

Symmetry-Mode Analysis of Displacive Phase Transitions using *International Tables for Crystallography*

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Abstract

The symmetry-mode analysis of a structural phase transition involves the use of methods of the representation theory of space groups. The aim of the paper is to present an alternative approach for the determination of the primary and secondary symmetry modes that contribute to the structural distortion of the low-symmetry phase. It only requires the systematic use of the data from *International Tables for Crystallography*, Vol. A, and is based on a fact, well known to crystallographers: the fully symmetrical displacements of any orbit of atoms (*i.e.* the modes compatible with the symmetry of the structure) follow in a straightforward way from the coordinate triplets of the corresponding Wyckoff positions. This property, systematically used for all intermediate subgroups between the space groups of the two phases, allows the determination of the relevant symmetry modes. Their distinction into primary and secondary modes comes out directly in the process of calculation. As an example, primary and secondary modes in the ferroelectric distortion of potassium selenate are divided.

1. Introduction

From a structural viewpoint, the main signature of a continuous or quasicontinuous structural phase transition of displacive type is the appearance in the low-symmetry phase of a symmetry-breaking distortion with respect to the high-symmetry phase (Landau & Lifshitz, 1980; Kocinski, 1990). This distortion is mainly caused by the freezing of some mode associated with the order parameter that we may call the *primary* mode. This mode corresponds to the degree of freedom of the system that becomes unstable at the phase transition. However, *secondary* modes are also triggered by the phase transition and can also have non-zero spontaneous amplitudes in the distorted structure (Cowley, 1980; Toledano & Toledano, 1987). A quantitative comparison

of the experimental structures of both phases is sufficient for determining the total structural distortion that relates them, but the separation of the unstable primary mode, which triggers the transition, from the secondary modes requires some symmetry analysis of the global distortion. This is usually done using symmetry modes (Mañes, Tello & Perez-Mato, 1982; Perez-Mato, Gaztelua, Madariaga & Tello, 1986; Withers, Hua, Welberry & Vincent, 1988; Hatch, Artman & Boerio-Goates, 1990; Stokes, Hatch & Wells, 1991). First, the symmetry modes of the parent phase compatible with the low-symmetry phase must be calculated and then, using their orthogonality properties, the global distortion is decomposed as a sum of the contributions of all of them. Finally, the *eigenvector* of the primary mode can be derived from the non-zero amplitudes of the symmetry modes associated with the order-parameter symmetry. Such an analysis is rather complex as it requires full use of group-theoretical methods: subduction properties of the irreducible representations, use of projectors to derive the symmetry modes *etc.* Here, we present an alternative method for the symmetry analysis of a given structural distortion. It only requires the systematic use of *International Tables for Crystallography* (1995), Vol. A (henceforth referred to as *IT95*). From these tables and for any space group, one can easily derive for any orbit of atoms the *fully symmetric* or *identity* modes, *i.e.* the modes that transform according to the identity representation of the group. It will be shown that this property, systematically used for all intermediate subgroups connecting the space groups of the two phases, yields a decomposition of the structural distortion in terms of *chain-adapted* modes. These modes are constructed and classified according to their compatibility with the different space groups in the subgroup chains. Although formally this symmetry classification is not the same as the one based on irreducible representations, in practice, it is equivalent in most cases and quite sufficient for a decomposition of the structural distortion into secondary and primary components. As an example, the method is applied to the symmetry break $Pnam \rightarrow Pna2_1(3a)$, which is present, for instance, in potassium selenate, and the results are compared with those previously published using con-

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ventional group-theoretical tools (Perez-Mato, Gaztelua, Madariaga & Tello, 1986).

2. Distortion-mode analysis

Let us consider a structural phase transition with the symmetry change $G \rightarrow H$, with $G > H$. The structural distortion relating the two phases can in general be decomposed into a homogeneous strain and an atomic displacement field, $u_\alpha(l, \kappa)$, representing the displacements of each atom (l, κ) in the low-symmetry structure, where l represents a unit cell of the high-symmetry structure, κ an atomic label within the corresponding unit cell and α stands for the three independent components (say x, y, z).[†] The displacement field $u_\alpha(l, \kappa)$ is calculated from the subtraction of the atomic positions of the two structures, each expressed in relative units. Thus, a displacement field $u_\alpha(l, \kappa) = 0$ would correspond to a phase where the structural distortion is totally described by a homogeneous strain of the high-symmetry structure.

In general, both the strain and the atomic displacements $u_\alpha(l, \kappa)$ contain a part that is also symmetry allowed in the high-symmetry phase. The determination of this part of the distortion requires some conventional reference structure within the space group G . This can be, for instance, the experimental G structure at some fixed temperature, or hypothetical G structure extrapolated into the thermal range of the H phase. The remaining part of the distortion is, by definition, symmetry forbidden in the high-symmetry phase and, therefore, its *spontaneous* non-zero magnitude in the H phase is uniquely determined. If G and H belong to different crystal systems, this symmetry-breaking part of the structural distortion includes some strain component, *i.e.* the transition is ferroelastic. The decomposition of the spontaneous strain relating both phases into irreducible components distinguishing primary and secondary strain components is in principle rather straightforward and well documented (Salje, 1990). We are interested in an analogous decomposition of the displacements $u_\alpha(l, \kappa)$, which, henceforth, are referred to as the *structural distortion*, obviating the strain component.

By definition, the order parameter or primary distortion describes completely the symmetry break of the transition. Hence, if $D^{q_0^*}$ is the active representation of the phase transition, *i.e.* the irreducible representation (irrep) associated with the order parameter, it should have as maximal invariance group, for some subspace, the group H . In group-theoretical language, the subduced representation ($D^{q_0^*} \downarrow H$) should contain the identity representation of H with some multiplicity, while for any other space group Z , such that $H < Z < G$, this multiplicity reduces in at least one unit (Jaric & Birman,

1977). One can say that H is an isotropy subgroup of G for the irrep $D^{q_0^*}$ (Stokes & Hatch, 1988).

Besides the primary distortion of symmetry $D^{q_0^*}$, the total distortion contains secondary distortions associated with other irreps. These remaining distortion components cannot produce any further symmetry break, *i.e.* they should all be compatible with the group H . The criteria to determine these other irreps can be found for instance in Kopsky (1980). Essentially, they must have isotropy subgroups that contain H or, in more formal terms, the representation subduced in H by the irrep D^{q^*} , say ($D^{q^*} \downarrow H$), should contain the identity representation of H at least once. This is easy to understand: being invariant subspaces, each (q^*) distortion should be kept unchanged by the action of the elements of H , as this is by definition the invariance group of the overall distortion. This necessarily requires the existence in the D^{q^*} -representation space of a subspace with an isotropy group equal to or higher than H . Therefore, besides the active representation, the irreps present in the structural distortion are those having as isotropy subgroups any space group Z intermediate between H and G . Hence, instead of the usual symmetry-mode description, it is possible to consider a decomposition of the total distortion in terms of components with different isotropy space groups:

$$u_\alpha(l, \kappa) = \sum_Z \sum_i C^Z(i) \xi_\alpha^Z(\kappa, l|i). \quad (1)$$

The first sum in (1) is over all possible space groups Z , such that $G > Z > H$, including the trivial cases G and H . A decomposition of the type of (1) was first introduced by Rae, Thompson, Withers & Willis (1990) for the particular case of bismuth titanate. The symmetry property that defines the modes $\xi_\alpha^Z(\kappa, l|i)$ is the invariance with respect to their isotropy space group Z and, by definition, for each set of Z modes, no linear combination exists with an isotropy group higher than Z . As shown in the next section, the derivation of this basis of symmetry-adapted modes requires the use of the structure of subgroup chains connecting H and G . Hence, we shall call them *chain-adapted* (symmetry) Z modes. For each orbit, the modes depend only on the type of Wyckoff position associated with it, *i.e.* the algebraic structure of the symmetry basis $\xi_\alpha^Z(\kappa, l|i)$ is the same for all orbits of the same Wyckoff type. Therefore, in the following, all expressions [including (1)] can be considered valid separately for each single orbit of atoms, and the set of atoms (l, κ) in (1) and following equations can be restricted to those related by the operations of G with one single atom in the asymmetric unit of the reference G structure. For each group Z , there can exist several Z modes in (1) and the index $i = 1, \dots, n^Z$ runs over them.

In Appendix A, it is shown that a symmetry decomposition of the structural distortion of the type (1) is, in many cases, equivalent to one using irreducible representations and, as shown in the next section, much

[†] A generalization to structural distortions with symmetry-breaking changes in the distribution of atomic occupation probabilities can be done. For the sake of simplicity, we restrict the expressions to distortions completely described through atomic displacements.

easier to derive. In particular, the low-symmetry space group H is usually an isotropy group of only one representation $\mathbf{D}^{\mathbf{q}_0^{\tau_0}}$.[†] In this case, the term in (1) corresponding to $Z = H$ coincides with the primary distortion $u_\alpha^0(l, \kappa)$ associated with the active representation:

$$u_\alpha^0(l, \kappa) = \sum_j C^H(j) \xi_\alpha^H(\kappa, l|j). \quad (2)$$

Furthermore (see Appendix A), the H modes in (2) have a direct relation with the $\mathbf{D}^{\mathbf{q}_0^{\tau_0}}$ modes. For instance, if the subspace, in the representation space of $\mathbf{D}^{\mathbf{q}_0^{\tau_0}}$, with isotropy group H , is one-dimensional (a rather common case, $d_H = 1$), the chain-adapted H modes $\xi_\alpha^H(\kappa, l|i)$ can be identified with symmetry-fixed linear combinations of the $\mathbf{D}^{\mathbf{q}_0^{\tau_0}}$ symmetry modes. If, on the other hand, d_H is equal to the total dimension of $\mathbf{D}^{\mathbf{q}_0^{\tau_0}}$ (which includes the rather common situation when the active irrep is one-dimensional), the chain-adapted H modes can be directly identified as the set of $\mathbf{D}^{\mathbf{q}_0^{\tau_0}}$ modes.

The set of Z modes in (1) with Z being strictly a supergroup of H are secondary distortions and they can be similarly related with those defined using the group-theoretical approach, so that, in many practical cases, the symmetry analysis of the distortion in terms of chain-adapted modes is equivalent to the one with a basis adapted to the irreps of G . Even in a quite general case, as discussed above, the description of the distortion in terms of chain-adapted modes is sufficient for distinguishing the primary structural distortion associated with the order parameter (given by the H modes), from secondary distortions with higher isotropy subgroups associated with secondary degrees of freedom. Only in the rather seldom case (Stokes & Hatch, 1988) when more than one irrep of G have H as an isotropy subgroup, the decomposition (1) would not be enough for the determination of the primary distortion. While in the approach using irreps a full use of the group-theoretical tools is required, decomposition (1), as explained below, is simpler to perform. It only needs to determine the set of modes that are *identity modes* for each intermediate space group between H and G . In the next sections, we will show how this information can be easily retrieved from IT95 for each Wyckoff orbit and, used in a combined manner through the subgroup chains connecting H and G , yields the desired basis of chain-adapted modes.

3. Identity symmetry modes and their determination from the data in *International Tables*

The conventional group-theoretical approach for the calculation of the symmetry modes transforming accord-

[†] This is the reason why the knowledge of the symmetry break $G \rightarrow H$ is in general sufficient for the identification of the active representation in a structural phase transition (Kocinski, 1990; Izyumov & Syromyatnikov, 1990).

ing to some irrep $\mathbf{D}^{\mathbf{q}^{\tau}}$ implies the construction of vibration representation $\mathbf{V}^{\mathbf{q}}$ of the little group $G^{\mathbf{q}}$ of the wave vector \mathbf{q} (see e.g. Izyumov & Syromyatnikov, 1990):

$$\mathbf{V}^{\mathbf{q}} = \{(\mathbf{P}^{\mathbf{q}} \otimes \mathbf{D}^{\mathbf{v}})(g), g \in G^{\mathbf{q}}\}. \quad (3)$$

Here, $\mathbf{P}^{\mathbf{q}}$ is the so-called permutation representation which shows how the r symmetrically equivalent atoms of the unit cell (i.e. the atoms belonging to an orbit O_G) permute under a space-group operation. Its $(r \times r)$ -dimensional matrices are given by

$$\mathbf{P}^{\mathbf{q}}(g)_{ij} = \begin{cases} 0, & g\mathbf{r}_j \neq \mathbf{r}_i \pmod{\mathbf{t}}, \quad \mathbf{t} \in \mathbf{L}, \\ \exp(-i\mathbf{k} \cdot \mathbf{t}_{ji}), & g\mathbf{r}_j = \mathbf{r}_i + \mathbf{t}_{ji}, \quad \mathbf{t}_{ji} \in \mathbf{L}, \\ & i, j = 1, \dots, r, g \in G^{\mathbf{q}}, \end{cases} \quad (4)$$

where $\mathbf{r}_k \equiv \mathbf{r}(l, \kappa)$, $\kappa = 1, \dots, r$, is the radius vector of the κ th atom of O_G and $\mathbf{t} \in \mathbf{L}$ is a translation lattice vector.

Following IT95, the elements g_i of a space group G are described as column-matrix pairs $(\mathbf{W}_i, \mathbf{w}_i)$, with a rotation part given by the matrix \mathbf{W}_i and a translation part by the column \mathbf{w}_i . The vector representation $\mathbf{D}^{\mathbf{v}}(\equiv \mathbf{D}^{\mathbf{q}^{\tau_0, \mathbf{v}}})$ of G is trivially constructed from the vector representation $\Gamma^{\mathbf{v}} = \{\mathbf{W}_1, \mathbf{W}_2, \dots, \mathbf{W}_n\}$ of the point group of G :

$$\mathbf{D}^{\mathbf{v}}(\mathbf{W}, \mathbf{w}) = \Gamma^{\mathbf{v}}(\mathbf{W}) = \mathbf{W}, \quad (\mathbf{W}, \mathbf{w}) \in G. \quad (5)$$

The polarization vectors of the symmetry modes follow from the matrix $\boldsymbol{\varepsilon}^{\mathbf{q}}$ ($\dim \boldsymbol{\varepsilon}^{\mathbf{q}} = 3r$), which reduces the vibration representation $\mathbf{V}^{\mathbf{q}}$ into irreps $\mathbf{D}^{\mathbf{q}^{\tau}}$ of the little group $G^{\mathbf{q}}$.

$$(\boldsymbol{\varepsilon}^{\mathbf{q}})^{-1} \mathbf{V}^{\mathbf{q}}(g) \boldsymbol{\varepsilon}^{\mathbf{q}} = \bigoplus_{\mathbf{q}^{\tau}} n(\mathbf{q}^{\tau}) \mathbf{D}^{\mathbf{q}^{\tau}}(g), \quad g \in G^{\mathbf{q}}. \quad (6)$$

The direct sum is over the little group irreps $\mathbf{D}^{\mathbf{q}^{\tau}}$ appearing in the vibration representation and $n(\mathbf{q}^{\tau})$ is the multiplicity of $\mathbf{D}^{\mathbf{q}^{\tau}}$ in $\mathbf{V}^{\mathbf{q}}$. The columns of the matrix $\boldsymbol{\varepsilon}^{\mathbf{q}}$ (known also as the *reduction matrix*) are labeled by the triple $(\mathbf{q}^{\tau}, m, j)$, with $j = 1, \dots, n(\mathbf{q}^{\tau})$ and $m = 1, \dots, d_{\tau}(\dim \mathbf{D}^{\mathbf{q}^{\tau}})$ and its rows by the pair (κ, α) , with $\kappa = 1, \dots, r$ and $\alpha = x, y, z$. The elements of $\boldsymbol{\varepsilon}^{\mathbf{q}}$ determine the polarization vectors $\boldsymbol{\varepsilon}_{\alpha}(\kappa | \mathbf{q}^{\tau}, m, j)$ of the modes which transform according to the rows of the irrep $\mathbf{D}^{\mathbf{q}^{\tau}}$ of $G^{\mathbf{q}}$.

For our further considerations, it is convenient to split and rewrite (6) for each irrep $\mathbf{D}^{\mathbf{q}^{\tau}}$ separately:

$$\mathbf{V}^{\mathbf{q}}(g) \boldsymbol{\varepsilon}_{\mathbf{q}^{\tau}} = \boldsymbol{\varepsilon}_{\mathbf{q}^{\tau}} \mathbf{D}^{\mathbf{q}^{\tau}}(g), \quad g \in G^{\mathbf{q}}. \quad (7)$$

Here, the rectangular matrices $\boldsymbol{\varepsilon}_{\mathbf{q}^{\tau}}$ consist of d_{τ} columns of $\boldsymbol{\varepsilon}^{\mathbf{q}}$ and correspond to the polarization vectors associated with one of the subspaces transforming according to the irrep $\mathbf{D}^{\mathbf{q}^{\tau}}$. The number of independent solutions of (7) equals the multiplicity $j = 1, \dots, n(\mathbf{q}^{\tau})$ of $\mathbf{D}^{\mathbf{q}^{\tau}}$ in $\mathbf{V}^{\mathbf{q}}$.

In the following, we will be mainly interested in the determination of the identity (symmetry) modes (*cf.* §2): Given a space group G , these are the modes whose polarization vectors correspond to the columns of the reduction matrix labeled by the identity representation $\mathbf{D}^1 (\equiv \mathbf{D}^{01}, \mathbf{q} = \mathbf{0}, \tau = 1)$. The methods for their calculation follow the approaches applied for the calculation of ε^q matrices either by the projection-operator technique or using the defining equations (7) as a system of linear equations in the elements of $\varepsilon_q \tau$.

Here, we present another technique for the determination. It is based on a fact well known to crystallographers: For a set of equivalent atoms occupying an orbit O_G , a combined displacement of all of them such that the orbit is maintained is clearly compatible (invariant) with the space-group symmetry of the structure and, therefore, constitutes a symmetry mode transforming according to the identity representation \mathbf{D}^1 of the space group G . These atomic displacements compatible with the orbit can be easily derived from the variable parameters of the corresponding Wyckoff position in *IT95*.

This 'dynamic' application of the data listed under Wyckoff positions in *IT95* can be rigorously demonstrated by comparing the definition for an orbit $O_G(X_0)$ of a point X_0 and the set of equations (12) for the determination of the reduction matrix. The crystallographic orbit of a point X_0 with respect to a space group G is defined as the set of all points X_i that are symmetrically equivalent to X_0 :

$$O_G(X_0) = \{X_i | (\mathbf{W}_i, \mathbf{w}_i + \mathbf{t}_i)X_0 = X_i, (\mathbf{W}_i, \mathbf{w}_i + \mathbf{t}_i) \in G\}. \quad (8)$$

The subgroup S_0 of G that leaves X_0 fixed is the site-symmetry group S_0 of G for the point X_0 :

$$S_0 = \{(\mathbf{W}_i, \mathbf{w}_i + \mathbf{t}_i) | (\mathbf{W}_i, \mathbf{w}_i + \mathbf{t}_i)X_0 = X_0, (\mathbf{W}_i, \mathbf{w}_i + \mathbf{t}_i) \in G\}. \quad (9)$$

The site-symmetry groups are of finite order; they are isomorphic to subgroups of the point group of the space group.

The set of equations (8) defining the orbit $O_G(X_0)$ of a point X_0 with respect to a group G can be considered as a nonhomogeneous system of linear equations in the coordinates of points X_i belonging to a G orbit:

$$(\mathbf{W}_j, \mathbf{w}_j + \mathbf{t}_j)X_0 = X_0, \quad \text{for } (\mathbf{W}_j, \mathbf{w}_j) \in S_0, \quad (10a)$$

$$(\mathbf{W}_i, \mathbf{w}_i + \mathbf{t}_i)X_0 = X_i, \quad \text{for } (\mathbf{W}_i, \mathbf{w}_i) \notin S_0. \quad (10b)$$

The coordinate triplets of the Wyckoff positions listed in *IT95* are solutions of such nonhomogenous systems. The solutions are composed of variable parameters which correspond to the general solutions of the associated homogenous systems and triples of real numbers which are particular solutions of the nonhomogenous system [equations (10)]. Wyckoff positions without variable

parameters correspond to the trivial solution of the associated homogenous system.

On the other hand, the system of linear equations for the elements of the reduction matrix [see (7)] describing the modes that transform according to the identity representation \mathbf{D}^1 of the space group reduces to the form

$$\mathbf{V}^q(g)\varepsilon = \varepsilon \mathbf{D}^1(g) = \varepsilon, \quad g \in G. \quad (11)$$

To simplify the notation, we have omitted the subindex of the matrix $\varepsilon (\varepsilon_j = \varepsilon)$, which is a single $3r$ column. The set of equations (11) is a homogeneous system of linear equations in its coefficients and the number of parameters in the general solution of the system (11) equals the multiplicity of \mathbf{D}^1 in \mathbf{V}^q . The important point is that it comprises exactly the homogeneous system of linear equations of the nonhomogeneous system (10). This is obvious if we consider the unknowns $(\varepsilon)_0$ of ε corresponding to the point X_0 . Taking into account the Kronecker-product structure of the vibration representation (3), the system (11) takes the form

$$\mathbf{W}_j(\varepsilon)_0 = (\varepsilon)_0, \quad (\mathbf{W}_j, \mathbf{w}_j) \in S_0, \quad (12a)$$

$$\mathbf{W}_i(\varepsilon)_0 = (\varepsilon)_i, \quad (\mathbf{W}_i, \mathbf{w}_i) \notin S_0. \quad (12b)$$

For the elements belonging to the site-symmetry group S_0 of the point X_0 , the set of equations (12a) forms a subsystem in the coefficients $(\varepsilon)_0$ while (12b) introduces relations between the coefficients $(\varepsilon)_0$ and $(\varepsilon)_i$ corresponding to the X_i point of the $O_G(X_0)$ orbit.

The possibility of reading directly the identity modes from the coordinate triplets giving the positions of the equivalent atoms of G orbits, listed under Wyckoff positions in *IT95*, follows from the relation between the solutions of the nonhomogeneous system of linear equations (10) and the solutions of the corresponding homogenous system of linear equations (12a), (12b). Solutions for the ε column matrix are obtained from the Wyckoff positions with variable parameters. The number of variable parameters of the Wyckoff position corresponds to the multiplicity of the identity representation \mathbf{D}^1 of G in the corresponding vibration representation. No solution for ε is obtained from Wyckoff positions without variable parameters, as they correspond to the trivial solutions of the homogenous system.

Example 1. Table 1 shows how the identity modes for an orbit of atoms at Wyckoff position 4(c) in a *Pnam* (a non-conventional setting of *Pnma*, No. 62)† structure can be directly derived from the set of triple coordinates describing the orbit. The 4(c) Wyckoff position is described by two variable parameters, so there are two identity modes for the atoms occupying this position. One possible choice for these modes follows directly from the coordinates of the 4(c) equivalent atoms and is

† A non-conventional setting of *Pnma* has been chosen in order to facilitate the comparison with the results of Perez-Mato, Gaztelua, Madariaga & Tello (1986) discussed below (see §5).

Table 1. *Identity symmetry modes for 4(c) atoms of Pnam*

Their number and patterns follow directly from the variable parameters of the 4(c) orbit of Pnam

Atom label	Coordinates of 4(c) atoms of Pnam		x mode			y mode			
	x	y	x	y	z	x	y	z	
1	x	y	1/4	1	0	0	0	1	0
2	-x + 1/2	y + 1/2	3/4	-1	0	0	0	1	0
3	-x	-y	3/4	-1	0	0	0	-1	0
4	x + 1/2	-y + 1/2	1/4	1	0	0	0	-1	0
	Normalization factors			1/2			1/2		

listed in Table 1. Similarly, one could write down the modes for the atoms occupying an orbit belonging to the general Wyckoff position 8(d) of Pnam. In this case, there are three independent displacive modes and they can be chosen following the coordinates of the 8(d) atoms, *i.e.* along the *a*, *b* and *c* axes.

4. Determination of chain-adapted symmetry modes

4.1. Group-subgroup chain with a maximal subgroup

Consider a group-subgroup chain $G > H$, where H is a maximal subgroup of G . Atoms that are symmetrically equivalent under G , *i.e.* belong to the same orbit of G , may become non-equivalent under H (the orbit splits) and/or their site symmetries can be reduced. It is important to note that this orbit behavior is the same for all orbits belonging to the same Wyckoff position (Wondratschek, 1993).

As explained in §3, the identity modes for the group G , say ϵ_j^G , $j = 1, \dots, n^G$, for atoms occupying a Wyckoff position $(WP)_G$ follow directly from its variable parameters. Similarly, one obtains the symmetry modes ϵ^H compatible with the subgroup H by examining the Wyckoff positions $(WP)_H$ into which $(WP)_G$ splits:

$$(WP)_G \rightarrow (WP)_1_H \cup (WP)_2_H \cup \dots \cup (WP)_k_H. \quad (13)$$

Here, Wyckoff positions of H , $(WP)_i_H$, originating from a Wyckoff position of G , $(WP)_G$, are connected by the union symbol. Taking into account the variable parameters of all $(WP)_i_H$ originating from $(WP)_G$, one obtains the identity modes ϵ_i^H , $i = 1, \dots, n^H$, for the atoms occupying the high-symmetry Wyckoff position $(WP)_G$. [Obviously, the number of ϵ_i^H modes corresponds to the number of variable parameters of all $(WP)_i_H$ in (13).] If it is possible to find some linear combinations of the ϵ^H modes that are also invariant with respect to $G > H$, then these linear combinations are the *chain-adapted* G modes ξ^G defined in §2. [Similar to the case of identity modes, here and below, we introduce a column-matrix notation ξ_j^G for the chain-adapted modes $\xi_\alpha^G(\kappa, l|j)$, defined in (1)]. The determination of ξ_j^G is straightforward as the chain-adapted G modes should correspond in number and form to the ϵ^G modes obtained for $(WP)_G$.

The relation between the ϵ^H modes and the chain-adapted G and H modes (ξ^G and ξ^H) can be expressed by a real square matrix X_G^H whose elements $(X_G^H)_{ij}$ are the coefficients necessary for the *chain-adaptation* procedure. Its dimension equals the number of ϵ^H modes.

$$\xi_i^Z = \sum_{j=1}^{n^H} \epsilon_j^H (X_G^H)_{ji}, \quad i = 1, \dots, n^H. \quad (14)$$

The matrix X_G^H can be chosen so that $\xi_i^Z = \xi_i^G$, for $i = 1, \dots, n^G$, and $\xi_i^Z = \xi_i^H$, for $i = n^G + 1, \dots, n^H$. One should note that the chain-adaptation procedure imposes restrictions only on the elements $(X_G^H)_{ji}$ of those columns of the matrix X_G^H (called *chain-adaptation matrix* in the following) that correspond to the G modes (*i.e.* $i = 1, \dots, n^G$). The rest of the coefficients $(X_G^H)_{ji}$ are restricted only by the orthogonal form of X_G^H .

It is worth noting that the chain-adaptation procedure of ϵ^H modes [*cf.* (14)] is always possible if the secondary modes ξ^G are existing, *i.e.* it is always possible to construct such linear combinations of ϵ^H modes that are also compatible with the G symmetry. Obviously, any solution of the defining system of linear equations (11) for the elements of the reduction matrix ϵ for the group G is also a solution of the system (11) reduced to the subgroup H .

Example 2. Consider the group-subgroup chain $Pnam > Pna2_1$ ($Pna2_1$ is a maximal *translationengleiche* subgroup of $Pnam$). In the transition to $Pna2_1$ symmetry, the orbits belonging to the 4(c) Wyckoff position of $Pnam$ do not split, their site symmetry is reduced and they become orbits of the general position 4(a) for the subgroup $Pna2_1$, which symbolically can be written as

$$4c(..m)x, y, 1/4 \rightarrow 4a(1)x, y, z. \quad (15)$$

Here, each Wyckoff position orbit is presented by its multiplicity, Wyckoff letter, site-symmetry group (in parentheses) and a coordinate triplet in the asymmetric unit. The identity $Pna2_1$ modes for the 4(a) atoms are listed in Table 2. Their relationships with the corresponding identity $Pnam$ modes of 4(c) atoms (Table 1) are evident. Obviously, the identity $Pna2_1$ mode (which we call $Pna2_1$ mode for short) along the *c* axis is a primary distortion for a hypothetical displacive $Pnam > Pna2_1$ phase transition. The *x* and *y* modes of $Pna2_1$ symmetry are secondary ones as they are also invariant with respect to $Pnam$. In this case, the chain-adaptation matrix (14) is a trivial three-dimensional unit matrix.

Example 3. Consider the group-subgroup chain $Pnam > Pnam(\mathbf{a}' = 3\mathbf{a})$. $Pnam(3\mathbf{a})$ is a maximal isomorphic subgroup of index 3 obtained by the tripling of the *a* axis. In that case, each of the 4(c) orbits splits into three $Pnam(3\mathbf{a})$ orbits of 4(c) type:

$$4c(..m)x, y, 1/4 \rightarrow 4c(..m)x, y, 1/4 \cup 4c(..m)x + 1, y, 1/4 \cup 4c(..m)x + 2, y, 1/4. \quad (16)$$

Table 2. Identity symmetry modes for 4(a) atoms of $Pna2_1$

Their number and patterns follow directly from the variable parameters of the 4(a) orbit of $Pna2_1$.

Atom label	Coordinates of 4(a) atoms of $Pna2_1$			x mode			y mode			z mode		
	x	y	z	x	y	z	x	y	z	x	y	z
1	x	y	z	1	0	0	0	1	0	0	0	1
2	$-x + 1/2$	$y + 1/2$	$z + 1/2$	-1	0	0	0	1	0	0	0	1
3	-x	-y	$z + 1/2$	-1	0	0	0	-1	0	0	0	1
4	$x + 1/2$	$-y + 1/2$	z	1	0	0	0	-1	0	0	0	1
	Normalization factors			1/2			1/2			1/2		

Table 3. Chain-adapted x modes of 4(c) atoms for $Pnam > Pnam(a' = 3a)$

Three consecutive cells along the x axis are considered. The chain-adapted modes are listed in the last columns of the table: there is one $Pnam$ mode and two $Pnam(a)$ modes.

Atom label	x coordinates			x symmetry modes					
	$Pnam$ basis	$Pnam(a'=3a)$ basis Coordinates	Orbit splitting	Identity $Pnam(3a)$ modes			Chain-adapted modes $Pnam$ $Pnam(3a)$		
1	x	x/3	x'	1	0	0	1	1	0
2	$-x + 1/2$	$-x/3 + 1/6$	$-x'' + 1/2$	0	-1	0	-1	1/2	-1
3	-x	-x/3	$-x'$	-1	0	0	-1	-1	0
4	$x + 1/2$	$x/3 + 1/6$	$x''' + 1/2$	0	0	1	1	-1/2	-1
1'	$x + 1$	$x/3 + 1/3$	x''	0	1	0	1	-1/2	1
2'	$-x + 3/2$	$-x/3 + 1/2$	$-x' + 1/2$	-1	0	0	-1	-1	0
3'	$-x + 1$	$-x/3 + 1/3$	$-x'''$	0	0	-1	-1	1/2	1
4'	$x + 3/2$	$x/3 + 1/2$	$x' + 1/2$	1	0	0	1	1	0
1''	$x + 2$	$x/3 + 2/3$	x''	0	0	1	1	-1/2	-1
2''	$-x + 5/2$	$-x/3 + 5/2$	$-x''' + 1/2$	0	0	-1	-1	1/2	1
3''	$-x + 2$	$-x/3 + 2/3$	$-x''$	0	-1	0	-1	1/2	-1
4''	$x + 5/2$	$x/3 + 5/6$	$x' + 1/2$	0	1	0	1	-1/2	1
	Normalization factors			1/2	1/2	1/2	$(1/12)^{1/2}$	$(1/6)^{1/2}$	$(1/8)^{1/2}$

Owing to the tripling of the cell along the a axis, there are 12 atoms in the unit cell of $Pnam(3a)$ occupying the three 4(c) orbits. They originate from the 4(c) orbit of $Pnam$ and their x coordinates are given in the second column of Table 3. [The coordinates of the atoms with primed labels are obtained from the coordinates of the original set by adding a translation (1, 0, 0) and those with double prime by adding the translation (2, 0, 0).] The distribution of the 12 atoms among the three 4(c) orbits of $Pnam(3a)$ (column 4 of Table 3) is easily obtained after the transformation of the coordinates of the atoms to the conventional basis of the subgroup (column 3 of Table 3) by the transformation matrix

$$P = \begin{pmatrix} 300 \\ 010 \\ 001 \end{pmatrix}.$$

For example, atoms 1, 3, 2' and 4' form the representative set of the first 4(c) orbit ($x' = x/3$), atoms 3, 1', 2'' and 4'' form the second one ($x'' = x/3 + 1/3$) etc.

Consider the three $\epsilon^{Pnam(3a)}$ modes along the a axis, which are listed under identity $Pnam(3a)$ modes in Table 3. The fact that they originated from one $Pnam$ x mode shows that there exists a linear combination of them that is compatible with $Pnam$ symmetry. Comparison with the $Pnam$ mode in Table 1 clearly shows that this mode should be the one listed as the chain-adapted $Pnam$ mode

in Table 3, i.e. a (1, 1, 1) combination of the three $Pnam(3a)$ modes and, therefore, the chain-adaptation matrix in this case can be chosen in the form

$$X_G^H = \begin{vmatrix} (1/3)^{1/2} & (2/3)^{1/2} & 0 \\ (1/3)^{1/2} & -(1/6)^{1/2} & (1/2)^{1/2} \\ (1/3)^{1/2} & -(1/6)^{1/2} & (1/2)^{1/2} \end{vmatrix}. \quad (17)$$

The coefficients in the first column of X_G^H determine the linear combination of $Pnam(3a)$ modes compatible with the $Pnam$ symmetry; the other two columns correspond to the two chain-adapted $Pnam(3a)$ modes, i.e. to the primary modes for a hypothetical symmetry break $Pnam > Pnam(3a)$.

4.2. Chain-adapted modes for an arbitrary group-subgroup chain

The generalization of the above-discussed procedure for the determination of the chain-adapted modes, for the case of an arbitrary group-subgroup chain, is straightforward:

(i) *Lattice of maximal subgroups.* Given a group-subgroup chain $G > H$, construct the lattice of maximal subgroups Z_i relating G and H (Fig. 1). The necessary data on maximal subgroups of space groups is partly available in IT95. A new volume of *International Tables for Crystallography*, supplementing Volume A on max-

imal subgroups of space groups, is in preparation† (*International Tables for Crystallography*, 1998, Vol. H, henceforth referred to as *ITH*).

(ii) *Splitting of Wyckoff positions.* Consider an occupied Wyckoff position $(WP)_G$ and determine its splitting scheme for a particular group-subgroup chain of maximal subgroups. The knowledge of the matrix (the so-called *transformation matrix*) relating the bases of the group Z_i and subgroup Z_{i+1} is of importance for the determination of the behavior of a Wyckoff position along a group-subgroup chain $Z_i > Z_{i+1}$. Such data are not available in *IT95*, but are given in *ITH*.

Determine the splitting schemes for all possible group-subgroup chains of the lattice of maximal subgroups $G > H$ and repeat the procedure for all occupied Wyckoff positions.

(iii) *Chain-adapted symmetry modes.* Consider a particular splitting scheme of a Wyckoff position (Fig. 2). Determine the (normalized) ϵ^H modes and apply the chain-adaptation procedure on the corresponding group-

† The complete data on maximal subgroups of space groups is available from the authors upon request.

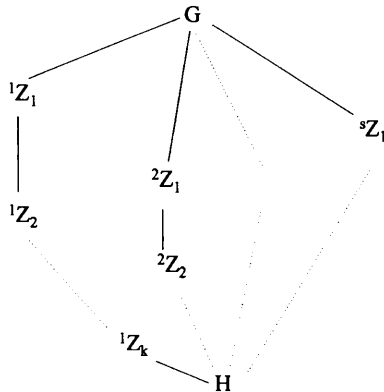


Fig. 1. Lattice of maximal subgroups for the group-subgroup chain $G > H$. The groups G and H are related by the subgroups kZ_i , where each of the intermediate subgroups kZ_i is a maximal subgroup of ${}^{k-1}Z_{i-1}$.

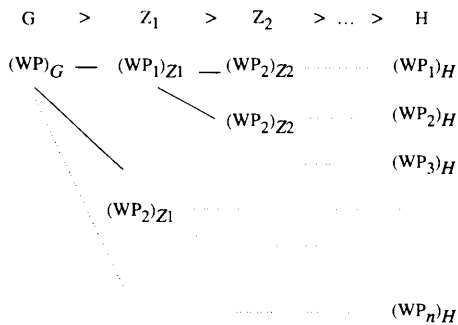


Fig. 2. Splitting of an occupied orbit belonging to a Wyckoff position $(WP)_G$ into $(WP)_H$ orbits following the chain $G > Z_1 > Z_2 > \dots > H$.

subgroup chain of maximal subgroups (Fig. 1): Starting from the ϵ^H modes and following up the group-subgroup chain, carry out a stepwise adaptation procedure, *i.e.* determine the adaptation matrix $X_{Z_i}^{Z_{i+1}}$ and apply (14) sequentially for each pair of subgroups $Z_{i+1} < Z_i$. The chain-adapted ξ_i^Z modes for a given group-subgroup change $G > H$ are obtained when this procedure is carried out along all possible chains of maximal subgroups comprising the subgroup lattice $G > H$ (Fig. 1). The possibility for a compatible adaptation of the ϵ^H modes along the different chains of maximal subgroups follows from the fact that the chain-adapted modes ξ_i^Z correspond either to different irreps of G or to different orthogonal subspaces within one irrep space.

5. Example

In the following, the example of potassium selenate K_2SeO_4 is discussed. The high-symmetry phase of potassium selenate K_2SeO_4 is orthorhombic with space group $Pnam$ (non-conventional setting of $Pnma$, No. 62). On cooling, the crystal undergoes a phase transition into a displacive incommensurate phase followed by a lock-in transition into a ferroelectric commensurate one of $Pna2_1$ symmetry characterized by a polar axis along c and a tripled a lattice constant (Iizumi, Axe, Shirane & Shimaoka, 1977; Perez-Mato, Gaztelua, Madariaga & Tello, 1986).

5.1. Lattice of maximal subgroups for $Pnam > Pna2_1(3a)$ (Fig. 3)

$Pna2_1(3a)$ is a general subgroup of $Pnam$ of index 6. The three antiphase domains of the low-symmetry phase correspond to the three conjugate subgroups $Pna2_1(3a)$, related by origin shifts. As it is seen from Fig. 3, there are two chains of maximal subgroups for each of the $Pna2_1(3a)$ subgroups: one over the *translationengleiche* subgroup $Pna2_1$ of index 2 and a second one over a *klassengleiche* subgroup $Pnam(3a)$ of index 3.

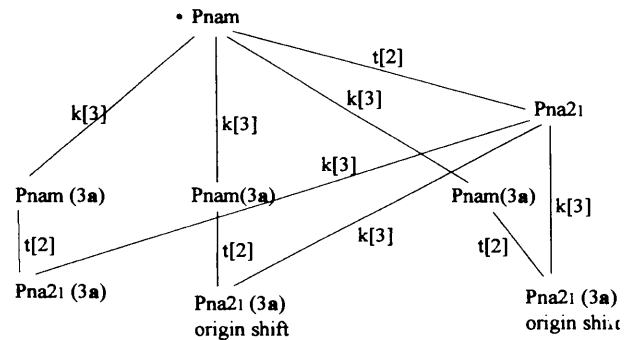


Fig. 3. Lattice of maximal subgroups for $Pnam > Pna2_1(3a)$. The symbols $k[3]$ and $t[2]$ indicate the type (k for *klassengleiche* and t for *translationengleiche*) and the index of the corresponding maximal subgroups.

Table 4. Chain-adapted z modes for $Pnam > Pna2_1(3a)$ (no origin shift)

Three consecutive cells along the x axis are considered. There is one $Pna2_1$ mode, and two $Pna2_1(3a)$ modes.

Atom label	z coordinates of 4(c) atoms			z symmetry modes					
	$Pnam$ basis	$Pna2_1$ basis	$Pna2_1(3a)$ basis	Identity			Chain-adapted modes		
				$Pna2_1(3a)$ modes			$Pna2_1$	$Pna2_1(3a)$	
1	1/4	z	z'	1	0	0	1	1	0
2	3/4	$z + 1/2$	$z'' + 1/2$	0	1	0	1	-1/2	1
3	3/4	$z + 1/2$	$z' + 1/2$	1	0	0	1	1	0
4	1/4	z	z''	0	0	1	1	-1/2	-1
1'	1/4	z	z'	0	1	0	1	-1/2	1
2'	3/4	$z + 1/2$	$z' + 1/2$	1	0	0	1	1	0
3'	3/4	$z + 1/2$	$z'' + 1/2$	0	0	1	1	-1/2	-1
4'	1/4	z	z'	1	0	0	1	1	0
1''	1/4	z	z''	0	0	1	1	-1/2	-1
2''	3/4	$z + 1/2$	$z'' + 1/2$	0	0	1	1	-1/2	-1
3''	3/4	$z + 1/2$	$z' + 1/2$	0	1	0	1	-1/2	1
4''	1/4	z	z'	0	1	0	1	-1/2	1
		Normalization factors		1/2	1/2	1/2	$(1/12)^{1/2}$	$(1/6)^{1/2}$	$(1/8)^{1/2}$

5.2. Splitting of Wyckoff positions

The high-temperature phase of K_2SeO_4 is described by Kalman, Stephens & Cruickshank (1970). The atoms either lie on a symmetry plane [4(c) Wyckoff position] or occupy the general 8(d) Wyckoff position.

The splitting of the 4(c) Wyckoff position for the two possible chains of maximal subgroups for $Pna2_1(3a)$ with no origin shift are given in Fig. 4. The diagrams of Wyckoff-position splitting (such as the one given in Fig. 4) are the same diagrams for the three conjugated subgroups of $Pna2_1(3a)$. However, it is very important to note that the distribution of the atoms of the $(WP)_G$ orbit into $(WP)_H$ orbits depends on the individual subgroup: it is different for the three $Pna2_1(3a)$ subgroups.

Consider the chain $Pnam > Pna2_1 > Pna2_1(3a)$. The 4(c) orbit of $Pnam$ does not split, but only its site symmetry is reduced [cf. Example 2, equation (15)]. In the transition to $Pna2_1(3a)$, the 4(a) orbit of $Pna2_1$ splits into three 4(a) orbits. The distribution of the 12 atoms in the unit cell of $Pna2_1(3a)$, with no origin shift, into the three orbits is easily seen after the transformation of the coordinates of the atoms by the same matrix \mathbf{P} as the one given in Example 3: atoms 1, 3, 2' and 4' form a representative set of the first 4(a) orbit ($x' = x/3$, $y' = y$, $z' = 1/4$), atoms 3, 1', 2'' and 4'' form the second one ($x'' = x/3 + 1/3$, $y'' = y$, $z'' = 1/4$) etc.

For the two subgroups $Pna2_1(3a)$ with origin shifts, the same transformation matrix \mathbf{P} can be used but in addition the new origins have to be taken into account: the relations between the conventional bases of $Pna2_1$ and each of the $Pna2_1(3a)$ subgroups are given by the column matrix pairs (\mathbf{P}, \mathbf{p}) , where \mathbf{p} are the columns

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 2 \\ 0 \\ 0 \end{pmatrix}.$$

For example, in the former case, the distribution of the atoms is as follows: atoms 1', 2', 3' and 4'' form the orbit

with $x' = x/3$; atoms 1'', 2', 3, 4 form the set for the orbit with $x'' = x/3 + 1/3$; and atoms 1, 2, 3'' and 4' form the set with $x''' = x/3 + 2/3$.

5.3. Chain-adapted symmetry modes for $Pnam > Pna2_1(3a)$

Owing to the splitting of the 4(c) Wyckoff position of $Pnam$ into three general positions of $Pna2_1(3a)$ (Fig. 4), there are nine symmetry modes compatible with the low-symmetry group, namely, three along \mathbf{a} , three along \mathbf{b} and three along \mathbf{c} .

According to the Wyckoff splitting schemes along the two chains (Fig. 4), there are three $Pna2_1(3a)$ z modes and one $Pna2_1$ z mode. The distribution of the 12 4(a) atoms in the unit cell of $Pna2_1(3a)$ among the three 4(a) orbits determines the corresponding $Pna2_1(3a)$ z modes, which are given in Table 4. The $Pna2_1$ z mode is obvious from the $Pnam > Pna2_1 > Pna2_1(3a)$ splitting in Fig. 4 [cf. also the corresponding z coordinates of the 4(c)

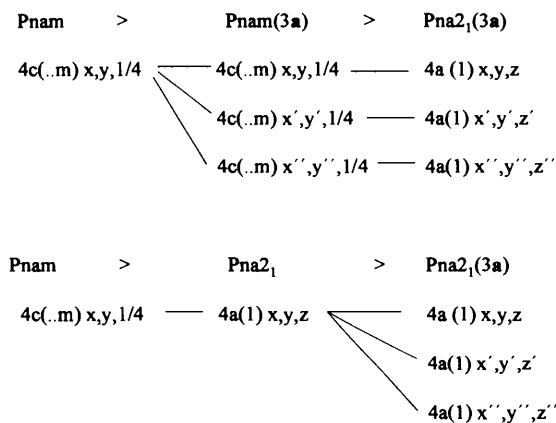


Fig. 4. Splitting of the 4(c) Wyckoff position for the two chains of maximal subgroups for $Pnam > Pna2_1(3a)$. Each Wyckoff position is specified by its multiplicity, Wyckoff letter, site symmetry group (in parentheses) and coordinates of a representative point.

Table 5. Chain-adapted z modes of 4(c) atoms for $Pnam > Pna2_1(3a)$ (origin shift 100)

Three consecutive cells along the a axis are considered. There are one $Pna2_1$ mode and two $Pna2_1(3a)$ modes.

Atom label	z coordinates of 4(c) atoms			z symmetry modes					
	$Pnam$ basis	$Pna2_1$ basis	$Pna2_1(3a)$ basis	Identity			Chain-adapted modes		
				$Pna2_1(3a)$ modes			$Pna2_1$	$Pna2_1(3a)$	
1	1/4	z	z'''	0	0	1	1	-1/2	-1
2	3/4	$z + 1/2$	$z''' + 1/2$	0	0	1	1	-1/2	-1
3	3/4	$z + 1/2$	$z'' + 1/2$	0	1	0	1	-1/2	1
4	1/4	z	z''	0	1	0	1	-1/2	1
1'	1/4	z	z	1	0	0	1	1	0
2'	3/4	$z + 1/2$	$z'' + 1/2$	0	1	0	1	-1/2	1
3'	3/4	$z + 1/2$	$z + 1/2$	1	0	0	1	1	0
4'	1/4	z	z'''	0	0	1	1	-1/2	-1
1''	1/4	z	z''	0	1	0	1	-1/2	1
2''	3/4	$z + 1/2$	$z + 1/2$	1	0	0	1	1	0
3''	3/4	$z + 1/2$	$z'' + 1/2$	0	0	1	1	-1/2	-1
4''	1/4	z	z	1	0	0	1	1	0
Normalization factors				1/2	1/2	1/2	$(1/12)^{1/2}$	$(1/6)^{1/2}$	$(1/8)^{1/2}$

Table 6. Chain-adapted x and y modes of 4(c) atoms for the symmetry break $Pnam > Pna2_1(3a)$ with no origin shift

The atoms of three consecutive cells along the x axis are considered. In both cases, there is one $Pnam$ mode and two $Pnam(3a)$ modes.

Atom label	$Pnam > Pna2_1(3a)$, no origin shift					
	Chain-adapted x modes			Chain-adapted y modes		
	$Pnam$	$Pnam(3a)$		$Pnam$	$Pnam(3a)$	
1	1	1	0	1	1	0
2	-1	1/2	-1	1	-1/2	1
3	-1	-1	0	-1	-1	0
4	1	-1/2	-1	-1	1/2	1
1'	1	-1/2	1	1	-1/2	1
2'	-1	-1	0	1	1	0
3'	-1	1/2	1	-1	1/2	1
4'	1	1	0	-1	-1	0
1''	1	-1/2	-1	1	-1/2	-1
2''	-1	1/2	1	1	-1/2	-1
3''	-1	1/2	-1	-1	1/2	-1
4''	1	-1/2	1	-1	1/2	-1
Factors	$(1/12)^{1/2}$	$(1/6)^{1/2}$	$(1/8)^{1/2}$	$(1/12)^{1/2}$	$(1/6)^{1/2}$	$(1/8)^{1/2}$

atoms given in Table 4]: all atoms should displace equally along z . This mode can be constructed as a linear combination of the three $Pna2_1(3a)$ modes. The resulting chain-adapted modes are listed in Table 4.

In Table 5, the chain-adapted z modes for $Pna2_1(3a)$ subgroup with an origin shift (1, 0, 0) are also listed. As expected, the modes show the same pattern, up to a cyclic permutation of the three consecutive cells of $Pnam$ along a .

In the case of the three x modes, it is sufficient to consider the chain $Pnam > Pnam(3a) > Pna2_1(3a)$. The three $Pna2_1(3a)$ modes are also invariant with respect to $Pnam(3a)$, *i.e.* the adaptation matrix can be chosen as the unit one for the $Pnam(3a) > Pna2_1(3a)$ chain step. Their further adaptation along the $Pnam > Pnam(3a)$ chain step gives one mode with $Pnam$ symmetry (*cf.* example 3, Table 3). Nothing new is learnt from the examination of the Wyckoff-position behavior for the chain $Pnam > Pna2_1 > Pna2_1(3a)$. The chain-adapted x modes for $Pnam > Pna2_1(3a)$ are given in Table 6.

The results for the three chain-adapted y modes are similar to the case of x modes: one is compatible with $Pnam$ symmetry and two are invariant with respect to $Pnam(3a)$. They are also listed in Table 6.

Therefore, the primary distortion for an orbit of 4(c) atoms is described by the two modes along the c axis listed in the last two columns of Table 4 and which are the only chain-adapted $Pna2_1(3a)$ modes.

5.4. Comparison with the conventional group-theoretical approach

The active irrep for the symmetry change $Pnam > Pna2_1(3a)$ is Σ_2 with the wave vector $\mathbf{q}_0 = 1/3a^*$ (Iizumi, Axe, Shirane & Shimaoka, 1977; Perez-Mato, Gaztelua, Madariaga & Tello, 1986), the order parameter being a complex amplitude: $Q = \rho \exp(i\theta)$. The space group $Pna2_1(3a)$ is the isotropy subgroup of the representation only for specific values of the order-parameter phase: $\theta = \pi/2 + n2\pi/6$.

Table 7. Polarization vectors of the Σ_2 modes for 4(c) atoms in a Pnam structure and the resulting chain-adapted $Pna2_1(3a)$ modes (last two columns) as obtained by the conventional group-theoretical approach (Perez-Mato, Gaztelua, Madariaga & Tello, 1986)

The cell index l has the values $l = 0, 1, 2$ for the three consecutive Pnam cells along the x axis; $a = \cos(2\pi x/3)$, $b = \sin(2\pi x/3)$, where x is the x coordinate of atom 1.

Atom label	$\epsilon_x(\kappa \Sigma_2, 1)$	$\epsilon_x(\kappa \Sigma_2, 2)$	$\theta_x(\kappa 1)$	$\theta_x(\kappa 2)$	$\cos[\mathbf{q}_0 \cdot \mathbf{r}(l, \kappa) + \pi/2 + \theta_x(\kappa 1)]$	$\cos[\mathbf{q}_0 \cdot \mathbf{r}(l, \kappa) + \pi/2 + \theta_x(\kappa 2)]$
1	1	i	0	$\pi/2$	$-a \sin(2\pi l/3) - b \cos(2\pi l/3)$	$-a \cos(2\pi l/3) + b \sin(2\pi l/3)$
2	1	$-i$	0	$3\pi/2$	$-a \sin(2\pi l/3 + 2\pi/6)$ $+ b \cos(2\pi l/3 + 2\pi/6)$	$a \cos(2\pi l/3 + 2\pi/6)$ $+ b \sin(2\pi l/3 + 2\pi/6)$
3	-1	i	π	$\pi/2$	$a \sin(2\pi l/3) - b \cos(2\pi l/3)$	$-a \cos(2\pi l/3) - b \sin(2\pi l/3)$
4	-1	$-i$	π	$3\pi/2$	$a \sin(2\pi l/3 + 2\pi/6)$ $+ b \cos(2\pi l/3 + 2\pi/6)$	$a \cos(2\pi l/3 + 2\pi/6)$ $- b \sin(2\pi l/3 + 2\pi/6)$

For the atoms in a 4(c) orbit, there are two independent modes of Σ_2 symmetry (Perez-Mato, Gaztelua, Madariaga & Tello, 1986). Their polarization vectors, $\epsilon_\alpha(\kappa|\Sigma_2, i)$, $i = 1, 2$, are listed in Table 7. According to (24) in Appendix A, the chain-adapted $Pna2_1(3a)$ modes derived above and listed in Table 4, which describe the primary distortion, can be related directly with the Σ_2 modes in the form:

$$\xi_\alpha^{Pna2_1(3a)}(\kappa, l|i) = C_N Q \epsilon_\alpha(\kappa|\Sigma_2, i) \exp[i\mathbf{q}_0 \cdot \mathbf{r}(l, \kappa)] + \text{c.c.} \quad (18)$$

Introducing one of the possible values for the order-parameter phase, say $\pi/2$, one can rewrite (18) as

$$\xi_\alpha^{Pna2_1(3a)}(\kappa, l|i) = C_N \rho |\epsilon_\alpha(\kappa|\Sigma_2, i)| \cos[\mathbf{q}_0 \cdot \mathbf{r}(l, \kappa) + \pi/2 + \theta_\alpha(\kappa|i)]. \quad (19)$$

Here, the component moduli $|\epsilon_\alpha(\kappa|\Sigma_2, i)|$ are all equal to one and $\theta_\alpha(\kappa|i)$ are the phases of the components of the mode polarization vectors. As seen from Table 7, the modes have non-zero components along \mathbf{c} only. Therefore, one can write:

$$\xi_z^{Pna2_1(3a)}(\kappa, l|i) \propto \cos[\mathbf{q}_0 \cdot \mathbf{r}(l, \kappa) + \pi/2 + \theta_z(\kappa|i)]. \quad (20)$$

The resulting chain-adapted $Pna2_1(3a)$ modes are given in the last two columns of Table 7. These two modes can be linearly combined in order to obtain the simpler ones listed in Table 8. The displacements of these modes for the 12 atoms in three consecutive cells coincide, as expected, with those listed in Table 4. The chain-adapted modes listed in Table 5 for the subgroup $Pna2_1(3a)$ with origin shift (1, 0, 0) correspond to another equivalent choice of the order-parameter phase in (18).

Apart from the two primary $Pna2_1(3a)$ modes analyzed above, Tables 4 and 6 contain all possible chain-adapted modes for the 4(c) orbits that have to be included in an expression like (1). It is interesting to identify them in terms of the conventional symmetry modes described by Perez-Mato, Gaztelua, Madariaga & Tello (1986). According to Tables 4 and 6, there are two Pnam modes (along \mathbf{a} and \mathbf{b}), one $Pna2_1$ mode along \mathbf{c}

Table 8. Chain-adapted $Pna2_1(3a)$ modes obtained by the conventional group-theoretical approach

Their form (which is obtained by a convenient linear combination of those of Table 7), facilitates the comparison with the modes listed in the last two columns of Table 4. The cell index l has the values $l = 0, 1, 2$ for the three consecutive Pnam cells along the x axis.

Atom label	$\xi_z^{Pna2_1(3a)}(\kappa, l 1)$	$\xi_z^{Pna2_1(3a)}(\kappa, l 2)$
1	$-\cos(2\pi l/3)$	$\sin(2\pi l/3)$
2	$\cos(2\pi l/3 + 2\pi/6)$	$\sin(2\pi l/3 + 2\pi/6)$
3	$-\cos(2\pi l/3)$	$-\sin(2\pi l/3)$
4	$\cos(2\pi l/3 + 2\pi/6)$	$-\sin(2\pi l/3 + 2\pi/6)$

and four Pnam(3a) modes (two along \mathbf{a} and two along \mathbf{b}). The Pnam and $Pna2_1$ modes are associated with irreps at the Brillouin-zone center and obviously represent directly modes of symmetry A_{1g} and B_{2u} as their isotropy groups correspond exactly to Pnam and $Pna2_1$. The Pnam(3a) modes must be associated with the irrep Σ_3 which is indeed the symmetry of two x models and two y modes. The relation between the Σ_3 modes, listed in Perez-Mato, Gaztelua, Madariaga & Tello (1986), and those given in Table 6 is given by an equation of the type (24) (see Appendix A) in a form analogous to the one described above for the primary Σ_2 modes.

6. Conclusions

Primary and secondary contributions present in a structural distortion resulting from a displacive phase transition can be identified and separated making use only of the information provided by *International Tables for Crystallography*. For any space group, the identity symmetry modes are directly deducible from the list of Wyckoff positions. This fact, together with the knowledge on the splitting of the Wyckoff orbits along the chains of maximal subgroups that connect the space groups of the two phases, can be systematically used for a symmetry analysis of the distortion. This analysis can in general identify the unstable (primary) component in the distortion that corresponds to the order parameter. The method is quite simple and does not require any use of the apparatus of representation theory.

APPENDIX A

In this Appendix, the relationship between the description of displacive distortions in terms of the chain-adapted (group-invariant) modes defined above and the conventional approach using modes transforming according to irreps of G is discussed. In the usual approach, the atomic displacements are decomposed into a sum of contributions of different symmetry modes:

$$u_\alpha(l, \kappa) = \sum_{\mathbf{q}^* \tau} \sum_j \sum_{\mathbf{q} \in \mathbf{q}^*} \sum_m C(\mathbf{q}\tau, m, j) \times \varepsilon_\alpha(\kappa|\mathbf{q}\tau, m, j) \exp[i\mathbf{q} \cdot \mathbf{r}(l, \kappa)], \quad (21)$$

where $\mathbf{r}(l, \kappa)$ is the position of atom (l, κ) in the reference structure of symmetry G and $\varepsilon_\alpha(\kappa|\mathbf{q}\tau, m, j)$ ($\alpha = x, y, z; \kappa = 1, \dots, s$) is the polarization vector of a particular symmetry mode with symmetry given by the irrep $\mathbf{D}^{\mathbf{q}^* \tau}$ of G and wavevector \mathbf{q} (belonging to the star of the representation, \mathbf{q}^*). The first sum in (21) refers to all irreps of G that are symmetry allowed in the structural distortion. The second sum [$j = 1, \dots, n(\mathbf{q}^* \tau)$] allows for the multiplicity of each irrep $\mathbf{D}^{\mathbf{q}^* \tau}$ in the decomposition of the vibration representation of the structure and the last two sums exhaust the dimension of each irrep, the first one running through the branches of the representation star, and the second ($m = 1, \dots, d_\tau; d_\tau = \text{dimension of } \tau$) through the components of the small representation τ . For multidimensional irreps, the symmetry-adapted coordinates $C(\mathbf{q}\tau, m, j)$, with (τ, j) fixed, may have some type of symmetry-forced relation among them in order to produce an H -invariant distortion.

For each orbit, the symmetry modes depend only on the type of Wyckoff positions associated with it. Therefore, similar to the main text, all expressions can be considered valid separately for each single orbit of atoms. Each orbit has in general different symmetry coordinates $C(\mathbf{q}\tau, m, j)$ but the symmetry modes are identical for orbits corresponding to the same Wyckoff positions.

Once obtained, the total distortion $u_\alpha(l, \kappa)$ from the experimental data and the relevant symmetry modes using group-theory tools, the values of the symmetry coordinates $C(\mathbf{q}\tau, m, j)$ are derived from (21) using the orthogonal properties of the symmetry modes (Perez-Mato, Gaztelua, Madariaga & Tello, 1986). The primary (order-parameter) distortion is associated with the mode or modes becoming unstable at the transition and its amplitude is described by the order-parameter components. It can be expressed in the form

$$u_\alpha^0(l, \kappa) = \sum_{\mathbf{q} \in \mathbf{q}_0^*} \sum_m Q(\mathbf{q}, m) \varepsilon_\alpha(\kappa|\mathbf{q}\tau_0, m) \exp[i\mathbf{q} \cdot \mathbf{r}(l, \kappa)], \quad (22)$$

where $\varepsilon_\alpha(\kappa|\mathbf{q}\tau_0, m)$ are the polarization vectors of the unstable degenerate normal modes and $Q(\mathbf{q}, m)$ the corresponding normal coordinates, *i.e.* the order-parameter components. On the other hand, the term in (21)

corresponding to the active irrep $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$ can also be identified with the *primary* distortion. Comparison of (21) and (22) shows that the *eigenvectors* $\varepsilon_\alpha(\kappa|\mathbf{q}\tau_0, m)$ of the primary distortion are determined by the values of the symmetry coordinates of the $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$ modes:

$$\varepsilon_\alpha(\kappa|\mathbf{q}\tau_0, m) = C_N \sum_j C(\mathbf{q}\tau_0, m, j) \varepsilon_\alpha(\kappa|\mathbf{q}\tau_0, m, j), \quad (23)$$

where C_N is a normalization constant.

According to the Landau description (Landau & Lifshitz, 1980), it should be expected that in (22) only the order-parameter components $Q(\mathbf{q}, m)$ are temperature dependent. Hence, the symmetry coordinates $C(\mathbf{q}\tau, m, j)$, for a fixed (\mathbf{q}, m) and for all orbits, must change with temperature in such a way that their relative values are maintained, keeping unchanged the *eigenvectors* described by (23). This is an important feature of the temperature variation of the structural distortion, implicit in the Landau description of a structural phase transition, and confirmed in several experimental cases (Perez-Mato, Gaztelua, Madariaga & Tello, 1986; Withers, Hua, Welberry & Vincent, 1988; Guelylah, Aroyo & Perez-Mato, 1996).

According to (21), (22) and (23), the H modes in (1) have a direct relationship with the $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$ modes. For instance, if the subspace, in the representation space of $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$, with isotropy group H , is one-dimensional (a rather common case, $d_H = 1$), the chain-adapted H modes $\xi_\alpha^H(\kappa, l|i)$ can be identified with:

$$\xi_\alpha^H(\kappa, l|i) = C_N \sum_{\mathbf{q} \in \mathbf{q}_0^*} \sum_m Q(\mathbf{q}, m) \times \varepsilon_\alpha(\kappa|\mathbf{q}\tau_0, m, i) \exp[i\mathbf{q} \cdot \mathbf{r}(l, \kappa)], \quad (24)$$

where C_N is again a suitable normalization constant and the multiplicity index i can be chosen the same on both sides of the equation. Thus, the H modes are symmetry-fixed linear combinations [described by the normal coordinates $Q(\mathbf{q}, m)$] of the $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$ symmetry modes. If, on the other hand, d_H is equal to the total dimension of $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$, then the set of chain-adapted H modes can be chosen in such a way that

$$\xi_\alpha^H(\kappa, l|j) = C_N \varepsilon_\alpha(\kappa|\mathbf{q}\tau_0, \mathbf{m}, \mathbf{i}) \exp[i\mathbf{q} \cdot \mathbf{r}(l, \kappa)] \quad (25)$$

and the multiplicity index j may be identified with the set of labels (\mathbf{q}, m, i) . Hence, in this particular case (which includes the rather common situation when the active irrep is one-dimensional), the chain-adapted H modes can be directly identified as the set of $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$ modes. In intermediate cases with $1 < d_H < d_{\mathbf{q}_0^* \tau_0}$, the H modes are particular (symmetry-fixed) linear combinations of the $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$ modes.

The case of the secondary distortion in (1), formed by the set of Z modes with Z being strictly a supergroup of H , is similar. Usually, in (21), each irrep $\mathbf{D}^{\mathbf{q}^* \tau}$, different from $\mathbf{D}^{\mathbf{q}_0^* \tau_0}$, has among its isotropy subgroups a single

supergroup of H and this supergroup does not coincide for different irreps. In this rather common case, each Z distortion can be identified with a particular irrep $D^{q\tau}$, and the corresponding Z modes are to be related with the $D^{q\tau}$ modes in a form analogous to the one explained above for the H modes.

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