Group-theoretical methods for obtaining distortions in crystals: Applications to vibrational modes and phase transitions

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We describe group-theoretical methods for projecting out global distortions in a crystal from distortions that are localized at a single site. We present a simple method for determining which sets of distortions are independent. We discuss and resolve the difficulties that arise when considering physically irreducible representations, which are reducible on the complex numbers. We illustrate these methods with examples. Applications of these methods to crystal vibrations and phase transitions are presented and illustrated with the BaTiO$_3$ structure.

**INTRODUCTION**

A crystal has the symmetry described by a space group. We define a distortion to be any change in the crystal which breaks this symmetry. Examples of distortions are (1) atomic displacements, such as in a lattice vibration or also in a displaceable phase transition, (2) changes in site occupation probabilities, such as in an order-disorder phase transition, and (3) changes in the directions of magnetic dipoles, such as in a spin wave or in a magnetic phase transition.

These distortions are “global.” They are distributed over the entire crystal. These distortions also have a microscopic characteristic. They can be broken down into individual “local” distortions. For example, a lattice vibration can be broken down into displacements of individual atoms. The displacement of an individual atom is a local distortion. The lattice vibration is a global distortion which consists of a large collection of these local distortions.

Distortions in a crystal are often classified by irreducible representations (IR’s) of the space group. In lattice vibrations, the IR’s classify the normal modes of oscillation. In phase transitions, the IR’s classify the order parameters.

Given a local distortion at a site in a crystal, group-theoretical methods can be used to obtain global distortions of which this local distortion is a part. In this paper, we show how this can be done in a systematic way. We also show how to resolve the difficulties that arise when considering physically irreducible representations, which are reducible on the real numbers but reducible on the complex numbers. We give examples that demonstrate how these methods can be applied.

**PROJECTION OF GLOBAL DISTORTIONS**

Consider a crystal with space-group symmetry $G$. Suppose we want to obtain global distortions classified by an IR $\Gamma^G$ of $G$. When we say that a distortion is classified by a particular IR of the space group, we mean that it can be broken into independent parts which transform like basis functions of the IR:

$$\theta(g)\psi^G_i(r) = \sum_{j=1}^{d^G} \psi_j^G(r)D^G(g)_{ij},$$

where $\psi_j^G(r)$ are basis functions of the IR, $g$ is an element of the space group, $D^G(g)$ is the $d^G$-dimensional matrix onto which the IR maps $g$, and $\theta(g)$ is an operation $g$ on the crystal. Elements of the space group are active operators (see pp. 47–50 in Ref. 1). They transform the crystal (via a rotation, reflection, translation, etc.) and leave the coordinate axes fixed. Functions $\psi_j^G(r)$ are “attached” to the crystal and move with it, so that

$$\theta(g)\psi_j^G(r) = \psi_j^G(g^{-1}r).$$

To obtain the possible global distortions of a certain type, we consider all possible local distortions of that type. For example, if the global distortion is to be a lattice vibration or a displaceable phase transition, we consider possible displacements for each of the atoms in the unit cell. Let $r_0$ be a site of a local distortion. The elements of the space group which leave $r_0$ fixed form a point group $H$. Just as global distortions can be classified by IR’s of the space-group $G$, local distortions can be classified by IR’s of the local point-group $H$. These local distortions at $r_0$ can be broken into parts which transform like basis functions of the point group IR:

$$\theta(h)\psi^H_i(r) = \sum_{j=1}^{d^H} \psi_j^H(r)D^H(h)_{ij},$$

where $\psi_j^H(r)$ are basis functions of the point-group IR, $h$ is an element of the point-group $H$, and $D^H(h)$ is the $d^H$-dimensional matrix onto which the IR maps $h$. All the $d^H$ functions $\psi_j^H(r)$ are associated with the same point $r_0$.

We must consider each point-group IR which classifies the type of local distortion we need. For example, if the global distortion is to be a lattice vibration or a displaceable phase transition, we consider “vector IR” of the point group. These are the IR’s whose basis functions transform like components of vectors, representing atomic displacements.

Let the basis functions $\psi^H_i(r)$ of the point-group IR $\Gamma^H$ be local distortions at the site $r_0$, and let the basis func-
ations \( \psi_i^G(r) \) of the space-group IR \( \Gamma^G \) be global distortions. We use the well-known projection operator technique (see pp. 54–56 in Ref. 1) to obtain the global distortions in terms of the local distortions:

\[
\psi_i^G(r) = \sum_{g \in G} D^G(g)^i_j \theta(g) \psi_i^G(r).
\]

(4)

We have omitted the usual multiplicative constant in front of the summation. Note that the global distortions are projected out from a single local distortion. We can use any one of the basis functions \( \psi_i^G(r) \) to obtain all possible global distortions. Here, we arbitrarily choose the first basis function \( \psi_1^G(r) \). Also note that in Eq. (4), the index \( i \) is arbitrarily chosen. For each value of \( i \), Eq. (4) produces a set of \( d^G \) global distortions that transform like the \( d^G \) basis functions of \( \Gamma^G \).

The expression in Eq. (4) can be cast in a more useful form if we break the space-group \( G \) into cosets with respect to the point-group \( H \).

\[
G = \sum_m g_m H.
\]

(5)

The first coset representative \( g_1 \) is chosen to be the identity operator. The others are chosen arbitrarily from each coset.

Equation (4) now becomes

\[
\psi_i^G(r) = \sum_m \theta(g_m) \psi_i^{G_m}(r),
\]

(6)

where

\[
\psi_i^{G_m}(r) = \sum_{i=1}^{d^G} D^G(g_m)^i_j \psi_i^G(r),
\]

(7)

\[
\psi_i^{G_m}(r) = \sum_{k=1}^{d^H} \alpha_{i/k}^m \psi_i^{G_m}(r),
\]

(8)

\[
\alpha_{i/k}^m = \sum_{h \in H} D^G(h)^i_j D^H(h^k_1).
\]

(9)

Equation (6) breaks the global distortion into a sum over local distortions at sites \( g_1 r_0, g_2 r_0, g_3 r_0, \ldots \). The function \( \psi_i^{G_m}(r) \) is a local distortion centered at \( r_0 \). (The local distortions at different sites are assumed to be independent.) The operation \( \theta(g_m) \) transforms the crystal, carrying the local distortion with it. Therefore, the function \( \theta(g_m) \psi_i^{G_m}(r) \) is a local distortion at site \( g_m r_0 \).

**INDEPENDENT SETS OF DISTORTIONS**

An index \( j \) appears in Eqs. (6)–(9). For each value of \( j \), a set of global distortions \( \psi_i^G(r) \) is generated. For some values of \( j \) it may happen that the functions \( \psi_i^G(r) \) are all zero. Furthermore, the nonzero sets of functions generated using different values of \( j \) may not all be linearly independent. We need some criteria for determining which values of \( j \) generate linearly independent sets of global basis functions.

Suppose that we have generated some sets of basis functions that are linearly independent. We label these \( \psi_i^{G_j} \). We then try another value of \( j \) and generate another set of basis functions \( \psi_i^{G_{j'}} \). This new set is linearly dependent on the previous sets if there exists a set of coefficients \( A_{i/k}^{j'} \) (at least one of them nonzero) such that

\[
\psi_i^{G_{j'}} = \sum_{j', k} A_{i/k}^{j'} \psi_i^{G_j}.
\]

(10)

If we apply the operation \( \theta(g) \) to both sides of this equation, we obtain

\[
\sum_{j', k} A_{i/k}^{j'} D^G(g)_{i/j} \psi_i^{G_j} = \sum_{j', k} A_{i/k}^{j'} D^G(g)_{i/k} \psi_i^{G_{j'}}.
\]

(11)

Since \( \psi_i^{G_j} \) are independent functions, their coefficients must be separately equal to each other in the above equation. This leads to the matrix equation,

\[
A_{i/k}^{j'} D^G(g)_{i/j} = D^G(g)_{i/k} A_{i/k}^{j'}.
\]

(12)

Since this must hold for any choice of operator \( \theta(g) \), \( g \in G \), we have from Schur’s lemma (see Theorem 1.3.7 on p. 19 in Ref. 1) that the matrix \( A_{i/k}^{j'} \) must be a constant times the unit matrix:

\[
A_{i/k}^{j'} = \lambda_{i/k} \delta_{i/k},
\]

(13)

where \( \lambda_{i/k} \) is some constant which may be different for various values of \( j' \). Putting this back into Eq. (10), we obtain

\[
\psi_i^{G_{j'}} = \sum_{j'} \lambda_{i/k} \psi_i^{G_j}.
\]

(14)

This means that the only way the new set of basis functions can be linearly dependent on the previous sets is for \( \psi_i^{G_{j'}} \) to be some linear combination of \( \psi_i^{G_1}, \psi_i^{G_2}, \ldots \), and for \( \psi_i^{G_j} \) to be the same linear combination of \( \psi_i^{G_1}, \psi_i^{G_2}, \ldots \), and for \( \psi_i^{G_{j'}} \) to be the same linear combination of \( \psi_i^{G_1}, \psi_i^{G_2}, \ldots \), etc.

From Eqs. (6)–(8), we find that Eq. (14) is exactly equivalent to

\[
\alpha_{i/k}^{j'} = \sum_{j'} \lambda_{i/k} \alpha_{i/k}^{j}.
\]

(15)

Equation (14) implies Eq. (15), and Eq. (15) implies Eq. (14). Thus if there exists a set of coefficients \( \lambda_{i/k} \) (at least one of them nonzero) which satisfies Eq. (15) for all values of \( i \) and \( k \), then the set of functions \( \psi_i^{G_{j'}} \) is not linearly independent from the previous sets of functions \( \psi_i^{G_j} \). Conversely, if there exists no solution to Eq. (15) except all \( \alpha_{i/k}^{j'} = 0 \), then the set of functions \( \psi_i^{G_{j'}} \) is linearly independent from the previous sets of functions \( \psi_i^{G_j} \).

If we form for each set \( j \) the \( d^G \times d^H \)-dimensional vector,

\[
\alpha^{j'} = [\alpha_{1,i}, \alpha_{2,i}, \ldots, \alpha_{1,j_{1}^{i}}, \alpha_{2,j_{2}^{i}}, \ldots, \alpha_{1,j_{d}^{i}}, \ldots, \alpha_{d,j_{d}^{i}}],
\]

(16)

then the test for independence of sets of basis functions simply becomes a test for linear independence of the vectors \( \alpha^{j} \).

This result is actually quite remarkable. The coefficients \( \alpha_{i,k}^{j} \) directly specify only the part of the global distortion which occurs at site \( r_0 \). We have thus shown that the independence of global distortions can be unambiguously determined from the independence of the part of those distortions that occur at the single site \( r_0 \).
PHYSICALLY IRREDUCIBLE REPRESENTATIONS

Physical distortions in a crystal must be described by real functions. This requires the matrices of the space-group representation to be real. If a space-group IR is complex, we form a physically irreducible representation from the direct sum of the IR with its complex conjugate. Such a representation can always be brought to real form using a similarity transformation. This representation is reducible with respect to complex numbers but irreducible with respect to real numbers.

We can obtain global distortions in this case using equations similar to Eqs. (6)–(9):

$$\psi_{i,m,\text{phys}}^G(r) = \sum_m \theta(g_m) \psi_{i,m,\text{phys}}^G(r),$$  \hspace{1cm} (17)

where

$$\psi_{i,\text{phys}}^G(r) = \sum_{i'} \sum_{i'=1}^{H} D_{i'i'}^G(g_{m}) \psi_{i',\text{phys}}^G(r),$$  \hspace{1cm} (18)

$$\psi_{i',\text{phys}}^G(r) = \sum_{k} \sum_{k'=1}^{H} \alpha_{k',k\text{phys}}^G r_k h_{k'}(r),$$  \hspace{1cm} (19)

$$\alpha_{k',k\text{phys}}^G = \sum_{h \in H} D_{i'i'}^G(h) r_k h_{k'}(h).$$  \hspace{1cm} (20)

In the above equations, $D_{i'i'}^G$ are matrices of the physically irreducible representation. The complex conjugation has been dropped since elements of $D_{i'i'}^G$ are real, i.e., we use the physically irreducible representations in their real form.

The method described in the previous section for determining the independent sets of distortions cannot be directly applied to the distortions $\psi_{i,\text{phys}}^G$ obtained here. In this case, Eq. (13) does not follow from Eq. (12), since Schur’s lemma is only valid for true irreducible representations.

The solution to this difficulty is straightforward. We use basis functions of true IR’s when testing for independence of sets.\(^2\) We thus need to transform the basis functions $\psi_{i,\text{phys}}^G$ obtained from Eqs. (17)–(20) into sets of basis functions which belong to true IR’s. To do this, we need a matrix $S$ which transforms the representation into block diagonal form.

Let us first consider IR’s of type 3, where the IR is not equivalent to its complex conjugate and the characters are complex (see p. 20 in Ref. 1). For this case, we want

$$S^{-1}D_{i'i'}^G(g)S = \begin{bmatrix} D_{i'i'}^G(g) & 0 \\ 0 & D_{i'i'}^G(g)^* \end{bmatrix},$$  \hspace{1cm} (21)

The basis functions of $\Gamma^G$ are

$$\psi_{i'}^G(r) = \sum_{i'=1}^{d_{i'}} \psi_{i',\text{phys}}^G(r)S_{i',i}^G,$$  \hspace{1cm} (22)

and the basis functions of $\Gamma^{G\ast}$ (the complex conjugate of $\Gamma^G$) are

$$\psi_{i'}^{G\ast}(r) = \sum_{i'=1}^{d_{i'}} \psi_{i',\text{phys}}^G(r)S_{i',i}^G + d_{i'}^G.$$  \hspace{1cm} (23)

In both cases, $i = 1, 2, \ldots, d_{i'}^G$, where $d_{i'}^G = \frac{1}{2}d_{i'}^G$. To test for independence, we form the $d_{i'}^G \times d_{i'}^G$-dimensional vector $\alpha^G$ as in Eq. (16) using the components,

$$\alpha_{i'i'}^G = \sum_{i'=1}^{d_{i'}} \alpha_{i',k,\text{phys}}^G S_{i',i}^G,$$  \hspace{1cm} (24)

and then proceed as in the previous section. Note that we do not need to consider the sets of basis functions of $\Gamma^{G\ast}$. Testing the independence of the sets of basis functions of $\Gamma^G$ also automatically tests the independence of the sets of basis functions of $\Gamma^{G\ast}$.

Let us next consider IR’s of type 2, where the IR is equivalent to its complex conjugate and the characters are real (see p. 20 in Ref. 1). For this case, we want

$$S^{-1}D_{i'i'}^G(g)S = \begin{bmatrix} D_{i'i'}^G(g) & 0 \\ 0 & D_{i'i'}^G(g) \end{bmatrix}. $$  \hspace{1cm} (25)

We require here that both $d_{i'}^G$-dimensional matrices $D_{i'i'}^G(g)$ be identical, element by element, in the block diagonal matrix. One set of basis functions of $\Gamma^G$ are

$$\psi_{i'}^G(r) = \sum_{i'=1}^{d_{i'}} \psi_{i',\text{phys}}^G(r)S_{i',i}$$  \hspace{1cm} (26)

and a second set of basis functions of $\Gamma^G$ are

$$\psi_{i'}^G(r) = \sum_{i'=1}^{d_{i'}} \psi_{i',\text{phys}}^G(r)S_{i',i} + d_{i'}^G.$$  \hspace{1cm} (27)

Both of these sets are independent and must be both used in testing independence from other sets. We thus form two $d_{i'}^G \times d_{i'}^G$-dimensional vectors, $\alpha^G$ and $\bar{\alpha}^G$, as in Eq. (16) using for one vector the components,

$$\alpha_{i'i'}^G = \sum_{i'=1}^{d_{i'}} \alpha_{i',k,\text{phys}}^G S_{i',i}^G,$$  \hspace{1cm} (28)

and for the other vector the components,

$$\bar{\alpha}_{i'i'}^G = \sum_{i'=1}^{d_{i'}} \alpha_{i',k,\text{phys}}^G S_{i',i}^G + d_{i'}^G.$$  \hspace{1cm} (29)

There is also the possibility that the IR $\Gamma^H$ of the point-group $H$ may be complex. In this case, we form physically irreducible IR’s $\Gamma^H_{\text{phys}}$ with matrices $D_{\text{phys}}^H$ which we use instead of $D_{\text{phys}}^H$ in Eqs. (17)–(20). All other results in the preceding discussion remain the same.

NUMBER OF INDEPENDENT SETS OF DISTORTIONS

The number of independent sets of distortions that can be obtained by using different values of $j$ in Eqs. (6)–(9) is exactly equal to the number of times the point-group IR $\Gamma^j$ appears in $\Gamma^{G\ast}$. The representation of $H$ subduced by the space-group IR $\Gamma^G$, formed by restricting the matrices of $\Gamma^G$ to elements of $H$. The number of independent sets can thus be calculated from

$$n = \frac{1}{|H|} \sum_{h \in H} \chi^G(h)^* \chi^G(h^*),$$  \hspace{1cm} (30)
where \(|H|\) is the number of elements in \(H\), and \(\chi^G\) and \(\chi^H\) are characters of the matrices in the IR's \(\Gamma^G\) and \(\Gamma^H\), respectively. Tables of these subduction frequencies may be found in Refs. 5 and 6.

The cases for reducible representations which are physically irreducible must be considered separately. For type 3 IR's, the number of independent sets is given by

\[
n = \frac{1}{2} \frac{1}{|H|} \sum_{h \in H} \chi^G_{\text{phys}}(h)^* \chi^H(h),
\]

(31)

and for type 2 IR's, the number of independent sets is given by

\[
n = \frac{1}{4} \frac{1}{|H|} \sum_{h \in H} \chi^G_{\text{phys}}(h)^* \chi^H(h).
\]

(32)

These results can be easily understood. For type 3 IR's, the \(n\) independent sets of \(2d^G\) basis functions of \(\Gamma^G_{\text{phys}}\) are constructed from \(n\) independent sets of \(d^H\) basis functions of \(\Gamma^H\) and \(n\) independent sets of \(d^G\) basis functions of \(\Gamma^G\). Since \(\Gamma^G_{\text{phys}}\) contains \(\Gamma^G\) once and \(\Gamma^G\) once, the summation in Eq. (31) gives us \(n\) for each of these IR's, and therefore we must multiply the weighted character sum by \(\frac{1}{2}\) to obtain \(n\).

For type 2 IR's, the \(n\) independent sets of \(2d^G\) basis functions of \(\Gamma^G_{\text{phys}}\) are constructed from \(2n\) independent sets of \(d^G\) basis functions of \(\Gamma^H\). Since \(\Gamma^G_{\text{phys}}\) contains \(\Gamma^G\) twice, the summation in Eq. (31) gives us \(2n\) twice, and therefore we must multiply the weighted character sum by \(\frac{1}{4}\) to obtain \(n\).

When the point-group representation is reducible but physically irreducible, we can simply substitute \(\chi^H_{\text{phys}}\) for \(\chi^H\) in Eqs. (30)–(32) without any further changes. All of the complex IR's that occur for crystallographic point groups are type 3. Thus, in Eq. (30), for example, the summation gives us the number of independent sets of functions that can be constructed from basis functions of \(\Gamma^H\) plus the number of independent sets of functions that can be constructed from basis functions of \(\Gamma^{H*}\). Since the basis functions of \(\Gamma^H\) and the basis functions of \(\Gamma^{H*}\) are independent from each other for a type 3 IR, the summation correctly gives us the total number of independent sets of functions that can be constructed from basis functions of \(\Gamma^H_{\text{phys}}\). Similar considerations also apply to Eqs. (31) and (32).

**EXAMPLES**

We now present some examples which demonstrate the principles and methods described above. In these examples, the labels of space-group IR's are from Ref. 7. The choices of matrices for these IR's are from Ref. 8. The labels of point-group IR's are from Ref. 1.

**Example 1**

Consider space group No. 22 \(F222\), space-group IR \(\Gamma^G = L_1\) (four-dimensional), site \(r_0 = (x,0,0,0)\) (Wyckoff position \(e\)), point-group \(H = 2\), and point-group IR \(\Gamma^H = A\). The elements of the point-group \(H\) are \(x, y, z\) and \(x, y, z\). The matrices onto which \(\Gamma^H\) and \(\Gamma^G\) map \(x, y, z\) are

\[
D^H(x, y, z) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\]

(33)

From Eq. (30), we find that there are \(n = 2\) independent sets of basis functions. From Eq. (9), we calculate the components of the vectors \(\alpha_j\):

\[
\begin{align*}
\alpha_1 &= (1,0,1,0), \\
\alpha_2 &= (0,1,0,1), \\
\alpha_3 &= (1,0,1,0), \\
\alpha_4 &= (0,1,0,1).
\end{align*}
\]

(34)

We see that only two of these vectors are independent, and we choose \(j = 1\) and \(j = 2\) for generating the two independent sets of basis functions. From Eqs. (6)–(9), we obtain

\[
\begin{align*}
\psi_1^G &= \theta(g_1) \psi^H - \psi^H - \theta(g_2) \psi^H + \psi^H + \cdots, \\
\psi_2^G &= \theta(g_2) \psi^H - \theta(g_4) \psi^H + \theta(g_6) \psi^H + \cdots, \\
\psi_3^G &= \theta(g_1) \psi^H + \theta(g_3) \psi^H + \theta(g_5) \psi^H + \cdots, \\
\psi_4^G &= \theta(g_3) \psi^H + \theta(g_4) \psi^H - \theta(g_6) \psi^H + \cdots. \\
\psi_5^G &= \theta(g_2) \psi^H - \theta(g_4) \psi^H + \theta(g_6) \psi^H + \cdots, \\
\psi_6^G &= \theta(g_1) \psi^H - \theta(g_3) \psi^H + \theta(g_5) \psi^H + \cdots, \\
\psi_7^G &= \theta(g_3) \psi^H + \theta(g_4) \psi^H + \theta(g_6) \psi^H + \cdots, \\
\psi_8^G &= \theta(g_1) \psi^H + \theta(g_2) \psi^H - \theta(g_5) \psi^H + \cdots.
\end{align*}
\]

(35)

Note that we have removed a common factor from each of these equations in Eqs. (34) and (35). We have carried these calculations out to six different sites so that it can be seen explicitly that each of the above eight functions are linearly independent of each other. In Table I, we give the six coset representatives \(g_i\), the sites \(g_i r_0\), and the IR matrices \(D^G(g_i)\). Note that global distortions do not contain a contribution from local distortions at every site \(g_i r_0\). For example, the global distortion \(\psi_1^G\) has contributions from the local distortions at \(g_1 r_0, g_3 r_0, g_5 r_0\) but no contribution from \(g_2 r_0, g_4 r_0, g_6 r_0\).

Let us extend this example further by considering a particular type of local distortion: atomic displacements. We see from Eq. (33) that the \(x\) component of a vector transforms like the basis function of the point-group IR. Thus, the local distortion \(\psi^H_i\) can be an atomic displacement in the \(x\) direction. Substituting this into Eqs. (35), we find that the global distortion \(\psi_1^G\) consists of a displacement of the atom at \(g_1 r_0\) in the \(x\) direction, a displacement of the atom at \(g_3 r_0\) in the \(-x\) direction, a displacement of the atom at \(g_5 r_0\) in the \(-x\) direction, etc. The global distortion \(\psi_2^G\) consists of a displacement of the atom at \(g_2 r_0\) in the \(-x\) direction, a displacement of the atom at \(g_4 r_0\) in the \(-x\) direction, etc. Note that the operations \(\theta(g_m)\) in Eqs. (35) not only move the local distortion to the site \(g_m r_0\) but may also reorient the distortion. For example, consider the term \(-\theta(g_4)\psi^H_i\) in the
expression for $\psi^G_2$. The function $-\psi^H$ represents a
displacement of the atom at $r_0=(x,0,0)$ in the $-x$ direction.
When $\theta(g_4)$ operates on this, the displaced atom is now
$g_4 r_0=(\bar{x}+\frac{1}{2},\frac{1}{2},0)$, and, since $g_4=\bar{x}+\frac{1}{2}, y+\frac{1}{2}, z$, the
operation also reorients the atomic displacement from the
$-x$ direction to the $x$ direction.

Example 2

Consider space group No. 52 Pnna, space-group IR
$\Gamma^G=S_1$ (two dimensional), site $r_0=(0,0,0)$ (Wyckoff position
$a$), point-group $H=1$, and point-group IR $\Gamma^H=A_2$.

The elements of the point-group $H$ are $x, y, z, x, y, z$.
The space-group IR $S_1$ is type 3. Its complex conjugate
is IR $S_2$. We form the physically irreducible representation $\Gamma^G$
via an appropriately chosen similarity transformation on the
direct sum of $S_1$ and $S_2$ so that the resulting
four-dimensional matrices are real. We denote this
physically irreducible representation by $S_1 S_2$.

The matrices onto which $\Gamma^H$ and $\Gamma^G$ maps $x, y, z$ are

$$D^H(x, y, z) = (-1),$$

$$D^G_{\text{phys}}(x, y, z) = \begin{pmatrix}
0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0 \\
1 & 0 & 0 & 0
\end{pmatrix}. \quad (36)$$

The transformation matrix that brings these matrices
back to block diagonal form is

$$S = \frac{1}{2} \begin{pmatrix}
1+i & 0 & 1-i & 0 \\
-1+i & 0 & -1-i & 0 \\
0 & 1+i & 0 & 1-i \\
0 & 1-i & 0 & 1+i
\end{pmatrix}. \quad (37)$$

From Eq. (31), we find that there is $n=1$ independent set
of basis functions. If we form the vectors $\alpha_j^x$ we obtain

$$\alpha^x_1 = (1,0,0,-1), \quad \alpha^x_2 = (0,1,-1,0),$$

$$\alpha^x_3 = (0,-1,1,0), \quad \alpha^x_4 = (-1,0,0,1). \quad (38)$$

The first two vectors seem to be independent of each oth-
er, and this demonstrates how the method fails for reduc-
tible representations. We must form instead the $\alpha_j^x$
for IR $S_1$ using Eq. (24), and we obtain

$$\alpha^x_1 = \frac{1}{2} (1+i, -1+i), \quad \alpha^x_2 = \frac{1}{2} (-1+i, 1-i),$$

$$\alpha^x_3 = \frac{1}{2} (1-i, 1+i), \quad \alpha^x_4 = \frac{1}{2} (-1-i, 1-i). \quad (39)$$

Each of these vectors is a multiple of the vector $(1, i)$, so
that only one of these vectors is linearly independent. We
choose $j=1$ for generating the set of basis functions.

From Eqs. (17)–(20), we obtain

$$\psi^G_{1,\text{phys}} = \theta(g_1) \psi^H + \theta(g_2) \psi^H + \cdots,$$

$$\psi^G_{2,\text{phys}} = -\theta(g_3) \psi^H + \theta(g_4) \psi^H + \cdots,$$

$$\psi^G_{3,\text{phys}} = \theta(g_3) \psi^H + \theta(g_4) \psi^H + \cdots,$$

$$\psi^G_{4,\text{phys}} = -\theta(g_1) \psi^H + \theta(g_2) \psi^H + \cdots. \quad (40)$$

Note that we have removed a common factor from each
of these equations in Eqs. (39) and (40). We have carried
these calculations out to four different sites so that it can
be seen explicitly that each of the above functions are
linearly independent of each other. In Table II, we give
the four coset representatives $g_i$, the sites $g_i r_0$, and
the matrices $D^G(g_i)$. Let us extend this example further by considering the
local distortions to be atomic displacements. We see from
Eq. (36) that any component of a vector transforms

\begin{table*}[h]
\begin{center}
\begin{tabular}{c|c|c|c}
\hline
$i$ & $g_i$ & $g_i r_0$ & $D^G(g_i)$ \\
\hline
1 & $x, y, z$ & $(0,0,0)$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ \\
2 & $x, y, z$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ \\
3 & $x, y, z$ & $(1,1,0,0,0,0,0,0,0,0,0,0)$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ \\
4 & $x, y, z$ & $(1,1,0,0,0,0,0,0,0,0,0,0)$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ \\
\hline
\end{tabular}
\end{center}
\caption{The coset representatives $g_i$, the sites $g_i r_0$, and the matrices $D^G(g_i)$ used in example 2. The rows of the matrices are separated by slashes.}
\end{table*}

\begin{table*}[h]
\begin{center}
\begin{tabular}{c|c|c|c}
\hline
$i$ & $g_i$ & $g_i r_0$ & $D^G(g_i)$ \\
\hline
1 & $x, y, z$ & $(0,0,0)$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ \\
2 & $x, y, z$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ \\
3 & $x, y, z$ & $(1,1,0,0,0,0,0,0,0,0,0,0)$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ \\
4 & $x, y, z$ & $(1,1,0,0,0,0,0,0,0,0,0,0)$ & $(1,0,0,0,0,0,0,0,0,0,0,0)$ \\
\hline
\end{tabular}
\caption{The coset representatives $g_i$, the sites $g_i r_0$, and the matrices $D^G(g_i)$ used in example 2. The rows of the matrices are separated by slashes.}
\end{center}
\end{table*}
like the basis function of the point-group IR. Thus, the local distortion $\psi^I_1$ can be an atomic displacement in any general direction. We form three independent sets of basis functions of $\Gamma^H$ from atomic displacements in the $x,y,z$ directions, respectively. Substituting these, one at a time, into Eqs. (40), we obtain three independent sets of basis functions of $\Gamma^G$. For example, in the first set, using an atomic displacement in the $x$ direction for $\psi^I_1$, we find that the global distortion $\psi^G_{1,\text{phys}}$ consists of a displacement of the atom at $g_1r_0$ in the $-x$ direction, a displacement of the atom at $g_2r_0$ in the $-x$ direction, etc. In the second set, using an atomic displacement in the $y$ direction for $\psi^I_1$, we find that the global distortion $\psi^G_{1,\text{phys}}$ consists of a displacement of the atom at $g_1r_0$ in the $y$ direction, a displacement of the atom at $g_2r_0$ in the $-y$ direction, etc. In the third set, using an atomic displacement in the $z$ direction for $\psi^I_1$, we find that the global distortion $\psi^G_{1,\text{phys}}$ consists of a displacement of the atom at $g_1r_0$ in the $z$ direction, a displacement of the atom at $g_2r_0$ in the $z$ direction, etc.

Example 3

Consider space group No. 158 $P3c1$, space-group IR $\Gamma^G = A_3$ (two-dimensional), site $r_0 = (0,0,0)$ (Wyckoff position $a$), point-group $H = 3$, and point-group IR $\Gamma^H = 1E$. The elements of the point-group $H$ are $x,y,z$; $y,x-y,z$; $x+y,x,z$. The point-group IR $E$ is type 3. We form the two-dimensional physically irreducible representation $E^*$ from $1E$ and its complex conjugate $E$. The space-group IR $A_3$ is type 2. It is equivalent to its own complex conjugate. We form the physically irreducible representation $\Gamma^G_{\text{phys}}$ via an appropriately chosen similarity transformation on the direct sum of $A_3$ with itself so that the resulting four-dimensional matrices are real. We denote this physically irreducible representation by $A_3 A_3$. The matrices onto which $\Gamma^G_{\text{phys}}$ and $\Gamma^G_{\text{phys}}$ map the elements of the point group are

$$ D^H_{\text{phys}}(y,x-y,z) = \begin{pmatrix} -\frac{1}{\sqrt{3}} & -\frac{1}{2}\sqrt{3} \\ \frac{1}{\sqrt{3}} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} , $$  

$$ D^H_{\text{phys}}(x+y,x,z) = \begin{pmatrix} -\frac{1}{\sqrt{3}} & -\frac{1}{2}\sqrt{3} \\ \frac{1}{\sqrt{3}} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} , $$  

$$ D^G_{\text{phys}}(y,x-y,z) = \begin{pmatrix} -\frac{1}{\sqrt{3}} & -\frac{1}{2}\sqrt{3} \\ 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} \end{pmatrix} , $$  

$$ D^G_{\text{phys}}(x+y,x,z) = \begin{pmatrix} -\frac{1}{\sqrt{3}} & -\frac{1}{2}\sqrt{3} \\ 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} \end{pmatrix} . $$

The transformation matrix that brings these matrices back to block diagonal form is

$$ S = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & -1 \\ -1 & 1 & i \\ -i & i & 1 \\ -i & -i & 1 \end{pmatrix} . $$

From Eq. (32), we find that there is $n = 1$ independent set of basis functions. If we form the vectors $\alpha^I_{\text{phys}}$, we obtain

$$ \alpha^1_{\text{phys}} = (1,0,0,1,0,0,0,0) , $$

$$ \alpha^2_{\text{phys}} = (0,-1,1,0,0,0,0,0) , $$

$$ \alpha^3_{\text{phys}} = (0,0,0,0,1,0,0,1) , $$

$$ \alpha^4_{\text{phys}} = (0,0,0,0,0,-1,1,0) . $$

All four of these vectors seem to be independent of each other, and this again demonstrates how the method fails for reducible representations. We must form instead the $\alpha^I$ vectors for IR $A_3$, two for each vector $\alpha^I_{\text{phys}}$ and, using Eqs. (28) and (29), we obtain

$$ \alpha^1 = \frac{1}{2}(1,-1,1,1) , \quad \alpha^2 = \frac{1}{2}(i,i,-i,i) , $$

$$ \alpha^3 = \frac{1}{2}(-1,-1,1,-1) , \quad \alpha^4 = \frac{1}{2}(i,-i,i,-i) . $$

Only the first two of these vectors are linearly independent. We choose $j = 1$ for generating the set of basis functions. From Eqs. (17)–(20), and we obtain

$$ \psi_{1,\text{phys}} = \theta(1) \psi^H_1 - \theta(2) \psi^H_2 + \cdots , $$

$$ \psi_{2,\text{phys}} = \theta(1) \psi^H_2 - \theta(2) \psi^H_2 + \cdots , $$

$$ \psi_{3,\text{phys}} = -\theta(1) \psi^H_2 + \theta(2) \psi^H_2 + \cdots , $$

$$ \psi_{4,\text{phys}} = \theta(1) \psi^H_2 + \theta(2) \psi^H_2 + \cdots . $$

Note that we have removed a common factor from each of these equations in Eqs. (44) and (45). We have carried these calculations out to four different sites. In Table III, we give the four coset representatives $g_i$, the sites $g_i r_0$, and the matrices $D^G_{\text{phys}}(g_i)$. Let us extend this example further by considering the local distortions to be atomic displacements. The two atomic displacements which transform like basis functions of the two-dimensional point-group IR $E^*$ lie in the plane perpendicular to the three-fold symmetry axis and are perpendicular to each other. We arbitrarily choose the second basis function to be an atomic displacement in the direction of the hexagonal $y$ axis. The first basis function is thus an atomic displacement in a direction perpendicular to the hexagonal $y$ axis. In terms of the hexagonal $x,y,z$ coordinates, the two basis functions are atomic displacements in the directions, $(\sqrt{4}/3, \sqrt{1}/3,0)$ and $(0,1,0)$, respectively.
TABLE III. The coset representatives $g_i$, the sites $g_ir_0$, and the matrices $D^G(g_i)$ used in example 3. The rows of the matrices are separated by slashes.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$g_i$</th>
<th>$g_ir_0$</th>
<th>$D^G(g_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$x,y,z$</td>
<td>$(0,0,z)$</td>
<td>$(1,0,0,0/0,1,0,0/0,1,0,0,0,1)$</td>
</tr>
<tr>
<td>2</td>
<td>$x+y,y,x+z + \frac{1}{2}$</td>
<td>$(0,0,z + \frac{1}{2})$</td>
<td>$(0,0,1/0,0,0,0,1/0,0,0,1,0,0)$</td>
</tr>
<tr>
<td>3</td>
<td>$x,y,z + 1$</td>
<td>$(0,0,2+)$</td>
<td>$(-1,0,0,0/0,1,0,0,0,0,1,0,0)$</td>
</tr>
<tr>
<td>4</td>
<td>$x+y,y,x+z + \frac{1}{2}$</td>
<td>$(0,0,z + \frac{1}{2})$</td>
<td>$(0,0,1/0,0,0,1,1/0,0,0,0,1,0,0)$</td>
</tr>
</tbody>
</table>

APPLICATION TO LATTICE VIBRATIONS

The IR’s of the space group classify the normal modes of the lattice vibrations (see, for example, Ref. 9). Modes classified by different IR’s are nondegenerate, i.e., they oscillate at different frequencies. Modes classified by the same IR are $d^G$-fold degenerate (or $d^G_{\text{phys}}$-fold degenerate for reducible but physically irreducible representations). The total number of $d^G$-fold degenerate normal modes classified by a given space-group IR is equal to the total number of independent sets of basis functions of the space-group IR which can be generated by basis functions of the vector IR’s of the point group at each kind of atomic site.

This is best illustrated by example. Consider a perovskite crystal like BaTiO$_3$. Its space-group symmetry is No. 221 P$m\bar{3}m$. Ba is at $(0,0,0)$ (Wyckoff position $a$), Ti is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Wyckoff position $b$), and O is at $(0, \frac{1}{2}, \frac{1}{2})$ (Wyckoff position $c$). Let us consider the modes of oscillation classified by the three-dimensional space-group IR $X^+_1$. There are three different types of sites occupied by atoms.

The Ba site has point-group symmetry $m\bar{3}m$. The vector IR for this point group is $T_{1u}$. Using Eq. (30), we find that $n = 0$, i.e., no sets of basis functions of $X^+_1$ can be generated from basis functions of $T_{1u}$ at the Ba site. Ba atoms do not oscillate in any of the modes classified by $X^+_1$.

The Ti site also has the point-group symmetry $m\bar{3}m$, and for this case we find that $n = 1$, i.e., one set of basis functions of $X^+_1$ can be generated from basis functions of $T_{1u}$ at the Ti site. Using Eqs. (6)–(9) and substituting atomic displacements for the basis functions $\psi^H_k$, we obtain

\begin{align*}
\psi^G_1(Ti) &= y_{Ti1} + \cdots, \\
\psi^G_2(Ti) &= x_{Ti1} + \cdots, \\
\psi^G_3(Ti) &= z_{Ti1} + \cdots,
\end{align*}

where $y_{Ti1}$ denotes a displacement of the Ti1 atom in the $y$ direction. The Ti1 atom is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

The O site has point-group symmetry $4/mmm$. The vector IR’s for this point group are $A_{2u}$ and $E_u$. Using Eq. (30), we find that $n = 0$ for $A_{2u}$ and $n = 1$ for $E_u$. One set of basis functions of $X^+_1$ can be generated from basis functions of $E_u$.

\begin{align*}
\psi^G_1(O) &= y_{O1} + y_{O3} + \cdots, \\
\psi^G_2(O) &= z_{O1} + z_{O3} + \cdots, \\
\psi^G_3(O) &= x_{O2} + x_{O3} + \cdots,
\end{align*}

where the O1, O2, and O3 atoms are at $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2}, 0)$, respectively.

All together, then, the two independent sets of basis functions of $X^+_1$ can be generated from atomic displacements of the Ti and O atoms. The normal modes of oscillation are linear combinations of these sets. Each mode is two-fold degenerate, one of the form, $a\psi^G_1(Ti) + b\psi^G_1(O)$, and the other of the form, $a\psi^G_2(Ti) + b\psi^G_2(O)$, where $a, b$ are constants. The values of $a, b$ cannot be determined by symmetry arguments. They can only be determined by solving the dynamical matrix equations which require some knowledge about the interatomic forces. From symmetry arguments alone, we can only say that there are two sets of two-fold degenerate modes classified by the space-group IR $X^+_1$. In each mode, the Ti and O atoms oscillate, but the Ba atoms do not.

APPLICATION TO PHASE TRANSITIONS

In the Landau theory of phase transitions in solids, the distortions which accompany transitions are classified by IR’s of $\Gamma^G$ of the space group of the higher-symmetry phase $G$. Using Eqs. (6)–(9), we can obtain global distortions $\psi^G_1$ which transform like basis functions of $\Gamma^G$. The distortion accompanying a phase transition is a linear combination of these:

\[ \psi^G(r) = \sum_{i=1}^{d^G} \eta_i \psi^G_i(r). \]

(48)

The coefficients $\eta_i$ are constants which constitute a $d^G$-dimensional vector $\eta = (\eta_1, \eta_2, \ldots, \eta_{d^G})$ called the order parameter. The relative weighting of the distortions $\psi^G_i(r)$ in the summation determines the space-group phase $G'$ of the lower-symmetry phase. The elements $g' \in G'$ are simply those operations in $G$ which leave the distortion $\psi^G_i(r)$ invariant.

As an example, consider possible displacive phase transitions in the perovskite crystal BaTiO$_3$ (space group No. 221 P$m\bar{3}m$). In the previous section, we examined the normal modes of oscillation classified by the IR $X^+_1$ of the space group. We use the very same approach in clas-
sifying the possible displaceable phase transitions in BaTiO$_3$, according to IR $X'_1$. For example, if the order parameter is $\eta=(a,0,0)$, where $a$ is an arbitrary constant, then, from Eq. (48), the distortion is simply $a\psi^{(G)}$. From Eqs. (46), we find that this distortion consists of a displacement of the Ti atom in the $\pm y$ direction. The sign on the direction depends on the sign of $a$. Similarly, from Eqs. (47), we find that this distortion also includes a displacement of the O1 atom in the $\pm y$ direction and a displacement of the O3 atom in the $\pm y$ direction. Again, the sign on the direction depends on the sign of $a$. However, whatever the sign of $a$, the displacement of the O3 atom is in the same direction as that of the O1 atom. Note that the value of $a$ is different for each set of distortions. Thus the magnitude of the O displacement is different from the magnitude of the Ti displacement. The sign on the direction of the O displacements also may or may not be the same as that of the Ti displacements. These questions cannot be answered by symmetry arguments alone. As with the modes of oscillation, no Ba atoms are displaced in this phase transition. The lower-symmetry space-group $G'$ determined by this distortion is $P4/mmm$ with the four-fold symmetry axis in the $y$ direction and a cell doubling in that same direction.

We can also consider distortions which consist of molecular rotations. A molecular rotation transforms like a pseudovector. We therefore use basis functions of point-group $\text{IR}$’s that transform like pseudovectors. As an example, consider possible phase transitions in the perovskite-like crystal Rb$_2$CdF$_4$ (space-group No. 139 I$4/mmm$) where the corner-linked octahedra CdF$_6$ rotate like nearly rigid units. We want to generate global distortions from local rotational distortions centered at the Cd site, $r_0=(0,0,0)$ (Wyckoff position $a$). The point-group symmetry at this site is 4/mmm. The pseudovector $\text{IR}$’s for this point group are $A_{2g}$ and $E_g$. If we consider, for example, global distortions that transform like basis functions of the two-dimensional space-group $\text{IR}$ $X''_1$, we find from Eq. (30) that $n=1$ for $A_{2g}$ and $n=0$ for $E_g$. One set of basis functions $X''_1$ can be generated from basis functions of $A_{2g}$:

\[
\psi_{G1}^{G1} = R_x \cdot z_{Cd} - R_z \cdot C_d + \cdots,
\]
\[
\psi_{G1}^{G2} = R_z \cdot C_d - R_x \cdot z_{Cd} + \cdots,
\]
where $R_z$ is a rotation about an axis in the $z$ direction. The Cd1, Cd2, Cd3, Cd4 sites are at (0,0,0), (1,0,0), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), respectively. Suppose the order parameter is $\eta=(a,0,0)$, where $a$ is an arbitrary constant. Then, from Eq. (48), the distortion is simply $a\psi^{(G)}$. From Eqs. (49), we see that this distortion consists of rotations of the octahedra centered at Cd3 and Cd4. The two octahedra rotate in opposite directions. The octahedra centered at Cd1 and Cd2 do not rotate at all. The lower-symmetry space-group $G'$ determined by this distortion is $P4/mmm$.

Likewise, we can consider order-disorder phase transitions where the distortions are changes in occupation probabilities. These probabilities transform like scalars. We therefore use basis functions of the unit $\text{IR}$’s of the point groups. As an example, consider the garnet Ca$_3$Fe$_{2}$Al$_{2}$Si$_{2}$O$_{12}$ (space group No. 230 I$\alpha$3d). The Fe and Al atoms are randomly distributed among the sites generated from $r_0=(0,0,0)$ (Wyckoff position $a$). The occupation probability $P_{Fe}$ of the Fe atom is the same at every one of these sites. An order-disorder phase transition occurs which takes this crystal to space group No. 70 P$\bar{4}$mm. The distortion accompanying this transition transforms like a basis function of the three-dimensional space-group IR $\Gamma^*_{\alpha}$ . The point group of the Fe-Al site is 3. The local distortion is the change $\delta$ in the occupation probability $P_{Fe}$. The scalar function $\delta$ transforms like the basis function of the point-group unit IR $A_{2g}$. We find from Eq. (30) that $n=1$ for this IR. One set of basis functions of $\Gamma^*_{\alpha}$ can be generated from basis functions of $A_{2g}$:

\[
\psi_{G1}^{G1} = \delta_1 + \delta_2 - \delta_3 - \delta_4 + \cdots,
\]
\[
\psi_{G1}^{G2} = \delta_1 - \delta_2 - \delta_3 + \delta_4 + \cdots,
\]

\[
\psi_{G1}^{G3} = \delta_1 - \delta_2 + \delta_3 - \delta_4 + \cdots,
\]

where $\delta_j$ is the change in $P_{Fe}$ at the $j$th site. Sites 1,2,3,4 are at (0,0,0), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), (0,$\frac{1}{2}$, $\frac{1}{2}$), ($\frac{1}{2}$,$\frac{1}{2}$,0), respectively. In this phase transition, the order parameter is $\eta=(a,0,0)$. Thus, depending on the sign of $a$, sites 1 and 2 become enriched (or depleted) in Fe atoms, and sites 3 and 4 become depleted (or enriched) in the Fe atoms. The magnitude of $\delta_j$ is the same at each site.

Ref. 8 are listed all of the phase transitions classified by each space-group $\text{IR}$ associated with $k$ points of symmetry. Approximately 15 000 phase transitions are contained in the list. For each phase transition listed, the order parameter and the space group of the lower-symmetry phase are given, along with some other useful information as well. Using the information in that list, we can use the methods described in this paper to obtain, in a very straightforward way, the distortions accompanying each of those transitions.

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