

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 BaTiO₃ 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 displacive 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 irreducible 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 Γ^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:

$$\theta(g)\psi_i^G(\mathbf{r}) = \sum_{j=1}^{d^G} \psi_j^G(\mathbf{r})D^G(g)_{ji}, \quad (1)$$

where $\psi_i^G(\mathbf{r})$ 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 $\psi_i^G(\mathbf{r})$ are “attached” to the crystal and move with it, so that

$$\theta(g)\psi_i^G(\mathbf{r}) = \psi_i^G(g^{-1}\mathbf{r}). \quad (2)$$

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 displacive phase transition, we consider possible displacements for each of the atoms in the unit cell. Let \mathbf{r}_0 be a site of a local distortion. The elements of the space group which leave \mathbf{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 \mathbf{r}_0 can be broken into parts which transform like basis functions of the point group IR:

$$\theta(h)\psi_i^H(\mathbf{r}) = \sum_{j=1}^{d^H} \psi_j^H(\mathbf{r})D^H(h)_{ji}, \quad (3)$$

where $\psi_i^H(\mathbf{r})$ 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 $\psi_i^H(\mathbf{r})$ are associated with the same point \mathbf{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 displacive phase transition, we consider “vector IR's” of the point group. These are the IR's whose basis functions transform like components of vectors, representing atomic displacements.

Let the basis functions $\psi_i^H(\mathbf{r})$ of the point-group IR Γ^H be local distortions at the site \mathbf{r}_0 , and let the basis func-

tions $\psi_i^G(\mathbf{r})$ of the space-group IR Γ^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:

$$\psi_i^{Gj}(\mathbf{r}) = \sum_{g \in G} D^G(g)_{ij}^* \theta(g) \psi_i^H(\mathbf{r}). \quad (4)$$

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 $\psi_i^H(\mathbf{r})$ to obtain all possible global distortions. Here, we arbitrarily choose the first basis function $\psi_1^H(\mathbf{r})$. Also note that in Eq. (4), the index j is arbitrarily chosen. For each value of j , Eq. (4) produces a set of d^G global distortions that transform like the d^G basis functions of Γ^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 .

$$G = \sum_m g_m H. \quad (5)$$

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

$$\psi_i^{Gj}(\mathbf{r}) = \sum_m \theta(g_m) \psi_{im}^{Gj}(\mathbf{r}), \quad (6)$$

where

$$\psi_{im}^{Gj}(\mathbf{r}) = \sum_{i'=1}^{d^G} D^G(g_m)_{i'i}^* \psi_{i'}^{Gj}(\mathbf{r}), \quad (7)$$

$$\psi_{i'k}^{Gj}(\mathbf{r}) = \sum_{k=1}^{d^H} \alpha_{i'k}^{j'} \psi_k^H(\mathbf{r}), \quad (8)$$

$$\alpha_{i'k}^{j'} = \sum_{h \in H} D^G(h)_{i'j}^* D^H(h)_{k1}. \quad (9)$$

Equation (6) breaks the global distortion into a sum over local distortions at sites $g_1 \mathbf{r}_0, g_2 \mathbf{r}_0, g_3 \mathbf{r}_0, \dots$. The function $\psi_{im}^{Gj}(\mathbf{r})$ is a local distortion centered at \mathbf{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 $\theta(g_m) \psi_{im}^{Gj}(\mathbf{r})$ is a local distortion at site $g_m \mathbf{r}_0$.

INDEPENDENT SETS OF DISTORTIONS

An index j appears in Eqs. (6)–(9). For each value of j , a set of global distortions $\psi_i^{Gj}(\mathbf{r})$ is generated. For some values of j it may happen that the functions $\psi_i^{Gj}(\mathbf{r})$ 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 $\psi_i^{Gj'}$. We then try another value of j and generate another set of basis functions ψ_i^{Gj} . This new set is linearly

dependent on the previous sets if there exists a set of coefficients $A_{ki}^{j'}$ (at least one of them nonzero) such that

$$\psi_i^{Gj} = \sum_{j',k} \psi_k^{Gj'} A_{ki}^{j'}. \quad (10)$$

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

$$\sum_{i',j',k'} \psi_{k'}^{Gj'} A_{k'i}^{j'} D^G(g)_{i'i} = \sum_{j',k,k'} \psi_{k'}^{Gj'} D^G(g)_{k'k} A_{ki}^{j'}. \quad (11)$$

Since $\psi_{k'}^{Gj'}$ are independent functions, their coefficients must be separately equal to each other in the above equation. This leads to the matrix equation,

$$A^{j'} D^G(g) = D^G(g) A^{j'}. \quad (12)$$

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 $A^{j'}$ must be a constant times the unit matrix:

$$A_{ki}^{j'} = \lambda^{j'} \delta_{ki}, \quad (13)$$

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

$$\psi_i^{Gj} = \sum_{j'} \lambda^{j'} \psi_i^{Gj'}. \quad (14)$$

This means that the only way the new set of basis functions can be linearly dependent on the previous sets is for ψ_1^{Gj} to be some linear combination of $\psi_1^{G1}, \psi_1^{G2}, \psi_1^{G3}, \dots$ and for ψ_2^{Gj} to be the *same* linear combination of $\psi_2^{G1}, \psi_2^{G2}, \psi_2^{G3}, \dots$ and for ψ_3^{Gj} to be the *same* linear combination of $\psi_3^{G1}, \psi_3^{G2}, \psi_3^{G3}, \dots$ etc.

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

$$\alpha_{ik}^{j'} = \sum_{j''} \lambda^{j''} \alpha_{ik}^{j''}. \quad (15)$$

Equation (14) implies Eq. (15), and Eq. (15) implies Eq. (14). Thus if there exists a set of coefficients $\lambda^{j'}$ (at least one of them nonzero) which satisfies Eq. (15) for all values of i and k , then the set of functions ψ_i^{Gj} is *not* linearly independent from the previous sets of functions $\psi_i^{Gj'}$. Conversely, if there exists no solution to Eq. (15) except all $\alpha^{j'} = 0$, then the set of functions ψ_i^{Gj} is linearly independent from the previous sets of functions $\psi_i^{Gj'}$. If we form for each set j the $d^G \times d^H$ -dimensional vector,

$$\alpha^j = [\alpha_{11}^j, \alpha_{12}^j, \dots, \alpha_{1d^H}^j, \alpha_{21}^j, \alpha_{22}^j, \dots, \alpha_{2d^H}^j, \dots, \alpha_{d^G d^H}^j], \quad (16)$$

then the test for independence of sets of basis functions simply becomes a test for linear independence of the vectors α^j .

This result² is actually quite remarkable. The coefficients $\alpha_{ik}^{j'}$ directly specify only the part of the global distortion which occurs at site \mathbf{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 \mathbf{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 very similar to Eqs. (6)–(9):

$$\psi_{i,\text{phys}}^{Gj}(\mathbf{r}) = \sum_m \theta(g_m) \psi_{im,\text{phys}}^{Gj}(\mathbf{r}), \quad (17)$$

where

$$\psi_{im,\text{phys}}^{Gj}(\mathbf{r}) = \sum_{i'=1}^{d_{\text{phys}}^G} D_{\text{phys}}^G(g_m)_{ii'} \psi_{i',\text{phys}}^{Gj}(\mathbf{r}), \quad (18)$$

$$\psi_{i',\text{phys}}^{Gj}(\mathbf{r}) = \sum_{k=1}^{d^H} \alpha_{i'k,\text{phys}}^j \psi_k^H(\mathbf{r}), \quad (19)$$

$$\alpha_{i'k,\text{phys}}^j = \sum_{h \in H} D_{\text{phys}}^G(h)_{i'j} D^H(h)_{k1}. \quad (20)$$

In the above equations, D_{phys}^G are matrices of the physically irreducible representation. The complex conjugation has been dropped since elements of D_{phys}^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 $\psi_{i,\text{phys}}^{Gj}$ 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 $\psi_{i,\text{phys}}^{Gj}$ 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

$$S^{-1} D_{\text{phys}}^G(g) S = \begin{bmatrix} D^G(g) & 0 \\ 0 & D^G(g)^* \end{bmatrix}. \quad (21)$$

The basis functions of Γ^G are

$$\psi_i^{Gj}(\mathbf{r}) = \sum_{i'=1}^{d_{\text{phys}}^G} \psi_{i',\text{phys}}^{Gj}(\mathbf{r}) S_{i'i}, \quad (22)$$

and the basis functions of Γ^{G*} (the complex conjugate of Γ^G) are

$$\psi_i^{G*j}(\mathbf{r}) = \sum_{i'=1}^{d_{\text{phys}}^G} \psi_{i',\text{phys}}^{Gj}(\mathbf{r}) S_{i',i+d^G}. \quad (23)$$

In both cases, $i = 1, 2, \dots, d^G$, where $d^G = \frac{1}{2} d_{\text{phys}}^G$. To test for independence, we form the $d^G \times d^H$ -dimensional vector α^j as in Eq. (16) using the components,

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

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

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

$$S^{-1} D_{\text{phys}}^G(g) S = \begin{bmatrix} D^G(g) & 0 \\ 0 & D^G(g) \end{bmatrix}. \quad (25)$$

We require here that both d^G -dimensional matrices $D^G(g)$ be identical, element by element, in the block diagonal matrix. One set of basis functions of Γ^G are

$$\psi_i^{Gj}(\mathbf{r}) = \sum_{i'=1}^{d_{\text{phys}}^G} \psi_{i',\text{phys}}^{Gj}(\mathbf{r}) S_{i'i}, \quad (26)$$

and a second set of basis functions of Γ^G are

$$\psi_i^{Gj}(\mathbf{r}) = \sum_{i'=1}^{d_{\text{phys}}^G} \psi_{i',\text{phys}}^{Gj}(\mathbf{r}) S_{i',i+d^G}. \quad (27)$$

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

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

and for the other vector the components,

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

There is also the possibility that the IR Γ^H of the point-group H may be complex. In this case, we form physically irreducible IR's Γ_{phys}^H with matrices D_{phys}^H which we use instead of D^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 Γ^H appears in $\Gamma^G \downarrow H$, the representation of H subduced by the space-group IR Γ^G , formed by restricting the matrices of Γ^G to elements of H . The number of independent sets can thus be calculated from^{3,4}

$$n = \frac{1}{|H|} \sum_{h \in H} \chi^G(h)^* \chi^H(h), \quad (30)$$

where $|H|$ is the number of elements in H , and χ^G and χ^H are characters of the matrices in the IR's Γ^G and Γ^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.² For type 3 IR's, the number of independent sets is given by

$$n = \frac{1}{2} \frac{1}{|H|} \sum_{h \in H} \chi_{\text{phys}}^G(h) \chi^H(h), \quad (31)$$

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

$$n = \frac{1}{4} \frac{1}{|H|} \sum_{h \in H} \chi_{\text{phys}}^G(h) \chi^H(h). \quad (32)$$

These results can be easily understood. For type 3 IR's, the n independent sets of $2d^G$ basis functions of Γ_{phys}^G are constructed from n independent sets of d^G basis functions of Γ^G and n independent sets of d^G basis functions of Γ^{G*} . Since Γ_{phys}^G contains Γ^G once and Γ^{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 Γ_{phys}^G are constructed from $2n$ independent sets of d^G basis functions of Γ^G . Since Γ_{phys}^G contains Γ^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 χ_{phys}^H for χ^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 Γ^H plus the number of independent sets of functions that can be constructed from basis functions of Γ^{H*} . Since the basis functions of Γ^H and the basis functions of Γ^{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 Γ_{phys}^H . 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 $\mathbf{r}_0 = (x, 0, 0)$ (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, \bar{y}, \bar{z} . The matrices onto which Γ^H and Γ^G map x, \bar{y}, \bar{z} are

$$D^H(x, \bar{y}, \bar{z}) = (1),$$

$$D^G(x, \bar{y}, \bar{z}) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \quad (33)$$

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 α^j :

$$\alpha^1 = (1, 0, 1, 0), \quad \alpha^2 = (0, 1, 0, 1),$$

$$\alpha^3 = (1, 0, 1, 0), \quad \alpha^4 = (0, 1, 0, 1). \quad (34)$$

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

$$\begin{aligned} \psi_1^{G1} &= \theta(g_1)\psi_1^H - \theta(g_3)\psi_1^H - \theta(g_5)\psi_1^H + \cdots, \\ \psi_2^{G1} &= \theta(g_2)\psi_1^H - \theta(g_4)\psi_1^H + \theta(g_6)\psi_1^H + \cdots, \\ \psi_3^{G1} &= \theta(g_1)\psi_1^H + \theta(g_3)\psi_1^H + \theta(g_5)\psi_1^H + \cdots, \\ \psi_4^{G1} &= \theta(g_2)\psi_1^H + \theta(g_4)\psi_1^H - \theta(g_6)\psi_1^H + \cdots, \\ \psi_1^{G2} &= \theta(g_2)\psi_1^H - \theta(g_4)\psi_1^H - \theta(g_6)\psi_1^H + \cdots, \\ \psi_2^{G2} &= \theta(g_1)\psi_1^H - \theta(g_3)\psi_1^H + \theta(g_5)\psi_1^H + \cdots, \\ \psi_3^{G2} &= \theta(g_2)\psi_1^H + \theta(g_4)\psi_1^H + \theta(g_6)\psi_1^H + \cdots, \\ \psi_4^{G2} &= \theta(g_1)\psi_1^H + \theta(g_3)\psi_1^H - \theta(g_5)\psi_1^H + \cdots. \end{aligned} \quad (35)$$

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 $g_i\mathbf{r}_0$, and the IR matrices $D^G(g_i)$. Note that global distortions do not contain a contribution from local distortions at every site $g_m\mathbf{r}_0$. For example, the global distortion ψ_1^{G1} has contributions from the local distortions at $g_1\mathbf{r}_0, g_3\mathbf{r}_0, g_5\mathbf{r}_0$ but no contribution from $g_2\mathbf{r}_0, g_4\mathbf{r}_0, g_6\mathbf{r}_0$.

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 ψ_1^H can be an atomic displacement in the x direction. Substituting this into Eqs. (35), we find that the global distortion ψ_1^{G1} consists of a displacement of the atom at $g_1\mathbf{r}_0$ in the x direction, a displacement of the atom at $g_3\mathbf{r}_0$ in the $-x$ direction, a displacement of the atom at $g_5\mathbf{r}_0$ in the $-x$ direction, etc. The global distortion ψ_2^{G1} consists of a displacement of the atom at $g_2\mathbf{r}_0$ in the $-x$ direction, a displacement of the atom at $g_4\mathbf{r}_0$ in the x direction, a displacement of the atom at $g_6\mathbf{r}_0$ in the $-x$ direction, etc. Note that the operations $\theta(g_m)$ in Eqs. (35) not only move the local distortion to the site $g_m\mathbf{r}_0$, but may also reorient the distortion. For example, consider the term $-\theta(g_4)\psi_1^H$ in the

TABLE I. The coset representatives g_i , the sites $g_i\mathbf{r}_0$, and the matrices $D^G(g_i)$ used in example 1. The rows of the matrices are separated by slashes.

i	g_i	$g_i\mathbf{r}_0$	$D^G(g_i)$
1	x, y, z	$(x, 0, 0)$	$(1, 0, 0, 0/0, 1, 0, 0/0, 0, 1, 0/0, 0, 0, 1)$
2	\bar{x}, y, \bar{z}	$(\bar{x}, 0, 0)$	$(0, 0, 0, 1/0, 0, 1, 0/0, 1, 0, 0/1, 0, 0, 0)$
3	$x + \frac{1}{2}, y + \frac{1}{2}, z$	$(x + \frac{1}{2}, \frac{1}{2}, 0)$	$(-1, 0, 0, 0/0, -1, 0, 0/0, 0, 1, 0/0, 0, 0, 1)$
4	$\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z}$	$(\bar{x} + \frac{1}{2}, \frac{1}{2}, 0)$	$(0, 0, 0, -1/0, 0, -1, 0/0, 1, 0, 0/1, 0, 0, 0)$
5	$x + \frac{1}{2}, y, z + \frac{1}{2}$	$(x + \frac{1}{2}, 0, \frac{1}{2})$	$(-1, 0, 0, 0/0, 1, 0, 0/0, 0, 1, 0/0, 0, 0, -1)$
6	$\bar{x} + \frac{1}{2}, y, \bar{z} + \frac{1}{2}$	$(\bar{x} + \frac{1}{2}, 0, \frac{1}{2})$	$(0, 0, 0, -1/0, 0, 1, 0/0, 1, 0, 0/-1, 0, 0, 0)$

expression for $\psi_2^{G_1}$. The function $-\psi_1^H$ represents a displacement of the atom at $\mathbf{r}_0 = (x, 0, 0)$ in the $-x$ direction. When $\theta(g_4)$ operates on this, the displaced atom is now at $g_4\mathbf{r}_0 = (\bar{x} + \frac{1}{2}, \frac{1}{2}, 0)$, and, since $g_4 = \bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z}$, 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 $\mathbf{r}_0 = (0, 0, 0)$ (Wyckoff position a), point-group $H = \bar{1}$, and point-group IR $\Gamma^H = A_u$. The elements of the point-group H are x, y, z and $\bar{x}, \bar{y}, \bar{z}$. The space-group IR S_1 is type 3. Its complex conjugate is IR S_2 . We form the physically irreducible representation Γ_{phys}^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_1S_2 . The matrices onto which Γ^H and Γ_{phys}^G map $\bar{x}, \bar{y}, \bar{z}$ are

$$D^H(\bar{x}, \bar{y}, \bar{z}) = (-1),$$

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

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 α_{phys}^j , we obtain

$$\alpha_{\text{phys}}^1 = (1, 0, 0, -1), \quad \alpha_{\text{phys}}^2 = (0, 1, -1, 0),$$

$$\alpha_{\text{phys}}^3 = (0, -1, 1, 0), \quad \alpha_{\text{phys}}^4 = (-1, 0, 0, 1). \quad (38)$$

The first two vectors seem to be independent of each other, and this demonstrates how the method fails for reducible representations. We must form instead the α^j vectors for IR S_1 using Eq. (24), and we obtain

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

$$\alpha^3 = \frac{1}{2}(1-i, 1+i), \quad \alpha^4 = \frac{1}{2}(-1-i, 1-i). \quad (39)$$

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

$$\psi_{1,\text{phys}}^{G_1} = \theta(g_1)\psi_1^H + \theta(g_2)\psi_1^H + \dots,$$

$$\psi_{2,\text{phys}}^{G_1} = -\theta(g_3)\psi_1^H + \theta(g_4)\psi_1^H + \dots,$$

$$\psi_{3,\text{phys}}^{G_1} = \theta(g_3)\psi_1^H + \theta(g_4)\psi_1^H + \dots,$$

$$\psi_{4,\text{phys}}^{G_1} = -\theta(g_1)\psi_1^H + \theta(g_2)\psi_1^H + \dots. \quad (40)$$

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 four functions are linearly independent of each other. In Table II, we give the four coset representatives g_i , the sites $g_i\mathbf{r}_0$, and the matrices $D_{\text{phys}}^G(g_i)$.

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

TABLE II. The coset representatives g_i , the sites $g_i\mathbf{r}_0$, and the matrices $D^G(g_i)$ used in example 2. The rows of the matrices are separated by slashes.

i	g_i	$g_i\mathbf{r}_0$	$D^G(g_i)$
1	x, y, z	$(0, 0, 0)$	$(1, 0, 0, 0/0, 1, 0, 0/0, 0, 1, 0/0, 0, 0, 1)$
2	$\bar{x} + \frac{1}{2}, \bar{y}, z$	$(\frac{1}{2}, 0, 0)$	$(1, 0, 0, 0/0, 1, 0, 0, 0/0, 0, -1, 0/0, 0, 0, -1)$
3	$\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, -1, 0/0, 0, 0, 1/1, 0, 0/0, 0, -1, 0, 0, 0)$
4	$x, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$	$(0, \frac{1}{2}, \frac{1}{2})$	$(0, 0, 1, 0/0, 0, 0, -1/1, 0, 0, 0/0, -1, 0, 0, 0)$

like the basis function of the point-group IR. Thus, the local distortion ψ_1^H can be an atomic displacement in any general direction. We form three independent sets of basis functions of Γ^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 Γ^G . For example, in the first set, using an atomic displacement in the x direction for ψ_1^H , we find that the global distortion $\psi_{1,\text{phys}}^{G1}$ consists of a displacement of the atom at $g_1\mathbf{r}_0$ in the x direction, a displacement of the atom at $g_2\mathbf{r}_0$ in the $-x$ direction, etc. In the second set, using an atomic displacement in the y direction for ψ_1^H , we find that the global distortion $\psi_{1,\text{phys}}^{G1}$ consists of a displacement of the atom at $g_1\mathbf{r}_0$ in the y direction, a displacement of the atom at $g_2\mathbf{r}_0$ in the $-y$ direction, etc. In the third set, using an atomic displacement in the z direction for ψ_1^H , we find that the global distortion $\psi_{1,\text{phys}}^{G1}$ consists of a displacement of the atom at $g_1\mathbf{r}_0$ in the z direction, a displacement of the atom at $g_2\mathbf{r}_0$ in the z direction, etc.

Example 3

Consider space group No. 158 $P3c1$, space-group IR $\Gamma^G = A_3$ (two dimensional), site $\mathbf{r}_0 = (0, 0, z)$ (Wyckoff position a), point-group $H = 3$, and point-group IR $\Gamma^H = {}^1E$. The elements of the point-group H are $x, y, z; \bar{y}, x - y, z; \bar{x} + y, \bar{x}, z$. The point-group IR 1E is type 3. We form the two dimensional physically irreducible representation E^* from 1E and its complex conjugate 2E . The space-group IR A_3 is type 2. It is equivalent to its own complex conjugate. We form the physically irreducible representation Γ_{phys}^G 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 Γ_{phys}^H and Γ_{phys}^G map the elements of the point group are

$$\begin{aligned}
 D_{\text{phys}}^H(\bar{y}, x - y, z) &= \begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}, \\
 D_{\text{phys}}^H(\bar{x} + y, \bar{x}, z) &= \begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}, \\
 D_{\text{phys}}^G(\bar{y}, x - y, z) &= \begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ 0 & 0 & \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}, \\
 D_{\text{phys}}^G(\bar{x} + y, \bar{x}, z) &= \begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2}\sqrt{3} \\ 0 & 0 & -\frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}.
 \end{aligned} \tag{41}$$

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

$$S = \frac{1}{2} \begin{bmatrix} 1 & 1 & i & -i \\ -1 & 1 & i & i \\ -i & i & 1 & 1 \\ -i & -i & -1 & 1 \end{bmatrix}. \tag{42}$$

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

$$\begin{aligned}
 \alpha_{\text{phys}}^1 &= (1, 0, 0, 1, 0, 0, 0, 0), \\
 \alpha_{\text{phys}}^2 &= (0, -1, 1, 0, 0, 0, 0, 0), \\
 \alpha_{\text{phys}}^3 &= (0, 0, 0, 0, 1, 0, 0, 1), \\
 \alpha_{\text{phys}}^4 &= (0, 0, 0, 0, 0, -1, 1, 0).
 \end{aligned} \tag{43}$$

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 α^j vectors for IR A_3 , two for each vector α_{phys}^j , and, using Eqs. (28) and (29), we obtain

$$\begin{aligned}
 \alpha^1 &= \frac{1}{2}(1, -1, 1, 1), & \bar{\alpha}^1 &= \frac{1}{2}(i, i, -i, i), \\
 \alpha^2 &= \frac{1}{2}(-1, -1, 1, -1) & \bar{\alpha}^2 &= \frac{1}{2}(i, -i, i, i), \\
 \alpha^3 &= \frac{1}{2}(-i, -i, i, -i), & \bar{\alpha}^3 &= \frac{1}{2}(1, -1, 1, 1), \\
 \alpha^4 &= \frac{1}{2}(-i, i, -i, -i), & \bar{\alpha}^4 &= \frac{1}{2}(-1, -1, 1, -1).
 \end{aligned} \tag{44}$$

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

$$\begin{aligned}
 \psi_{1,\text{phys}}^{G1} &= \theta(g_1)\psi_1^H - \theta(g_3)\psi_1^H + \dots, \\
 \psi_{2,\text{phys}}^{G1} &= \theta(g_1)\psi_2^H - \theta(g_3)\psi_2^H + \dots, \\
 \pi_{3,\text{phys}}^{G1} &= -\theta(g_2)\psi_1^H + \theta(g_4)\psi_1^H + \dots, \\
 \psi_{4,\text{phys}}^{G1} &= \theta(g_2)\psi_2^H - \theta(g_4)\psi_2^H + \dots.
 \end{aligned} \tag{45}$$

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 $g_i\mathbf{r}_0$, and the matrices $D_{\text{phys}}^G(g_i)$.

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 $g_i\mathbf{r}_0$, and the matrices $D^G(g_i)$ used in example 3. The rows of the matrices are separated by slashes.

i	g_i	$g_i\mathbf{r}_0$	$D^G(g_i)$
1	x, y, z	$(0, 0, z)$	$(1, 0, 0/0/1, 0, 0/0, 0, 1, 0/0, 0, 0, 1)$
2	$\bar{x} + y, y, z + \frac{1}{2}$	$(0, 0, z + \frac{1}{2})$	$(0, 0, 1/0/0, 0, 0, -1/-1, 0, 0, 0/0, 1, 0, 0)$
3	$x, y, z + 1$	$(0, 0, z + 1)$	$(-1, 0, 0/0/0, -1, 0, 0/0, 0, -1, 0/0, 0, 0, -1)$
4	$\bar{x} + y, y, z + \frac{3}{2}$	$(0, 0, z + \frac{3}{2})$	$(0, 0, -1/0/0, 0, 0, 1/1, 0, 0, 0/0, -1, 0, 0)$

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_{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 $Pm\bar{3}m$. 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 ψ_k^H , we obtain

$$\begin{aligned}\psi_1^{G1}(\text{Ti}) &= y_{\text{Ti1}} + \cdots, \\ \psi_2^{G1}(\text{Ti}) &= z_{\text{Ti1}} + \cdots, \\ \psi_3^{G1}(\text{Ti}) &= x_{\text{Ti1}} + \cdots,\end{aligned}\quad (46)$$

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 .

$$\begin{aligned}\psi_1^{G1}(\text{O}) &= y_{\text{O1}} + y_{\text{O3}} + \cdots, \\ \psi_2^{G1}(\text{O}) &= z_{\text{O1}} + z_{\text{O2}} + \cdots, \\ \psi_3^{G1}(\text{O}) &= x_{\text{O2}} + x_{\text{O3}} + \cdots,\end{aligned}\quad (47)$$

where the O1, O2, and O3 atoms are at $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, 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, $a\psi_1^{G1}(\text{Ti}) + b\psi_1^{G1}(\text{O})$, and the other of the form, $a\psi_2^{G2}(\text{Ti}) + b\psi_2^{G2}(\text{O})$, 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,¹⁰ the distortions which accompany transitions are classified by IR's Γ^G of the space group of the higher-symmetry phase G . Using Eqs. (6)–(9), we can obtain global distortions ψ_i^{Gj} which transform like basis functions of Γ^G . The distortion accompanying a phase transition is a linear combination of these:

$$\psi^{Gj}(\mathbf{r}) = \sum_{i=1}^{d^G} \eta_i \psi_i^{Gj}(\mathbf{r}). \quad (48)$$

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

As an example, consider possible displacive phase transitions in the perovskite crystal BaTiO_3 (space group No. 221 $Pm\bar{3}m$). 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 displacive phase transitions in BaTiO₃, 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 $a\psi_1^{G_1}$. From Eqs. (46), we find that this distortion consists of a displacement of the Ti1 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 IR's that transform like pseudovectors. As an example, consider possible phase transitions in the perovskitelike crystal Rb₂CdF₄ (space-group No. 139 $I4/mmm$) where the corner-linked octahedra CdF₆ rotate like nearly rigid units.^{11,12} 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 that site is $4/mmm$. The pseudovector 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 IR X_2^+ , we find from Eq. (30) that $n=1$ for A_{2g} and $n=0$ for E_g . One set of basis functions X_2^+ can be generated from basis functions of A_{2g} .

$$\begin{aligned}\psi_1^{G_1} &= R_{z,Cd3} - R_{z,Cd4} + \dots, \\ \psi_2^{G_1} &= R_{z,Cd1} - R_{z,Cd2} + \dots,\end{aligned}\quad (49)$$

where R_z is a rotation about an axis in the z direction. The Cd1, Cd2, Cd3, Cd4 sites are at $(0,0,0)$, $(1,0,0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$, respectively. Suppose the order parameter is $\eta=(a,0,0)$, where a is an arbitrary constant. Then,

from Eq. (48), the distortion is simply $a\psi_1^{G_1}$. 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 $P4/mbm$.

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* IR's of the point groups. As an example,¹³ consider the grandite garnet Ca₃Fe_{2x}Al_{2(1-x)}Si₃O₁₂ (space group No. 230 $Ia\bar{3}d$). 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 $Fddd$. The distortion accompanying this transition transforms like a basis function of the three-dimensional space-group IR Γ_5^+ . The point group of the Fe-Al site is $\bar{3}$. The local distortion is the change δ in the occupation probability P_{Fe} . The scalar function δ transforms like the basis function of the point-group unit IR A_g . We find from Eq. (30) that $n=1$ for this IR. One set of basis functions of Γ_5^+ can be generated from basis functions of A_g :

$$\begin{aligned}\psi_1^{G_1} &= \delta_1 + \delta_2 - \delta_3 - \delta_4 + \dots, \\ \psi_2^{G_1} &= \delta_1 - \delta_2 - \delta_3 + \delta_4 + \dots, \\ \psi_3^{G_1} &= \delta_1 - \delta_2 + \delta_3 - \delta_4 + \dots,\end{aligned}\quad (50)$$

where δ_i is the change in P_{Fe} at the i th site. Sites 1,2,3,4 are at $(0,0,0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, 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 δ_i is the same at each site.

In Ref. 8 are listed all of the phase transitions classified by each space-group 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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