Introduction to
Isotropy Subgroups and Displacive Phase Transitions

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This is an introduction to the concepts of isotropy subgroups and how they are applied to the description of displacive phase transitions. We try to use a physically intuitive approach here. We begin with atomic displacements in a crystal, then show how the application of symmetry leads to the concepts of irreducible representations and finally isotropy subgroups. This paper is divided into two parts, theory and examples. They should be read in parallel. The theoretical principles explained in part 1 are illustrated by examples in part 2.

Part 1. Theory

Space-Group Symmetry and Atomic Displacements

Consider a crystalline solid containing N atoms. Let $\vec{r}_i$ be the position of the ith atom. Let the space-group symmetry of the crystal be G. Operators in G have the form $g = \{R|\vec{v}\}$, a point operation R followed by a translation $\vec{v}$ so that $g\vec{r}_i = R\vec{r}_i + \vec{v}$. The operator g moves an atom from position $\vec{r}_i$ to position $\vec{r}_j = R\vec{r}_i + \vec{v}$. Since each operator in G leaves the crystal invariant, there must be an atom at $\vec{r}_j$ of the same type as the atom at $\vec{r}_i$.

Now let us consider atomic displacements. Let $\vec{u}_i$ be the displacement of the atom at $\vec{r}_i$. After the displacement, the position of the ith atom is $\vec{r}_i + \vec{u}_i$. When g operates on this new atomic position, we obtain $g(\vec{r}_i + \vec{u}_i) = \vec{r}_j + R\vec{u}_i$, where $\vec{r}_j = R\vec{r}_i + \vec{v}$ is the position of that atom after the operation. We see that the displacement of the atom at $\vec{r}_j$ after the operation is now $R\vec{u}_i$ which may or may not be equal to its displacement $\vec{u}_j$ before the operation of g.

Let us denote the displacements of all of the atoms in the crystal by a vector in a $3N$-dimensional space S. The $3N$ coordinates of the vector are given by $\{u_{i\alpha}\}$, where $\alpha = 1, 2, 3$ refer to the x, y, z coordinates of $\vec{u}_i$, respectively. Every possible set of atomic displacements in the crystal can be denoted by a vector in S. The operation of g on a vector in S causes a permutation of atomic positions as well as a rotation of the displacements, as described above.

Subspaces and Representations

Let ϕ be a vector in S. The vector ϕ denotes a particular set of atomic displacements in the crystal. If we operate on ϕ by every g in G, we obtain a collection of vectors $\{g\phi\}$

which spans an n-dimensional subspace S' of S. All linear combinations of these vectors belong to S'. Furthermore, S' is closed under all operations g in G, i.e., the operation of g on any vector in S' produces a vector also in S'.

Let us define a set of n basis vectors ϕ_i of S' such that any vector in S' can written as a linear combination of the basis vectors. An operation g on any one of the basis vectors results in some vector in S' which can, of course, be expressed as a linear combination of the basis vectors:

$$g\phi_i = \sum_{j=1}^{n} \phi_j D_{ji}(g), \tag{1}$$

where the n-dimensional matrix $D(g)$ is generally different for different operators g. From Eq. (1), it follows that $D(g_i)D(g_j) = D(g_ig_j)$ so that the matrices $D(g)$ have the same multiplication table as the operators g, and therefore the homomorphic mapping of g onto $D(g)$ is a group representation of G.

If we now choose some vector ϕ orthogonal to every vector in S', we can repeat the above procedure, obtaining a collection of vectors $\{g\phi\}$ which spans another subspace S'' of S. The subspaces S' and S'' do not overlap. Every vector in S'' is orthogonal to every vector in S'.

We repeat this process until S is completely decomposed into subspaces. The sum of the dimensions of these subspaces is equal to $3N$. The $3N$ basis vectors of these subspaces constitute a complete set of orthogonal basis vectors of S.

Irreducible Subspaces and Representations

Let us return to the n-dimensional subspace S'. Suppose that we can find some vector ϕ' in S' such that the vectors $\{g\phi'\}$ span a subspace of dimension less than n. In this case, the subspace S' is reducible and can be further decomposed into subspaces. The representation $D(g)$ is said to be reducible. Mathematically, this means that there exists a similarity transformation T such that $TD(g)T^{-1}$ is a block-diagonal matrix for every g in G.

We can repeatedly decompose every subspace into subspaces of smaller dimensions until they can be decomposed no further. These subspaces are irreducible. For each such subspace, we choose basis vectors and, through operations similar to those in Eq. (1), we obtain a set of matrices $D(g)$ called an irreducible representation (IR) of G. Every subspace is associated with an IR.

Some subspaces can be further decomposed into subspaces of smaller dimensions if we are allowed to consider complex vectors. In these cases, a complex transformation T is required to bring the matrices $D(g)$ into block-diagonal form. Since displacements in the physical world are real, we require the vectors and the representations to be real. We

say that this real representation is "physically irreducible". It is actually reducible under complex numbers and is equivalent to the direct sum of a complex IR and its complex conjugate. Real IRs are called type 1. A complex IR which is equivalent to its complex conjugate is called type 2. A complex IR which is not equivalent to its complex conjugate is called type 3. From this point, we will simply refer to all physically irreducible representations as IRs without distinction between actual type-1 real IRs and those containing type-2 and type-3 complex IRs.

Two subspaces are associated with the same IR if basis vectors can be chosen such the operations in Eq. (1) generate the same set of matrices $D(g)$. Mathematically, two IRs $D(g)$ and $D'(g)$ are equivalent if there exists a similarity transformation T such that $TD'(g)T^{-1} = D(g)$ for every g in G. We assume that we always choose basis vectors so that the resulting matrices $D(g)$ are identical in every subspace associated with the same IR.

Two vectors in different subspaces which are associated with nonequivalent IRs are always orthogonal to each other. Subspaces associated with equivalent IRs can be chosen so that vectors in one subspace are orthogonal to vectors in the other subspaces. Finally, if we choose the basis vectors of each subspace to be orthogonal to each other, the basis vectors of all of the irreducible subspaces of S together form a set of $3N$ orthogonal basis vectors of S. Any set of atomic displacements in the crystal can be written as a linear combination of these basis vectors.

Symmetry of Distortions

Consider a general vector ϕ in S. The vector ϕ denotes a set of atomic displacements and, in general, these displacements lower the space-group symmetry of the crystal. The new space-group symmetry G' is a subgroup of G and consists of all operators g in G which leave ϕ invariant, i.e., $g\phi = \phi$.

For the moment, let us confine our considerations to vectors contained in a single subspace S' associated with an IR which maps g onto $D(g)$. Every vector in S' lowers the symmetry of the crystal from G to some subgroup G'. (Actually, one of the IRs, the "identity" IR, maps every g onto 1 so that the vectors in S' do not lower the symmetry of the crystal, i.e., $G' = G$.) If we collect all of the distinct subgroups that we can obtain by considering every possible vector in S', we obtain a finite list of subgroups. If we consider these subgroups one at a time, the vectors in S' that lower the crystal symmetry to that subgroup symmetry define a subspace S'' of S'. Every vector in S'' is invariant under every operation g in the subgroup. Thus, the subgroup symmetries define a decomposition of S' into invariant subspaces (which are generally non-orthogonal), each of which contain vectors that are invariant under operations g in some subgroup of G. These subgroups are called isotropy subgroups belonging to the IR associated with S'.

Every vector in S' can be written as a linear combination of the basis vectors of S':

$$\phi = \sum_{i=1}^{n} \eta_i \phi_i. \tag{2}$$

Using Eq. (1), we obtain

$$g\phi = \sum_{j=1}^{n} \left(\sum_{i=1}^{n} D_{ji}(g)\eta_i \right) \phi_j. \tag{3}$$

From this result, we see that we can consider g to operate on the coefficients η_i rather than on the basis vectors ϕ_i:

$$g\eta_i = \sum_{j=1}^{n} D_{ij}(g)\eta_j. \tag{4}$$

We can also consider the coefficients η_i to be components of an n-dimensional vector $\vec{\eta}$ in "representation space". Space-group operations g in this space are carried out by the matrices $D(g)$, so that Eq. (4) is simply written as $g\vec{\eta} = D(g)\vec{\eta}$.

Now we can view the decomposition of S' by the isotropy subgroups as a decomposition of representation space. Given an isotropy subgroup G', the collection of all vectors $\vec{\eta}$ which satisfy $g\vec{\eta} = \vec{\eta}$ for all g in G' defines an invariant subspace of the representation space. This subspace is invariant under operators in G'. Some of the invariant subspaces of representation space may be one-dimensional, others two-dimensional, etc. One of the isotropy subgroups will define an n-dimensional subspace which includes the entire representation space. This subgroup is called the kernel of the IR and consists of all operators g which are mapped by the IR onto a unit matrix, i.e., $D(g)$ is a unit matrix so that $g\vec{\eta} = \vec{\eta}$ is satisfied for every vector $\vec{\eta}$ in the representation space.

Consider a particular isotropy subgroup G' determined by a vector $\vec{\eta}$. Operators g in G but not in G' generate isotropy subgroups $gG'g^{-1}$ which are determined by vectors $g\vec{\eta}$. These subgroups are equivalent to G'. In phase transitions, they represent different domains in the lower-symmetry phase. Lists of isotropy subgroups usually list only one representative from each group of equivalent subgroups.

Consider two different subspaces, S' and S'', associated with the same IR. Since space-group operations g in the representation spaces associated with S' and S'' are carried out by the identical IR matrices $D(g)$, the same vector $\vec{\eta}$ in either representation space results in the same subgroup symmetry. As a result, a given linear combination of basis vectors in S' has the same effect on the symmetry of the crystal as the same linear combination of basis vectors in S'', even though the actual atomic displacements represented by vectors in S' and S'' may be very different from each other. Furthermore, given an isotropy subgroup G', the collection of all vectors $\vec{\eta}$ which satisfies $g\vec{\eta} = \vec{\eta}$ for all g in G' defines the same subspace in either representation space.

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Let us summarize what we have done so far. In this treatment, we start with arbitrary sets of displacements, from which we generate subspaces, which we decompose into irreducible subspaces, from which we generate IRs of the space group. We used this approach in an attempt to give physical meaning to IRs. We do not actually use this approach in practice. It is much simpler to start with IRs. There exist well-known group-theoretical methods for generating all of the IRs of any given space group without reference to any atomic positions. Given an IR, we can form vectors $\vec{\eta}$ in representation space and determine the possible isotropy subgroups, again without reference to any atomic positions. Once we specify the atomic positions, we can then use straightforward group-theoretical techniques to generate all subspaces of S associated with the IR. (We may find none. In that case, this IR is not associated with any atomic displacements in the crystal.) We then use Eq. (2) to find the sets of atomic displacements that lower the symmetry of the crystal to that of the isotropy subgroup determined by $\vec{\eta}$.

Phase Transitions and Order Parameters

Now we consider a structural phase transition where some set of atomic displacements lowers the symmetry of the crystal from G to G'. We represent the atomic displacements as a vector ϕ in S. We can always decompose ϕ into a linear combination of basis vectors from subspaces of S. The contribution from each subspace can be written as a vector $\vec{\eta}$ in the representation space of the IR associated with the subspace. These vectors $\vec{\eta}$ are called order parameters of the phase transition and each define some isotropy subgroup of G. One order parameter is called "primary". It drives the phase transition and defines an isotropy subgroup with symmetry G', i.e., its action alone can lower the symmetry from G to G'. The other order parameters are called "secondary".

In practice, we can find the order parameters of a phase transition without reference to atomic positions. First, we generate a list of candidate IRs. (The generation of this list is based on a straightforward group-theoretical method which we will not describe here.) Second, for each candidate IR, we try to find an invariant subspace of representation space where the vectors $\vec{\eta}$ satisfy the equation $D(g)\vec{\eta} = \vec{\eta}$ for every operator g in G'. If we are successful, we then look for additional operators g in G but *not* in G' that also satisfy that equation. The collection of all operators that satisfy that equation constitutes an isotropy subgroup G'' associated with the IR. In general, G'' will be a supergroup of G'. As before, once we specify the atomic positions, we can use group-theoretical methods to generate all subspaces of S associated with the IR and hence the sets of atomic displacements belonging to that order parameter.

In the high-symmetry state of the crystal, all of the order parameters are zero. During the phase transition, the primary order parameter is driven to a nonzero value. Secondary order parameters also become nonzero due to coupling with the primary order parameter.

In some cases, none of the order parameters alone define a subgroup symmetry equal to G'. They all define subgroup symmetries which are supergroups of G'. In this case,

two or more order parameters are required to act simultaneously to lower the symmetry of the crystal to G'. We call them coupled order parameters, and together they are considered the primary order parameter of the phase transition.

Part 2. Examples

Symmetry operators and atomic positions. We begin with an example using a point group instead of a space group. Consider a two-dimensional object with point-group symmetry $G = 4$. The point group contains 4 operators: (1) E, the identity operator, (2) C_{2z}, 180° rotation about the z axis, (3) C_{4z}^+, 90° rotation about the z axis, and (4) C_{4z}^-, −90° rotation about the z axis. We will consider 4 atoms in this object, their positions being at $\vec{r}_1 = (p, 0)$, $\vec{r}_2 = (0, p)$, $\vec{r}_3 = (\bar{p}, 0)$, and $\vec{r}_4 = (0, \bar{p})$. The operators in G permute the positions of these atoms. For example, $C_{4z}^+ \vec{r}_1 = \vec{r}_2$.

Atomic displacements and vector space. We define a displacement $\vec{u}_i$ of the atom at $\vec{r}_i$. The coordinates of the atomic displacements of all 4 atoms define an 8-dimensional space S. Vectors in S have components $(u_{1x}, u_{1y}, u_{2x}, u_{2y}, u_{3x}, u_{3y}, u_{4x}, u_{4y})$. The operation of C_{4z}^+ on this vector gives us $(-u_{4y}, u_{4x}, -u_{1y}, u_{1x}, -u_{2y}, u_{2x}, -u_{3y}, u_{3x})$.

Subspace. Let us choose an arbitrary vector $\phi = (a, 0, 0, 0, 0, 0, 0, 0)$. The set of vectors $\{g\phi\}$ is given by
$\{(a, 0, 0, 0, 0, 0, 0, 0), (0, 0, 0, a, 0, 0, 0, 0), (0, 0, 0, 0, \bar{a}, 0, 0, 0), (0, 0, 0, 0, 0, 0, 0, \bar{a})\}$. These 4 vectors span a 4-dimensional subspace S' of S. However, S' is reducible.

Irreducible subspaces and representations. For example, the vector $\phi = (a, 0, 0, a, \bar{a}, 0, 0, \bar{a})$ is invariant under every operation in G. It spans a 1-dimensional irreducible subspace of S'. Since $g\phi = \phi$ for every g, we obtain the IR, $D(g) = 1$ for every g.

The vector $\phi = (a, 0, 0, \bar{a}, \bar{a}, 0, 0, a)$ also defines a 1-dimensional irreducible subspace where $D(E) = D(C_{2z}) = 1$ and $D(C_{4z}^+) = D(C_{4z}^-) = -1$.

Physically irreducible representation. The 2 vectors, $\phi_1 = (a, 0, 0, a, a, 0, 0, a)$ and $\phi_2 = (a, 0, 0, \bar{a}, a, 0, 0, \bar{a})$ define a 2-dimensional irreducible subspace. For example, $C_{4z}^+ \phi_1 = -\phi_2$. The IR matrices are given by

$$D(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad D(C_{2z}) = \begin{pmatrix} \bar{1} & 0 \\ 0 & \bar{1} \end{pmatrix}, \quad D(C_{4z}^+) = \begin{pmatrix} 0 & 1 \\ \bar{1} & 0 \end{pmatrix}, \quad D(C_{4z}^-) = \begin{pmatrix} 0 & \bar{1} \\ 1 & 0 \end{pmatrix}.$$

This subspace is actually reducible under complex numbers. If we allow complex displacements, the two vectors, $\phi_3 = \phi_1 + i\phi_2$ and $\phi_4 = \phi_1 - i\phi_2$ define irreducible 1-dimensional subspaces. For example, $C_{4z}^+ \phi_3 = i\phi_3$ and $C_{4z}^+ \phi_4 = -i\phi_4$. The 2-dimensional IR defined by the above matrices is physically irreducible.

Three-dimensional crystal. Now we consider a three-dimensional crystal, $BaTiO_3$, with space group symmetry $G = Pm\bar{3}m$. The unit cell is a cube of side a with the Ba atom at $\vec{r}_1 = (\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a)$, the Ti atom at $\vec{r}_2 = (0, 0, 0)$, and the O atoms at $\vec{r}_3 = (\frac{1}{2}a, 0, 0)$, $\vec{r}_4 = (0, \frac{1}{2}a, 0)$, and $\vec{r}_5 = (0, 0, \frac{1}{2}a)$.

Space group. The space group $G = Pm\bar{3}m$ contains 48 point operators with generators (1) C_{4z}^+, 90° rotation about the z axis, (2) C_{31}^+, 120° rotation about the [111] axis, and (3) I, the inversion which takes x, y, z to $\bar{x}, \bar{y}, \bar{z}$.

Irreducible representations. IRs of space groups are associated with k points in the first Brillouin zone. For each k point, we can generate a finite number of IRs. For example, the Γ point is at $\vec{k} = (0, 0, 0)$. There are 10 IRs associated with the Γ point: 4 of them are 1-dimensional (Γ_1^+, Γ_2^+, Γ_1^-, Γ_2^-), 2 of them are 2-dimensional (Γ_3^+, Γ_3^-), and 4 of them are 3-dimensional (Γ_4^+, Γ_5^+, Γ_4^-, Γ_5^-).

The IR Γ_4^- has direct physical meaning. It maps each operator onto the rotation matrix corresponding to the operator. The generators are given by

$$D(C_{4z}^+) = \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad D(C_{31}^+) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad D(I) = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.$$

Invariant subspaces of representation space. There are six non-equivalent invariant subspaces in the 3-dimensional representation space of Γ_4^-. They are defined by the vectors $\vec{\eta} = (a, 0, 0)$, $(a, a, 0)$, (a, a, a), $(a, b, 0)$, (a, a, b), (a, b, c), where a, b, c are arbitrary constants. The first 3 are 1-dimensional, the next 2 are 2-dimensional, and the last one is 3-dimensional and includes the entire representation space.

Isotropy subgroups. The isotropy subgroups which correspond to each of the subspaces contain the operators for which $D(g)\vec{\eta} = \vec{\eta}$. For example, if $\vec{\eta} = (a, 0, 0)$, there are eight matrices $D(g)$ which satisfy the equation, $D(g)\vec{\eta} = \vec{\eta}$:

$$D(g) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \pm 1 & 0 \\ 0 & 0 & \pm 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & \pm 1 \\ 0 & \pm 1 & 0 \end{pmatrix}.$$

The operators g that Γ_4^- maps onto these matrices are E, C_{4x}^+, C_{4x}^-, C_{2z}, σ_y, σ_z, σ_{dd}, and σ_{df}. Given these operators, we can identify the isotropy subgroup symmetry to be space-group $P4mm$. Similarly, we can identify the isotropy subgroups that correspond to the other invariant subspaces of representation space.

Subspaces of S. Now, let us consider subspaces of the $3N$-dimensional space S of atomic displacements. For the Γ-point IRs, all atomic displacements are the same in every unit cell, so we can designate the $3N$-dimensional vectors in S with the 15 components of the displacements $\{u_{i\alpha}\}$ for atoms in a single unit cell.

Only two of the Γ-point IRs, Γ_4^- and Γ_5^-, can generate subspaces of S. Since Γ_4^- and Γ_5^- are both 3-dimensional IRs, the subspaces are also 3-dimensional. The basis vectors of those belonging to Γ_4^- are (1) $\{u_{1x} = 1\}$, $\{u_{1y} = 1\}$, $\{u_{1z} = 1\}$, (2) $\{u_{2x} = 1\}$, $\{u_{2y} = 1\}$, $\{u_{2z} = 1\}$, (3) $\{u_{3x} = 1\}$, $\{u_{4y} = 1\}$, $\{u_{5z} = 1\}$, (4) $\{u_{4x} = u_{5x} = 1\}$, $\{u_{3y} = u_{5y} = 1\}$,

$\{u_{3z} = u_{4z} = 1\}$, where the subscript 1 refers to Ba, 2 refers to Ti, and 3,4,5 refers to O. The basis vectors of the subspace belonging to Γ_5^- are (1) $\{u_{4z} = -u_{3z} = 1\}$, $\{u_{5x} = -u_{4x} = 1\}$, $\{u_{3y} = -u_{5y} = 1\}$.

Sets of Distortions. We obtain distortions belonging to a particular isotropy subgroup by applying the vector $\vec{\eta}$ to the basis vectors of the subspaces of S. For example, the distortions associated with the isotropy subgroup $P4mm$ belonging to Γ_4^- are obtained by applying $\vec{\eta} = (a, 0, 0)$ to the three basis vectors of every subspace of S generated by Γ_4^-. In the case of $(a, 0, 0)$, these would be the first basis vector in each subspace: $\{u_{1x} = a_1\}$, $\{u_{2x} = a_2\}$, $\{u_{3x} = a_3\}$, $\{u_{4x} = u_{5x} = a_4\}$, where a_1, a_2, a_3, a_4 are independent arbitrary constants. Any one of these four distortions can lower the $Pm\bar{3}m$ symmetry of BaTiO$_3$ to $P4mm$.

As another example, consider $\vec{\eta} = (a, a, b)$. This represents a 2-dimensional invariant subspace of representation space. The isotropy subgroup symmetry determined by this $\vec{\eta}$ is the monoclinic space group Cm. Applying $\vec{\eta}$ to the basis vectors of the subspaces of S, we obtain the following 8 distortions belonging to Cm: $\{u_{1x} = u_{1y} = a_1\}$, $\{u_{1z} = b_1\}$, $\{u_{2x} = u_{2y} = a_2\}$, $\{u_{2z} = b_2\}$, (3) $\{u_{3x} = u_{4y} = a_3\}$, $\{u_{5z} = b_3\}$, (4) $\{u_{4x} = u_{5x} = u_{3y} = u_{5y} = a_4\}$, $\{u_{3z} = u_{4z} = b_4\}$, where $a_1, b_1, a_2, b_2, a_3, b_3, a_4, b_4$ are independent arbitrary constants. In order to lower the $Pm\bar{3}m$ symmetry of BaTiO$_3$ to Cm, however, at least one of a_1, a_2, a_3, a_4 and one of b_1, b_2, b_3, b_4 must be nonzero.

Phase transitions and order parameters. Consider a phase transition in BaTiO$_3$ from the cubic $Pm\bar{3}m$ structure to the monoclinic Cm structure discussed above. The primary order parameter is (a, a, b), belonging to the IR Γ_4^-. There is only one secondary order parameter which produces atomic displacements: $(0, a, \bar{a})$, belonging to the IR Γ_5^-. This order parameter generates the isotropy subgroup $Amm2$, which is a supergroup of Cm. There is only one distortion belonging to $Amm2$: $\{u_{5x} = -u_{4x} = -u_{3y} = u_{5y} = a\}$. In the phase transition, the 8 distortions associated with the primary order parameter and the distortion associated with the secondary order parameter will all appear. There are 9 independent distortions in all, equal to the number of free atomic position variables in the Cm structure.

Coupled order parameters. Suppose we couple the order parameter $(a, 0, 0)$ belonging to Γ_4^- with the order parameter $(0, a, 0)$ belonging to Γ_5^-. This means that we superimpose the distortions associated with those two order parameters. The order parameter $(a, 0, 0)$ belonging to Γ_4^- lowers the symmetry to $P4mm$, and the order parameter $(0, a, 0)$ belonging to Γ_5^- lowers the symmetry to $P\bar{4}m2$. Together, they lower the symmetry to $Pmm2$, which is a subgroup of both $P4mm$ and $P\bar{4}m2$. A phase transition from the $Pm\bar{3}m$ structure to this $Pmm2$ structure can only happen if the coupling between the two order parameters is strong enough so that both order parameters become nonzero simultaneously.

Bibliography

C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon, Oxford, 1972).
This book is a good source for the method of generating IRs of space groups.

S. C. Miller and W. F. Love, *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups* (Pruett, Boulder, 1967).
This is essentially the same as A. P. Cracknell, B. L. Davies, S. C. Miller, and W. F. Love, *Kronecker Product Tables*, Vol. 1 (Plenum, New York, 1979).
These two books contain tables of IRs of space groups.

H. T. Stokes and D. M. Hatch, "Coupled Order Parameters in the Landau Theory of Phase Transitions in Solids," *Phase Transitions* **34**, 53–67 (1991).
This paper explains in detail the concepts of primary and secondary order parameters and how they couple.

D. M. Hatch and H. T. Stokes, "The Complete Listing of Order Parameters for a Crystalline Phase Transition: A Solution to the Generalized Landau Problem." *Phys. Rev. B* **65**, 014113–1–4 (2002).
This paper explains the algorithm for finding all order parameters, given the change of symmetry at a phase transition.

H. T. Stokes, D. M. Hatch, and J. D. Wells, "Group-Theoretical Methods for Obtaining Distortions in Crystals: Applications to Vibrational Modes and Phase Transitions," *Phys. Rev. B* **43**, 11010–11018 (1991).
This paper presents an algorithm for generating sets of atomic displacements for a given IR.

H. T. Stokes and D. M. Hatch, *Isotropy Subgroups of the 230 Crystallographic Space Groups* (World Scientific, Singapore, 1988).
This book contains tables of isotropy subgroups and IR matrices.

stokes.byu.edu/isotropy.html. Internet URL for software packages, ISOTROPY and ISODISPLACE, which generate information about isotropy subgroup and related atomic displacements.

C. J. Howard and H. T. Stokes, "Group Theoretical Analysis of Octahedral Tilting in Perovskites," *Acta Cryst. B* **54**, 782–789 (1998). Erratum in *Acta Cryst. B* **58**, 565 (2002).

H. T. Stokes, E. H. Kisi, D. M. Hatch, and C. J. Howard, "Group Theoretical Analysis of Octahedral Tilting in Ferroelectric Perovskites." *Acta Cryst. B* **58**, 934–936 (2002).

C. J. Howard and H. T. Stokes, "Octahedral Tilting in Cation-Ordered Perovskites—a Group-Theoretical Analysis." *Acta Cryst. B* **60**, 674–684 (2004).

C. J. Howard and H. T. Stokes, "Structures and Phase Transitions in Perovskites—a Group-Theoretical Approach." *Acta Cryst. A* **61**, 93–111 (2005).

These four papers give good examples of using the ISOTROPY software to find symmetry changes in certain kinds of phase transitions.