

## AMPLIMODES: Symmetry mode analysis on the Bilbao Crystallographic Server

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AMPLIMODES is a computer program available on the Bilbao Crystallographic Server that can perform a 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, expressing all quantities for an asymmetric unit of the low-symmetry structure. Distorted structures are often related with their higher symmetry counterparts by temperature and/or pressure driven phase transitions; ferroic phase transitions being a particular example. The automatic symmetry mode analysis done by AMPLIMODES can be very useful for establishing the driving mechanisms of such structural phase transitions or the fundamental instabilities at the origin of the distorted phases.

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### 1. Introduction

The structure of many materials can be seen as the result of a distortion with respect to a configuration of higher symmetry. This structure of higher symmetry may be another phase of the compound or a latent virtual arrangement that can be used as reference for the observed structure and often for other phases of the same compound. Let us call this structure (real or virtual) of higher symmetry *parent* structure or *parent* phase, a group-subgroup relation necessarily exists between their space groups, and the structural distortion that relates them can be qualified as a symmetry breaking distortion. Usually small distortions imply that the parent phase can be thermally stabilized, and one or several structural phase transitions towards the arrangement of higher symmetry may happen as temperature is increased. Ferroic materials and ferroic phase transitions are a particular case of such general phenomena. Structural distortions can be of displacive type or can include some type of order-disorder component. Here, we only consider distorted structures of displacive type.

The structural distortion present in a distorted (pseudosymmetric) structure contains in general a primary component, which corresponds to a mode or modes which are unstable in the parent high-symmetry configuration, and are fundamental for explaining the stability of the distorted structure. In addition, the distortion can also contain other secondary contributions of less importance associated with modes which are allowed by symmetry and become frozen through coupling with the primary ones. This is well known to happen in phases related with symmetry breaking structural phase transitions, and is the basis of their treatment within the Landau theory (Landau &

Lifshitz, 1969). But even without the existence of phase transitions, the use of symmetry-adapted modes in the description of distorted structures is expected to introduce a natural physical hierarchy among the structural parameters. The presence of distortion modes associated with different irreducible representations (in the following referred to as *irreps*) of the parent space group have in general quite different origin, and are bound to have quite different responses to external perturbations. Also for crystallographic purposes, a structural description in terms of symmetry modes can be specially useful, as the parameters used are more adequate for a controlled refinement of the structure, or for comparing structures or materials with the same or different symmetries.

The separation of the contributions of the different modes in a structural distortion is usually done using the so-called symmetry-mode analysis (*cf.* Mañes *et al.* (1982), Perez-Mato *et al.* (1986), Withers *et al.* (1988), Hatch *et al.* (1990), Stokes *et al.* (1991), Aroyo & Perez-Mato (1998)). First, it is necessary to determine a basis of symmetry-modes of the parent phase compatible with the low-symmetry phase, and then, to decompose the structural distortion as a sum of the contributions of all of them. Despite its advantages, a symmetry-mode description is rarely used in phase-transition studies, or in the characterization of pseudosymmetric structures. The probable reason is that such symmetry analysis is rather complex as it requires full use of group-theoretical methods, including detailed knowledge of group-subgroup relations between space groups and their irreps. Free computer tools that allow (total or partial) symmetry-mode analysis have appeared recently (ISARAh (Wills, 2000), ISOTROPY (Stokes & Hatch, 2002), MODY (Sikora *et al.*,

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2004), BasIreps (Rodriguez-Carvajal, 1993)). However, the use of a parameterization quite distant from crystallographic conventions has hampered their widespread use in crystallography. These tools use the setting of the parent structure and the parent space group to describe modes and distortions, without explicit use of the space-group symmetry of the distorted structure.

The aim of the present contribution is to report on the development of a systematic procedure and a new computer program for the symmetry-mode analysis of any displacive distorted structure. The program is available at the Bilbao Crystallographic Server (Aroyo *et al.* (2006a) and Aroyo *et al.* (2006b)). Given the parent and the distorted structure of lower symmetry, AMPLIMODES calculates the atomic displacements relating both structures if their magnitudes lay within some tolerance range. A complete basis of symmetry-adapted distortion modes is then determined and defined. The program finally decomposes the distortion in terms of this basis of symmetry modes, and calculates the polarization vectors and amplitudes for each of the symmetry-adapted distortions present in the distorted structure. A fundamental feature of the program is that the parameterization of the structural distortion is done in a form close to the conventional crystallographic form. Modes are given in terms of atomic displacements in relative units for the atoms of the asymmetric unit of the distorted phase, so that the actual atomic positions describing the structure in the conventional approach are readily obtained from the listed modes and their amplitudes. This should facilitate a direct translation from a conventional to a mode description and viceversa. Three illustrative examples are presented to explain the necessary input data and provide details on the output.

## 2. The method

### 2.1. Input structure data

Let  $\mathcal{G}$  and  $\mathcal{H}$  be the space groups of the parent and the distorted structure (of lower symmetry) so that we are considering a symmetry break  $\mathcal{G} \rightarrow \mathcal{H}$  with  $\mathcal{G} > \mathcal{H}$ . For the systematic analysis of the global distortion it is necessary to specify the transformation matrix-column pair  $(\mathbf{P}, \mathbf{p})$  that relates the coordinate system of the group to that of the subgroup: the square matrix  $\mathbf{P}$  defines the transformation of the conventional basis  $(\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{G}}$  of  $\mathcal{G}$  to the conventional basis  $(\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{H}}$  of  $\mathcal{H}$ :

$$(\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{H}} = (\mathbf{a}, \mathbf{b}, \mathbf{c})_{\mathcal{G}} \mathbf{P} \quad (1)$$

The column  $\mathbf{p} = (p_1, p_2, p_3)$  gives the coordinates of the origin  $O_{\mathcal{H}}$  of  $\mathcal{H}$  referred to the coordinate system of  $\mathcal{G}$ .

The program requires as only input the distorted and parent structures described in conventional settings, and the matrix-column  $(\mathbf{P}, \mathbf{p})$  described above, that relates both settings.

Thus, for the default example shown by the program, the following input data are introduced:

High symmetry (parent) structure:

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

Low symmetry (distorted) structure:

```
38
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
```

and the transformation  $(\mathbf{P}, \mathbf{p})$  relating the (conventional) bases of the two structures:

$$\left( \begin{array}{ccc|c} 0 & 1 & 1 & 0 \\ 0 & -1 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{array} \right) \quad (2)$$

The first row in the two sets of structural data refers to the space group number according to the International Tables for Crystallography, Vol. A (referred to as ITA in the following (Hahn, 2002)), *i.e.*  $Pm\bar{3}m$  (No. 221) and  $Amm2$  (No. 38). The third row indicates the number of atoms in the asymmetric unit.

This input example corresponds to the orthorhombic phase of the well-known ferroelectric  $BaTiO_3$ , with its cubic perovskite structure taken as the parent phase. The structural data for the orthorhombic phase has been taken from Kwei *et al.* (1993). This case will be used as an example in parallel to the general description of the program.

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 of symmetry  $\mathcal{H}$  one can construct an ideal parent structure whose symmetry group  $\mathcal{G}$  (with  $\mathcal{G} > \mathcal{H}$ ) 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 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 is due only to contributions of symmetry modes compatible with  $\mathcal{G}$ , *i.e.* the so-called *totally symmetric* modes<sup>1</sup>. The contributions of the much more important symmetry-breaking distortion modes present in the distorted phase do not depend on any choice of the variable atomic coordinates of the parent structure.

In order to perform the symmetry-mode analysis two concepts have to be properly defined, namely, the structural distortion relating the parent and the distorted phases, and the basis with respect to which this distortion can be decomposed. The structural distortion is defined by the so-called *displacement field* which is calculated from the atomic positions of the low-

<sup>1</sup> These are modes transforming as the *totally symmetric*, *trivial*, or *identity* irrep that are compatible with the high-symmetry structure. Their number equals the number of variable (free) parameters in the high-symmetry atomic coordinates.

and high-symmetry structures expressed in relative comparable coordinates. The basis with respect to which this displacement field can be decomposed is formed by the symmetry modes compatible with the symmetry break between  $\mathcal{G}$  and  $\mathcal{H}$ .

## 2.2. Atomic displacement field

The structural distortion relating the two phases can be decomposed into two contributions, a homogeneous strain and an atomic *displacement field* given by the displacements of each atom in the low symmetry structure with respect to its position in the given parent structure. This distinguishes the elastic degrees of freedom from the internal atomic degrees of freedom, and is done automatically if the atomic displacements are obtained by subtracting the corresponding atomic coordinates in both structures expressed in relative units with respect to equivalent bases. Thus, if this set of atomic displacements would be zero, the distortion between the two structures would only be due to a homogeneous strain. In general, the strain component of the distortion can be directly derived from the comparison of the unit cells of both phases (again referred to equivalent bases).

For full mathematical consistency (orthogonality and completeness of the set of symmetry modes, *etc.*), the mode analysis of the distorted structure should be done disregarding the strain component of the structural distortion. The strain present in the real structure can subsequently be added in a straightforward manner, by just taking the *real* unit cell instead of the idealized unstrained one, while keeping the same relative coordinates. In the following, we obviate this last step and when referring to the structural or global distortion we generally mean the internal distortion of the atomic coordinates given by the above-mentioned atomic displacement field.

The atomic displacement field is completely defined by the atomic displacements  $\mathbf{u}(\mu, i)$  within an asymmetric unit of the low-symmetry structure. The index  $\mu$ ,  $\mu = 1, \dots, s$  labels the atoms of the asymmetric unit of the high-symmetry parent structure, and  $i$ ,  $i = 1, \dots, n_\mu$ , distinguishes the possible split atomic positions in the low symmetry asymmetric unit, due to the symmetry break  $\mathcal{G} \rightarrow \mathcal{H}$  (Wondratschek, 1992). The set of atomic positions  $\mathbf{r}(\mu, i)$ , within an  $\mathcal{H}$ -asymmetric unit, describing the distorted structure can be expressed as:

$$\mathbf{r}(\mu, i) = \mathbf{r}_o(\mu, i) + \mathbf{u}(\mu, i) \quad (3)$$

where  $\mathbf{r}_o(\mu, i)$  stands for the atomic positions in the parent structure with space group  $\mathcal{G}$ .

Independently of the  $\mathcal{H}$ -asymmetric unit introduced in the input for the distorted structure, the program defines for the distorted structure a new asymmetric unit, by transforming to the  $\mathcal{H}$  basis the  $\mathcal{G}$ -asymmetric unit of the parent phase of the input. If necessary, additional atoms resulting from the splitting of some of the Wyckoff orbits are added, in accordance with equation (3).

Thus, for our example, the program first gives the high symmetry structure transformed in the subgroup basis, described as:

4.	0.0060	5.6653	5.6653	90	90	90
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	

where the O orbit is splitted into two. The  $\mathcal{H}$  asymmetric unit so defined is the one which is relevant for all further output, and referred to as *reference structure*. The program determines the displacement field  $\mathbf{u}(\mu, i)$  from the comparison of the atomic positions of this  $\mathcal{H}$  transformed asymmetric unit of the parent structure with the atomic positions of the distorted structure, both expressed in relative coordinates. The program only proceeds further if it is able to find a mapping of both structures with a set of displacements  $\mathbf{u}(\mu, i)$  with absolute values smaller than a given tolerance value.

Note that the cell parameters listed in the reference structure above correspond to the transformation of those associated with the parent structure. Thus, for our example,  $b = c = \sqrt{2}a$ , according to the transformation (2). These cell parameters are used by the program for computing (when needed) the absolute values of the components of the atomic displacements  $\mathbf{u}(\mu, i)$ . In other words, the calculation of these displacements in Amstrongs is done disregarding any strain of the distorted structure with respect to the parent one.

The determination of the atomic displacement field requires special attention if the distorted structure is of *polar* type. The arbitrariness of the origin of the structure along the polar direction(s) introduces some arbitrariness in the atomic displacements defining its relation with the parent phase. It is convenient in most cases to change the choice of origin of the distorted polar phase, so that no global translation of the structure is included in the atomic displacements relating both structures, *i.e.* the arithmetic centre of the structure is not displaced when parent and distorted structures are mapped through the displacement field. Therefore, in the case of a polar distorted phase, the program, in general, introduces an origin shift, to obtain a displacement field fulfilling:

$$\sum_{\mu, i} mult(\mu, i) \mathbf{u}(\mu, i) = 0, \quad (4)$$

where  $mult(\mu, i)$  is the multiplicity of the atomic site  $(\mu, i)$  within the *primitive* unit cell of the space group  $\mathcal{H}^2$ .

Note that one can find in the literature another form of displacement-field calculations for the cases of polar distorted phases: it is based on the so-called *center-of-mass* condition which requires that the centre of mass of the structure is left at rest during the transformation (see *e.g.* Perez-Mato *et al.* (2004)).

The space group of the distorted phase *Amm2* is polar along  $z$ , and the origin shift required is (0, 0, -0.00508). The resulting displacement field given by the program is shown in the following table. In this output,  $u_x, u_y, u_z$  are the components of the displacements in relative units, while  $|u|$  is the absolute displacement given in Å. The maximum atomic displacement between the two structures is therefore smaller than 0.13 Å.

<sup>2</sup> This multiplicity is not the conventional one of ITA for centered space groups, as the latter refers to a centered unit cell.

WP		Atoms	Atomic Distances			
			ux	uy	uz	u
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

The set of atomic displacements defining any distortion present in a  $\mathcal{H}$  distorted phase can be considered as the components of a multidimensional vector defined in a vector space with the scalar product given by the sum of conventional three dimensional scalar products for all displacements within a  $\mathcal{H}$  primitive unit cell. The set of displacements  $\mathbf{u}(\mu, i)$  restricted to the  $\mathcal{H}$  asymmetric unit, *i.e.* with  $\mu = 1, \dots, s, i = 1, \dots, n_\mu$ , unambiguously defines the whole displacement field. By definition, the distortion maintains the symmetry given by the space group  $\mathcal{H}$ . Therefore, the displacement of an atom related with an atom  $(\mu, i)$  of the asymmetric unit by a symmetry operation of  $\mathcal{H}$  represented by a matrix-column pair  $(\mathbf{W}, \mathbf{w})$  is given by  $\mathbf{W}\mathbf{u}(\mu, i)$ . Considering that any operation  $\mathbf{W}$  is unitary, the scalar product of two arbitrary distortions defined by the sets  $\mathbf{u}(\mu, i)$  and  $\mathbf{v}(\mu, i)$  can then be calculated using the expression:

$$\sum_{\mu,i} \text{mult}(\mu, i) \mathbf{u}(\mu, i) \cdot \mathbf{v}(\mu, i). \quad (5)$$

which is restricted to the  $\mathcal{H}$  asymmetric unit. The magnitude of a displacive distortion can be measured by the norm or amplitude of its displacement field, given by:

$$A = \sqrt{\sum_{\mu,i} \text{mult}(\mu, i) |\mathbf{u}(\mu, i)|^2}. \quad (6)$$

This amplitude depends on the specific values of the cell parameters that have been associated with the reference parent structure, but its variation will be minimal so long as these cell parameters, even if corresponding to a hypothetical unstrained phase, are kept within reasonable values, implying small strains of the actual lattice of the distorted structure.

The dimension  $D$  of the vector space of  $\mathcal{H}$ -compatible distortions, is equal to the number of free atomic coordinates in the conventional description of the structure. Thus, in the *Amm2* structure of BaTiO<sub>3</sub> this dimension  $D$  is 5 (this includes the global translation along the polar axis) and from the table of displacements, given above, one can derive from equation (6) that the distortion present in the *Amm2* has a total amplitude of 0.165Å.

### 2.3. Symmetry-modes basis

In general, any  $\mathcal{H}$  distortion can be expressed as the sum of the contributions of a set of symmetry-adapted distortion modes. In other words, one can choose within the  $D$ -dimensional space of  $\mathcal{H}$  distortions a basis of specific distortions or *modes*,  $\epsilon(j|\mu, i), j = 1, \dots, D$ , with certain symmetry properties, such that

$$\mathbf{u}(\mu, i) = \sum_j A_j \epsilon(j|\mu, i). \quad (7)$$

The symmetry properties of a mode  $\epsilon$  is characterized by an irrep of the high-symmetry space group  $\mathcal{G}$ , defining its transformation properties under the operations of this group. In general, the modes should satisfy some additional restrictions so that they are compatible with  $\mathcal{H}$ . Each distortion mode in equation (7) is compatible with a space group  $\mathcal{Z}$  that is intermediate between  $\mathcal{G}$  and  $\mathcal{H}$  ( $\mathcal{G} \geq \mathcal{Z} \geq \mathcal{H}$ ), *i.e.* its *isotropy group* (Hatch & Stokes, 2002) is a supergroup of  $\mathcal{H}$ . This implies that the symmetry modes in (7) are in general restricted to a specific subspace within the representation space associated with their associated irrep. This restriction is always present if we are working with a fixed space group  $\mathcal{H}$ , and therefore the irrep associated with each mode can be used as a single label for describing its symmetry properties (leaving implicit the additional restriction forced by the space group  $\mathcal{H}$ ).

In the following, we will use two indices  $\tau$  and  $m$  to distinguish the members of the basis of symmetry modes. The index  $\tau$  is a global label to enumerate the different irreps present in the basis, while  $m$  ( $m = 1, \dots, n_\tau$ ) distinguishes the different independent modes for a given irrep  $\tau$ . We can then rewrite equation (7) as:

$$\mathbf{u}(\mu, i) = \sum_{\tau,m} A_{\tau,m} \epsilon(\tau, m|\mu, i), \quad (8)$$

where  $A_{\tau,m}$  is the amplitude of the symmetry mode  $(\tau, m)$  in the structural distortion.

The basis of symmetry modes  $\epsilon(\tau, m)$  is chosen orthonormalized (with Ångströms (Å) as length unit):

$$\sum_{\mu,i} \text{mult}(\mu, i) \epsilon(\tau, m|\mu, i) \cdot \epsilon(\tau', m'|\mu, i) = \delta_{\tau\tau'} \delta_{mm'}, \quad (9)$$

where the sum is over all atoms  $(\mu, i)$  in the  $\mathcal{H}$  asymmetric unit. The orthogonality property is automatically satisfied by modes corresponding to different irreps, while in the case of modes associated with the same irrep, a systematic orthogonalization procedure can be applied. Note that this implies that the basis of symmetry modes is in general not unique and for any practical calculation a certain arbitrary choice must be done.

The normalized distortion given by the so-called polarization vector  $\epsilon(\tau, m|\mu, i)$  defines the symmetry mode  $(\tau, m)$  except for a global amplitude; therefore henceforth we will use the terms *mode* and *mode polarization vector* as practically synonymous.

The set of displacements of each Wyckoff orbit of the parent structure form an invariant subspace for all symmetry operations, so that the basis of symmetry modes can be chosen considering separate modes for each Wyckoff orbit in the parent structure, *i.e.*  $\epsilon(\tau, m|\mu, i) = 0$  for all atoms  $\mu$  except one. Furthermore, the symmetry constraints of the polarization vector of a given mode only depends on the type of Wyckoff position,

so that the set of displacements defining the mode polarization vectors can be chosen identical for all crystallographic orbits of the same Wyckoff position. Hence, in practice, the index  $m$  in the symmetry-mode basis  $\epsilon(\tau, m)$  labeling the modes associated with a given irrep  $\tau$ , can be decomposed into two labels: one giving the atom representative  $\mu$  of the Wyckoff orbit having displacements in this mode, and an additional index for further enumeration in case of multiplicity. Whenever it is possible, we will maintain however for simplicity a single label  $m$ , as a short symbolic notation for enumerating the basis modes for a given irrep.

The basis of symmetry modes that is used by AMPLIMODES in the description of the  $Amm2$  structure of  $BaTiO_3$ , is given in the following table. It consists, as expected, of five modes: four corresponding to the irrep  $GM4-(\Gamma_4^-)$  and one to  $GM5-(\Gamma_5^-)$  with wave vector  $k = (0, 0, 0)^3$ . The program lists the basis of symmetry modes, using as mode labels, apart from their irrep, the relevant atom within the  $\mathcal{G}$  asymmetric unit and a multiplicity index:

mode	label	atom	$\delta x$	$\delta y$	$\delta z$
GM4-	Ba1 1	Ba1	0.00	0.000000	0.176512
GM4-	Ti1 1	Ti1	0.00	0.000000	0.176512
GM4-	O1 1	O1	0.00	0.062406	0.062406
		O2	0.00	0.000000	0.124813
GM4-	O1 2	O1	0.00	-0.088256	0.088256
		O2	0.00	0.000000	0.000000
GM5-	O1 1	O1	0.00	-0.062406	-0.062406
		O2	0.00	0.000000	0.124813

The displacements  $\delta x$ ,  $\delta y$ ,  $\delta z$  associated with each mode are given in relative units with respect to the low symmetry unit cell, and they fulfill the mentioned orthonormalization conditions if transformed into absolute displacements using the  $\mathcal{H}$ -transformed unit cell of the parent structure. In the example, these displacements are in fact quite simple fractions when expressed in absolute distance units. For instance, modes (GM4- Ba1 1) and (GM4- Ti1 1) are displacements of the corresponding atoms by 1 Å along the  $z$  direction of the  $Amm2$  setting, while those of the mode (GM5- O1 1) for O1 and O2 atoms are  $(0, -1/\sqrt{8}, -1/\sqrt{8})$  and  $(0, 0, 2/\sqrt{8})$ , also in Å. The definition and use of the basis symmetry modes in the setting of the low symmetry distorted structure, and in relative units, are a key point of the parameterization used by the program. Although they apparently complicate the expressions for the polarization vectors of the modes, they allow in fact to express all mode relations in accordance with crystallographic conventions. In this way, their effect on the  $\mathcal{H}$  structure become self-evident, and can be applied directly on the relative coordinates of the asymmetric unit of the  $\mathcal{H}$ -reference structure.

<sup>3</sup> The irreps are defined by a wave vector  $\mathbf{k}$  representative of its star of wave vectors, plus a label defining its transformation properties for pure lattice translational operations. For the labels of irreps AMPLIMODES follows the notation used by ISOTROPY (Stokes & Hatch, 2002), which is essentially the one of Cracknell *et al.* (1979).

## 2.4. Decomposition

Expression (8) can be considered as a change of basis in the description of the atomic displacement field as a vector in the  $D$ -dimensional  $\mathcal{H}$  distortion space, *i.e.* a linear transformation between the atomic parameters  $\mathbf{u}(\mu, i)$ , that define the atomic positions in the distorted structure and the amplitudes  $A_{\tau, m}$ , of the chosen basis of symmetry adapted modes. The determination of the contribution of each of the symmetry-allowed modes to the distortion, given by these amplitudes  $A_{\tau, m}$ , is straightforward taking into account the orthonormal properties of the symmetry modes:

$$A_{\tau, m} = \sum_{\mu, i} mult(\mu, i) \epsilon(\tau, m | \mu, i) \cdot \mathbf{u}(\mu, i) \quad (10)$$

The amplitudes  $A_{\tau, m}$  have length as dimension and can be expressed in absolute length units. This allows the comparison of the contributions of different distortion modes even if they represent collective atomic displacements of very different type. These amplitudes weakly depend on the chosen parent unit cell, since the absolute atomic displacements are calculated for the undistorted lattice. This minor ambiguity is unavoidable, since in general an unstrained  $\mathcal{G}$  compatible lattice has to be considered for both atomic displacements and symmetry modes in order to achieve a mathematically consistent mode analysis.

From a physical/chemical viewpoint, if we are interested in the atomistic mechanism at the origin of a certain distorted structure, it is convenient to distinguish and separate, for each possible irrep, the amplitude of the distortion with this symmetry, and its normalized polarization vector. For instance, in our  $BaTiO_3$  example, according to equation (10), the amplitudes in Å obtained for the chosen orthonormalized mode basis are:

GM4-	Ba1 1:	0.028780
GM4-	Ti1 1:	0.125091
GM4-	O1 1:	-0.041823
GM4-	O1 2:	-0.094725
GM5-	O1 1:	-0.005609

The amplitude of the total distortion is therefore given by the norm of the five dimensional vector defined by these five components, *i.e.* 0.1650 Å, in accordance with the norm calculated directly from the atomic displacements, *cf.* Section 2.2. Within this total distortion, the amplitude of the GM4- distortion is given by the norm of a vector limited to the first four amplitudes above, while the specific combination of the four GM4- basis modes, which is not forced by symmetry present in the observed GM4- distortion, *i.e.* the polarization vector of the actual GM4- distortion, is given by the normalization of the corresponding 4-component vector:

$$\begin{aligned} \text{Amplitude}(GM4-) &= 0.1649 \text{Å} \\ \mathbf{e}(GM4-) &= (0.174511, 0.758503, -0.253598, -0.574375) \end{aligned} \quad (11)$$

This is the form in which AMPLIMODES first presents the weight and internal structure of the symmetry components

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present in the analyzed distorted structure, separating their amplitude and expressing their normalized polarization vector in terms of the basis of symmetry modes. Henceforth, we shall call these symmetry adapted distortion modes for each irrep, present in the distorted structure, *irrep distortions*. The program also indicates for each irrep distortion the subspace within the irrep space in which the distortion is restricted, using the notation of ISOTROPY (Stokes & Hatch, 2002).

Within the range of stability of the analyzed phase one expects that the amplitudes of each irrep distortion should be in general strongly temperature, pressure or composition dependent, and with different behaviors for different irreps, while the polarization vector would be rather invariant. In other words, frozen distortions of a given symmetry may change rather easily in amplitude, but their internal structure or polarization vector in general is bound to be quite “rigid”. Furthermore, a hierarchy of amplitudes among the different irrep distortions is expected, depending on their relevance on the stabilization of the distorted phase.

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 relating this phase with the cubic perovskite. The GM4- distortion is therefore at the origin of this ferroelectric phase, while the GM5- distortion is secondary, allowed by symmetry but marginal in the phase stabilization. Thus, the strong difference of amplitudes of the two frozen distortions is the signature of the underlying lattice dynamics mechanism that causes this phase.

In general, the program lists the irrep distortion for each irrep, giving its amplitude:

$$A_\tau = (\sum_m (A_{\tau,m})^2)^{\frac{1}{2}} \quad (12)$$

and its polarization vector in terms of components for the basis of symmetry modes of this irrep:

$$\mathbf{e}(\tau) = (a_{\tau,1}, a_{\tau,2}, \dots, a_{\tau,n_\tau}) \quad (13)$$

with  $a_{\tau,m} = A_{\tau,m}/A_\tau$ .

For crystallographic purposes, the program also lists the polarization vector of each irrep distortion in the atomic basis, listing the atomic displacements  $\mathbf{e}(\tau|\mu, i)$  within the asymmetric unit, calculated as

$$\mathbf{e}(\tau|\mu, i) = \sum_m a_{\tau,m} \boldsymbol{\epsilon}(\tau, m|\mu, i) \quad (14)$$

A virtual structure with only the  $\tau$ -component of the distortion can then be obtained by adding to the  $\mathcal{H}$  transformed asymmetric unit of the reference structure the displacements:

$$\mathbf{u}(\tau|\mu, i) = A_\tau \boldsymbol{\epsilon}(\tau, m|\mu, i) \quad (15)$$

Hence for our example, the polarization vector of the GM4- distortion (see equation (11)) is alternatively listed as:

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

The displacements are listed in relative units, which multiplied by 0.1649 and added to the reference asymmetric unit listed above, produce a virtual *Amm2* structure with only the GM4- component of the experimental structure. Note that these displacements include a subtle correlation due to their GM4- symmetry, namely the displacements of the oxygens O1 and O1\_2 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 very small amplitude, this non-crystallographic relation is approximately maintained by the atomic coordinates of the experimental structure.

## 3. The program

### 3.1. Implementation

The displacement field described in the previous section is calculated by the combined action of two modules. A first module, TRANSTRU, transforms the high-symmetry structure to the basis of the low-symmetry phase. Although the change of structure description is conceptually clear and simple it can become technically complicated especially when the symmetry break  $\mathcal{G} \rightarrow \mathcal{H}$  involves an enlargement of the unit cell. The robustness of the transformation procedure is achieved by a parallel calculation of the splitting schemes of the occupied atomic positions for the transformation  $\mathcal{G} > \mathcal{H}$ . The program first decomposes  $\mathcal{G}$  in right cosets with respect to  $\mathcal{H}$ , and then the split orbits are calculated. Given the space-group types of  $\mathcal{G}$  and  $\mathcal{H}$ , and the transformation matrix between their conventional bases, TRANSTRU produces the transformed high-symmetry structure, explicitly indicating the coordinate triplets of the representatives of the split atomic positions. An important feature of this tool is that it provides the Wyckoff labels and multiplicity for each atom representative in the transformed structure.

The second module, COMPSTRU, searches an optimal atom *mapping* between the high- and low-symmetry structures and calculates the corresponding atomic displacement field. It compares the (relative) coordinate triplets of the high-symmetry structure referred to the basis of  $\mathcal{H}$  with those of the low-symmetry structure and forms pairs of atoms between the two structures so that the corresponding displacements are within the maximal allowed distance (tolerance length) defined in advance. The pairing procedure becomes complicated if the transformation  $\mathcal{G} \rightarrow \mathcal{H}$  involves large atomic displacements. An optimization routine has to supplement the pairings procedure when atoms of the same type occupy several independent orbits that belong to the same Wyckoff position type. The program stops if it is unable to find a mapping of the two structures within the given tolerance. If the space group  $\mathcal{H}$  is polar, the atomic displacement field obtained by COMPSTRU is modified to cancel any global translation, shifting the origin of the distorted structure.

Due to their utility for other structural calculations both programs, TRANSTRU and COMPSTRU, are also accessible

online on the Bilbao Crystallographic Server as independent tools.

The basis of orthonormal symmetry modes necessary for the symmetry-mode analysis are obtained using the program SYMMODES (Capillas *et al.*, 2003) that is already available on the Bilbao Crystallographic Server. The symmetry mode calculation performed by SYMMODES is based on the program COPL (Hatch & Stokes, 2002). For a given symmetry break  $\mathcal{G} \rightarrow \mathcal{H}$ , and a specified Wyckoff atomic orbit, SYMMODES, calculates the polarization vectors of a complete basis of symmetry modes that can contribute to the structural distortion. The symmetry of the modes is specified by their irrep, their direction in the representation space and their isotropy subgroup. SYMMODES (Capillas *et al.*, 2003) provides the mode polarization vector of each mode in the setting of the high-symmetry space group, giving the atomic displacements for the whole Wyckoff orbit extended to the  $\mathcal{H}$  unit cell, without forcing normalization or orthogonalization of modes of the same symmetry.

In the AMPLIMODES procedure, first SYMMODES is called to provide the allowed symmetry modes for all Wyckoff positions occupied in the parent structure. This information is then transformed to the setting of the distorted structure. In addition, the modes are internally transformed to a Cartesian basis applying the so-called Standard Root Tensor routine (Schlenker *et al.*, 1978), to be subsequently normalized, and orthogonalized if necessary using the Gram-Schmidt procedure. For the decomposition of the displacement field with respect to this basis of symmetry modes, the displacement field is also transformed to the same Cartesian basis. Simple scalar product calculations result in the determination of the amplitudes  $A_{\tau,m}$  of the symmetry modes, *cf.* equation (10). The amplitudes  $A_{\tau}$  for all irrep distortions and the components of their polarization vectors are calculated following directly from the corresponding definitions, *cf.* equations (12), (13) in Section 2.4.

### 3.2. Input and output

In the **Input** block the user is expected to introduce the structural data for the high- and low-symmetry phases. The data can be introduced either using CIF files (with certain restrictions), or keyed by hand or introduced by copy/paste in the provided field. The necessary structure information includes the space group number (as given in ITA), the cell parameters, the number of independent atoms in the asymmetric unit and the coordinates of these atoms. Each atom must be specified by its chemical symbol, a sequential number for each species, the Wyckoff position of the occupied orbit and the atomic coordinates in relative units. If unknown, the Wyckoff position label can be substituted by some arbitrary character. The program in fact identifies the actual labels of the occupied Wyckoff orbits, independently of the Wyckoff symbols introduced, and indicates the correct ones in the output. Fractional coordinate  $1/3$ ,  $2/3$ , *etc.* have to be introduced with six digits for a proper identification.

The program AMPLIMODES only accepts structure data given with respect to the default ITA settings of the space groups

used by the programs of the Bilbao Crystallographic Server<sup>4</sup>. The transformation matrix that relates the conventional bases of the high- and low-symmetry space groups should be provided either as a matrix-column pair  $(\mathbf{P}, \mathbf{p})$  or in the concise form:  $P_{11}\mathbf{a} + P_{21}\mathbf{b} + P_{31}\mathbf{c}, P_{12}\mathbf{a} + P_{22}\mathbf{b} + P_{32}\mathbf{c}, P_{13}\mathbf{a} + P_{23}\mathbf{b} + P_{33}\mathbf{c}; p_1, p_2, p_3$ .

Normally the matrix  $\mathbf{P}$  of the transformation  $(\mathbf{P}, \mathbf{p})$  can easily be obtained from the knowledge of the lattice parameters of the two structures. The knowledge of the relevant origin shift, on the other hand, can be a more complicated matter. In general, the tool SUBGROUPGRAPH (Ivantchev *et al.*, 2000) also available on the Bilbao Crystallographic Server, can be used for the purpose of determining the relevant transformation  $(\mathbf{P}, \mathbf{p})$ . This program only requires the index of  $\mathcal{H}$  as subgroup of  $\mathcal{G}$  (easily derived from the knowledge of the number of formula units  $Z$  per unit cell in both structures), to produce all possible distinct subgroups of  $\mathcal{G}$  of type  $\mathcal{H}$ , and their corresponding transformations  $(\mathbf{P}, \mathbf{p})$ . Often there may be distinct (non-equivalent) subgroups of type  $\mathcal{H}$  with the same matrix  $\mathbf{P}$ , but different shifts  $\mathbf{p}$ . In these cases, the server tool WYCKSPLIT (Kroumova *et al.*, 1998) can be used to check the splitting of the Wyckoff orbits for each of the possible subgroups. A comparison of this Wyckoff splitting with the occupied Wyckoff orbits in the distorted structure is usually sufficient to identify the relevant class of subgroups  $\mathcal{H}$  and its possible transformations  $(\mathbf{P}, \mathbf{p})$ .

Finally, the user should indicate a maximum allowed distance (tolerance length)  $\Delta$  in Å for the displacement field. The tolerance length limits the allowed atomic displacements for COMPSTRU and reasonable values will rarely exceed 1 Å. For tolerance lengths much larger than this value, the pairing routine in COMPSTRU may be unable to reach an acceptable displacement field, and some specific constraints about the possible pairings may be introduced by the user, to restrict the possibilities. In any case, if a successful comparison of the non-distorted and distorted structures done by the program requires atomic displacements that greatly exceed 1 Å, the user should carefully check if the atomic pairs determined by the program are sterically reasonable.

The **Output** of the program consists of two main blocks: a structure-data block and a block where a summary of the main results of the symmetry-mode analysis are displayed:

- *Structural data* The output begins by showing the input provided by the user, *i.e.* the high- and the low-symmetry structures and the transformation matrix. Then follows the high-symmetry structure transformed to the subgroup basis *i.e.* the *reference structure*. The atomic labels of the reference structure are used to identify the atoms throughout the rest of the program output. The next two tables describe the displacement field. The first table lists the pairings found by the program: for each atom in the asymmetric unit of the reference structure an atom from the unit cell of the distorted structure is assigned. The corresponding atomic displacements calculated in terms

<sup>4</sup> For space groups with more than one description in ITA, the following conventional settings are taken as default: *unique axis b*, *cell choice 1* for monoclinic groups, *hexagonal axis* setting for rhombohedral groups, and *origin choice 2* for centrosymmetric groups listed with respect to two origins in ITA.

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of relative displacements  $u_x, u_y$  and  $u_z$  with respect to the reference unit cell are listed in the second table. A measure of the total displacement in Ångströms is given in its fourth column, using for the calculation the unit cell of the reference structure. In the case of polar structures type, the user is asked to indicate the polar direction which is used for the calculation of the origin shift necessary to avoid the inclusion of a global translation in the displacement field. The tables describing the displacement field are shown twice: without and with the calculated origin shift. It is not unusual for the maximum atomic displacement to increase after the origin shift.

- **Summary block** Two tables sum up the main results of the symmetry-mode analysis. The first one lists the type of basis modes and their number for each occupied orbit of the non-distorted structure, specified by an atomic label and the corresponding Wyckoff position. The symmetry modes are distinguished by the label of the irrep to which they belong (see footnote<sup>3</sup> for explanations on the notation). The second table lists the amplitudes  $A_\tau$  of the irrep distortions present in the distorted structure also listing for each allowed irrep its representative wave vector, its corresponding isotropy subgroups and the distortion dimension (the number of independent basis symmetry-modes involved).

The option *Detailed information*, extends further the output of the program by providing details on the basis of symmetry modes used for the analysis, and the decomposition of the displacement field.

- **Symmetry modes** The polarization vectors of the basis of symmetry modes used are listed, labeling them by their irrep, the atom label corresponding to the representative of the  $\mathcal{G}$  Wyckoff orbit having displacements for this mode, and an additional index for further enumeration in case of multiplicity. For each polarization vector, the program only lists the atomic displacements (in relative units with respect to the unit cell of the reference structure) of the atoms of the relevant  $\mathcal{G}$  Wyckoff orbit which are present in the asymmetric unit of the reference structure. The number of atoms in the list is therefore equal to the number of  $\mathcal{H}$  Wyckoff orbits originated from the splitting of the relevant  $\mathcal{G}$  Wyckoff orbit. The assigned labels of the symmetry modes are used throughout the rest of the output.
- **Decomposition** The results of the decomposition of the displacement field are shown in sub-blocks: the data for each of the irrep distortions that contribute to the structural distortion (*cf.* equation (8)) are given in a separate sub-block. Each sub-block is entitled by the corresponding irrep symmetry label followed by the isotropy subgroup and the transformation matrix-column pair  $(\mathbf{P}, \mathbf{p})$  that relates the conventional bases of the high-symmetry group  $G$  and the corresponding isotropy subgroup. The subspace within the  $n$ -dimensional irrep space, within which the distortion is restricted to fulfill the symmetry compatibility with this isotropy subgroup is indicated

in the form of a generic  $n$ -dimensional vector, termed in the output as *direction*, following the conventions of ISOTROPY (Stokes & Hatch, 2002).

The program lists the global amplitude  $A_\tau$  (in Å) and the components  $a_{\tau,m}, m = 1, \dots, n_\tau$  describing the normalized polarization vector  $\mathbf{e}(\tau|\mu, i)$  (in the chosen basis of symmetry modes) *cf.* equations (13), (14). The last table in the sub-block shows the same polarization vector in terms of displacements (in relative units) of the atoms in the asymmetric unit of the reference structure and normalized with respect to its primitive unit cell. The option "Virtual structure" produces a virtual structure corresponding to the presence of only this irrep distortion.

### 3.3. Availability

The program AMPLIMODES forms part of the Bilbao Crystallographic Server, <http://www.cryst.ehu.es>, (Aroyo *et al.* (2006a) and Aroyo *et al.* (2006b)) and uses the databases and the results from other programs available on this server. The program can be used from any computer with a www-browser *via* Internet. The URL is <http://www.cryst.ehu.es/cryst/amplimodes.html> where also an on-line manual with a description of input and output of the program is available.

### 4. Examples

The following two examples illustrate the use of the computer program AMPLIMODES for the symmetry-mode analysis of specific distorted structures. In addition, the results obtained by the program are compared with results from the literature.

#### 4.1. Example 1: SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>

The Aurivillius family includes compounds with the general formula  $\text{Bi}_{2m}\text{A}_{n-m}\text{B}_n\text{O}_{3(n+m)}$  that are formed by  $[\text{Bi}_2\text{O}_2]$  slabs separating perovskite-like blocks. These compounds show a paraelectric-ferroelectric phase transition from a tetragonal to orthorhombic or monoclinic phases. The main features of AMPLIMODES can be demonstrated by its application to the ferroelectric structure of one of the most studied materials of the Aurivillius family, SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> namely SBT. The symmetry-mode analysis of SBT, published in Perez-Mato *et al.* (2004) can be compared with the results of the program.

The format of the input structure data for AMPLIMODES is illustrated by the high- and low-symmetry data of SBT shown in Table 1. The experimental data for the tetragonal  $I4/mmm$  phase is taken from Hervoches *et al.* (2001) while the orthorhombic  $Cmc2_1$  data corresponds to the data given by Rae *et al.* (1992). Note that the original structure description of the low-symmetry phase in Rae *et al.* (1992), has been previously transformed to the conventional setting  $Cmc2_1$ . The automatic tool SETSTRU (<http://www.cryst.ehu.es/cryst/setstru.html>) also available in the Bilbao Crystallographic Server can be used for this purpose.

The transformation matrix relating the conventional bases of  $I4/mmm$  and  $Cmc2_1$  can be given either in a concise form, *i.e.* as  $\mathbf{c}, \mathbf{a} - \mathbf{b}, \mathbf{a} + \mathbf{b}; 1/4, -1/4, 0$ , or written in a matrix form:



$$\left( \begin{array}{ccc|c} 0 & 1 & 1 & 1/4 \\ 0 & -1 & 1 & -1/4 \\ 1 & 0 & 0 & 0 \end{array} \right)$$

The output produced by AMPLIMODES starts with the reference structure (Table 2). The tables of pairings and displacement field (Table 3) are recalculated after indicating the polar direction ((0, 0, 1) in our case).

**Table 1**

High- and low-symmetry structures for SBT. The asymmetric unit of each structure is given in the conventional basis of the space group.

# Space Group ITA number					
139					
# Lattice parameters					
3.9121 3.9121 24.984 90 90 90					
7					
# [atom type] [number] [WP] [x] [y] [z]					
Sr	1	2a	0	0	0
Ta	1	4e	0	0	0.5856
Bi	1	4e	0	0	0.2002
O	1	2b	0	0	0.5
O	2	4e	0	0	0.6593
O	3	4d	0	0.5	0.25
O	4	8g	0	0.5	0.0772
# Space Group ITA number					
36					
# Lattice parameters					
24.9839 5.5344 5.5306 90 90 90					
8					
# [atom type] [number] [WP] [x] [y] [z]					
Sr	1	4a	0.5000	0.2554	0.0220
Bi	1	8b	0.7007	0.2232	0.0486
Ta	1	8b	0.5849	-0.2478	0.0137
O	1	4a	0.5000	-0.2928	0.0131
O	2	8b	0.6591	-0.19455	0.0071
O	3	8b	0.2492	-0.0093	-0.2183
O	4	8b	0.5697	0.0056	-0.2414
O	5	8b	0.5831	-0.4835	-0.2625

**Table 2**

Reference structure for SBT. This structure is obtained by expressing the high symmetry structure in the low symmetry basis. Note that the number of independent atoms on this basis increases due to a splitting of the high symmetry O4 orbit.

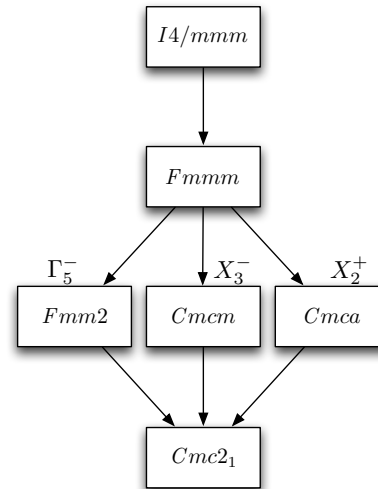
036					
24.983999 5.532545 5.532545 90.000000 90.000000 90.000000					
8					
Sr	1	4a	0.000000	0.750000	0.000000
Ta	1	8b	0.585600	0.750000	0.000000
Bi	1	8b	0.200200	0.750000	0.000000
O	1	4a	0.500000	0.750000	0.000000
O	2	8b	0.659300	0.750000	0.000000
O	3	8b	0.250000	0.500000	0.250000
O	4	8b	0.077200	0.500000	0.250000
O	4 <sub>2</sub>	8b	0.077200	0.000000	0.750000

**Table 3**

Displacement field for SBT. The components of the displacement field  $u_x$ ,  $u_y$  and  $u_z$  are given in relative units.  $\|u\|$  is the absolute displacement in Å.

Atom	$u_x$	$u_y$	$u_z$	$\ u\ $
Sr1	0.0000	0.0054	0.0220	0.1253
Ta1	-0.0007	0.0022	0.0137	0.0787
Bi1	0.0005	-0.0268	0.0486	0.3073
O1	0.0000	-0.0428	0.0131	0.2476
O2	-0.0002	0.0554	0.0071	0.3093
O3	0.0008	0.0093	0.0317	0.1839
O4	-0.0075	-0.0056	0.0086	0.1958
O4 <sub>2</sub>	0.0059	0.0165	-0.0125	0.1867

The three types of irrep distortions that can contribute to the symmetry break  $I4/mmm \rightarrow Cmc2_1$  are shown in the graph of maximal subgroups (Figure 1 obtained with SUBGROUP-GRAPH (Ivantchev *et al.*, 2000) or SYMMODES (Capillas *et al.*, 2003).



**Figure 1**

Maximal subgroup graph between space groups  $I4/mmm$  and  $Cmc2_1$ . The irrep labels indicate the irrep distortions (and the related isotropy subgroup) that can contribute to the symmetry break  $I4/mmm \rightarrow Cmc2_1$ . The label X corresponds to the wave vector  $(1/2, 1/2, 0)$  in the Brillouin zone of the  $I4/mmm$  structure.

It can be seen that a single irrep distortion is not sufficient to explain the full symmetry break of the transformation; a combination of at least two distortions belonging to different irreps is necessary. The SBT orthorhombic structure requires a basis of 22 symmetry modes (equal to the number of free parameters of the low-symmetry structure) and their distribution into irrep types is shown in the symmetry-mode summary table of the output of AMPLIMODES reproduced in Table 4. There are 4 modes of symmetry  $\Gamma_1^+$ , 8 of symmetry  $\Gamma_5^-$ , 7 corresponding to  $X_3^-$  and 3 modes of symmetry  $X_2^+$ . Part of the data on the  $\Gamma_5^-$  symmetry modes shown by the program under the *Detailed information* option are summarized in Table 5. The patterns of the symmetry mode are specified by the relative atomic displacements  $\delta x$ ,  $\delta y$ ,  $\delta z$  of one orbit representative. Due to the splitting of the O4 orbit (Wyckoff position 8g) during the symmetry reduction  $I4/mmm \rightarrow Cmc2_1$ ,

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$(8g)_{I4/mmm} \longrightarrow 2 * (8d)_{Cmc2_1}$ , the relative displacements of two O4 atoms are necessary for the pattern description of the modes O4 1 and O4 2.

**Table 4**

Summary of the basis of the symmetry modes in the distortion of SBT, distributed per type of Wyckoff position. Numbers in parenthesis indicate the number of modes for each irrep.

Atoms	WP	Modes
O4	8g	$\Gamma_1^+(1) \Gamma_5^-(2) X_2^+(2) X_3^-(1)$
O2 Bi1 Ta1	4e	$\Gamma_1^+(1) \Gamma_5^-(1) X_3^-(1)$
O3	4d	$\Gamma_5^-(1) X_2^+(1) X_3^-(1)$
O1	2b	$\Gamma_5^-(1) X_3^-(1)$
Sr	2a	$\Gamma_5^-(1) X_3^-(1)$

**Table 5**

Symmetry modes of SBT for the  $\Gamma_5^-$  irrep. Each symmetry mode involves a single atom in the asymmetric unit of the high-symmetry structure. The modes O4 1 and O4 2 contain displacements in to two orbits of the reference structure because they originate in the splitting of a single one in the high-symmetry structure. The displacements are normalized with respect the reference unit cell and given in relative units with respect to its lattice parameters. The displacements of the remaining atoms within the unit cell can be obtained from those listed by applying the  $Cmc2_1$  symmetry.

Mode label	Atom	$\delta x$	$\delta y$	$\delta z$
Sr1 1	Sr1	0.00	0.00	0.1278
Ta1 1	Ta1	0.00	0.00	0.0903
Bi1 1	Bi1	0.00	0.00	0.0903
O1 1	O1	0.00	0.00	0.1278
O2 1	O2	0.00	0.00	0.0903
O3 1	O3	0.00	0.00	0.0903
O4 1	O4	0.00	-0.0451	0.0451
	O4,2	0.00	-0.0451	0.0451
O4 2	O4	0.00	-0.0451	0.0451
	O4,2	0.00	-0.0451	0.0451

The amplitudes of the irrep distortions present in the  $Cmc2_1$  structure of SBT calculated by AMPLIMODES are given in Table 6. While not numerically equal, they are equivalent to the results reported in Perez-Mato *et al.* (2004). The differences are explained taking into account two considerations. First, the polar  $\Gamma_5^- (= E_u)$  mode depends on the origin of the  $Cmc2_1$  phase. While AMPLIMODES satisfies the 'arithmetic-centre' condition keeping the arithmetic centre fixed, the calculation in Perez-Mato *et al.* (2004) kept the center of mass fixed. Also another normalization was used. AMPLIMODES normalizes the symmetry modes with respect to the low symmetry basis, the normalization in the mentioned reference was done with respect to the high symmetry basis.

**Table 6**

Summary of the mode decomposition of SBT, indicating the amplitudes in Å of all intervening irrep distortions.

K-vector	Irrep	Dir.	Isotropy Subgroup	Dim.	Ampl. (Å)
(0, 0, 0)	$\Gamma_1^+$	(a)	$I4/mmm$ (139)	4	0.07
(0, 0, 0)	$E_u (= \Gamma_5^-)$	(a, a)	$Fmm2$ (42)	8	0.51
(1/2, 1/2, 0)	$X_3^-$	(a, -a)	$Cmca$ (64)	3	0.89
(1/2, 1/2, 0)	$X_2^+$	(a, -a)	$Cmcm$ (63)	7	0.26

Tables 7 and 8 show the normalized polarization vector for the  $\Gamma_5^-$  mode, first in terms of the symmetry modes given on

table 5 (see equation (13)) and as crystallographic displacements next, this mode can be seen on figure 2.

**Table 7**

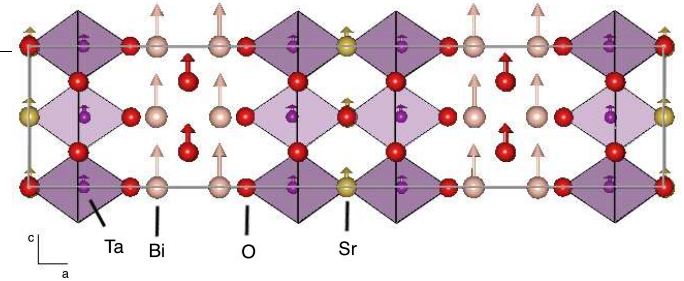
Normalized polarization vector for the  $\Gamma_5^-$  distortion of SBT

Sr1 1	Ta1 1	Bi1 1	O1 1	O2 1	O3 1	O4 1	O4 2
0.09	-0.06	0.70	-0.05	-0.20	0.33	-0.52	-0.28

**Table 8**

Normalized polarization vector for the  $\Gamma_5^-$  distortion of SBT expressed as displacements in relative units for the reference asymmetric unit.

Atom	$\delta x$	$\delta y$	$\delta z$
Sr1	0.0000	0.0000	0.0110
Ta1	0.0000	0.0000	-0.0053
Bi1	0.0000	0.0000	0.0632
O1	0.0000	0.0000	-0.0065
O2	0.0000	0.0000	-0.0182
O3	0.0000	0.0000	0.0301
O4	0.0000	0.0107	-0.0360
O4,2	0.0000	0.0107	-0.0360



**Figure 2**

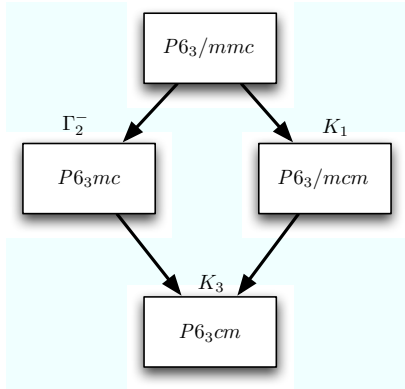
Description of the  $\Gamma_5^-$  distortion mode for SBT. The direction of the atomic displacements correspond to the direction of the arrows while their lengths are proportional to the amplitudes of the displacements. The figure was prepared using the program FP\_Studio included on the FullProf Suite.

As stressed in Perez-Mato *et al.* (2004) the mode decomposition of the distortion in SBT evidences the hierarchy of the three intervening irrep distortions. The two primary order parameters present on this phase can be identified as those with largest amplitude. The  $X_3^-$  distortion, having the largest amplitude can be considered the most unstable one, and an intermediate phase compatible with only this distortion and of symmetry  $Cmcm$ , can be predicted. This conclusion is in agreement with the results of *ab initio* calculations (Perez-Mato *et al.*, 2004) and experimental results (Hervoches *et al.*, 2001). The  $X_3^-$  and  $\Gamma_5^-$  distortion modes of the experimental structure could be identified as the two most unstable normal modes of the parent structure.

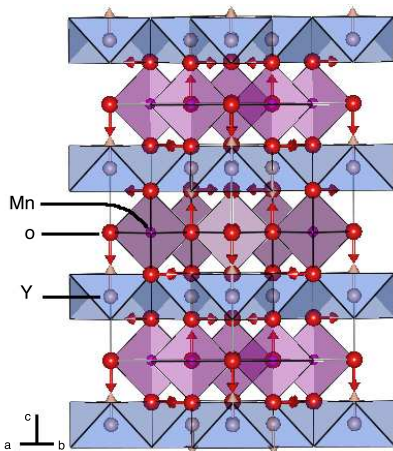
## 5. YMnO<sub>3</sub>

Our second example deals with the ferroelectric phase transition of YMnO<sub>3</sub> and the results of AMPLIMODES are compared with those of Fennie & Rabe (2005). The compound is

ferroelectric of symmetry  $P6_3cm$  at room temperature and paraelectric with space  $P6_3/mmc$  above 1270K.



**Figure 3**  
Maximal subgroup graph between space groups  $P6_3/mmc$  and  $P6_3cm$ . The irrep labels indicate the irrep distortions (and the related isotropy subgroup) that can contribute to the symmetry break  $P6_3/mmc \rightarrow P6_3cm$ . The label K corresponds to the wave vector  $(1/3, 1/3, 0)$  in the Brillouin zone of the  $P6_3/mmc$  structure.



**Figure 4**  
Description of the  $K_3$  distortion mode for  $YMnO_3$  in a  $[110]$  projection. The direction of the atomic displacements correspond to the direction of the arrows. For clarity the lengths have not been kept proportional. The figure was prepared using the program FP\_Studio included on the FullProf Suite.

The room temperature lattice implies a three-fold multiplication of the unit cell with respect to the  $P6_3/mmc$  parent structure.  $YMnO_3$  can be considered a multiferroic, and its sequence of phase transitions has been the subject of discussion in the literature. Some research groups have reported or proposed an intermediate phase (Lonkai *et al.* (2004), Nénert *et al.* (2007)), with the possibility of having a proper ferroelectric transition. This intermediate phase, however, has not been observed in other studies (Katsufuji *et al.*, 2002), while Fennie & Rabe (2005)

by means of *ab-initio* calculations have concluded that the symmetry break  $P6_3/mmc \rightarrow P6_3cm$  is the result of a single instability, *i.e.* a single phase transition,  $YMnO_3$  being in fact an *improper* ferroelectric.

**Table 9**  
High- and low-symmetry structure data for  $YMnO_3$

194						
	3.61	3.61	11.39	90	90	120
4						
Mn	1	2c	0.33333	0.66667	0.25	
O	1	2b	0	0	0.25	
O	2	4f	0.33333	0.66667	0.087	
Y	1	2a	0	0	0	
185						
	6.1387	6.1387	11.4071	90.	90.	120.
7						
Mn	1	6c	0	0.3352	0	
O	1	2a	0	0	-0.0218	
O	2	4b	0.33333	0.66667	0.0186	
O	3	6c	0.3083	0	0.1627	
O	4	6c	0.3587	0	-0.1628	
Y	1	2a	0	0	0.2743	
Y	2	4b	0.33333	0.66667	0.2335	

Figure 3 shows the chain of maximal subgroups relating parent and distorted symmetries in this case, with indication of the allowed irrep distortions that should be present in the room temperature structure. One can directly derive from the figure the three possible mechanisms for the symmetry break. A primary (unstable) mode of symmetry  $K_3$  (this mode can be seen on Figure 4), would be sufficient to explain the symmetry break with a single phase transition. In this case, one expects that the  $P6_3cm$  room temperature structure will have a strong dominant  $K_3$  component, while the symmetry allowed  $\Gamma_2^-$  or  $K_1$  distortions would be secondary weaker distortions. The spontaneous polarization produced by the polar distortion  $\Gamma_2^-$  would be then a secondary induced effect, and  $YMnO_3$  would be an *improper* ferroelectric. On the other hand, if both  $\Gamma_2^-$  or  $K_1$  were unstable primary distortions, they could also explain the observed room temperature symmetry, and in this case an intermediate phase would be expected. The intermediate phase would correspond to the condensation of only one of the two primary modes (in principle, the one with largest amplitude), and in this case the ferroelectric properties of  $YMnO_3$  would be those of a *proper* ferroelectric. In this second scenario, the hierarchy of amplitudes of the three distortions is expected to be completely different: the  $K_3$  distortion as a secondary mode would have a significantly smaller amplitude than the primary  $\Gamma_2^-$  and  $K_1$  distortions. Therefore, a mere mode decomposition of the experimental distorted structure can be sufficient to derive which of the two scenarios is more plausible, and if the existence of an intermediate phase is to be expected<sup>5</sup>. Fennie & Rabe (2005) did this mode decomposition and showed it was in accordance with the first model: a dominant  $K_3$  distortion. This result was also confirmed by their *ab-initio* calculations that show that the parent  $P6_3/mmc$  structure has a  $K_3$  unstable degenerate mode, and that no unstable modes of  $\Gamma_2^-$  or  $K_1$  symmetry exists. Moreover,

<sup>5</sup> in Lonkai *et al.* (2004) a third scenario was proposed with an isosymmetric transition between a paraelectric intermediate phase and the final ferroelectric phase. This is however based on incorrect arguments, as the authors overlooked the necessary condensation of a polar mode as a secondary distortion, in the first non-polar — polar symmetry break

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the polarization vector of the experimental  $K_3$  distortion agrees very well with the one of the calculated unstable mode.

**Table 10**

Reference structure for  $\text{YMnO}_3$

185					
6.2527 6.2527 11.3900 90.0000 90.0000 120.0000					
7					
Mn	1	6c	0.000000	0.333330	0.000000
O	1	2a	0.000000	0.000000	0.000000
O	1_2	4b	0.666667	0.333333	0.000000
O	2	6c	0.000000	0.333330	0.837000
O	2_2	6c	0.333330	0.333330	0.663000
Y	1	2a	0.000000	0.000000	0.750000
Y	1_2	4b	0.666667	0.333333	0.750000

Here, we show how this illuminating mode decomposition can be done automatically by AMPLIMODES. The structures introduced as input are shown in Table 9. The high-symmetry structure is taken from Lukaszewicz & Karut-Kalicinska (1974) while the low-symmetry phase is from van Aken *et al.* (2001). The matrix relating the settings of both structures is  $\mathbf{a} - \mathbf{b}$ ,  $\mathbf{a} + 2\mathbf{b}$ ,  $\mathbf{c}$ ; 0, 0, 1/4. The origin shift 1/4 along the polar z direction is chosen in view of the arbitrary choice of  $z=0$  for the Mn atom done in the distorted structure, to make the positions in both structures comparable. The reference structure is given in Table 10. The program then only requires a shift of the origin along z of 0.00043 in relative units to keep the arithmetic centre unmoved. The displacement field obtained by comparison of the reference and the low symmetry structures is shown in Table 11.

**Table 11**

Displacement field for  $\text{YMnO}_3$ .  $u_x$ ,  $u_y$  and  $u_z$  are given in relative units.  $\|u\|$  is the absolute displacement in Å.

Atom	$u_x$	$u_y$	$u_z$	$\ u\ $
Mn1	0.0000	0.0019	-0.0004	0.0127
O1	0.0000	0.0000	-0.0222	0.2532
O1_2	0.0000	-0.0000	0.0182	0.2070
O2	0.0000	0.0254	-0.0002	0.1587
O2_2	-0.0250	-0.0250	-0.0007	0.1567
Y1	0.0000	0.0000	0.0239	0.2719
Y1_2	0.0000	-0.0000	-0.0169	0.1928

A summary of the distortion amplitudes obtained by AMPLIMODES are shown in Table 12. The amplitudes directly coincide with the ones in Fennie & Rabe (2005). The amplitude for mode  $K_3$  is much larger than the other two modes, indicating that we are dealing with a phase which is the result of a single antiferrodistortive phase transition, with its ferroelectricity being of improper character. It must be stressed that, the amplitude of the polar mode  $\Gamma_2^-$  strongly depends on the choice of origin along the polar axis. It is sufficient a shift of 0.05 in relative units, to change the amplitude of the  $\Gamma_2^-$  distortion to 3.1 Å, while those of the other modes remain unchanged. This is due to the spurious global translation of the structure that the mode  $\Gamma_2^-$  would include in this case. It is therefore important for a proper comparison of mode amplitudes, the cancellation of this arbitrary component of the polar mode by means of an adequate origin choice.

**Table 12**

Summary of the mode decomposition of the  $P6_3cm$  structure of  $\text{YMnO}_3$ .

K-vector	Irrep	Dir.	Isotropy Subgroup	Dim.	Ampl. (Å)
(0, 0, 0)	$\Gamma_1^+$	(a)	$P6_3/mmc(194)$	1	0.01
(0, 0, 0)	$\Gamma_2^-$	(a)	$P6_3mc(186)$	4	0.16
(1/3, 1/3, 0)	$K_1$	(a, 0)	$P6_3/mcm(193)$	2	0.03
(1/3, 1/3, 0)	$K_3$	(a, 0)	$P6_3cm(185)$	3	0.93

**Table 13**

Normalized polarization vectors for the  $\Gamma_2^-$ ,  $K_1$  and  $K_3$  distortions in  $\text{YMnO}_3$

Mn1 1	O1 1	O2 1	Y1 1
0.0000	-0.1432	0.0020	0.0809

Mn1 1	O2 1
-0.9921	-0.1255

O1 1	O2 1	Y1 1
-0.5702	0.5858	0.5759

**Table 14**

Normalized polarization vectors for the  $\Gamma_2^-$ ,  $K_1$  and  $K_3$  distortions expressed as displacements for the asymmetric unit of the reference structure, in relative units with respect to the reference unit cell.

Atom	$\delta x$	$\delta y$	$\delta z$
Mn1	0.0000	0.0000	0.0000
O1	0.0000	0.0000	0.0312
O1_2	0.0000	0.0000	0.0312
O2	0.0000	0.0000	-0.0003
O2_2	0.0000	0.0000	-0.0003
Y1	0.0000	0.0000	-0.0176
Y1_2	0.0000	0.0000	-0.0176

Atom	$\delta x$	$\delta y$	$\delta z$
Mn1	0.0000	0.0648	0.0000
O1	0.0000	0.0000	0.0000
O1_2	0.0000	0.0000	0.0000
O2	0.0000	0.0058	0.0000
O2_2	0.0058	0.0058	0.0000
Y1	0.0000	0.0000	0.0000
Y1_2	0.0000	0.0000	0.0000

Atom	$\delta x$	$\delta y$	$\delta z$
Mn1	0.0000	0.0000	0.0000
O1	0.0000	0.0000	-0.0289
O1_2	0.0000	0.0000	0.0145
O2	0.0000	0.0270	0.0000
O2_2	-0.0270	-0.0270	0.0000
Y1	0.0000	0.0000	0.0292
Y1_2	0.0000	0.0000	-0.0146

The crystallographic format of the distortion modes provided by AMPLIMODES, separating amplitude and normalized polarization vector, and listing the polarization vector in two forms (in terms of components of the basis modes and as relative displacements within an asymmetric unit, tables 13 and 14) can be compared with the form used in Fennie & Rabe (2005), where absolute atomic displacements are listed. From the description in terms of the components of the basis modes, one can immediately observe that the  $K_1$  distortion involves mainly displacements of Mn1 along the y direction, while this atom is not involved in the other two irrep distortions, either because is not symmetry allowed, or because its displacements are rather negligible. On the other hand, the polar mode  $\Gamma_2^-$  is

basically an antiphase displacement along  $z$  of the Y and oxygens O2 and O2\_2 (O3 and O4 in the original structure), while the large primary distortion  $K_3$  which is at the origin of this phase is a concerted mode where the symmetry modes for Y and O atoms participate with similar weight.

## 6. Conclusions

The symmetry-mode analysis of a distorted structure decomposes its structural distortion in a natural basis which is not only symmetry-adapted but also adapted to the physics underlying its stability. Distortion modes of different symmetry have in general different behaviours for internal or external perturbations, as composition, temperature, pressure, stress, electric or magnetic fields. Their relative amplitudes in the total distortion follow in general a hierarchy which directly evidences their different roles played in the stabilization of the phase. The polarization vectors of the modes define the correlated atomic displacements, which are involved in each of them and are a valuable information for understanding and manipulating, if wished, the structural and physical properties of the phase. In general, the structure response to external perturbations can be approximated to variations of the amplitudes of the different symmetry-adapted distortions, while variations of their polarization vectors are relatively weak. A mode decomposition can thus provide important information on the character, origin, and properties of a distorted phase, including possible ferroic properties, expected thermal behaviour and probable phase transitions. The program AMPLIMODES can perform this mode analysis for any displacively distorted crystalline phase of any symmetry. Only the distorted structure and its high-symmetry reference, with respect to which the analysis is desired, must be provided. The time required on the Bilbao Crystallographic Server can vary between seconds to a few minutes for structures of reasonable size (one hundred atoms per unit cell or less). The program uses an asymmetric unit of the low symmetry phase as a common reference. It gives the results in a conventional crystallographic format which can be directly used to construct and analyze virtual structures with any of the modes considered in the mode decomposition. A comprehensive review of results that this program can provide and their relevance in the investigation of a wide range of specific materials will be presented elsewhere.

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 also 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 (Campbell *et al.*, 2007). In collaboration with J. Rodríguez-Carvajal we have recently included in AMPLIMODES this possibility as an additional option. A special output is provided to be directly used with FullProf (Rodríguez-Carvajal, 1993), and this refinement program can now use the amplitudes of the basis of symmetry modes defined by AMPLIMODES as *positional* parameters alternative to the

atomic coordinates. A detailed report on the use and possibilities of this combined use of AMPLIMODES and FullProf is in preparation.

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