

## **Tutorial on the use of the program *AMPLIMODES* of the Bilbao Crystallographic Server ([www.cryst.ehu.es](http://www.cryst.ehu.es)).**

J. Manuel Perez-Mato, D. Orobengoa, Mois I. Aroyo and C. Capillas  
Dept. de Fisica de la Materia Condensada, Facultad de Ciencia y  
Tecnologia, Universidad del Pais Vasco, Apto. 644, 48080 Bilbao, Spain.

(see also D. Orobengoa, C. Capillas, M.I. Aroyo & J. M. Perez-Mato. J. Appl. Cryst. (2009), A42, 820-833 )

We know since the works of Landau that the natural language to deal with the static frozen distortions present in displacively distorted structures is the one of *modes*. Modes are collective correlated atomic displacements fulfilling certain symmetry properties. Structural distortions in distorted structures can be decomposed into contributions of modes with different symmetries given by irreducible representations of the parent space group. One can then distinguish primary and secondary (induced) distortions, which will have in general quite different weights in the structure, and will respond differently to external perturbations.

In general, the use of symmetry-adapted modes in the description of distorted structures introduces a natural physical hierarchy among the structural parameters. This can be useful not only for investigating the physical mechanisms that stabilize these phases, but also for pure crystallographic purposes. The set of structural parameters used in a mode description of a distorted phase will in general be better adapted for a controlled refinement of the structure, or for instance for comparative studies between different materials or for ab-initio calculations.

AMPLIMODES is a computer program available on the Bilbao Crystallographic Server that can perform the symmetry-mode analysis of any distorted structure of displacive type. The analysis consists in decomposing the symmetry-breaking distortion present in the distorted structure into contributions from different symmetry-adapted modes. Given the high- and the low-symmetry structures, AMPLIMODES determines the atomic displacements that relate them, defines a basis of symmetry-adapted modes, and calculates the amplitudes and polarization vectors of the distortion modes of different symmetry frozen in the structure. The program uses a mode parameterization that is as close as possible to the crystallographic conventions, using an asymmetric unit of the low-symmetry structure for describing modes and distortions.

AMPLIMODES uses internally SYMMODES to produce the basis of symmetry-adapted modes to be used in the decomposition of the structural distortion, but instead of describing the modes in the high-symmetry setting, as SYMMODES, works in the setting of the subgroup.

Let us consider as an example the Amm2 structure of the ferroelectric distorted perovskite BaTiO<sub>3</sub> at 190K (Kwei et al. (1993)). The only data needed by AMPLIMODES are the parent structure and the distorted structure to be analyzed (both structures described in standard settings). This, together with the transformation relating the space groups of the two structures, is sufficient for running the program:

### High symmetry structure

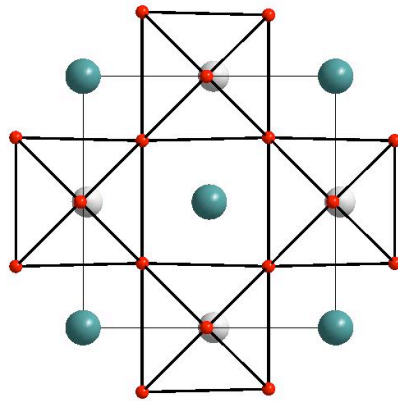
```
221
4.006 4.006 4.006 90 90 90
3
Ba 1 1a 0.0 0.0 0
Ti 1 1b 0.5 0.5 0.5
O 1 3c 0.5 0.0 0.5
```

### Low symmetry structure

```
36
3.9828 5.6745 5.6916 90 90 90
4
Ba 1 2a 0.0 0.0 0.0
Ti 1 2b 0.5 0.0 0.5170
O 1 2a 0.0 0.0 0.4890
O 2 4e 0.5 0.2561 0.2343
```

### Transformation matrix

```
[ 0 1 1 ] [ 0 ]
[ 0 -1 1 ] [ 0 ]
[ 1 0 0 ] [ 0 ]
```



**Figure 1:** Structure of the Amm2 phase of BaTiO<sub>3</sub>

This orthorhombic is one the three ferroelectric phases of BaTiO<sub>3</sub>, caused by the condensation at low temperatures of an unstable polar distortion. A three-fold degenerate polar instability associated with a single active 3-dim irrep produces three successive ferroelectric phases, by changing its direction within the 3-dim irrep space.

### Reference Structure:

The program first transforms the input high-symmetry parent structure into the setting of the low symmetry phase (using TRANSTRU). This structure is the so-called REFERENCE STRUCTURE. This structure, and in particular the specific asymmetric unit chosen by the program, will be used as the reference configuration for the atomic displacements describing the low-symmetry structure:

## Reference Structure

### Transformed high symmetry structure in the subgroup basis

```
038
4.006000 5.665339 5.665339 90.000000 90.000000 90.000000
4
Ba      1      2a      0.000000      0.000000      0.000000
Ti      1      2b      0.500000      0.000000      0.500000
O       1      4e      0.500000      0.250000      0.250000
O       1_2    2a      0.000000      0.000000      0.500000
```

This listing describes the parent structure, but expressed in the low-symmetry space group. The number of atoms in the asymmetric unit increases in general with respect to the description in the high-symmetry group. Some Wyckoff orbits may split. In the present case, the number of independent atoms increases from 3 to 4, because the orbit of O1 splits into two.

Note that the cell parameters listed in the reference structure above correspond to the transformation of the unit cell associated with the parent structure. Thus, they fulfill exactly  $b = c = \sqrt{2}a$ , according to the group-subgroup transformation. If the mode analysis demanded to the program really makes sense, this unit cell should not differ much from the one of the input low-symmetry structure, and this should be checked by the user.

These idealized cell parameters of the reference structure will be used by the program for computing (when needed) the absolute values of the atomic displacements. In other words, the calculation of these displacements (in Å) is done disregarding the strain of the lattice of the low-symmetry structure with respect to the parent one.

### Atom Mapping:

Once the asymmetric unit of the reference structure has been defined, the program does an “atom mapping” or “pairing” identifying the atoms in the low symmetry structure that correspond to those listed in the asymmetric unit of the reference structure. From the comparison of these pairs of atomic positions in the high and low symmetry structures, the atomic displacements are calculated:

#### Atom pairings and distances

Atom Mappings					
WP	Atom	Coordinates in $S_1$	Atom	Coordinates in $S_2$	
2a	(0,0,z)	Ba1	(0,0,0)	Ba1	(0,0,0)
2b	(1/2,0,z)	Ti1	(1/2,0,1/2)	Ti1	(1/2,0,0.51700)
4e	(1/2,y,z)	O1	(1/2,1/4,1/4)	O2	(1/2,0.25610,0.23430)
2a	(0,0,z)	O1_2	(0,0,1/2)	O1	(0,0,0.48900)

WP	Atom	Atomic Distances				
		$u_x$	$u_y$	$u_z$	d	
2a	(0,0,z)	Ba1	0.0000	0.0000	0.0000	0.0000
2b	(1/2,0,z)	Ti1	0.0000	0.0000	0.0170	0.0963
4e	(1/2,y,z)	O1	0.0000	0.0061	-0.0157	0.0954
2a	(0,0,z)	O1_2	0.0000	0.0000	-0.0110	0.0623

NOTE:  $d_x$ ,  $d_y$  and  $d_z$  are given in relative units. |d| is the absolute distance given in Å

**Maximum atomic displacement in the distortion,  $\Delta$ : 0.0963 Å**

**Total distortion amplitude: 0.1771 Å**

The pairing is only done if the magnitude of the atomic displacements (for all atoms) is smaller than a given tolerance. This tolerance, which by default is 1 Å, can be increased by the user, but one should consider that a successful pairing with atomic displacements much larger than 1 Å may be nonsensical from a stereochemical viewpoint, and should be crosschecked carefully.

The displacements  $\mathbf{u}$  for the atoms in the asymmetric unit of the reference structure, listed in the last table above defines completely the displacive distortion relating the two structures. The space group of the low symmetry structure forces that any atom not present in this asymmetric unit, but related by a space group operation  $(\mathbf{R}, \mathbf{t})$  with one atom in it having a displacement  $\mathbf{u}$ , must have a displacement given by the rotation or roto-inversion operation  $\mathbf{R}$ :  $\mathbf{R}\mathbf{u}$ .

Apart from the maximal atomic displacement, the output yields the amplitude of the total distortion, which is given by the square root of the sum of the square of all atomic displacements within a primitive unit cell of the reference structure.

### Polar structures:

The Amm2 structure is polar along the z direction. This means that the displacive distortion relating both structures may include some global translation of the structure as a whole, due to the arbitrary choice of the origin along z in the Amm2 structure. For polar structures, the program shifts its origin to eliminate this global displacement. If this shift is not desired, the user can put (0,0,0) as the polar direction in a second input menu, only appearing for polar structures. If we introduce the correct direction (0,0,1), the program does the mentioned origin shift, yielding the new displacive distortion without global displacement along z:

#### After origin shift

Relative origin shift to eliminate a global displacement: (0.00000, 0.00000, -0.00508)

Atom Mappings					
WP	Atom	Coordinates in $S_1$		Atom	Coordinates in $S_2$
2a	(0,0,z)	Ba1	(0,0,0)	Ba1	(0,0,0.00508)
2b	(1/2,0,z)	Ti1	(1/2,0,1/2)	Ti1	(1/2,0,0.52208)
4e	(1/2,y,z)	O1	(1/2,1/4,1/4)	O2	(1/2,0.25610,0.23938)
2a	(0,0,z)	O1_2	(0,0,1/2)	O1	(0,0,0.49408)

WP	Atom	Atomic Distances				
		$u_x$	$u_y$	$u_z$	d	
2a	(0,0,z)	Ba1	0.0000	0.0000	0.0051	0.0288
2b	(1/2,0,z)	Ti1	0.0000	0.0000	0.0221	0.1251
4e	(1/2,y,z)	O1	0.0000	0.0061	-0.0106	0.0694
2a	(0,0,z)	O1_2	0.0000	0.0000	-0.0059	0.0335

NOTE:  $d_x$ ,  $d_y$  and  $d_z$  are given in relative units. |d| is the absolute distance given in Å

Maximum atomic displacement in the distortion,  $\Delta$ : 0.1251 Å

Total distortion amplitude: 0.1650 Å

Note that the origin shift done has slightly increased the maximal atomic displacement, but has decreased the total amplitude of the distortion.

One should take into account that in the case of polar structures, its origin choice, relative to the one of the high-symmetry configuration, may include such a large

global displacement of the structure that AMPLIMODES can be unsuccessful to find an appropriate pairing of the two structures. In this case, one has two possibilities:

- i) Try AMPLIMODES with a series of equivalent low-symmetry structures with the origin shifted systematically (this shifted structures can be constructed automatically with TRANSTRU) until the program achieves a correct pairing or
- ii) Apply PSEUDO to the low-symmetry structure to get a first choice for the origin shift minimizing somehow the atomic displacements.

### Summary Output:

The program then calls the program SYMMODES to obtain a basis of symmetry-adapted modes for describing the displacive distortion, makes the mode decomposition of the distortion with this basis, and lists the results. First, a summary appears:

#### Symmetry Modes Summary

Atoms	WP	Modes
O1	3c	<b>GM4-(2)</b> <b>GM5-(1)</b>
Ti1	1b	<b>GM4-(1)</b>
Ba1	1a	<b>GM4-(1)</b>

Note: The primary mode is written in bold letters

#### Summary of Amplitudes

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM4-	(a,a,0)	Amm2 (38)	4	0.1649
(0,0,0)	GM5-	(0,a,-a)	Amm2 (38)	1	0.0056

Global distortion: 0.1650 Å

The basis of symmetry-adapted modes are chosen such that each mode is restricted to displacements within a single Wyckoff orbit of the high temperature structure. The first Table in this summary lists the number of basis symmetry modes and their irreps, that describe the atomic displacements of the atoms in each occupied Wyckoff orbit of the high symmetry phase. For each Wyckoff type, the table lists the relevant irreps and in parenthesis the number of basis modes corresponding to this irrep and this Wyckoff orbit. This information only depends on the type of Wyckoff orbit, therefore all atoms with the same type of orbit are included in a single row.

In our example, there are a total of five modes, four corresponding to irrep GM4- and one to irrep GM5-. The single mode GM5- only involves displacements of the high-symmetry orbit of atoms represented by O1.

The total number of modes must coincide with the total number of free structural parameters that are necessary to describe the structure. Indeed, if we inspect the original asymmetric unit of the Amm2 structure, it can be seen that there are five atomic components that are “free” by symmetry, although one of them has been arbitrarily chosen zero due to the polar character of the structure.

The second Table in this summary is the most important one. It lists the two irreps present in the distortion and the absolute amplitudes of these two symmetry components of the global distortion. The table gives for each irrep its wave vector, the restricted direction within the irrep space that the modes fulfill, their isotropy subgroup, and the dimension of its subspace. This dimension is the number of basis symmetry-adapted modes of this symmetry. The GM4- subspace is four-dimensional. In order to

describe a GM4- distortion four components must be given corresponding to the four GM4- (orthonormal) basis modes, one for the Ba atoms, one for the Ti atoms, and two for the oxygens. The GM5- subspace is one dimensional as only one basis mode of this symmetry exists.

The four dimensional character of the GM4- subspace is however misleading, as it includes the global translation of the structure. Fixing the origin, as in a standard crystallographic description, reduces the number of degrees of freedom within this type of distortions to three.

It is remarkable that the isotropy subgroup of the two irreps is Amm2. Therefore any of the two could be the active irrep. However, the amplitudes obtained for the two symmetry-adapted distortions are very different. The amplitude of GM5- distortion is more than 20 times smaller. This is an extreme case of what we expect in distorted structures resulting (according to Landau theory) from the instability of an order parameter with symmetry properties given, by a single active irrep. In our example, the GM4- distortion corresponds approximately to a specific combination of the three-fold degenerate unstable polar normal modes which cause the successive ferroelectric phases in BaTiO<sub>3</sub>. Its amplitude can be identified with the Landau order parameter connecting this phase with the cubic perovskite. The GM4- distortion is therefore at the origin of this ferroelectric phase, while the GM5- distortion is only a secondary effect allowed by symmetry, but marginal in the phase stabilization. Therefore, the strong difference of amplitudes of the two frozen distortions is the signature of the underlying lattice dynamics mechanism causing this phase.

Note that the amplitude of the total distortion, 0.1650 Å is again given in this summary. It is in fact a cross check of the calculation done previously summing the square of the atomic displacements of the total distortion. Here, the calculation is done taking the square root of the sum of the square of the amplitudes listed in the Table for all irreps (The Pythagoras theorem is fulfilled by the amplitudes: as we are in a vector space!). In this example:  $0.1650 = [(0.1649)^2 + (0.0056)^2]^{1/2}$ .

### Basis of symmetry-adapted modes:

The subsequent detailed output includes first a list of the basis of symmetry-adapted modes used in the decomposition:

#### Normalized Symmetry modes

The modes are normalized to the low symmetry unit cell and are given as relative displacements in this cell.

#### Irrep GM4-

##### GM4- Mode Ba1 1

Atom	$\delta x$	$\delta y$	$\delta z$
Ba1	0.000000	0.000000	0.176512

##### GM4- Mode Ti1 1

Atom	$\delta x$	$\delta y$	$\delta z$
Ti1	0.000000	0.000000	0.176512

##### GM4- Mode O1 1

Atom	$\delta x$	$\delta y$	$\delta z$
O1	0.000000	0.062406	0.062406
O1_2	0.000000	0.000000	0.124813

GM4- Mode O1 2

Atom	$\delta x$	$\delta y$	$\delta z$
O1	0.000000	-0.088256	0.088256
O1_2	0.000000	0.000000	0.000000

**Irrep GM5-**

GM5- Mode O1 1

Atom	$\delta x$	$\delta y$	$\delta z$
O1	0.000000	-0.062406	-0.062406
O1_2	0.000000	0.000000	0.124813

The five basis symmetry-adapted modes used by the program are shown. They are listed separately for each irrep. They are labelled using the atom label of the representative of the corresponding Wyckoff orbit, plus a numeric index that enumerates the modes in case that more than one exists.

The basis modes are given listing the displacements of only the atoms of the relevant Wyckoff orbit that are present in the asymmetric unit of the reference structure. These displacements are expressed in relative units with respect to the unit cell parameters of the subgroup cell. If transformed into absolute values (in Å) using the reference unit cell, the square of these displacements, when summed for all atoms within a primitive unit cell of the low symmetry space group, must yield  $1 \text{ \AA}^2$ :

$$\sum_i \mathbf{u}^2(i) = 1 \text{ \AA}^2$$

This means that the basis modes are normalized to  $1 \text{ \AA}$ . We can check that for instance for mode (O1 ,1):

$$2x[(0.062406 \times 5.665339)^2 + (0.062406 \times 5.665339)^2] + 1x[(0.124813 \times 5.665339)^2] = 0.999995$$

where we have used the fact that  $b=c= 5.665339 \text{ \AA}$  in the reference structure, and that the multiplicity of the splitted orbits of the oxygens O1 and O1\_2, reduced to a primitive unit cell, are 2 and 1, respectively. Note that the inclusion in the sum of the atoms not listed in the Table can be done simply by multiplying by the respective multiplicities (for a primitive cell) the contribution of the atoms in the Table, because, due to the symmetry condition mentioned above, the modules of their rotated displacements will be the equal to those of the corresponding atom in the asymmetric unit.

The basis modes are also orthogonal:

$$\sum_i \mathbf{u}_{\text{mode1}}(i) \cdot \mathbf{u}_{\text{mode2}}(i) = 0$$

Let us check this condition for the modes (O1, 1) and (O1, 2):

$$2x[(0, 0.062406 \times 5.665339, 0.062406 \times 5.665339) \cdot (0, -0.088256 \times 5.665339, 0.088256 \times 5.665339)] \\ + 1x[(0, 0, 0.124813 \times 5.665339) \cdot (0, 0, 0)] = 1.12331 \times 10^{-7}$$

where again the sum for the full orbit can be done by multiplying the dot products of the atom representatives by their multiplicities.

We can observe in the above table of basis modes the symmetry constraints associated with each type of symmetry. For instance, the displacements of the O1 and O1\_2 atoms in the mode GM5- are such that the displacement of the O1\_2 atom is restricted to the z-direction (subgroup setting), and is twice the value of the equal displacement of the O1 atom along the y and z directions. O1 and O1\_2 are independent atomic positions in the Amm2 group, but the GM5- mode correlates their displacements. It is the free combination of the GM5- and GM4- modes for the two atoms, both allowed in the Amm2 space group, that makes the two atomic sites independent.

### Irrep Distortions. Amplitudes and polarization vectors:

Once the basis of symmetry-adapted modes is defined, the output gives the details of the mode decomposition. For each irrep, the parameters describing the distortion of this symmetry (irrep distortion) present in the low-symmetry structure are listed:

**K-vector: GM = (0,0,0)**

**Irrep: GM4-**

**Direction: (a,a,0)**

**Isotropy Subgroup: 38 Amm2 C2v-14**

Transformation matrix:

$$\begin{bmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

The amplitude of this distortion is:

$$A_{GM4-} = 0.1649 \text{ \AA}$$

Normalized polarization vector: (in terms of the amplitudes of the (normalized)

Ba1 1	Ti1 1	O1 1	O1 2
0.1745	0.7585	-0.2536	-0.5744

NOTE: A second number next to the label counts the different symmetry modes that

Normalized polarization vector expressed as displacements (in cell relative un Ångström)

Atom	$\delta x$	$\delta y$	$\delta z$
Ba1	0.0000	0.0000	0.0308
Ti1	0.0000	0.0000	0.1339
O1	0.0000	0.0349	-0.0665
O1_2	0.0000	0.0000	-0.0317

**Virtual structure** with only this symmetry component of the distortion frozen.

After a detailed information on the symmetry of the irrep distortion: wave vector, restricted direction, isotropy subgroup, and transformation matrix, the output



lists the amplitude of this irrep distortion and its normalized so-called *polarization vector*.

The polarization vector of the irrep distortion is the set of normalized correlated atomic displacements of all atoms that multiplied by the given amplitude yields the actual distortion of this symmetry, which is present in the low-symmetry structure.

The polarization vector is expressed in two equivalent forms, one algebraic, and one crystallographic. In our example, the space of GM4- distortions is 4-dimensional, and four different basis modes of this symmetry were listed above. Any GM4-distortion can be expressed as a vector in this 4-dim space, by means of its four components with respect to this basis. The output gives these four components:

$$(0.1745, 0.7585, -0.2536, -0.5744)$$

indicating the basis mode corresponding to each of them: (Ba1,1), (Ti1,1), (O1,1) and (O1,2), respectively. The vector is normalized:

$$0.1745^2 + 0.7585^2 + (-0.2536)^2 + (-0.5744)^2 = 1.00002$$

The program is just saying that the GM4- distortion present in the structure can be obtained by combining the four basis modes in the form given by this 4-dim normalized vector and multiplying the resulting distortion by an amplitude of 0.1649.

This algebraic form of expressing the irrep distortion can be very useful to compare different distorted structures, obtained for instance at different temperatures, for similar compounds, or to compare experimental and theoretical (ab-initio) structures. In general, one expects the polarization vector of the active/primary irrep distortion to be rather invariant to temperature variations, modelizations, or composition, while its amplitude may vary considerably.

We can compare an irrep distortion in two different isomorphic structures by comparing separately their amplitudes, and their polarization vectors. The amplitude just compares the magnitude of the distortion, while the polarization vector compares the type of distortion within a certain symmetry restriction. The polarization vector defines a direction in the 4-dimensional vector space of the GM4- distortions. Two distortions would be of same type, independently of their magnitude, if the dot product of their 4-component vectors is one. The closer to one this dot product is, the more similar are the two distortions.

For instance, the Amm2 structure was also determined at 250K (Kwei et al. (1993), and the polarization vector of the GM4- distortion for this structure determined with AMPLIMODES is:

$$(0.2084, 0.7073, -0.1889, -0.6486)$$

The similarity of this vector with the one corresponding to the structure at 190K discussed until now, can be clearly seen by comparing each component. But a more quantitative comparison is just given by their dot product, which is 0.9933.

The output on each irrep distortion also includes a crystallographic description of its polarization vector. For the asymmetric unit of the reference structure, a table is given with the correlated atomic displacements (in relative units), which describe the normalized polarization vector of the irrep distortion.

This Table is just obtained by multiplying the components of the polarization vector by the corresponding basis modes. Thus, for instance, the atomic displacements of the oxygens O1 and O1\_2 in the table above can be obtained by just combining the two GM4- basis modes for these atoms, each multiplied by the corresponding component in the four-dimensional vector:

$$\begin{array}{|c|c|c|c|} \hline \text{O1} & 0.0000 & 0.0349 & -0.0665 \\ \hline \text{O1\_2} & 0.0000 & 0.0000 & -0.0317 \\ \hline \end{array} = -0.2536 \times \begin{array}{|c|c|c|c|} \hline \text{GM4- Mode O1 1} \\ \hline \text{Atom} & \delta x & \delta y & \delta z \\ \hline \text{O1} & 0.000000 & 0.062406 & 0.062406 \\ \hline \text{O1\_2} & 0.000000 & 0.000000 & 0.124813 \\ \hline \end{array} + (-0.5744) \times \begin{array}{|c|c|c|c|} \hline \text{GM4- Mode O1 2} \\ \hline \text{Atom} & \delta x & \delta y & \delta z \\ \hline \text{O1} & 0.000000 & -0.088256 & 0.088256 \\ \hline \text{O1\_2} & 0.000000 & 0.000000 & 0.000000 \\ \hline \end{array}$$

For the GM5- distortion the output is somehow simpler, since it is a 1-dim subspace:

**Irrep: GM5-**

**Direction: (0,a,-a)**

**Isotropy Subgroup: 38 Amm2 C2v-14**

Transformation matrix:

$$\begin{bmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

The amplitude of this distortion is:

$$A_{\text{GM5-}} = 0.0056 \text{ \AA}$$

There is one mode with this symmetry, and its amplitude in Ångströms is:

O1 1
-0.0056

Normalized polarization vector expressed as displacements (in cell relative units) of the structure:(normalization unit: 1 Ångström)

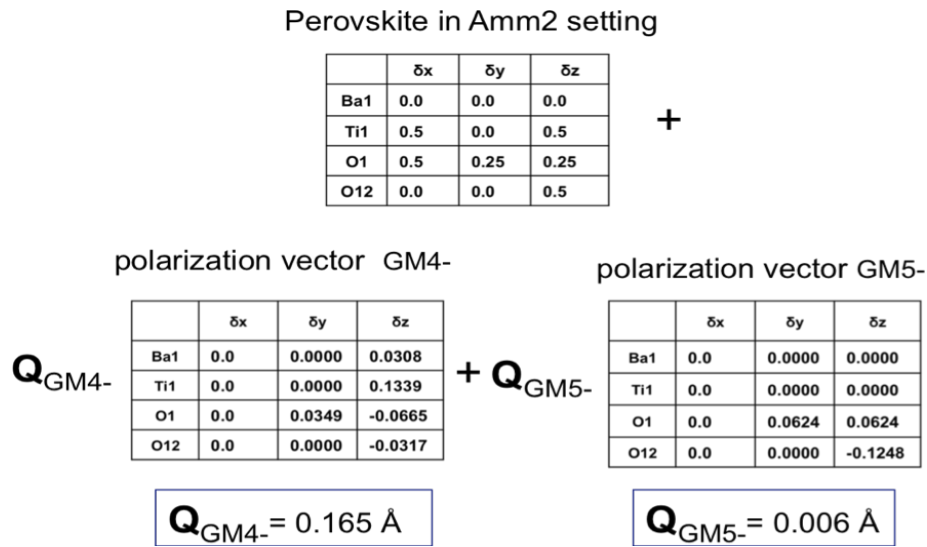
Atom	$\delta x$	$\delta y$	$\delta z$
Ba1	0.0000	0.0000	0.0000
Ti1	0.0000	0.0000	0.0000
O1	0.0000	0.0624	0.0624
O1_2	0.0000	0.0000	-0.1248

with only this symmetry component of the distortion frozen.

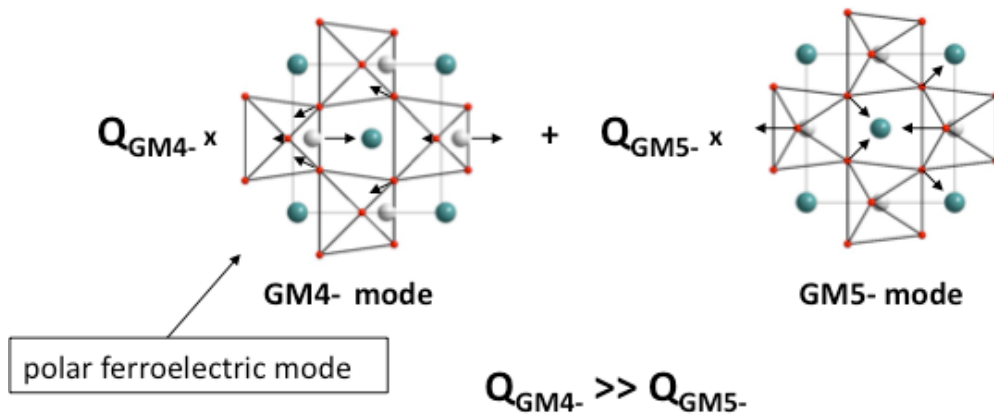
For each irrep, the program can provide a virtual structure with only the distortion of this symmetry, which has been calculated and is present in the input distorted structure.

The output of the program for our example can be summarized as follows. The Amm2 structure can be understood as the sum of two distortions with symmetry properties given by two different irreps. The amplitudes of the two irrep distortions are

very different. The correlated atomic displacements corresponding to each them, are given by the listed polarization vectors. Schematically we can say that the observed Amm2 structure can be described in the following form:



We can represent graphically this mode decomposition as:



In the figures we have represented the effect of each of the two irrep distortions in an exaggerated way by increasing arbitrarily their amplitudes.

Note that the displacements corresponding to the GM4- symmetry include a subtle hidden correlation, namely the displacements of the oxygens O1 and O1<sub>2</sub> fulfill  $\delta y O1 + \delta z O1 + \delta z O1_2 = 0$ . This implies in the resulting structure a **non-crystallographic** symmetry constraint:  $y O1 + z O1 + z O1_2 = 0$ . As the GM5- distortion, that breaks this relation, is a secondary marginal distortion with a very small amplitude, this non-crystallographic relation is approximately maintained by the atomic coordinates of the experimental structure.

Finally, it is important to emphasize that for doing a meaningful symmetry mode analysis of a distorted structure with AMPLIMODES is NOT necessary to know a specific *real* parent structure. Starting from the distorted phase one can construct an

ideal parent structure whose symmetry group is determined by the structural pseudosymmetry of the low-symmetry phase, either by hand, from previous knowledge of similar compounds, or using computer tools as PSEUDO, also available on the Bilbao Crystallographic Server. If the atomic coordinates of the parent high-symmetry structure include some values not forced by symmetry, it is sufficient to give them reasonable approximate values. The structural differences between the ideal parent structure, constructed in such a way, and any other possible parent structure of this symmetry are only due to contributions of symmetry modes compatible with the high space groups, i.e. the so called *totally symmetric* modes transforming according to the identity irrep. The contributions of the much more important symmetry-breaking distortion modes do not depend on the choice of the variable atomic coordinates of the parent structure.

**Exercise 1:**  $S_2Sn_2P_6$  has a monoclinic P21/c phase at high temperatures (J. Sol. State Chem. (1992) 96, 294) and a ferroelectric non-centrosymmetric phase of symmetry Pc at low temperatures (Z. Naturf. B. (1974) 29, 312-317) :

```

14
6.5500 7.4930 11.3157 90.00 124.19 90.00
5
Sn  1  4e  -0.2842  0.3692 -0.2431
P   1  4e   0.3723  0.3914 -0.0671
S   1  4e   0.1362  0.4975 -0.2629
S   2  4e   0.21  0.309  0.0328
S   3  4e   0.5988  0.1976 -0.057

7
6.513000 7.488000 11.309900 90.000000 124.000000 90.000000
10
Sn  1  2a   0.304600  0.385600  0.277000
Sn  2  2a   0.740900  0.124500  0.777900
P   1  2a   0.372800  0.860800  0.433600
P   2  2a   0.626600  0.644700  0.567400
S   1  2a   0.140700  0.751100  0.239800
S   2  2a   0.203800  0.946200  0.528800
S   3  2a   0.602100  0.051700  0.444200
S   4  2a   0.865200  0.743700  0.764900
S   5  2a   0.785900  0.563300  0.464700
S   6  2a   0.402500  0.448000  0.555000

```

i) Obtain with AMPLIMODES that the ferroelectric structure has two distortion modes, a primary one that yields the Pc space group, i.e. the order parameter distortion, and a secondary one compatible with the parent symmetry.

ii) Change arbitrarily some of the coordinates of P21/c, but displacing the positions only a small amount (below 1 Å). Check that AMPLIMODES gives the same results (amplitude and polarization vector) for the symmetry-breaking mode, changing only the form of the fully symmetric mode GM1.

iii) Which atoms are moving more strongly in the transition? Derive the atomic positions of the Sn atoms in two virtual Pc structures having only the experimental primary ferroelectric mode with an amplitude of 0.1Å and of 0.2 Å. One could use such virtual structures in an ab-initio calculation to characterize the energy variation of the system as a function of the ferroelectric mode.

## Exercise 2. “Complex” phase of Ga under pressure

Ga under pressure exhibits a phase with symmetry  $C222_1$  and 52 atoms per primitive unit cell (see below). It has been reported as a “complex” structure and described in terms of some sequence of atomic layers along the c axis (PRL 93, 205502 (2004)).

- i) Using the program AMPLIMODES show that the structure can be understood as a distorted structure of a simple  $Fddd$  structure, with its unit cell having the same a and b parameters, and c being 13 times smaller, and with only a single independent Ga atom at position 8a (1/8,1/8,1/8). (origin shift of the transformation between the two space groups: -1/8 1/8 -3/8).
- ii) Identify the Ga atom in the  $C222_1$  structure with the largest displacement with respect to the ideal  $Fddd$  position.
- iii) From the output identify the prevailing primary mode and its wave vector.
- iv) Check that the two next dominant modes have wave vectors corresponding to a second and third harmonic of the primary mode.
- v) If the structure is described with these three first harmonics that have much larger amplitudes, how many parameters are required? Compare this number with the number of parameters required in a conventional crystallographic description.

GaII structure:

# space group  $C222_1$

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

## SYSTEMATIC WEAKNESS OF SECONDARY DISTORTIONS

The case of the  $Amm2$  structure of  $BaTiO_3$  is an extreme example of the systematic hierarchy that usually happen between primary distortions, associated with the active irrep of the symmetry break, and the secondary ones.

Let us consider as a second example the room-temperature  $P6_3cm$  phase of  $KNiCl_3$ :

185

11.795 11.795 5.926 90 90 120

5

```

K      1      6c      0.3353 0.3353 0.3294
Ni     1      2a      0 0 0
Ni     2      4b      0.333333 0.666667 0.1230
Cl     1      6c      0.1598 0 0.2604
Cl     2      12d     0.5056 0.1732 0.3852

```

This structure has the following virtual  $P6_3/mmc$  parent structure:

```

194
6.80985 6.80985 5.926 90 90 120
3
Ni     1      2a      0.0 0.0 0.0
K      1      2d      0.333333 0.666667 0.75
Cl     1      6h      0.16 0.32 0.25

```

This virtual structure can be obtained for instance using the program PSEUDO of the server, or just by looking at the  $P6_3/mmc$  structure of similar compounds. **Note that the special coordinates 1/3, 2/3 are given with 6 digits. This is important, as in other programs of the server, for the program to recognise the special value of the coordinate.**

From the comparison of the multiplicities of the atomic positions, it is straightforward to see that the number of formula unit per primitive unit cell is  $Z=2$  for the parent phase, while  $Z=6$  in the non-centrosymmetric phase. This means a triplication of the unit cell ( $i_k=3$ ). Using CELLSUB or SUBGROUPGRAPH it is then immediate to obtain the transformation matrix relating both space groups:  $(\mathbf{a}+2\mathbf{b}, -2\mathbf{a}-\mathbf{b}, \mathbf{c}; 0\ 0\ 0)$ . This transformation is only one of a set of possible ones, which are fully equivalent. In fact the cell parameters of the virtual parent structure have been chosen to fulfill the cell transformation exactly.

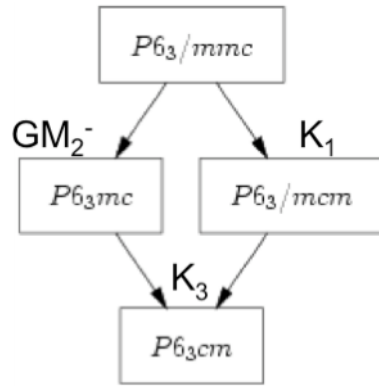
We use then AMPLIMODES to perform the mode decomposition of the  $P6_3cm$  structure with the following basic result:

### Summary of Amplitudes

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM1+	(a)	$P6_3/mmc$ (194)	1	0.0167
(0,0,0)	GM2-	(a)	$P6_3mc$ (186)	3	0.2069
(1/3,1/3,0)	K1	(a,0)	$P6_3/mcm$ (193)	3	0.0684
(1/3,1/3,0)	K3	(a,0)	$P6_3cm$ (185)	2	1.7018

**Global distortion: 1.7158 Å**

It is convenient to analyse this result, having in mind the graph of minimal subgroups connecting the high and low symmetries:



**Figure 2:** Graph of maximal subgroups connecting the parent and low-symmetry space groups of  $\text{KNiCl}_3$

One can see that there is a primary active irrep with wave vector  $(1/3, 1/3, 0)$  and label  $K_3$  and two secondary active irreps, associated with two intermediate isotropy subgroups. The  $K_1$  distortion also corresponds to a wave vector  $(1/3, 1/3, 0)$ , so that it produces the same cell multiplication as  $K_3$ , but maintains the point group of the parent phase, while the second distortion,  $GM_2^-$  at the Brillouin zone centre, keeps the parent lattice and is a polar mode, which should be responsible of some spontaneous polarization in the distorted phase.

The mode decomposition provided by AMPLIMODES shows the extreme prevailing role of the primary distortion corresponding the irrep  $K_3$ . From a total amplitude of  $1.72 \text{ \AA}$  of the total distortion, the contribution of the  $K_3$  component is  $1.70 \text{ \AA}$ . This  $K_3$  distortion involves only 2 of the 9 structural degrees of freedom present in the  $P6_3cm$  structure. The much larger amplitude of the  $K_3$  distortion is a clear indication that it can be identified with the primary order parameter of this phase, and it can be further inferred that  $K_1$  and  $GM_2^-$  are induced secondary effects. The material is then a ferroelectric of improper character, the spontaneous polarization (of symmetry  $GM_2^-$ ) being an induced secondary effect.

The polarization vector of the  $K_3$  dominant distortion is given by AMPLIMODES as:

Atom	$\delta x$	$\delta y$	$\delta z$
Ni1	0.0000	0.0000	-0.0482
Ni1_2	0.0000	0.0000	0.0241
K1	0.0000	0.0000	0.0000
Cl1	0.0000	0.0000	-0.0489
Cl1_2	0.0000	0.0000	0.0244

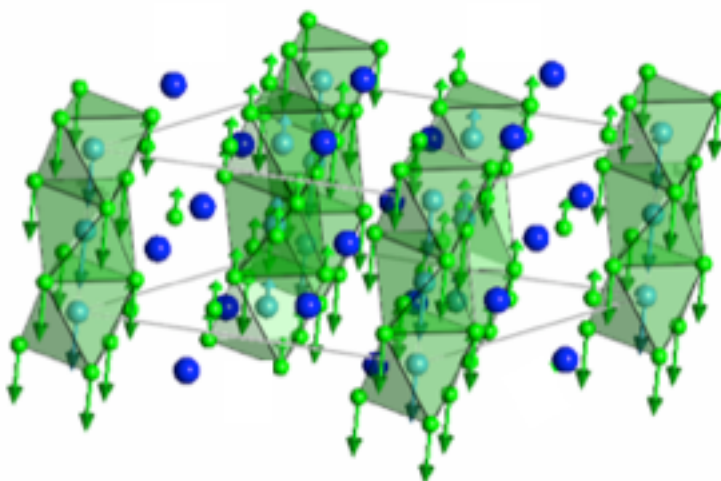
This table only acquires a full meaning when combined with the Table defining the reference structure and the asymmetric unit chosen by the program:

### Reference Structure:

```
185
11.795007 11.795007 5.926000 90.000000 90.000000 120.000000
5
Ni 1 2a 0.000000 0.000000 0.000000
Ni 1_2 4b 0.666667 0.333333 0.000000
K 1 6c 0.333334 0.000000 0.750000
Cl 1 6c 0.160000 0.000000 0.250000
Cl 1_2 12d 0.826667 0.333333 0.250000
```

This list defines the atoms in the Table that describes the polarization vector of the K3 mode. The splitted Ni1 and Ni1\_2 atoms within the asymmetric unit of the distorted structure move in opposite directions along z, with a  $\frac{1}{2}$  relation among its displacements. The same relation exists among the displacements of the two Cl sites. These correlations are forced by the K3 symmetry. But the table shows an additional correlation between the displacements of the Cl and Ni sites, namely the displacements of Ni1 and Cl1 are practically the same, and this is not forced by symmetry.

Combining AMPLIMODES with FULLPROF (J. Rodriguez-Carvajal, <http://www.ill.eu/sites/fullprof/>) one can obtain in a straightforward manner a graphical scheme of this K3 distortion (see below for a more detailed explanation of the combined use of AMPLIMODES and FULLPROF):

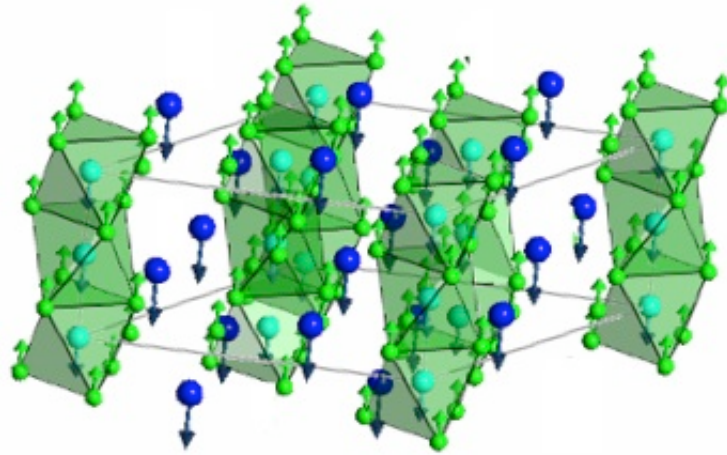


**Figure 3:** Scheme of the K3 distortion present in  $\text{KNiCl}_3$

The correlation of the Ni and Cl displacements implies that the K3 distortion involves global displacements of the  $\text{NiCl}_3$  columns as rigid units. This feature of the primary K3 distortion is forced neither by symmetry, nor by a strong rigidity of the Ni positions within the octahedra. In the observed structure in fact the Ni atoms clearly displace relatively to their surrounding  $\text{Cl}_6$  octahedra, and approach along the c axis one of the two  $\text{Cl}_3$  triangles forming the octahedron. But these Ni displacements are not part of the K3 distortion; they follow a pattern according to the GM2- symmetry. The  $-\frac{1}{2}$  relation between the displacements of the Cl1\_2, Ni1\_2 atoms and the Cl1 and Ni1 atoms (this relation indeed forced by the K3 symmetry) yields the antiphase shift of the  $\text{NiCl}_3$  octahedral columns within the  $\text{P6}_3\text{cm}$  unit cell, with respect to those on the vertices, causing the tripling of the cell. It important to note that the secondary modes break in general these strict K3-correlations of the displacements between atomic



sites, which are crystallographically independent. For instance the GM2- mode introduces displacements with completely different correlations:



**Figure 4:** Scheme of the GM2- distortion present in  $\text{KNiCl}_3$

But the prevailing role of the K3 distortion makes that its atomic correlations are also approximately fulfilled by the total distortion, despite the presence of the secondary distortions. Hence the structure has approximate non-crystallographic constraints coming from the physical mechanism, which stabilizes the phase.

### Exercise 3: Constrained structural model of $\text{SrMnO}_3$

A  $C222_1$  structural model for  $\text{SrMnO}_3$  has been recently proposed (Phys. Rev. B 75 (2007) 104417). The structure is listed below.

- i) Decompose this structure into modes with respect to the structure of higher symmetry,  $P6_3/mmc$ , observed at 350K (also listed below) and check that the structure has an active irrep and a strong primary distortion with this symmetry, and that two secondary distortions have amplitudes, which are practically negligible.
- ii) Comparing the atomic coordinates of the model with the general form of the corresponding Wyckoff positions, check that several refinable coordinates have been restricted *a priori* in the model. How many degrees of freedom have been in practice used in the refinement compared with a full conventional refinement under the  $C222_1$  space group? How many degrees of freedom would have been used in the refinement if the secondary modes would have been set *a priori* to zero.
- iii) By checking the form of the polarization vector of the primary mode, derive that this model has also included an unjustified restriction on the form of the primary distortion, which is not forced by symmetry considerations

$\text{SrMnO}_3$  at 350K:

194  
 5.461 5.461 9.093 90 90 120  
 5

Sr	1	2a	0 0 0
Sr	2	2c	0.3333333 0.666667 0.25
Mn	1	4f	0.3333333 0.666667 0.61264
O	1	6g	0.5 0 0
O	2	6h	-0.81858 0.81858 0.75

#### SrMnO<sub>3</sub> at 100K:

```

20
5.4435 9.4122 9.0630
7
Sr 1 4a 0.0096 0 0
Sr 2 4b 0 0.3333333 0.25
Mn 1 8c -0.0123 0.3333333 0.6131
O 1 4a 0.5212 0 0
O 2 8c 0.7712 0.25 0.0085
O 3 4b 0 -0.1798 0.25
O 4 8c 0.2696 0.0899 0.2412

```

### Exercise 4: Hexagonal BaMnO<sub>3</sub>

BaMnO<sub>3</sub> has been determined at 1.7K and at 80K (*Chem. Mater.* 12 (2000) 831-838) with space group P6<sub>3</sub>cm (see structures below). These structures are supposed to be distorted structures from an ideal P6<sub>3</sub>/mmc ABX<sub>3</sub> structure with atoms at positions A 2a, B 2d and O 6h (x, 2x, 0.25), with x about 0.15. (It is a similar situation to the one of the example of KNiCl<sub>3</sub> discussed above).

- Draw with SUBGROUPGRAPH the graph of maximal subgroups relating both symmetries.
- Decompose with AMPLIMODES the two structures into symmetry-adapted modes with respect to the ideal parent phase. Identify the primary dominant distortion. Try to understand and characterize this dominant mode.
- How many positional atomic parameters are necessary to refine these structures and how many are required to describe the dominant primary distortion?
- Compare the mode decomposition of the two structures corresponding to different temperatures. First, compare the total amplitudes for each irrep distortion mode, and check if the result is plausible. Second compare the polarization vectors of each distortion mode, by inspection, and by calculating their dot products. Detect that there is some inconsistency in the models for one of the secondary modes (the atomic displacements are more or less opposite in the two models, relative to those of the primary mode). So probably one of the structures is wrong (corresponding to a false minimum in the refinement).
- Compare the mode decomposition with the one of the example KNiCl<sub>3</sub> discussed above.

#### BaMnO<sub>3</sub> at 1.7K:

```

185
9.8467 9.8467 4.8075 90.00 90.00 120.00
5
Ba 1 6c 0.339 0.339 0.230
Mn 1 2a 0 0 0
Mn 2 4b 0.666667 0.333333 0.952
O 1 6c 0 0.1492 0.248
O 2 12d 0.6644 0.4824 0.200

```

#### BaMnO<sub>3</sub> at 80K:

```

185
9.8467 9.8467 4.8075 90.00 90.00 120.00
5

```

Ba	1	6c	0.332	0.332	0.238
Mn	1	2a	0	0	0
Mn	2	4b	0.666667	0.333333	0.963
O	1	6c	0	0.150	0.250
O	2	12d	0.667	0.484	0.212

## AMPLIMODES COMBINED WITH FULLPROF

A symmetry mode decomposition can be done not only *a posteriori*, *i.e.* once the low symmetry structure is known, but may be very useful for the actual process of determining the structure. The expected hierarchy among the distortions of different symmetry and the essential invariance of their polarization vectors can make very advantageous a direct refinement of the amplitudes of a basis of symmetry modes, as collective coordinates, instead of the usual individual atomic coordinates. In collaboration with J. Rodriguez-Carvajal we have included in AMPLIMODES an option, which creates a special output to be directly used by FullProf (J. Rodriguez-Carvajal, <http://www.ill.eu/sites/fullprof/>), for doing such type of refinement. By this means, FullProf can now use in the refinement process the amplitudes of the basis of symmetry modes defined by AMPLIMODES as refinable *positional* parameters, alternative to the atomic coordinates.

This option can also be used to generate, using FullProf, figures of the distortion modes, and of the basis of symmetry-adapted modes, in general.

The FullProf option can be chosen in the starting menu, and the program completely changes its output with respect to what has been explained above. Concerning the input, the inclusion of a specific low-symmetry distorted structure becomes optional.

In this option, AMPLIMODES creates a so-called pcr file to be used as input for FullProf. This pcr file, by default, is intended to be an input file for simulating with FullProf a neutron powder diffraction diagram. If FullProf is executed using this pcr file, not only the simulated diffraction diagram, but also .fst files are created that can be read by FullProf Studio to represent graphically the different irrep distortions present in the distorted structure.

The pcr file created by AMPLIMODES can be easily changed by the user to become the starting pcr file for a refinement of diffraction data, with the amplitudes of the basis of symmetry-adapted modes defined by AMPLIMODES as refinable parameters, instead of the conventional atomic coordinates.

Let us take again the example of the Amm2 phase of BaTiO<sub>3</sub> discussed above. AMPLIMODES under the FullProf option gives two alternative outputs. One is a set of text lines which can be introduced by copy/paste in a working pcr file of the user, to allow the direct refinement of the amplitudes of basis of symmetry-modes defined by AMPLIMODES:

You can copy and paste the following text on your .pcr file

```

038 <--Space group symbol
!Atom Typ X Y Z Biso Occ In Fin N_t Spc /Codes
Bal BA 0.000000 0.000000 0.000000 0.500000 0.250000 0 0 0 1
 0.00 0.00 0.00 0.00 0.00
Til TI 0.500000 0.000000 0.500000 0.500000 0.250000 0 0 0 1
 0.00 0.00 0.00 0.00 0.00
O1 O 0.500000 0.250000 0.250000 0.500000 0.500000 0 0 0 1
 0.00 0.00 0.00 0.00 0.00
O1_2 O 0.000000 0.000000 0.500000 0.500000 0.250000 0 0 0 1
 0.00 0.00 0.00 0.00 0.00
! Polarisation Vectors of Symmetry Modes for each atom
V_MODES 8
! Nm Atm Irrep Vx Vy Vz Coeff
1 Bal GM4- 0.000000 0.000000 0.176512 1.00
2 Til GM4- 0.000000 0.000000 0.176512 1.00
3 O1 GM4- 0.000000 0.062406 0.062406 1.00
3 O1_2 GM4- 0.000000 0.000000 0.124813 1.00
4 O1 GM4- 0.000000 -0.088256 0.088256 1.00
4 O1_2 GM4- 0.000000 0.000000 0.000000 1.00
5 O1 GM5- 0.000000 -0.062406 -0.062406 1.00
5 O1_2 GM5- 0.000000 0.000000 0.124813 1.00
!Amplitudes of Symmetry Modes
A_MODES 5 2
A1_GM4- 0.000000 1.00
A2_GM4- 0.096311 1.00
A3_GM4- -0.082524 1.00
A4_GM4- -0.123505 1.00
A5_GM5- -0.005609 1.00

```

You can download the full .pcr file for a default neutron simulation [here](#)

The first lines define the reference structure. Its atomic coordinates are set constant, and will not be refined. Then, the set of 5 symmetry modes defined by AMPLIMODES are listed. The modes are numbered from 1 to 5, and the first column of each line indicates to which mode belongs the triad of displacements listed in this line. For instance, the mode GM4- labelled (O1 1) in the previous output is here mode 3, and the displacements for atoms O1 and O1\_2 corresponding to this mode are given in two consecutive rows headed by the number 3. The number of lines necessary to define all basis modes using this format is 8, which is the variable V\_MODES. A\_MODES is the number of basis symmetry modes (5 in our example). It should coincide with the number of refinable positional parameters in a conventional treatment. The digit 2 in the same row controls the output of .fst graphic files (consult the webpage of Fullprof for other graphical options).

The last lines introduce, as starting model for the eventual refinement, the amplitudes of the 5 basis symmetry modes that have calculated by AMPLIMODES by decomposing the input low-symmetry structure. If no low-symmetry structure is included in the input, these amplitudes would appear with null values, and the starting model would be the reference structure. The value 1.00 after the 5 amplitudes sets them by default as refinable parameters.

Compared with the output of AMPLIMODES in its normal option, the amplitudes for the basis modes listed here are obtained by multiplying the corresponding component of the irrep polarization vector by the amplitude of this irrep distortion. But one should take into account that in the FullProf option no origin shift is introduced for polar structures. Therefore, for a comparison, the origin shift should be avoided in the normal option by introducing (0,0,0) as polar direction.

**Polar Structures:** In the FullProf option, AMPLIMODES does not introduce an origin shift of the low symmetry polar structure, since the amplitudes of the modes are only

intended as starting values for a refinement. This is the reason why the amplitude of the GM4- mode for Ba1 is zero, since in the input structure its z-coordinate is fixed to zero. Similarly as it happens with a conventional refinement, in a direct refinement of the mode amplitudes, the amplitude of either mode 1 or mode 2, which involve only atomic displacements along z, should be fixed, while the other amplitudes are refined.

As an alternative, AMPLIMODES can create a full pcr file for the simulation of a neutron powder diffraction diagram:

```

COMM AMPLIMODES for FullProf
! Files => DAT-file: myDAT_file PCR-file: myPCR_file
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
  3 7 1 0 2 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 1
!
! Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
  0 0 1 0 1 0 4 0 0 3 0 0 0 0 0 0 0 0 0 0 0
!
! lambda1 Lambda2 Ratio Bkpos Wdt Cthm muR AsyLim Rpolarz ->Patt# 1
1.227200 1.227200 0.0000 50.0000 10.0000 0.0000 0.0000 170.00 0.0000
!
! INCY Eps R_at R_an R_pr R_gl Thmin Step Thmax PSD Sent0
  1 0.10 1.00 1.00 1.00 1.00 1.0000 0.050000 170.0000 0.000 0.000
!
! Excluded regions (LowT HighT) for Pattern# 1
  0.00 2.00
  170.00 180.00
!
!
! 0 !Number of refined parameters
!
! Zero Code SyCos Code SySin Code Lambda Code MORE ->Patt# 1
  0.00000 0.0 0.00000 0.0 0.00000 0.0 0.000000 0.00 0
!
! Background coefficients/codes for Pattern# 1
  100.00 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
  0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
!-----
! Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1: 0
!-----
AMPLIMODES for FullProf FIX xyz
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
  4 0 0 0.0 0.0 1.0 6 0 0 0 5 0.000 0 7 0
038 <---Space group symbol
!Atom Typ X Y Z Biso Occ In Fin N_t Spc /Codes
Ba1 BA 0.000000 0.000000 0.000000 0.500000 0.250000 0 0 0 1
  0.00 0.00 0.00 0.00 0.00
Ti1 TI 0.500000 0.000000 0.500000 0.500000 0.250000 0 0 0 1
  0.00 0.00 0.00 0.00 0.00
O1 O 0.500000 0.250000 0.250000 0.500000 0.500000 0 0 0 1
  0.00 0.00 0.00 0.00 0.00
O1_2 O 0.000000 0.000000 0.500000 0.500000 0.250000 0 0 0 1
  0.00 0.00 0.00 0.00 0.00
! Polarisation Vectors of Symmetry Modes for each atom
V MODES 8
! Nm Atom Irrep Vx Vy Vz Coeff
  1 Ba1 GM4- 0.000000 0.000000 0.176512 1.00
  2 Ti1 GM4- 0.000000 0.000000 0.176512 1.00
  3 O1 GM4- 0.000000 0.062406 0.062406 1.00
  3 O1_2 GM4- 0.000000 0.000000 0.124813 1.00
  4 O1 GM4- 0.000000 -0.088256 0.088256 1.00
  4 O1_2 GM4- 0.000000 0.000000 0.000000 1.00
  5 O1 GM5- 0.000000 -0.062406 -0.062406 1.00
  5 O1_2 GM5- 0.000000 0.000000 0.124813 1.00
! Amplitudes of Symmetry Modes
A MODES 5 2
  A1_GM4- 0.000000 1.00
  A2_GM4- 0.096311 1.00
  A3_GM4- -0.082524 1.00
  A4_GM4- -0.123505 1.00
  A5_GM5- -0.005609 1.00
!
! Scale Shape1 Bov Str1 Str2 Str3 Strain-Model
  2.00 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0
  0.00000 0.000 0.000 0.000 0.000 0.000 0.000
!
! U V W X Y GauSiz LorSiz Size-Model
  0.176020 -0.197809 0.091458 0.000000 0.030039 0.000000 0.000000 0
  0.000 0.000 0.000 0.000 0.000 0.000 0.000
!
! a b c alpha beta gamma #Cell Info
  4.006000 5.665339 5.665339 90.000000 90.000000 90.000000 0.000000 -0.15 1.15 -0.15 1.15
  0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S L D L
  0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
  0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! 2Th1/TOF1 2Th2/TOF2 Pattern # 1
  10.000 100.000 1

```

Running FullProf with this pcr file, apart from creating the simulated diffraction diagram, produces a .fst file for each irrep distortion present in the structure according to the mode amplitudes given in the .pcr file. These .fst files can be read by FullProf Studio to represent graphically the distortion modes.

Note that the cell parameters in this .pcr file are those of the reference high symmetry structure in the low symmetry setting. For FullProf refinements you will have to change by hand these cell parameters to introduce the experimental values of the low-symmetry phase. Note however that, in this case, the symmetry and orthogonal properties of the modes will in general be broken in a degree that depends on the magnitude of the strain between the two cells. This will be not a problem for refinements (except for extreme unrealistic strains), but a proper visualization with FullProf Studio and a correct interpretation of the symmetry modes will require the use of the reference unit cell provided in the .pcr file provided by AMPLIMODES.

A final caution remark: If the reference unit cell is very large the default values used for the pcr file may fail and FullProf may crash. This problem can usually be palliated by changing the U, V, ... peak profile parameters, making the peaks thinner.

**Exercise 5:**

- i) Run the default example of AMPLIMODES for the Amm2 structure of BaTiO<sub>3</sub>, but making the program not to shift the origin. Inspecting the output of this run, check that the values of the amplitudes for the basis modes in the pcr file above are correct.
- ii) If you are familiar with FullProf, create the pcr file for this default example, and use it to obtain with FullProf Studio a graphical representation of the GM4- and GM5- distortions in the Amm2 phase of BaTiO<sub>3</sub>.