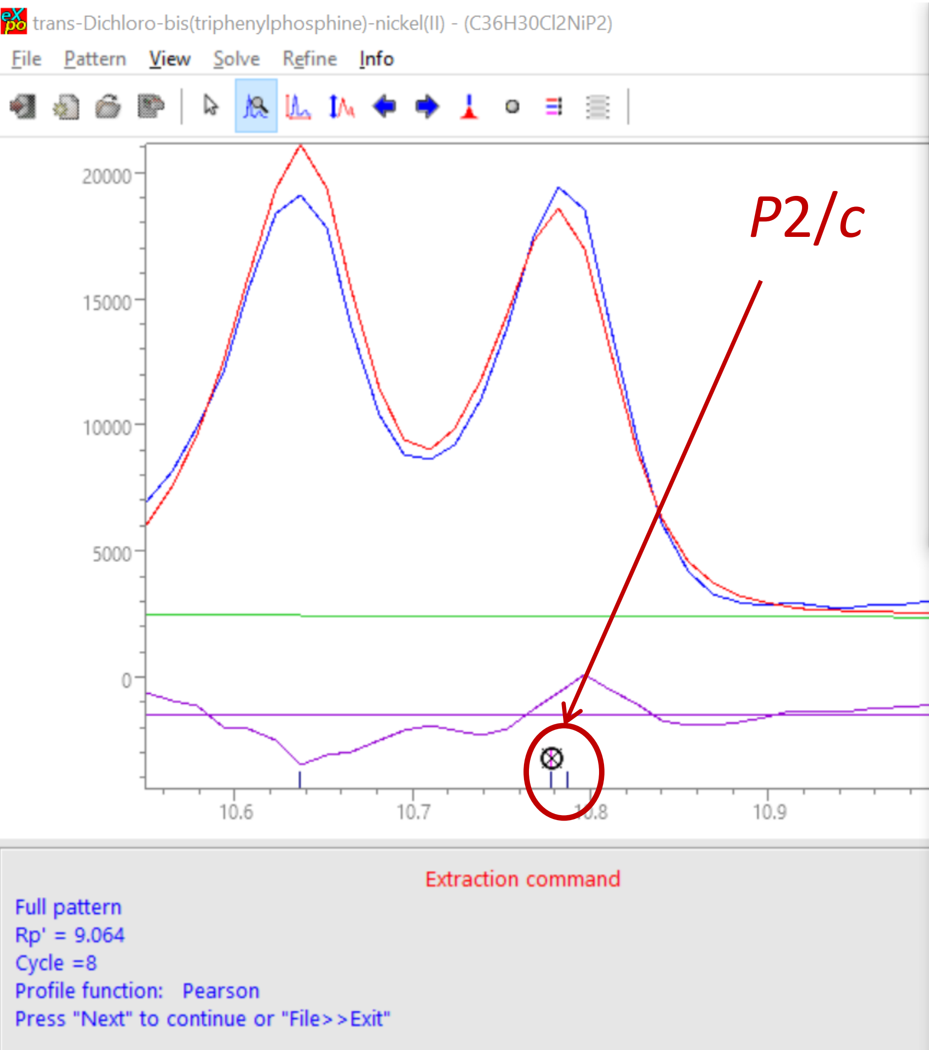

List of systematically absent reflections

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
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
28	1	0	3	c (h 0 l : l)	0.718	Single

Close

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

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Space group determination by EXPO in case of pseudotranslational effects

Pseudotranslational simmetry effects are present when a non-negligible part of the electron density [*i.e.*, $\rho_p(\mathbf{r})$] satisfies a vector **u** that is not a crystallographic translation:

$$\rho_p(\mathbf{r}) \approx \rho_p(\mathbf{r}+\mathbf{u})$$

These effects often occur in case of structures containing heavy atoms.

Due to pseudotranslational effects, the normalized intensities of some classes of reflections are greater and those ones of some other classes are smaller than the expected ones, simulating the presence of symmetry operator(s).

⇓

A space group determination process that does not take into account the pseudo-translational effects could be misleading.

Space group determination by *EXPO* in case of pseudotranslational effects

In case of psedotranslational simmetry (detected by a statistical analysis of the integrated intensities) ***EXPO*** provided, in the output file only, a second list in which the extinction symbols are ranked according to probability values taking into account the effects of pseudotranslation.

If the most probable ES of the two lists are different, that one of the second list, taking into account the pseudotranslational effects, could be the right one.

BAMO: $BaMo_3O_{10}$

X-ray laboratory data - Published space group: $\boxed{P2_1}$

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*******************************
Correction by Pseudotranslation
*******************************

Extinction Group          Fig.Mer
  P 1 21 1                 0.506
  P 1 21/n 1               0.394
  P 1 _ 1                  0.056
  P 1 n 1                  0.044
  P 1 21/c 1               0.000
  P 1 21/a 1               0.000
  P 1 a 1                  0.000
  P 1 c 1                  0.000
  I 1 _ 1                  0.000
  I 1 a 1                  0.000
  A 1 n 1                  0.000
  A 1 _ 1                  0.000
  C 1 c 1                  0.000
  C 1 _ 1                  0.000
```

Find space group

Pseudotranslational effects not taken into account:

Space Group	Extinction symbol	FoM	Nabs	Nasym	No. in CSD	% of CSD	Rank	Chiral
P 21/n	P 1 21/n 1	0.758	21	14	279041	34.57	1	no
P 21	P 1 21 1	0.142	2	28	41791	5.18	5	yes
P 21/m	P 1 21 1	0.142	2	14	4023	0.50	17	no
P 2/n	P 1 n 1	0.084	19	14	5232	0.65	14	no
P n	P 1 n 1	0.084	19	28	3447	0.43	18	no
P 2	P 1 - 1	0.016	0	28	142	0.02	96	yes
P 2/m	P 1 - 1	0.016	0	14	110	0.01	111	no
P m	P 1 - 1	0.016	0	28	21	0.00	202	no
P 21/c	P 1 21/c 1	0.000	25	14	279041	34.57	1	no

List OK Cancel

Final remarks

The outcomes of the space group determination process by EXPO are based on statistical analysis of the integrated intensities, that are affected by errors

The most probable extinction symbol (ES) suggested by EXPO could be wrong.

To increase the probability of identifying the correct space group:

- Check by visual inspection ***via*** graphic interface if the extinction conditions, stated by the most probable ES, agree with the experimental diffraction pattern.
- If more space groups are compatible with the same ES and no prior information is available, the structure solution can be carried out by trying one of the possible space groups, according to the order in the list given by *EXPO*.
- Check the *EXPO* output file: in case of crystal structures characterized by pseudotranslational effects, the correct ES could be that one whose probability value takes into account the pseudotranslational effects.
- In case of failure of structure solution process *via* the most plausible space group(s), further attempts should be tried by considering the less probable space groups.

FOR YOUR ATTENTION