Tutorial on the use of the program *PSEUDO* of the Bilbao Crystallographic Server (www.cryst.ehu.es)

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(see also E. Kroumova, M. I. Aroyo, J. M. Perez-Mato, S. Ivantchev, J. M. Igartua and H. Wondratschek, J. Appl. Cryst. (2001) 34, 783)

If a structure, with space group H, is such that all its atomic positions $\mathbf{r}_i$ can be described as $\mathbf{r}_i^o + \mathbf{u}_i$, with $\mathbf{u}_i$ being small displacements, while the virtual atomic positions $\mathbf{r}_i^o$ have a higher symmetry described by a supergroup G > H, we say that the structure has pseudosymmetry G, or is pseudosymmetric for the space group G.

The detection of pseudosymmetry can be very useful for several purposes:

- Prediction of symmetry and structure of some other phase of the material
- Prediction of phase transitions.
- Identification of ferroic materials: ferroelectrics, ferroelastics,…
- Determination of an optimized virtual parent structure
- Detection of false symmetry assignments (overlooked symmetry)
- Identification of the space group symmetry of a theoretical structure calculated without symmetry restrictions (ab-initio calculations).

The Bilbao Crystallographic server provides three tools for pseudosymmetry search in a given structure: PSEUDO, DOPE and BPLOT.

PSEUDO is a new version of a previous program (*J. Appl. Cryst. (2001). 34, 783*), which examines the possible pseudosymmetry for a given supergroup G of H by applying on the structure the coset representatives of the left coset decomposition of G with respect to the observed symmetry H. The program then checks the approximate coincidence of the transformed structures with the original one through an identification of the atomic displacements relating the two configurations. If these displacements are smaller than a tolerance, the structure is flagged as pseudosymmetric.

DOPE works similarly as PSEUDO, but it does the quantitative comparison of the original and transformed structures by checking the degree of superposition of their virtual electronic densities, obtained from the standard atomic diffusion factors assigned to each atom. Results can be more difficult to interpret than those of PSEUDO, since superposition of atoms of different type may contribute to the calculated degree of pseudosymmetry.

BPLOT is a modified version (adapted for the Bilbao server with the collaboration of its author) of the program KPLOT (Hundt, R. (1979). KPLOT. A Program for Plotting and Investigating Crystal Structures). BPLOT is intended for searching and identifying *symmetry* rather than *pseudosymmetry*. It transforms the input structure to a structure with space group P1 and does not assume a priori any rotational symmetry. In contrast

with PSEUDO, generally BPLOT only works properly if the pseudosymmetry is very high, with displacements of the order of 0.1A or smaller.

The program PSEUDO

PSEUDO is designed to detect pseudosymmetry in a given structure, and derive a virtual parent high-symmetry structure. The program is intended for the detection, analysis and characterization of displacively distorted structures. It can be used as a preliminary step before the use of AMPLIMODES for a full symmetry mode analysis (if we lack a structural model for the parent high-symmetry structure, required as part of the input in AMPLIMODES).

The program is expected to work successfully and detect pseudosymmetry if the maximal atomic displacements relating the input structure with a high symmetry configuration are not larger than about 1 Å. For much larger displacements, the program will not be capable in many cases to detect the pseudosymmetry although it may exist if large distortions are considered.

The program is not in principle applicable to structures with order-disorder features in their distortion. However, in many cases some tricks can be done to analyse the displacive component of these distortions, as using average positions of the disordered positions, or treating as distinct atom types the atomic sites with different occupation probabilities.

PSEUDO only requires as input the structure to be investigated in the conventional setting of the International Tables for Crystallography (for space groups with two conventional settings the default normally used in this server should be used). A CIF file can be used to introduce the structure.

If G is a supergroup of the space group H of the structure to be checked as possible pseudosymmetry, the program first uses the program COSETS (also available in this server as an independent program) to do the left coset decomposition of G with respect to H, choosing a set of coset representatives $\{1,g_2, \ldots,g_n\}$:

$$G = H + g_2H + \ldots.. + g_nH$$

The operations $\{1,g_2, \ldots,g_n\}$ are representatives of the operations of G not belonging to H. All operations belonging to a given coset g_iH, i.e. all operations of type g_ih, with h belonging to H, transform the H-symmetric structure in the same form.

If we call S the input structure, the structures g_iS obtained by transforming the structure S by the action of the left coset representatives g_i are calculated by the program and compared with the original structure S. If the structures g_iS differ from S below a given tolerance for the atomic distances, the space group G is then flagged as pseudosymmetry. This tolerance Δ_{max} is the maximum value allowed for the distances Δ between any atomic site of the structure S and the atomic sites that would supposedly coincide with it in the transformed structures g_iS if the operation g_i were actually a symmetry operation. For supergroups of index 2, this distance Δ for each atom is twice the atomic displacement between the hypothetical high symmetry position and the

observed one. The tolerance value Δ_{max} is by default 1 Å, and generally it should not exceed 2 Å. For larger values, the atomic displacements allowed are so large, in many cases comparable to the unit cell parameters, that the comparison of the transformed structures, if successful, may include nonsensical associations between the atoms in both structures.

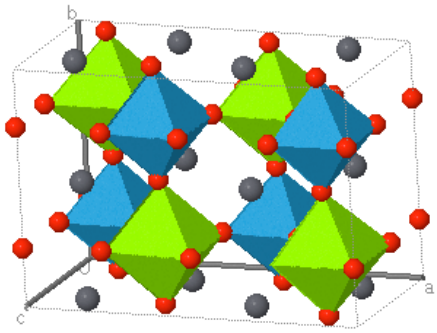
The pseudosymmetry search is done by default checking the minimal supergroups of the actual space group of the structure. Monoclinic and triclinic structures, due to their freedom in the choice of unit cell, require some special additional processing, and this is not yet fully available in the present version of the program.

Several options are available when using PSEUDO:

Option 1: search of maximal pseudosymmetry stepwise, climbing up through minimal supergroups.

Let us consider the following rather simple example of the orthorhombic Pnma structure of Pb_2MgWO_6 [*Acta Cryst.* (1995). B51, 668-673]:

```
62
11.4059 7.9440 5.6866 90.00 90.00 90.00
8
Pb     1    8d     0.1422 0.0032 0.7804
Mg     1    4c     0.3772 0.25 0.7519
W      1    4c     0.1161 0.25 0.2577
O      1    8d     0.1314 0.4907 0.2365
O      2    4c     0.0027 0.25 0.0133
O      3    4c     0.0103 0.25 0.4991
O      4    4c     0.237 0.25 -0.0153
O      5    4c     0.2491 0.25 0.4745
```



The structure is introduced in a quite obvious format. In consecutive rows the following information is listed: space group number, unit cell parameters, number of atoms in the asymmetric unit, and one row for each atom with atom type, label number, Wyckoff label (can be left unfilled, but substituted by any character) and relative coordinates. This is also the format for the description of a structure in other programs of the Bilbao Crystallographic Server. Also, a CIF structure file can be used as input.

We choose first the default option, i.e. option1: Minimal supergroups. We leave the tolerance in the default value of 1Å, and run the program:

List of distinct minimal supergroups:

A list of minimal supergroups of Pnma will appear on the screen (by definition, a minimal supergroup of a group H has no subgroup that is also supergroup of H). This list contains *all* distinct minimal supergroups of Pnma of a type different than Pnma, and a *subset* of the infinite series of minimal isomorphic supergroups (i.e. minimal supergroups of type Pnma). This subset of minimal isomorphic supergroups includes those with the smallest indices (for most space groups those with index up to 7 are listed).

Select minimal supergroups of space group *Pnma* (62)

The next step is to select the supergroups which the pseudosymmetry should be searched for. Each supergroup in the table can be selected b marking the corresponding checkbox.

No. #	Select	HM Symb.	IT Numb.	Index	Index i_k	Transformation (P,p)	Transformed Cell
1	☑	*Pbam*	055	2	2	**-a,2c,b** ; 1/2,1/2,0	11.4059 5.6866 3.9720 90.00 90.00 90.00
2	☐	*Pbcm*	057	2	2	**-b,-c,2a** ; 1,1/2,0	2.8433 11.4059 7.9440 90.00 90.00 90.00
3	☑	*Pmmn*	059	2	2	**-2c,-b,-a** ; -1/2,0,1	5.6866 7.9440 5.7030 90.00 90.00 90.00
4	☑	*Pnma*	062	3	3	**-3a,-b,c** ; 3/2,0,1/2	3.8020 7.9440 5.6866 90.00 90.00 90.00
5	☐	*Pnma*	062	3	3	**-a,-3b,c** ; 1/2,0,1/2	11.4059 2.6480 5.6866 90.00 90.00 90.00
6	☐	*Pnma*	062	3	3	**-a,-b,3c** ; 1/2,0,3/2	11.4059 7.9440 1.8955 90.00 90.00 90.00
7	☐	*Pnma*	062	5	5	**-5a,-b,c** ; 5/2,0,1/2	2.2812 7.9440 5.6866 90.00 90.00 90.00
8	☐	*Pnma*	062	5	5	**-a,-5b,c** ; 1/2,0,1/2	11.4059 1.5888 5.6866 90.00 90.00 90.00
9	☐	*Pnma*	062	5	5	**-a,-b,5c** ; 1/2,0,5/2	11.4059 7.9440 1.1373 90.00 90.00 90.00
10	☐	*Pnma*	062	7	7	**-7a,-b,c** ; 7/2,0,1/2	1.6294 7.9440 5.6866 90.00 90.00 90.00
11	☐	*Pnma*	062	7	7	**-a,-7b,c** ; 1/2,0,1/2	11.4059 1.1349 5.6866 90.00 90.00 90.00
12	☐	*Pnma*	062	7	7	**-a,-b,7c** ; 1/2,0,7/2	11.4059 7.9440 0.8124 90.00 90.00 90.00
13	☑	*Cmcm*	063	2	2	**-b,-c,a** ; 1/2,1/2,0	5.6866 11.4059 7.9440 90.00 90.00 90.00
14	☑	*Cmcm*	063	2	2	**-c,-a,b** ; 1/4,3/4,1/2	7.9440 5.6866 11.4059 90.00 90.00 90.00
15	☑	*Cmca*	064	2	2	**b,-a,c** ; 1/4,-1/4,1/2	7.9440 11.4059 5.6866 90.00 90.00 90.00
16	☑	*Imma*	074	2	2	**-a,-b,c** ; 1/2,0,1/2	11.4059 7.9440 5.6866 90.00 90.00 90.00

Show

If a structure of space group H is pseudosymmetric for a supergroup G >H, then the structure will also be pseudosymmetric for any intermediate space group H' between G and H, and therefore it will be pseudosymmetric for *at least* one of the minimal supergroups of H, which will necessarily be in a chain of minimal supergroups G> … > H'>…>H, connecting G and H. We can therefore assess the pseudosymmetry of a structure by checking the pseudosymmetry for the minimal supergroups, and if successful for one of them, repeat the process anew for its minimal supergroups, and so on, until the maximal pseudosymmetry is reached.

Note that the program procedure may fail to detect the pseudosymmetry if all possible chains of minimal supergroups connecting the two space groups include an isomorphic supergroup of an index larger than 7, which will not appear in the list of minimal supergroups proposed by the program for checking. In these cases, a more elaborated process using the option 3 of the program can be used (see below).

From the list of minimal supergroups provided by the program, many of them can be discarded beforehand, avoiding the subsequent lengthy check, which is bound to be unsuccessful or give non-sensical results. The data provided in the list of minimal supergroups helps the user for choosing the actual minimal supergroups that can make sense. The list gives the index between the two groups and the k-index which indicates the multiplication of the primitive unit cell of the group with respect to the one of the supergroup, the transformation relating both conventional cells, and the actual cell parameters of the hypothetical supergroups.

In many cases, the cell parameters of the supergroup will be absurd or unrealistic, or very far from fulfilling the symmetry conditions imposed by the crystalline class of the supergroup. Furthermore, the number of molecules in the primitive unit cell of the structure should be divisible by the k-index, so that the number of molecules in the supergroup primitive unit cell is an integer. In the present example, using these considerations, you can discard many of the listed supergroups. In many cases, the isomorphic supergroups can be discarded because they imply unrealistic divisions of the input unit cell.

The program then lists the supergroups that have been checked and the ones for which pseudosymmetry has been detected under the required tolerance. In our example, only the minimal supergroup Pmmn (2c,b,a;0,0,0) gives a positive result:

Summary search results

Pseudosymmetry search among minimal supergroups.

Case #	Supergroup G	Index i	Index i_k	(P,p)	Tr. Matrix	Δ_{max}	u_{max}
1	*Pbam* (055)	2	2	**-a,2c,b** ; 1/2,1/2,0	[-1 0 0] [1/2] [0 0 1] [1/2] [0 2 0] [0]	>tol	-
2	*Pmmn* (059)	2	2	**-2c,-b,-a** ; -1/2,0,1	[0 0 -1] [-1/2] [0 -1 0] [0] [-2 0 0] [1]	0.3457	0.1729
3	*Cmcm* (063)	2	2	**-b,-c,a** ; 1/2,1/2,0	[0 0 1] [1/2] [-1 0 0] [1/2] [0 -1 0] [0]	>tol	-
4	*Cmcm* (063)	2	2	**-c,-a,b** ; 1/4,3/4,1/2	[0 -1 0] [1/4] [0 0 1] [3/4] [-1 0 0] [1/2]	>tol	-
5	*Cmca* (064)	2	2	**b,-a,c** ; 1/4,-1/4,1/2	[0 -1 0] [1/4] [1 0 0] [-1/4] [0 0 1] [1/2]	>tol	-
6	*Imma* (074)	2	2	**-a,-b,c** ; 1/2,0,1/2	[-1 0 0] [1/2] [0 -1 0] [0] [0 0 1] [1/2]	>tol	-

You can inspect in detail the rest of the output for this detected pseudosymmetry. The program derives a Pmmn structure as close as possible to the input structure, and lists

the atomic displacements of the asymmetric unit of the Pnma structure with respect to this idealized Pmmn configuration. The maximum atomic displacement between the two structures is of the order of 0.17A:

Idealized structures

2# Supergroup *Pmmn* (059): -2c,-b,-a ; -1/2,0,1 and index 2

Displacements:

Atom	Idealized Coordinates	u_x	u_y	u_z	|u|
Pb1	(0.1422, 0.0032, 0.7500)	0.000000	0.000000	0.030400	0.1729
Mg1	(0.3772, 0.2500, 0.7500)	0.000000	0.000000	0.001900	0.0108
W1	(0.1161, 0.2500, 0.2500)	0.000000	0.000000	0.007700	0.0438
O1	(0.1314, 0.4907, 0.2500)	0.000000	0.000000	-0.013500	0.0768
O2	(0.0065, 0.2500, 0.0071)	-0.003800	0.000000	0.006200	0.0559
O3	(0.0065, 0.2500, 0.4929)	0.003800	0.000000	0.006200	0.0559
O4	(0.2430, 0.2500, 0.0051)	-0.006050	0.000000	-0.020400	0.1350
O5	(0.2430, 0.2500, 0.4949)	0.006050	0.000000	-0.020400	0.1350

This symmetrized structure is given first in the subgroup Pnma setting, as above, but also in the Pmmn supergroup setting:

```
059
5.6866 7.9440 5.7030 90.00 90.00 90.00
6
Pb     1    -  0.2500  0.0032  0.2844
Mg     1    -  0.2500  0.2500  0.7544
W      1    -  0.7500  0.2500  0.2322
O      1    -  0.7500  0.4907  0.2628
O      2    -  0.9929  0.2500  0.0130
O      4    -  0.9949  0.2500  0.4861
```

The number of atoms in the asymmetric unit has been reduced, due to the higher symmetry. Due to the reduction of the unit cell, the Wyckoff orbits has smaller multiplicities for those atoms with no orbit-merging, We can check this point using the program WPASSIGN of the Bilbao server:

```
59
5.6866 7.9440 5.7030 90.00 90.00 90.00
6
Pb     1    4e     0.2500 0.0032 0.2844
Mg     1    2a     0.2500 0.2500 0.7544
W      1    2b     0.7500 0.2500 0.2322
O      1    4e     0.7500 0.4907 0.2628
O      2    4f     0.9929 0.2500 0.0130
O      4    4f     0.9949 0.2500 0.4861
```

A more detailed report of the pseudosymmetry assessment is also available with a click at the end of the summary provided by the program. This report contains a full comparison of the original structure with the transformed ones obtained by the application of the coset representatives of the supergroup with respect to the subgroup.

Doing copy-paste, we can now use the symmetrized Pmmn structure as a new input for PSEUDO, so that we can continue the search for pseudosymmetry among the minimal supergroups of this symmetry.

We can discard again beforehand many of the minimal supergroups provided by the program. From the rest, only the space group Immm (**a,b,c** ; 1/4,1/4,1/4) will be flagged as acceptable with maximal displacements of the order of 0.2A.

Continue the process introducing the symmetrized Immm structure as input in PSEUDO, following the same steps. Now, I4/mmm (**b**,**c**,**a**; 0,1/2,0) will be flagged a pseudosymmetry space group with a maximal atomic displacement smaller than 0.03A, and a symmetrized structure given by:

```
139
5.7030 5.6866 7.9440 90.00 90.00 90.00
5
Pb    1   -  0.5000  0.0000  0.2500
Mg    1   -  0.0000  0.0000  0.5000
W     1   -  0.5000  0.5000  0.5000
O     1   -  0.5000  0.5000  0.7407
O     2   -  0.2598  0.7402  0.5000
```

It is important to take into account that the cell parameters given by the program for the supergroup are in general not symmetrized, and correspond exactly to the result of the transformation relating the supergroup-group unit cells, taking as data the cell parameters of the subgroup. In the case that the supergroup belongs to a different crystalline class, the resulting unit cell for the supergroup will include in general some symmetry breaking strain, which should be small, if the pseudosymmetry attribution makes sense. In the present case, for instance, the parameters a and b are not exactly equal, as demanded by the tetragonal symmetry.

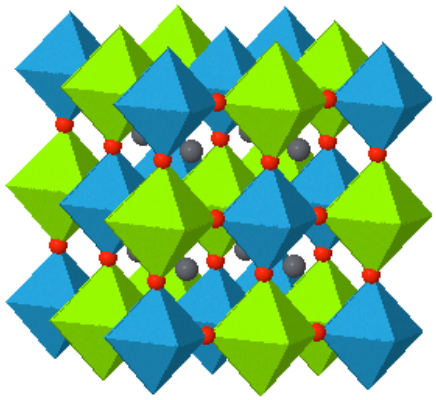
If this idealized structure is to be used in other contexts, obviously the cell parameters provided by PSEUDO will require a hand-made symmetrization. For instance, in this example, the tetragonal a parameter would be (a+b)/2, with a and b being the ones provided by PSEUDO. **However, if we are going to use the structure for a new step further up in the search of maximal pseudosymmetry, it is much better to keep the unsymmetrized unit cell provided by PSEUDO, so that the real lattice of the experimental structure is maintained up to the last step of the process**, and the symmetry breaking strain in the final maximal pseudosymmetry space group can be assessed. PSEUDO can work consistently even if a non-tetragonal unit cell is provided, for the tetragonal lattice, because the action of the symmetry operation is calculated on the atomic relative coordinates. The unit cell parameters are only used for producing the transformed unit cells.

We use then again this symmetrized I4/mmmm structure as input, and check reasonable minimal supergroups, with the result:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*P4/mmm* (123)	2	2	**a-b,a+b,2c** ; 0,0,0	>tol	-
2	*Fm*-3*m* (225)	3	1	**1/2a-1/2b,1/2a+1/2b,c** ; 0,0,0	0.0040	0.0026

We arrive then to a cubic pseudosymmetry. Note that in this case the maximal atomic displacement is not half the maximal Δ parameter, because the index of the supergroup/group relation is 3. The resulting symmetrized Fm-3m configuration provided by PSEUDO will be (Wyckoff labels added using WPASSIGN):

```
225
8.0537 8.0537 7.9440 90.00 90.00 90.17
4
Pb     1    8c     0.2500 0.7500 0.2500
Mg     1    4b     0.0000 0.0000 0.5000
W      1    4a     0.5000 0.0000 0.5000
O      1    24e    0.5000 0.0000 0.7404
```



Note the slight deformation of the unit cell with respect to the required conditions within the cubic crystalline class. The actual symmetrized cell parameter will be the mean value of three a,b,c values, while the angle γ has to be corrected to 90º.

The symmetrized Fm-3m structure can be further checked for pseudosymmetry with respect to its only minimal cubic supergroup Pm-3m proposed by PSEUDO, with negative results. In fact this supergroup could be discarded directly, since from the multiplicity of the atomic positions, one can see that the primitive unit cell of the Fm-3m configuration already contains a single formula unit, and therefore, no higher symmetry through smaller primitive cells is possible, while the point-group symmetry is already maximal.

Additional Note: *This example compound is in fact a double-perovskite where the composition ABO_3 is changed to $A_2BB'O_3$. The Fm-3m configuration corresponds to a perovskite cell duplicated along the three directions due to the ordering of the B and B' cations within the O_6 octahedra. This is a simple quite trivial example of a Bärninghausen relation between the space groups Pm-3m --- Fm-3m (**2a,2b,2c** ; 0,0,0) through the ordering of the Mg and W atoms in the B site of the Pm-3m perovskite. This can be checked with PSEUDO if we introduce as input the above Fm-3m structure with the atoms Mg and W artificially substituted by the same atom type:*

```
225
8.0537 8.0537 7.9440 90.00 90.00 90.17
4
Pb     1    8c     0.2500 0.7500 0.2500
A      1    4b     0.0000 0.0000 0.5000
A      2    4a     0.5000 0.0000 0.5000
O      1    24e    0.5000 0.0000 0.7404
```

Now the search for pseudosymmetry with respect to the Pm-3m space group will be successful:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*Pm*-3*m* (221)	2	2	**2a,2b,2c** ; 0,0,0	0.1546	0.0773

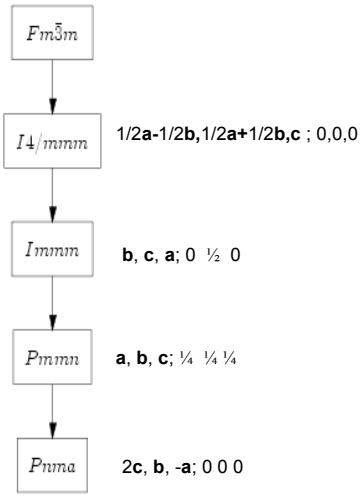
Atom	Idealized Coordinates	u_x	u_y	u_z	|u|
Pb1	(0.2500, 0.7500, 0.2500)	0.000000	0.000000	0.000000	0.0000
A1	(0.0000, 0.0000, 0.5000)	0.000000	0.000000	0.000000	0.0000
A2	(0.5000, 0.0000, 0.5000)	0.000000	0.000000	0.000000	0.0000
O1	(0.5000, 0.0000, 0.7500)	0.000000	0.000000	-0.009600	0.0763

with the obtained symmetrized structure being of course the cubic perovskite:

```
221
4.0269 4.0269 3.9720 90.00 90.00 90.17
3
Pb    1   1b    0.5000 0.5000 0.5000
A     1   1a    0.0000 0.0000 0.0000
O     1   3d    0.0000 0.0000 0.5000
```

where again a small strain in the unit cell is to be corrected by hand. Disregarding the ordering of the atoms Mg and W in the B-sites, the distortion of the Fm-3m configuration with respect to a Pm-3m perovskite structure is minimal, with the oxygens displacements below 0.1Å.

Coming back to the main result: for the actual observed structure with ordering of the Mg and W atoms within the B-sites of the perovskite, the maximal pseudosymmetry is Fm-3m, with the parent structure given above. The process has been a bit long, but we have arrived to an end in a repetitive process of pseudosymmetry check along the following chain of minimal supergroups:



Expressing each of the transformations (P,p) in the chain as a 4-dim matrix (see International Tables for Crystallography), we can obtain the global transformation relating the space groups Fm-3m and Pnma, by multiplying the four matrices:

1/2	1/2	0	0
-1/2	1/2	0	0
0	0	1	0
0	0	0	1

0	0	1	0
1	0	0	1/2
0	1	0	0
0	0	0	1

1	0	0	1/4
0	1	0	1/4
0	0	1	1/4
0	0	0	1

0	0	1	0
0	1	0	0
2	0	0	0
0	0	0	1

with the following result:

1	0	-1/2	1/2
-1	0	-1/2	1/4
0	1	0	1/4
0	0	0	1

This means the global transformation relating the two groups is:

a-b,c,-1/2a-1/2b ; 1/2,1/4,1/4

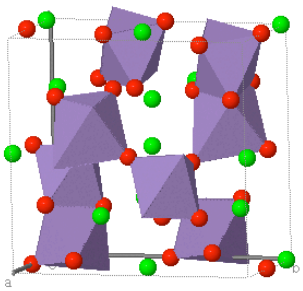
Using SUBGROUPGRAPH, we could also obtain this transformation or an equivalent one. We only need to introduce the two end space groups Fm-3m and Pnma and their index, which is 24. SUBGROUPGRAPH will provide all equivalent classes of subgroups of Fm-3m, of type Pnma. One of these classes corresponds to our specific case. The class contains all equivalent subgroups corresponding to equivalent domain-related structures. The transformations obtained above does not necessarily appears in the list, but an equivalent one will be listed. The figure above describing the lattice of minimal supergroups connecting the two symmetries has been produced with this program.

Note that in this example there is a single chain of minimal supergroups connecting the two space groups. In general, the graph of minimal supergroups connecting the pseudosymmetry space group and observed symmetry can be more complex with several different chains of minimal supergroups connecting both symmetries. In these cases, pseudosymmetry will be detected for several minimal supergroups, and one can choose in principle any of them, for continuing the process and proceed to the next step up to the maximal pseudosymmetry. Generally it is convenient to choose the minimal supergroup with minimal displacements.

Let us consider a second example where this happens. Let us take a hypothetical structure of symmetry $C222_1$ (N. 20):

```
20
5.4435 9.4122 9.0630 90 90 90
7
A     1    4a     0.0790 0 0
A     2    4b     0 0.385 0.25
B     1    8c     -0.0323 0.3562 0.6231
C      1    4a     0.5412 0 0
C      2    8c     0.7812 0.222 0.0385
C      3    4b     0 -0.1998 0.25
C      4    8c     0.2596 0.0999 0.2312
```

C222_1
a=5,444Å
b=9,412Å
c=9,063Å
α=90,0°
β=90,0°
γ=90,0°



We apply then PSEUDO with option 1 and tolerance 2 Å, discarding from the list of minimal supergroups those with inconsistent cells or impossible k-indices:

No. #	Select	HM Symb.	IT Numb.	Index	Index i_k	Transformation (P,p)	Transformed Cell
1	☑	*P*222$_1$	017	2	2	**2a,2b,c** ; 0,0,0	2.7218 4.7061 9.0630 90.00 90.00 90.00
2	☐	*C*222$_1$	020	3	3	**3a,b,c** ; 0,0,0	1.8145 9.4122 9.0630 90.00 90.00 90.00
3	☐	*C*222$_1$	020	3	3	**-b,-3a,-c** ; 0,0,3/4	3.1374 5.4435 9.0630 90.00 90.00 90.00
4	☐	*C*222$_1$	020	3	3	**a,b,3c** ; 0,0,0	5.4435 9.4122 3.0210 90.00 90.00 90.00
5	☐	*C*222$_1$	020	5	5	**5a,b,c** ; 0,0,0	1.0887 9.4122 9.0630 90.00 90.00 90.00
6	☐	*C*222$_1$	020	5	5	**-b,-5a,-c** ; 0,0,3/4	1.8824 5.4435 9.0630 90.00 90.00 90.00
7	☐	*C*222$_1$	020	5	5	**a,b,5c** ; 0,0,0	5.4435 9.4122 1.8126 90.00 90.00 90.00
8	☐	*C*222$_1$	020	7	7	**7a,b,c** ; 0,0,0	0.7776 9.4122 9.0630 90.00 90.00 90.00
9	☐	*C*222$_1$	020	7	7	**-b,-7a,-c** ; 0,0,3/4	1.3446 5.4435 9.0630 90.00 90.00 90.00
10	☐	*C*222$_1$	020	7	7	**a,b,7c** ; 0,0,0	5.4435 9.4122 1.2947 90.00 90.00 90.00
11	☑	*C*222	021	2	2	**a,b,2c** ; 0,0,1/2	5.4435 9.4122 4.5315 90.00 90.00 90.00
12	☑	*F*222	022	2	2	**b,c,a** ; ¼,0,1/4	9.0630 5.4435 9.4122 90.00 90.00 90.00
13	☑	*Cmcm*	063	2	1	**a,b,c** ; 0,0,0	5.4435 9.4122 9.0630 90.00 90.00 90.00
14	☑	*Cmcm*	063	2	1	**-b,-a,-c** ; 0,0,3/4	9.4122 5.4435 9.0630 90.00 90.00 90.00
15	☑	*Cmca*	064	2	1	**a,b,c** ; ¼,0,0	5.4435 9.4122 9.0630 90.00 90.00 90.00
16	☑	*Cmca*	064	2	1	**-b,-a,-c** ; ¼,0,3/4	9.4122 5.4435 9.0630 90.00 90.00 90.00
17	☐	*P*4$_1$22	091	2	1	**a-b,a+b,c** ; 0,0,1/8	5.4365 5.4365 9.0630 90.00 90.00 60.09
18	☐	*P*4$_1$22	091	2	1	**-a+b,-a-b,-c** ; 0,0,1/8	5.4365 5.4365 9.0630 90.00 90.00 60.09

19	☐	$P4_12_12$	092	2	1	**a-b,a+b,c** ; 0,0,1/4	5.4365 5.4365 9.0630 90.00 90.00 60.09
20	☐	$P4_12_12$	092	2	1	**-a+b,-a-b,-c** ; 0,0,1/4	5.4365 5.4365 9.0630 90.00 90.00 60.09
21	☐	$P4_322$	095	2	1	**a-b,a+b,c** ; 0,0,3/8	5.4365 5.4365 9.0630 90.00 90.00 60.09
22	☐	$P4_322$	095	2	1	**-a+b,-a-b,-c** ; 0,0,3/8	5.4365 5.4365 9.0630 90.00 90.00 60.09
23	☐	$P4_32_12$	096	2	1	**a-b,a+b,c** ; 0,0,1/4	5.4365 5.4365 9.0630 90.00 90.00 60.09
24	☐	$P4_32_12$	096	2	1	**-a+b,-a-b,-c** ; 0,0,1/4	5.4365 5.4365 9.0630 90.00 90.00 60.09
25	☐	$P6_122$	178	3	1	**-a+b,-a-b,c** ; 0,0,5/12	5.4365 5.4365 9.0630 90.00 90.00 60.09
26	☐	$P6_122$	178	3	1	**-a+b,-a-b,c** ; -1/2,1/2,5/12	5.4365 5.4365 9.0630 90.00 90.00 60.09
27	☐	$P6_122$	178	3	1	**a-b,a+b,-c** ; 0,0,5/12	5.4365 5.4365 9.0630 90.00 90.00 60.09
28	☐	$P6_122$	178	3	1	**a-b,a+b,-c** ; -1/2,1/2,5/12	5.4365 5.4365 9.0630 90.00 90.00 60.09
29	☑	$P6_122$	178	3	1	**-a-b,-a+b,c** ; 0,0,2/3	5.4365 5.4365 9.0630 90.00 90.00 119.91
30	☑	$P6_122$	178	3	1	**-a-b,-a+b,c** ; -1/2,-1/2,2/3	5.4365 5.4365 9.0630 90.00 90.00 119.91
31	☑	$P6_122$	178	3	1	**a+b,a-b,-c** ; 0,0,2/3	5.4365 5.4365 9.0630 90.00 90.00 119.91
32	☑	$P6_122$	178	3	1	**a+b,a-b,-c** ; -1/2,-1/2,2/3	5.4365 5.4365 9.0630 90.00 90.00 119.91
33	☐	$P6_522$	179	3	1	**-a+b,-a-b,c** ; 0,0,1/12	5.4365 5.4365 9.0630 90.00 90.00 60.09
34	☐	$P6_522$	179	3	1	**-a+b,-a-b,c** ; -1/2,1/2,1/12	5.4365 5.4365 9.0630 90.00 90.00 60.09
35	☐	$P6_522$	179	3	1	**a-b,a+b,-c** ; 0,0,1/12	5.4365 5.4365 9.0630 90.00 90.00 60.09
36	☐	$P6_522$	179	3	1	**a-b,a+b,-c** ; -1/2,1/2,1/12	5.4365 5.4365 9.0630 90.00 90.00 60.09
37	☑	$P6_522$	179	3	1	**-a-b,-a+b,c** ; 0,0,1/3	5.4365 5.4365 9.0630 90.00 90.00 119.91
38	☑	$P6_522$	179	3	1	**-a-b,-a+b,c** ; -1/2,-1/2,1/3	5.4365 5.4365 9.0630 90.00 90.00 119.91
39	☑	$P6_522$	179	3	1	**a+b,a-b,-c** ; 0,0,1/3	5.4365 5.4365 9.0630 90.00 90.00 119.91
40	☑	$P6_522$	179	3	1	**a+b,a-b,-c** ; -1/2,-1/2,1/3	5.4365 5.4365 9.0630 90.00 90.00 119.91
41	☐	$P6_322$	182	3	1	**-a+b,-a-b,c** ; 0,0,1/4	5.4365 5.4365 9.0630 90.00 90.00 60.09
42	☐	$P6_322$	182	3	1	**-a+b,-a-b,c** ; -1/2,1/2,1/4	5.4365 5.4365 9.0630 90.00 90.00 60.09

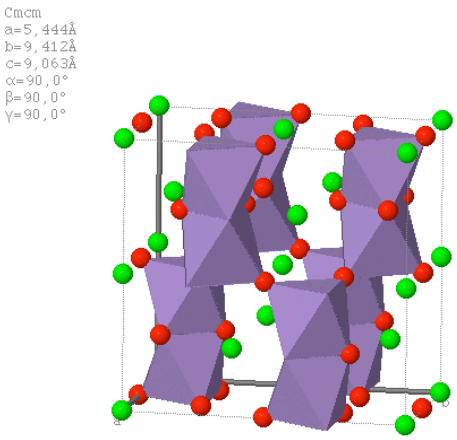
43	☑	$P6_322$	182	3	1	**a+b,a-b,-c** ; 0,0,1	5.4365 5.4365 9.0630 90.00 90.00 119.91
44	☑	$P6_322$	182	3	1	**a+b,a-b,-c** ; -1/2,-1/2,1	5.4365 5.4365 9.0630 90.00 90.00 119.91

with the following results:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	$P222_1$ (017)	2	2	**2a,2b,c** ; 0,0,0	>tol	-
2	$C222$ (021)	2	2	**a,b,2c** ; 0,0,1/2	>tol	-
3	$F222$ (022)	2	2	**b,c,a** ; 1/4,0,1/4	>tol	-
4	*Cmcm* (063)	2	1	**a,b,c** ; 0,0,0	0.9382	0.4691
5	*Cmcm* (063)	2	1	**-b,-a,-c** ; 0,0,3/4	>tol	-
6	*Cmca* (064)	2	1	**a,b,c** ; 1/4,0,0	>tol	-
7	*Cmca* (064)	2	1	**-b,-a,-c** ; 1/4,0,3/4	>tol	-
8	$P6_122$ (178)	3	1	**-a-b,-a+b,c** ; 0,0,2/3	>tol	-
9	$P6_122$ (178)	3	1	**-a-b,-a+b,c** ; -1/2,-1/2,2/3	>tol	-
10	$P6_122$ (178)	3	1	**a+b,a-b,-c** ; 0,0,2/3	>tol	-
11	$P6_122$ (178)	3	1	**a+b,a-b,-c** ; -1/2,-1/2,2/3	>tol	-
12	$P6_522$ (179)	3	1	**-a-b,-a+b,c** ; 0,0,1/3	>tol	-
13	$P6_522$ (179)	3	1	**-a-b,-a+b,c** ; -1/2,-1/2,1/3	>tol	-
14	$P6_522$ (179)	3	1	**a+b,a-b,-c** ; 0,0,1/3	>tol	-
15	$P6_522$ (179)	3	1	**a+b,a-b,-c** ; -1/2,-1/2,1/3	>tol	-
16	$P6_322$ (182)	3	1	**a+b,a-b,-c** ; 0,0,1	0.8427	0.4863
17	$P6_322$ (182)	3	1	**a+b,a-b,-c** ; -1/2,-1/2,1	>tol	-

Two minimal supergroups have been flagged. We take for the next step *upwards* the symmetrized structure with smallest atomic displacements, i.e. the structure Cmcm (**a,b,c** ; 0,0,0):

```
063
5.4435 9.4122 9.0630 90.00 90.00 90.00
7
A      1    -  0.0000  0.0000  0.0000
A      2    -  0.0000  0.3850  0.2500
B      1    -  0.0000  0.3562  0.6231
C      1    -  0.5000  0.0000  0.0000
C      2    -  0.7500  0.2500  0.0000
C      3    -  0.0000  0.8002  0.2500
C      4    -  0.2596  0.0999  0.2500
```

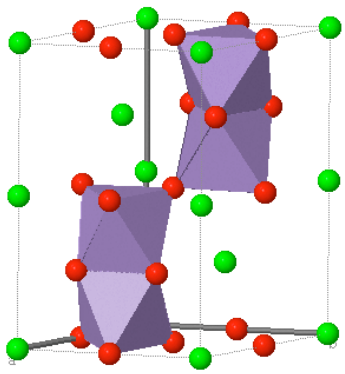


with the following result:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*Pmma* (051)	2	2	**2b,2c,a** ; 0,0,0	>tol	-
2	*Cmmm* (065)	2	2	**-b,a,2c** ; 0,0,0	>tol	-
3	*Fmmm* (069)	2	2	**c,b,-a** ; 1/4,1/4,0	>tol	-
4	*P6$_3$/mmc* (194)	3	1	**-a-b,a-b,c** ; 0,0,0	0.8427	0.4863
5	*P6$_3$/mmc* (194)	3	1	**-a-b,a-b,c** ; -1/2,-1/2,0	>tol	-

Taking again the symmetrized structure P6$_3$/mmc with the smallest distortion for further pseudosymmetry check (Wyckoff labels added with WPASSIGN):

```
194
5.4365 5.4365 9.0630 90.00 90.00 119.91
5
A      1    2a     0.0000 0.0000 0.0000
A      2    2c     0.333333 0.666667 0.2500
B      1    4f     0.333333 0.666667 0.6231
C      1    6g     0.5000 0.5000 0.0000
C      3    6h     0.8136 0.1864 0.2500
```

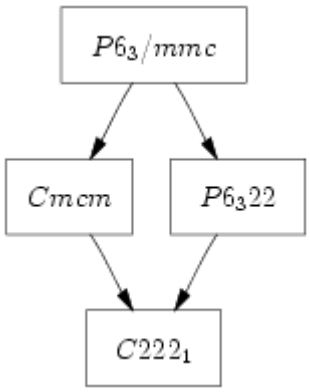


Important: *Note that we have modified the output of PSEUDO including 6 decimal digits for the special coordinates 1/3 and 2/3. To use PSEUDO and other programs of*

this server, it is important that special coordinates 1/3, 2/3, etc… are expressed including a maximum number of digits in its numerical expression, so that the programs recognise them as exact simple fractions.

Applying PSEUDO again to this structure, the result is negative for all consistent minimal supergroups and tolerance 2 Å. P63/mmc is therefore the pseudosymmetry of the structure, with the structural model listed above as P63/mmc reference structure (The cell has some strain to be corrected by hand).

The graph of maximal subgrousp connecting this space group with the actual observed symmetry $C222_1$ is the following (obtained with SUBGROUPGRAPH):



One can see now why both supergroups of type Cmcm and $P6_322$ were flagged by PSEUDO, as they are both intermediate symmetries with respect to $P6_3/mmc$. If we had taken the symmetrized $P6_322$ structure in the second step, the result would have been the same.

Option 3: Search of pseudosymmetry for a specific supergroup defined by the transformation (P,p)

Retaking the first example of the Pnma structure of Pb_2MgWO_6, we can use the option 3 of the program, in which a given supergroup specified by its transformation matrix can be checked, to confirm that this Pnma structure is indeed pseudosymmetric with respect to the symmetry Fm-3m, as obtained step by step checking a chain of minimal supergroups.

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*Fm*-3*m* (225)	24	4	**a-b,c,-1/2a-1/2b** ; 1/2,1/4,1/4	0.5243	0.2627

Atom	Idealized Coordinates	u_x	u_y	u_z	|u|
Pb1	(0.1250, 0.0000, 0.7500)	0.017200	0.003200	0.030400	0.2627
Mg1	(0.3750, 0.2500, 0.7500)	0.002200	0.000000	0.001900	0.0273
W1	(0.1250, 0.2500, 0.2500)	-0.008900	-0.000000	0.007700	0.1106
O1	(0.1250, 0.4904, 0.2500)	0.006400	0.000317	-0.013500	0.1060

O2	(0.0048, 0.2500, 0.0096)	-0.002108	0.000000	0.003683	0.0319
O3	(0.0048, 0.2500, 0.4904)	0.005492	0.000000	0.008717	0.0799
O4	(0.2452, 0.2500, 0.0096)	-0.008192	0.000000	-0.024917	0.1697
O5	(0.2452, 0.2500, 0.4904)	0.003908	0.000000	-0.015883	0.1007

We can see now directly the atomic displacements relating the actual Pnma structure with the proposed ideal Fm-3m configuration. These displacements are smaller than 0.27A.

Option 3 is in principle intended for obtaining a symmetrized structural model of a structure for which we know its pseudosymmetry, and the transformation matrix relating both space groups. But it can also be used to start the determination of some unknown pseudosymmetry in structures which due to their large unit cell may have in their chains of minimal pseudosymmetric supergroups isomorphic space groups with indices larger than those considered in option 1.

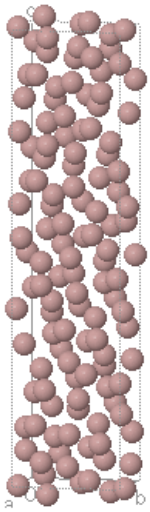
Example of combined application of option 3 and 1:

The apparently complex phase of the phase Ga-II of Ga under pressure:

Let us consider for instance the phase of Ga under pressure called Ga-II (Phys. Rev. Lett. 93, 205502 (2004)):

```
20
5.976 8.576 35.758 90 90 90
14
Ga    1   4b    0.5000 0.1802 0.2500
Ga    2   8c    0.6956 0.4684 0.2716
Ga    3   8c    0.5804 0.7858 0.2861
Ga    4   8c    0.2772 0.5622 0.3081
Ga    5   8c    -0.0341 0.7809 0.3292
Ga    6   8c    0.8482 0.4567 0.3430
Ga    7   8c    0.5632 0.6919 0.3666
Ga    8   8c    0.2324 0.4838 0.3851
Ga    9   8c    0.6129 0.2914 0.4003
Ga    10  8c    0.8276 0.5660 0.4250
Ga    11  8c    -0.0030 0.2613 0.4435
Ga    12  4a    0.2460 0.0 0.5000
Ga    13  8c    0.1052 0.3090 0.5170
Ga    14  8c    0.3574 0.5518 0.5409
```

C222_1
a=5,976Å
b=8,576Å
c=35,758Å
α=90,0°
β=90,0°
γ=90,0°

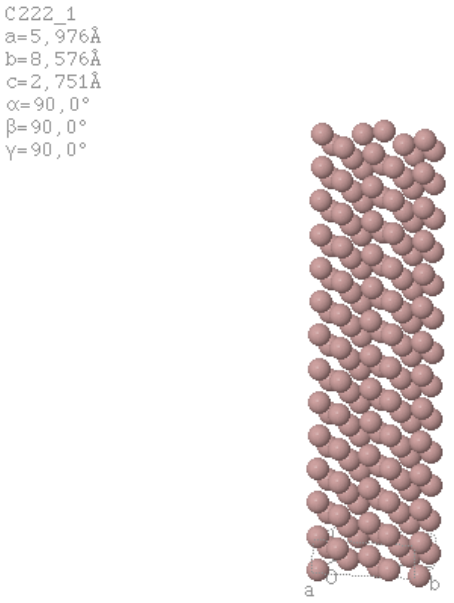


This orthorhombic structure, with space group C2221, has 104 Ga atoms in the conventional centred unit cell. Its unit cell is much elongated along the c axis. One can suspect that the system may be a superstructure of a more proportioned cell, with a division of the cell parameter along the c axis. The observed cell would be then a multiple of a smaller cell, the multiplication factor being necessarily a divisor of 104. Divisors giving reasonable values for the c parameter may be 13, 8, 4, 2. If the structure is a superstructure with the unit cell multiplied along c by a factor 13, the option 1 would not detect it, since this cell multiplication would correspond to an isomorphic supergroup with index 13, above the limit considered in this option. But we can try this possibility by introducing the specific isomorphic supergroup with option 3. Using the program SERIES we can look to the whole series of isomorphic supergroups of C2221, check the existence of one with a division of the cell by 13, and get the corresponding origin shift, if any. In this case the transformation matrix is rather trivial, with no origin shift needed, and introducing a tolerance of 2 Å, PSEUDO reports a positive result, with maximal atomic displacements smaller than 0.8 A:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Tr. Matrix	Δ_{max}	u_{max}
1	$C222_1$ (20)	13	13	**a,b,13c** ; 0,0,0	[1 0 0] [0] [0 1 0] [0] [0 0 13] [0]	1.6288	0.7794

The resulting symmetrized structure is :

```
20
5.9760 8.5760 2.7506 90.00 90.00 90.00
2
Ga     1    -  0.5000  0.2484  0.2500
Ga     10   -  0.7504  0.5000  0.5000
```



Hence, to obtain this very regular structure with a much smaller cell (with c = 2.751 Å) the atomic displacements that have been required are smaller than 0.8 Å. This symmetrized structure can be now checked further for pseudosymmetry using option 1, checking the minimal supergroups.

Decreasing now the tolerance to 1Å, and dropping the tetragonal and hexagonal minimal supergroups because they have unit cells very far from the symmetry requirements, and some of the orthorhombic ones because of their inconsistent unit cell, we obtain that the structure is only pseudosymmetric for the minimal supergroup F222 (**-b,-c,a** ; 3/4,0,1/4) with the following symmetrized reference structure, that requires atomic displacements smaller than 0.01 Å:

Atom	Idealized Coordinates	u_x	u_y	u_z	|u|
Ga1	(0.5000, 0.2500, 0.2500)	0.000000	-0.001600	0.000000	0.0137
Ga10	(0.7500, 0.5000, 0.5000)	0.000400	0.000000	0.000000	0.0024

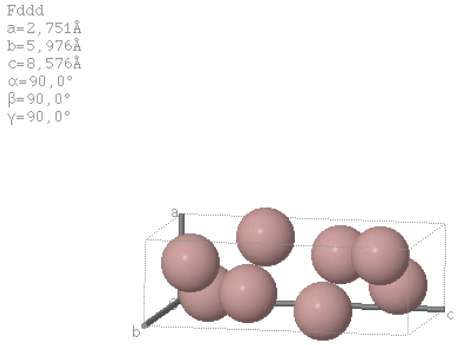
```
022
2.7506 5.9760 8.5760 90.00 90.00 90.00
2
Ga     1    -  0.0000  0.5000  0.0000
Ga     10   -  0.2500  0.2500  0.7500
```

This structure can be further checked for pseudosymmetry with option 1, considering consistent minimal supergroups, and in fact, the structure is detected as having Fddd symmetry, with no additional displacement required:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*P*222 (016)	2	2	**-2a,-2b,2c** ; 0,0,0	>tol	-
2	*F*222 (022)	3	3	**b,c,3a** ; 0,0,0	>tol	-
3	*F*222 (022)	3	3	**c,3a,b** ; 0,0,0	>tol	-

4	*Fmmm* (069)	2	1	**-a,-b,c** ; 0,0,0	>tol	-
5	*Fmmm* (069)	2	1	**a,b,c** ; 1/4,1/4,1/4	>tol	-
6	*Fddd* (070)	2	1	**-a,-b,c** ; 1/8,1/8,1/8	>tol	-
7	*Fddd* (070)	2	1	**a,b,c** ; 3/8,3/8,3/8	0	0.0000

```
070
2.7506 5.9760 8.5760 90.00 90.00 90.00
1
Ga     1    -  0.3750  0.8750  0.3750
```



So, in fact, phase GaII is a distorted Fddd structure with a single atom in the asymmetric unit, with its position fully fixed by symmetry.

We can obtain the actual distortion relating both structures, using again PSEUDO with option 3, introducing the supergroup Fddd with the adequate transformation, multiplying, as in the previous case, the three 4x4 matrices corresponding to the three steps done along the chain minimal supergroups: (**-b**,**-c**,13**a**; 1/8, 3/8, 5/8). A summary of the result is:

Case #	**Supergroup G**	**Index i**	**Index i_k**	**(P,p)**	**Δ_{max}**	**u_{max}**
1	*Fddd* (70)	52	26	**-b,-c,13a** ; 1/8,3/8,5/8	1.6288	0.7729

Atom	**Idealized Coordinates**	**u_x**	**u_y**	**u_z**	**|u|**
Ga1	(0.5000, 0.2500, 0.2500)	-0.000000	-0.069800	0.000000	0.5986
Ga2	(0.7500, 0.5000, 0.2692)	-0.054400	-0.031600	0.002369	0.4316
Ga3	(0.5000, 0.7500, 0.2885)	0.080400	0.035800	-0.002361	0.5764
Ga4	(0.2500, 0.5000, 0.3077)	0.027200	0.062200	0.000408	0.5578
Ga5	(0.0000, 0.7500, 0.3269)	-0.034100	0.030900	0.002277	0.3441
Ga6	(0.7500, 0.5000, 0.3462)	0.098200	-0.043300	-0.003154	0.7036
Ga7	(0.5000, 0.7500, 0.3654)	0.063200	-0.058100	0.001216	0.6267
Ga8	(0.2500, 0.5000, 0.3846)	-0.017600	-0.016200	0.000485	0.1751
Ga9	(0.5000, 0.2500, 0.4038)	0.112900	0.041400	-0.003546	0.7729
Ga10	(0.7500, 0.5000, 0.4231)	0.077600	0.066000	0.001923	0.7350
Ga11	(0.0000, 0.2500, 0.4423)	-0.003000	0.011300	0.001192	0.1074

Ga12	(0.2500, 0.0000, 0.5000)	-0.004000	-0.000000	0.000000	0.0239
Ga13	(0.0206, 0.2685, 0.5211)	0.084617	0.040527	-0.004079	0.6307
Ga14	(0.2679, 0.5200, 0.5366)	0.089521	0.031812	0.004287	0.6198

Therefore, phase GaII is in fact a modulated structure of a simple Fddd structure, with maximal atomic displacements below 0.78A (Phys. Rev. Lett. **97**, 115501 (2006)).

Option 2: Search among supergroups with a fixed k-index

Sometimes, we may be sure that the system is pseudosymmetric with respect to a supergroup from which we know the multiplication factor of its primitive unit cell (k-index). We may be interested for instance to search the pseudosymmetry among supergroups with the no change of lattice, except for some strain (k-index=1), or with a primitive unit cell containing half the number of formula unit than the actual observed one (k-index=2). In this case, option 2 can be more direct. It provides the supergroups for a given k-index (up to 4), and one can choose one by one the desired supergroups. If we want to check a specific supergroup this option spares the user to have to know beforehand (as it happens in option 3) the transformation matrix relating the checked supergroup with the actual space group (only the k-index must be known).

Exercises 1: Using PSEUDO, find the pseudosymmetry of the following structure and the symmetrized reference structure.

```
1
7.0000 4.0000 4.5000 95.00 100.00 82.00
1
A     1   -  0.2800  0.0500  0.09500
A     2   -  0.7500  0.9800  0.9700
```

This is a case that can be easily deduced from inspection of the structure (you can use *VISUALIZE* in the Bilbao crystallographic server to visualize the structure with Jmol).

Exercise 2: GeF_2, having the $P2_12_12_1$ (N. 19) structure given below, is reported to have at higher temperature an unknown tetragonal phase, with the primitive unit cell volume being essentially maintained. Using PSEUDO, with the option 2, which allows to check supergroups with a fixed k-index (multiplication of the primitive unit cell) postulate a probable space group or groups and a starting structural model for this high-temperature phase.

```
19
4.682 5.158 8.312 90 90 90
3
Ge 1    4a      0.2340  0.0083  0.1311
F  1    4a      0.029   0.083   -0.018
F  2    4a      0.067   0.246   0.279
```

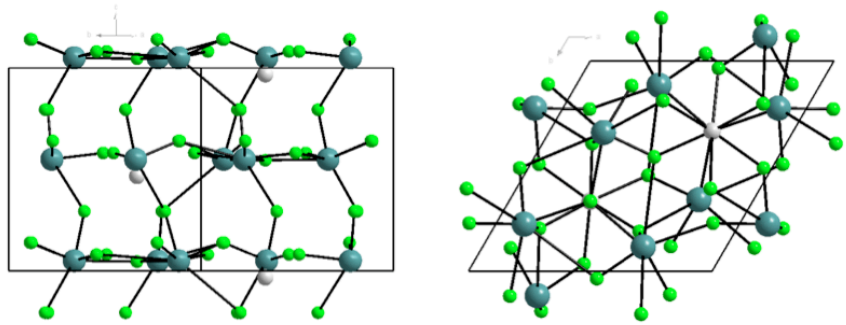
Polar structures:

If the structure to be checked for pseudosymmetry is polar, its origin along the polar direction(s) has in general been chosen arbitrarily. A proper search of non-polar pseudosymmetry requires then to optimize somehow the origin of the non-polar (or less polar) supergroup with respect to the input polar structure (formally, the number of distinct non-polar supergroups is infinite due to the possible distinct choices of origin). This optimization is done in PSEUDO by making the pseudosymmetry check for a grid of origin choices for the polar structure whose density is controlled by the user, while the transformation matrix (P,p) defining the origin of the non-polar supergroup is not varied.

Let us consider as an example the case of the $P6_3$ room-temperature structure of $NaSb_3F_{10}$ (J. Appl. Cryst. (2009). 42, 58–62):

```
173
8.285 8.285 7.600 90 90 120
6
Sb     1    6c     -0.1163 0.2243 0.55
Na     1    2b     0.333333 0.666667 0.467
F      1    6c     0.204 0.393 0.294
F      2    6c     0.111 0.229 0.640
F      3    6c     0.035 0.491 0.581
F      4    2b     0.666667 0.333333 0.545
```

(*we have introduced an arbitrary shift of the origin to the structure reported in the reference above, to simulate a more general case, with unknown pseudosymmetry*)



Two projections of the experimental P63 structure of NaSb3F10

This compound has been predicted to be ferroelectric due to its small deviation from a non-polar configuration. The symmetries P6322 and P63/mmc have been proposed for two successive non-polar phases at higher temperatures.

The first output of PSEUDO with the list of minimal supergroups includes now a note indicating the polarity of the structure, and allowing the user to introduce the desired maximal distance among the points of the grid to be tried for the origin choice, the default being 0.5 Å (the maximum number of points is however internally limited to 40 along any polar direction). One should take into account that very dense grids can increase computer times to unacceptable values. It is therefore advisable to keep this grid parameter as large as possible.

No. #	Select	HM Symb.	IT Numb.	Index	Index i_k	Transformation (P,p)	Transformed Cell
1	☑	*P*6	168	2	2	**a,b,2c** ; 0,0,2t	8.2850 8.2850 3.8000 90.00 90.00 120.00
2	☐	*P*6$_3$	173	3	3	**a,b,3c** ; 0,0,3t	8.2850 8.2850 2.5333 90.00 90.00 120.00
3	☐	*P*6$_3$	173	3	3	**a-b,a+2b,c** ; 0,0,t	4.7833 4.7833 7.6000 90.00 90.00 120.00
4	☐	*P*6$_3$	173	4	4	**2a,2b,c** ; 0,0,t	4.1425 4.1425 7.6000 90.00 90.00 120.00
5	☐	*P*6$_3$	173	5	5	**a,b,5c** ; 0,0,5t	8.2850 8.2850 1.5200 90.00 90.00 120.00
6	☐	*P*6$_3$	173	7	7	**a,b,7c** ; 0,0,7t	8.2850 8.2850 1.0857 90.00 90.00 120.00
7	☐	*P*6$_3$	173	7	7	**a-2b,2a+3b,c** ; 0,0,t	3.1314 3.1314 7.6000 90.00 90.00 120.00
8	☐	*P*6$_3$	173	7	7	**-2a-3b,-a+2b,-c** ; 0,0,-t	3.1314 3.1314 7.6000 90.00 90.00 120.00
9	☑	*P*6$_3$/*m*	176	2	1	**a,b,c** ; 0,0,t	8.2850 8.2850 7.6000 90.00 90.00 120.00
10	☑	*P*6$_3$22	182	2	1	**a,b,c** ; 0,0,t	8.2850 8.2850 7.6000 90.00 90.00 120.00
11	☑	*P*6$_3$*cm*	185	2	1	**a,b,c** ; 0,0,t	8.2850 8.2850 7.6000 90.00 90.00 120.00
12	☑	*P*6$_3$*mc*	186	2	1	**a,b,c** ; 0,0,t	8.2850 8.2850 7.6000 90.00 90.00 120.00

HINT: The initial structure is polar, which means that, in general, an origin shift will be necessary to minimize the displacements between the initial polar structure and the hypothetical idealized parent one. Please, insert a minimum grid for the optimization (in Angstroms)

Note the continuous parameter t appearing in the transformation matrix of the listed minimal supergroups, indicating the possible arbitrary choice of its origin along the z-axis. Instead of varying this parameter, the program sets it to zero, while the origin of the input structure is varied according to the defined grid.

All isomorphic supergroups can be discarded beforehand because the structure contains only 2 formula unit per primitive cell, and therefore the cell divisions implied by these supergroups (inverse of their k-index) are incompatible. For the rest, with a tolerance of 2 A, the summary of the pseudosymmetry check is the following:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*P*6 (168)	2	2	**a,b,2c** ; 0,0,0	>tol	-
2	*P*6$_3$/*m* (176)	2	1	**a,b,c** ; 0,0,0	1.4010	0.7005
3	*P*6$_3$22 (182)	2	1	**a,b,c** ; 0,0,0	1.3984	0.6992
4	*P*6$_3$*cm* (185)	2	1	**a,b,c** ; 0,0,0	>tol	-
5	*P*6$_3$*mc* (186)	2	1	**a,b,c** ; 0,0,0	0.8948	0.4474

Three minimal supergroups are therefore detected. The first two are non-polar, while the third one is also polar along z. For the non-polar ones the program indicates an optimal origin shift within the resolution given by the grid used and lists besides the symmetrized structure, the original one with the optimized origin. For instance for the first flagged supergroup:

2# Supergroup $P6_3/m$ (176): a,b,c ; 0,0,0 and index 2
Displacements:

Atom	Idealized Coordinates	u_x	u_y	u_z	|u|
Sb1	(0.8837, 0.2243, 0.2500)	0.000000	0.000000	0.033333	0.2533
Na1	(0.3333, 0.6667, 0.2500)	0.000000	0.000000	-0.049667	0.3775
F1	(0.1575, 0.3110, 0.0770)	0.046500	0.082000	-0.049667	0.7005
F2	(0.1575, 0.3110, 0.4230)	-0.046500	-0.082000	-0.049667	0.7005
F3	(0.0350, 0.4910, 0.2500)	0.000000	0.000000	0.064333	0.4889
F4	(0.6667, 0.3333, 0.2500)	0.000000	0.000000	0.028333	0.2153

NOTE: u_x, u_y and u_z are given in relative units. |u| is the absolute displacement given in Å.

Optimized polar structure:

Origin shifted with t = (0.000000, 0.000000, 0.733333)
173
8.2850 8.2850 7.6000 90.00 90.00 120.00
6
Sb 1 - 0.883700 0.224300 0.283333
Na 1 - 0.333333 0.666667 0.200333
F 1 - 0.204000 0.393000 0.027333
F 2 - 0.111000 0.229000 0.373333
F 3 - 0.035000 0.491000 0.314333
F 4 - 0.666667 0.333333 0.278333

Idealized structure (subgroup setting):

173
8.2850 8.2850 7.6000 90.00 90.00 120.00
6
Sb 1 - 0.8837 0.2243 0.2500
Na 1 - 0.3333 0.6667 0.2500
F 1 - 0.1575 0.3110 0.0770
F 2 - 0.1575 0.3110 0.4230
F 3 - 0.0350 0.4910 0.2500
F 4 - 0.6667 0.3333 0.2500

Idealized structure (supergroup setting):

176
8.2850 8.2850 7.6000 90.00 90.00 120.00
5
Sb 1 - 0.8837 0.2243 0.2500
Na 1 - 0.3333 0.6667 0.2500
F 1 - 0.1575 0.3110 0.0770
#F 2 - 0.1575 0.3110 0.4230
F 3 - 0.0350 0.4910 0.2500
F 4 - 0.6667 0.3333 0.2500

Notes:
* Idealized structure with space group 176 related with the given by the transformation a,b,c ; 0,0,0 and index 2
* Cell parameters have not been symmetrized. They may include in general some symmetry breaking strain, to be removed by hand.
* A commented atom means a redundant atom, due to the merging of the Wyckoff orbit with another one in the supergroup

The origin shift done by the program is therefore (0,0,0.733), and it is the same for the other non-polar supergroup $P6_322$. If we increase the density of grid points, the origin choice can be further optimized decreasing the maximum atomic displacements between the symmetrized and the input structure. For instance, if we put for the grid parameter 0.1 A, the pseudosymmetry check gives the following results:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*P*6 (168)	2	2	**a,b,2c** ; 0,0,0	>tol	-
2	$P6_3/m$ (176)	2	1	**a,b,c** ; 0,0,0	1.2824	0.6412
3	$P6_322$ (182)	2	1	**a,b,c** ; 0,0,0	1.3072	0.6536
4	$P6_3cm$ (185)	2	1	**a,b,c** ; 0,0,0	>tol	-
5	$P6_3mc$ (186)	2	1	**a,b,c** ; 0,0,0	0.8948	0.4474

The corresponding results for the supergroup $P6_3/m$ are now:

Optimized polar structure:

Origin shifted with t = (0.000000, 0.000000, 0.250000)
173
8.2850 8.2850 7.6000 90.00 90.00 120.00
6
Sb 1 - 0.883700 0.224300 0.800000
Na 1 - 0.333333 0.666667 0.717000
F 1 - 0.204000 0.393000 0.544000
F 2 - 0.111000 0.229000 0.890000
F 3 - 0.035000 0.491000 0.831000
F 4 - 0.666667 0.333333 0.795000

Idealized structure (subgroup setting):

173
8.2850 8.2850 7.6000 90.00 90.00 120.00
6
Sb 1 - 0.8837 0.2243 0.7500
Na 1 - 0.3333 0.6667 0.7500
F 1 - 0.1575 0.3110 0.5770
F 2 - 0.1575 0.3110 0.9230
F 3 - 0.0350 0.4910 0.7500
F 4 - 0.6667 0.3333 0.7500

Idealized structure (supergroup setting):

176
8.2850 8.2850 7.6000 90.00 90.00 120.00
5
Sb 1 - 0.8837 0.2243 0.7500
Na 1 - 0.3333 0.6667 0.7500
F 1 - 0.1575 0.3110 0.5770
#F 2 - 0.1575 0.3110 0.9230
F 3 - 0.0350 0.4910 0.7500
F 4 - 0.6667 0.3333 0.7500

Note that the origin shift is quite different from the one proposed for the 0.5 Å grid. However, the proposed symmetrized P63/m reference structure is the same. In fact, it is an equivalent description of the same structure (the origin is shifted (0 0 ½), which is an operation of the normalizer of P63/m- see program NORMALIZER in the server-). The same happens for the other flagged non-polar supergroup

Important: once the program has detected pseudosymmetry for a given non-polar symmetry, it is in principle not necessary to try to optimize further the origin choice

with PSEUDO by minimizing the maximum atomic displacements. In most cases, the best or more sensible origin choice does not correspond to this minimization. For instance, it can be more convenient to take the origin that cancels any global translation when the two structures are compared, so that its geometric centre remains unmoved by the distortion. Once the reference symmetrized structure is known and independently of the magnitude of the atomic displacements, the calculation of this optimal origin choice is straightforward, as done by AMPLIMODES in this server.

Continuing with the example, we take now the (polar) symmetrized $P6_3mc$ structure:

```
186
8.2850 8.2850 7.6000 90.00 90.00 120.00
6
Sb    1   -  0.8297  0.1703  0.5500
Na    1   -  0.3333  0.6667  0.4670
F     1   -  0.1965  0.3930  0.2940
F     2   -  0.1145  0.2290  0.6400
F     3   -  0.0350  0.5175  0.5810
F     4   -  0.6667  0.3333  0.5450
```

which is the one with the smallest distortion. We use it for a further step up, checking with PSEUDO its pseudosymmetry.

To be noticed is the fact that for this symmetry no origin shift has been done by the program, as this supergroups is also polar along z, and the magnitude of the atomic displacements between the distorted and the symmetrized structures do not depend on the origin choice along z.

Keeping the grid parameter in 0.1 Å, pseudosymmetry for P63/mmc is detected, with the following values:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*P6mm* (183)	2	2	**a,b,2c** ; 0,0,0	>tol	-
2	*P6$_3$/mmc* (194)	2	1	**a,b,c** ; 0,0,0	1.2792	0.6396

Optimized polar structure:

```
# Origin shifted with t = (0.000000, 0.000000, 0.250000)
186
8.2850 8.2850 7.6000 90.00 90.00 120.00
6
Sb 1 -  0.829700 0.170300 0.800000
Na 1 -  0.333300 0.666700 0.717000
F 1 -  0.196500 0.393000 0.544000
F 2 -  0.114500 0.229000 0.890000
F 3 -  0.035000 0.517500 0.831000
F 4 -  0.666700 0.333300 0.795000
```

Idealized structure (subgroup setting):

```
186
8.2850 8.2850 7.6000 90.00 90.00 120.00
6
Sb   1  - 0.8297  0.1703  0.7500
Na   1  - 0.3333  0.6667  0.7500
F    1  - 0.1555  0.3110  0.5770
F    2  - 0.1555  0.3110  0.9230
```

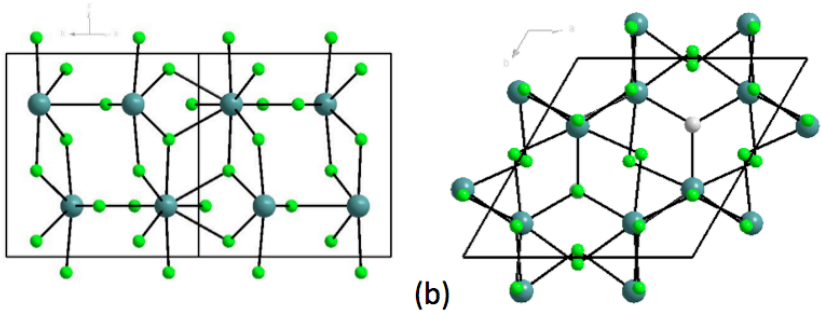
F 3 - 0.0350 0.5175 0.7500
F 4 - 0.6667 0.3333 0.7500

Idealized structure (supergroup setting):

194
8.2850 8.2850 7.6000 90.00 90.00 120.00
5
Sb 1 - 0.8297 0.1703 0.7500
Na 1 - 0.3333 0.6667 0.7500
F 1 - 0.1555 0.3110 0.5770
#F 2 - 0.1555 0.3110 0.9230
F 3 - 0.0350 0.5175 0.7500
F 4 - 0.6667 0.3333 0.7500

The optimized origin shift is the same as obtained in the previous step for the non-polar supergroups. The reference symmetrized $P6_3/mmc$ structure with Wyckoff labels is:

```
194
8.2850 8.2850 7.6000 90.00 90.00 120.00
5
Sb     1    6h     0.8297 0.1703 0.7500
Na     1    2d     0.333333 0.666667 0.7500
F      1    12k    0.1555 0.3110 0.5770
F      3    6h     0.0350 0.5175 0.7500
F      4    2c     0.666667 0.333333 0.7500
```



Two projections of the P63/mmc structure obtained with *PSEUDO* as ideal symmetrized configuration of $NaSb_3F_{10}$. The maximal atomic displacement of the displacive distortion relating this structure with the experimental one (see previous figure (a)) is of the order of 0.65 Å.

Although the rotational symmetry is already maximal, as there are still two formula units per primitive unit cell, we can still check the pseudosymmetry of this structure for supergroups with k-index=2. There is only a supergroup of this type, but the pseudosymmetry check is negative:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*P6/mmm* (191)	2	2	**a,b,2c** ; 0,0,0	>tol	-

In fact if we increase sufficiently the tolerance, this supergroup P6/mmm is flagged by the program with Δ_{max}=3.8 Å (u_{max}= 1.9 Å), but this is due to the fact that c/4 =1.9 A, and therefore with this enormous tolerance atomic sites can change their z-coordinate from 0.75 to 0.0, and similar jumps, changing completely the structure.

Summarizing, and considering the two steps done with PSEUDO, the $NaSb_3F_{10}$ structure has $P6_3/mmc$ pseudosymmetry with a transformation matrix (**a**, **b**, **c**; 0, 0, 0) relating its setting with the observed $P6_3$ space group. We can then use the option 3 of PSEUDO, which also allows a origin optimization for polar cases, for a direct check of this pseudosymmetry and a direct comparison of the two structures:

Case #	Supergroup G	Index i	Index i_k	(P,p)	Δ_{max}	u_{max}
1	*P6₃/mmc* (194)	4	1	**a,b,c** ; 0,0,0	1.3072	0.6536

Idealized structures

1# Supergroup *P6₃/mmc* (194): a,b,c ; 0,0,0 and index 4

Displacements:

Atom	Idealized Coordinates	u_x	u_y	u_z	|u|
Sb1	(0.8297, 0.1703, 0.7500)	0.054000	0.054000	0.050000	0.5870
Na1	(0.3333, 0.6667, 0.7500)	0.000000	0.000000	-0.033000	0.2508
F1	(0.1555, 0.3110, 0.5770)	0.048500	0.082000	-0.033000	0.6426
F2	(0.1555, 0.3110, 0.9230)	-0.044500	-0.082000	-0.033000	0.6402
F3	(0.0350, 0.5175, 0.7500)	0.000000	-0.026500	0.081000	0.6536
F4	(0.6667, 0.3333, 0.7500)	0.000000	0.000000	0.045000	0.3420

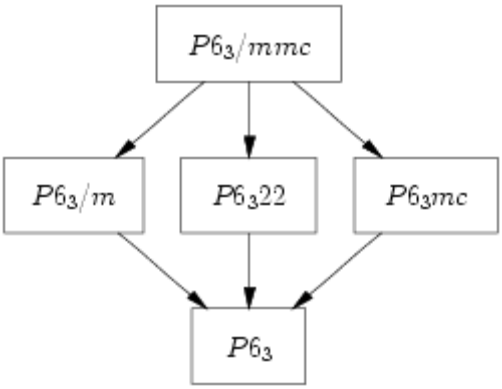
NOTE: ux, uy and uz are given in relative units. |u| is the absolute displacement given in Å

Idealized structure (supergroup setting):

```
194
8.2850 8.2850 7.6000 90.00 90.00 120.00
5
Sb   1  - 0.8297  0.1703  0.7500
Na   1  - 0.3333  0.6667  0.7500
F    1  - 0.1555  0.3110  0.5770
#F   2  - 0.1555  0.3110  0.9230
F    3  - 0.0350  0.5175  0.7500
F    4  - 0.6667  0.3333  0.7500
```

The symmetrized structure is the same as the one obtained stepwise through a chain of minimal supergroups.

If we search with SUBGROUPGRAPH (also in the server) the possible subgroups $P6_3$ of $P6_3/mmc$ of index 4 (the index of the one here), we can observe that there is a single class and a single subgroup $P6_3$, with the following lattice of minimal subgroups relating both space groups:



It is then clear that the pseudosymmetry for $P6_3/mmc$ makes the system pseudosymmetric for the three intermediate space groups, and this is the reason why the three supergroups were detected by PSEUDO in the first step up the chain of minimal supergroups. Obviously, for the second step we could have used any of the three symmetrized structures to reach the ultimate global supergroup.

In (J. Appl. Cryst. (2009). 42, 58–62) only pseudosymmetry for the space groups $P6_322$ and $P6_3/mmc$ was detected. The other two intermediate subgroups seem to have been overlooked, and the symmetry $P6_322$ was proposed for a possible intermediate phase inferred from experimental results. However, the other two intermediate may be more appropiate candidates for an intermediate phase, since the distortion in the structure with $P6_322$ symmetry, quantified with AMPLIMODES, is marginal compared with those associated with the symmetries $P6_3/m$ and $P6_3mc$.

Exercise 3: The compound Nd4GeO8 is reported to have the following structure with $Pmc2_1$ symmetry (Doklady Akademii Nauk SSSR (1978) 241, 353-356):

26
7.475 5.727 17.927 90 90 90
20

Nd	1	2a	0.000000	0.265100	0.000000
Nd	2	2b	0.500000	0.231400	0.973700
Nd	3	2a	0.000000	0.292500	0.205700
Nd	4	2b	0.500000	0.787400	0.270500
Nd	5	4c	0.241600	0.768900	0.090200
Nd	6	4c	0.261000	0.274100	0.383800
Ge	1	2b	0.500000	0.258100	0.180900
Ge	2	2a	0.000000	0.755800	0.298600
O	1	2a	0.000000	0.531400	0.104500
O	2	2b	0.500000	0.063000	0.100800
O	3	2a	0.000000	0.040900	0.114200
O	4	2b	0.500000	0.545400	0.143500
O	5	4c	0.186400	0.668100	0.248000
O	6	4c	0.312100	0.192400	0.236700
O	7	2a	0.000000	0.055500	0.319800
O	8	2a	0.000000	0.539900	0.366300
O	9	2b	0.500000	0.004300	0.370900
O	10	2b	0.500000	0.512400	0.362800
O	11	4c	0.215300	0.009700	0.486700
O	12	4c	0.258000	0.492400	0.497300

Show using *PSEUDO* (option 1) that this structure can be considered a small distortion of a Cmcm structure. Using *SUBGROUPGRAPH* show the graph of maximal subgroups connecting the two symmetries. Using again *PSEUDO* (option 3) obtain the atomic displacements relating the two structures. Calculate the theoretical value for the spontaneous polarization of the compound using nominal charges for the ions.

Exercise 4: The ICSD database contains the following structural model for $Ca_2Ge_7O_{16}$ (Doklady Akademii Nauk SSSR (1979) 245, 110-113):

```
32
11.340 11.340 4.6400 90 90 90
13
Ge   1  2a   0 0 0
Ge   2  4c   0.1335 0.1336 0.4996
Ge   3  4c   0.0666 0.3122 -.0107
Ge   4  4c   0.3123 0.0667 0.0095
Ca   1  4c   0.3350 0.3348 0.4970
O    1  4c   0.0012 0.1167 0.7467
O    2  4c   0.0288 0.2197 0.2695
O    3  4c   0.1686 0.2658 0.7246
O    4  4c   0.2657 0.1697 0.2645
O    5  4c   0.1171 0.0006 0.2411
O    6  4c   0.2198 0.0282 0.7180
O    7  4c   0.1398 0.4316 0.1548
O    8  4c   0.4327 0.1403 0.8306
```

Despite the 4/mmm Laue symmetry of the diffraction diagram the authors of this publication were unable to find an appropiate tetragonal structural model, and refined this Pba2 structure

Using *PSEUDO*, demonstrate that this structure differs from a tetragonal one with space group P-4b2, by atomic displacements which are practically negligible or within experimental accuracy, so that in fact this structure file should be considered incorrect, being a case of "overlooked symmetry".
The extreme pseudosymmetry of this structure was reported in (Acta Cryst. B (2002) 58, 921) and the compound has been recently confirmed to have P-4b2 symmetry by a new study of the structure (Acta Cryst. C (2007) 63, i47)

Option 4: Monoclinic and triclinic structures

Monoclinic and triclinic structures have a great deal of freedom in the choice of their conventional unit cell, and therefore the checking of their pseudosymmetry with respect to space groups of a higher symmetry class requires in general a specific analysis of the pseudosymmetry of its Bravais lattice. This is provided by option 4 of PSEUDO, which uses a tool of the CCTBX library (http://cci.lbl.gov/cctbx/).

This option is still under construction.