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ISODISPLACE: a web-based tool for exploring structural distortions

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ISODISPLACE is a new internet-server tool for exploring structural phase transitions. Given parent-phase structural information, it generates atomic displacement patterns induced by irreducible representations of the parent space-group symmetry and allows a user to visualize and manipulate the amplitude of each distortion mode interactively. *ISODISPLACE* is freely accessible at http://stokes.byu.edu/isodisplace.html *via* common internet browsers.

1. Introduction

When studying a phase transition *via* diffraction techniques, one typically needs to generate a low-symmetry structural model that can be tested in a refinement package against experimental data. One may likewise want to use the model as the starting point for a computational energy minimization. The maximal subgroup listings in the *International Tables of Crystallography* are an invaluable tool for this purpose, though considerable care is required to handle the change of basis and origin correctly. When the symmetry of the new phase is not a maximal subgroup of the parent, the problem must be solved in multiple steps, and more than one chain of subgroups may be possible. The exploration of a single candidate symmetry can become very complicated to manage 'by hand'; hence the need for computational tools such as those available in the *ISOTROPY* software suite (Stokes & Hatch, 2000; Capillas *et al.*, 2003) and other packages (Kroumova *et al.*, 2003; Kopský, 2003).

The subroutines of the *ISOTROPY* suite are powerful tools by themselves and can be combined in many different ways to solve practical crystallographic problems that are of interest to researchers in physics, chemistry, biology, mechanical engineering and materials science. However, it is a simple fact that most researchers in these fields cannot afford the steep learning curve (theory, mathematics, jargon, command language, *etc.*) that will allow them to take full advantage of *ISOTROPY*'s breadth and flexibility. The present *ISODISPLACE* software brings several of these tools to bear on a specific problem of widespread interest and provides a simple internet-based GUI that largely eliminates the learning curve. Without requiring an understanding of the group-theoretical methods involved, *ISODISPLACE* guides the user through the process of selecting a distortion and provides an interactive Java applet for graphically visualizing and interactively manipulating the free parameters of the corresponding low-symmetry phase.

Applications of *ISODISPLACE* may include (i) the enumeration of possible low-symmetry distortions consistent with incomplete experimental evidence of a phase transition, (ii) the differentiation amongst possible distortions based on their physical characteristics, (iii) the validation of a transition obtained experimentally or computationally, (iv) the efficient creation of distortion models that can be exported to other software packages for experimental or computational analysis, (v) the systematic theoretical exploration of a class of transitions such as the well studied perovskite tilting patterns (Glazer, 1972; Hatch & Stokes, 1987; Howard & Stokes, 1998), and (vi) the creation and enjoyment of beautiful distortion modes, *i.e.* 'art for art's sake'.

2. Group theoretical concepts

ISODISPLACE has been designed for use by researchers who are not experts in the mathematical theory of crystallographic symmetry. Without much mathematical rigor, we will here describe the group-theoretical concepts employed for those who wish to gain a better understanding of the nature of *ISODISPLACE* output. Several examples will be presented that involve distortions of cubic perovskite ABO_3, which has space-group symmetry $Pm\bar{3}m$ and unique atoms located at Wyckoff sites $A{:}b(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $B{:}a(0,0,0)$, and $\mathrm{O}{:}d(\frac{1}{2},0,0)$.

2.1. Space-group irreps and the irrep basis of distortion space

A space-group representation is a homomorphic mapping of an infinite number of space-group symmetry operations onto an often finite group of representative matrix operations called the 'image' of the representation. The abstract n-dimensional vector space in which the matrices of a representation operate is called the 'carrier space' of the representation. The 'dimension' of the representation is the dimension of its matrices, and the 'order' of the image is the number of its distinct matrices. An irreducible representation or 'irrep' is a representation that cannot be unitarily transformed into block-diagonal form. A reducible representation is one that can be unitarily transformed into block-diagonal form, such that each block is occupied by an instance of one of the available irreps.

The term 'distortion' is an intuitive reference to the set of structural degrees of freedom in the low-symmetry phase that results from a phase transition. Even users who are not well acquainted with representation theory will benefit from an appreciation of the fact that any distortion can be described as a vector in the abstract carrier space of a representation of the parent structure, which we loosely refer to here as 'distortion space'. Once a basis of a distortion space has been identified, one can describe any conceivable combination of macroscopic strain and microscopic atomic displacement patterns within that distortion space in terms of vector components along each of the basis vector directions. Irreps are extremely useful in this regard because they are associated with basis vectors that can always be chosen to be orthogonal to one another and to those of other irreps (Eyring *et al.*, 1944). They not only form a complete basis, but also provide for a unique description of any distortion.

The reciprocal-space *k*-point or wavevector of a phase transition indicates the location of any superlattice diffraction peaks that may arise in the low-symmetry phase. The set of distinct *k* vectors related by the symmetries of the space group are referred to collectively as the 'star' of *k*. As is typical, we use the term '*k*-point' to refer to the entire star of *k*. 'Special *k*-points' are those that lie on points of symmetry in reciprocal space. The *k*-points that lie along special lines (*i.e.* lines of symmetry) or within special planes (*i.e.* planes of symmetry), but which are not points of symmetry are called 'non-special *k*-points'. One typically groups non-special *k*-points of the same type (*i.e.* same line or plane of symmetry) and refers to them with a common *k*-point label. Similarly, all fully general *k*-points share a common label 'GP'.

ISODISPLACE uses the subroutines of the *ISOTROPY* software suite to generate atomic displacement patterns induced by representations of the parent space-group symmetry at reciprocal-space *k*-points. In general, space-group irreps are defined relative to specific *k*-points. A space-group irrep of the parent structure can only induce distortions that produce the reciprocal superlattice defined by its *k*-point. In the case of cubic $Pm\bar{3}m$ ABO_3 perovskite, *ISODISPLACE* lists six irreps for the special *R*-point ($k = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$), R_1^+, R_3^+, R_4^+, R_5^+, R_2^- and R_4^-, and four irreps for the non-special Σ-point ($k = [a, a, 0]$), Σ_1, Σ_2, Σ_3 and Σ_4. Even for distinct *k*-points with the same label, the irreps defined at those points are distinct (*e.g.* $[\frac{1}{3}, \frac{1}{3}, 0]\Sigma_1$ *versus* $[\frac{1}{4}, \frac{1}{4}, 0]\Sigma_1$). While many phase transitions can be described in terms of the basis vectors of a single irrep, some require reducible representations that couple multiple irreps (Hatch & Stokes, 1991).

2.2. Isotropy subgroups (distortion symmetries)

When a crystal experiences a symmetry-lowering structural distortion, some of the symmetry elements of the parent space group are lost, while others persist in the resulting superstructure. Those elements that persist form the space-group symmetry of the low-symmetry phase, which is called an 'isotropy subgroup' of the parent space group (Stokes & Hatch, 1987). Within a given isotropy subgroup, many distinct distortions can be achieved by arbitrarily choosing the values of the new degrees of freedom available. The isotropy subgroup simply defines the common symmetry that each such distortion will possess, and can be more intuitively referred to as the 'distortion symmetry'. Hereafter, we will use the terms 'isotropy subgroup' and 'distortion symmetry' interchangeably.

A distortion will not possess all of the parent space-group symmetry operations; yet it must, by definition, possess the subgroup symmetries that persist in the superstructure. In other words, the distortion vector is left invariant by the subgroup symmetry operations. It follows that the set of all possible distortion vectors sharing the same distortion symmetry forms an 'invariant subspace' of the carrier space (Bradley & Cracknell, 1972).

It is impossible to tabulate all possible distortion symmetries of a parent space-group symmetry simply because there are an infinite number of them. While there are only a finite number of distortion symmetries for a given *k*-point, there are an infinite number of possible *k*-points in continuous reciprocal space. Stokes & Hatch (1987) have tabulated all of the isotropy subgroups of each of the 230 crystallographic space groups induced at special *k*-points by a single irrep of the parent. *ISOTROPY* and *ISODISPLACE* further permit one to explore those associated with non-special *k*-points and coupled irreps.

2.3. Irrep kernels

Because an irrep mapping is homomorphic rather than isomorphic, it is possible for many group elements (even an infinite number) to be mapped onto the same matrix operator. The group of all symmetry operators that are mapped by a representation onto the identity matrix is called the 'kernel' of the representation. In the case of cubic ABO_3 perovskite, the kernel of the two-dimensional R_3^+ irrep has space-group symmetry *Fmmm*, and the kernel of the three-dimensional R_4^+ irrep has space-group symmetry $P\bar{1}$. In either case, the identity matrix represents each element of the kernel, so that the kernel leaves all distortions in the entire carrier space of the irrep invariant. Thus, the kernel of an irrep is an isotropy subgroup (*i.e.* distortion symmetry) of the parent space-group symmetry and also corresponds to the largest invariant subspace (*i.e.* the whole carrier space) belonging to that irrep.

2.4. Order parameters and order-parameter directions

Only three things are required to specify a given distortion symmetry uniquely: a *k*-point, an irrep and one of its order-parameter directions. The term 'order-parameter direction' (OPD) refers to a direction, or rather a subspace, in the carrier space of the irrep. Each distinct vector within such a subspace will correspond to a different distortion. More specifically, the OPD identifies the invariant subspace containing all of the distortion vectors that possess the corresponding distortion symmetry. For a given irrep, the kernel will always be the distortion symmetry with the most general OPD. For a three-dimensional irrep, we express the OPD of the kernel with three variable components (a, b, c) to indicate that any vector in the three-dimensional carrier space is permitted.

Many irreps also induce intermediate distortion symmetries that contain the kernel as a subgroup. These intermediate distortion symmetries have smaller invariant subspaces, lower-dimensional OPDs, higher space-group symmetries, and fewer degrees of freedom than the kernel. For example, $(a, a, 0)$ is a one-dimensional OPD of a three-dimensional irrep, and refers to a more restrictive one-dimensional subspace of (a, b, c). *ISODISPLACE* lists the OPDs of all intermediate distortion symmetries. The list will tend (but not strictly) towards lower symmetry from top to bottom, with the general OPD appearing at the bottom. For cubic ABO_3 perovskite, the three-dimensional R_4^+ irrep of $Pm\bar{3}m$ yields six OPDs: $(a, 0, 0)$, $(a, a, 0)$, (a, a, a), $(a, b, 0)$, (a, a, b) and (a, b, c).

When working within the kernel distortion symmetry of an irrep, each structural degree of freedom provided by *ISODISPLACE* is a vector component (*i.e.* amplitude) that corresponds to exactly one of the irrep basis vectors. However, when working within an intermediate distortion symmetry, one structural degree of freedom may instead activate a symmetry-adapted linear combination of several irrep basis vectors that takes advantage of the higher space-group symmetry. In general, we will call these symmetry-adapted linear combinations 'distortion modes'. In the context of phase transitions, the mode amplitudes are referred to as 'order-parameter components'. An arbitrary distortion can be thus decomposed into distortion modes, one for each structural degree of freedom. Each amplitude then determines how much of its corresponding mode to mix into the overall atomic displacement pattern.

The precise definition of 'order parameter' is somewhat difficult to organize here because the term is commonly used in different ways in the context of phase transitions. When a transition involving multiple irreps and OPDs gives rise to a distortion vector, one might define the order parameter to be the complete set of its vector components over the multi-irrep basis, where components within the same mode may be linearly dependent. Or it may be more convenient to define it as the complete set of independent vector components. Alternatively, it is common to define an order parameter to be a vector in distortion space that lies along a specific OPD of a specific irrep at a specific *k*-point. Under this definition, an arbitrary distortion vector can be composed of multiple order parameters, some of which may be multi-dimensional themselves. This is the definition used by *ISODISPLACE*.

3. Physical considerations

The fundamental advantages of the irrep-induced distortion modes are (i) that they form a complete basis of distortion space, and (ii) that the free energy of a crystalline solid can be expressed very simply in terms of the corresponding order parameters (Landau, 1937; Landau & Lifshitz, 1980). These symmetry-adapted distortion modes often involve polyhedral stretches, rotations, shears, bucklings, and other familiar geometric displacement patterns, which tend to have clear physical meaning with respect to the interatomic interaction forces that drive a phase transition. In most cases, the principal component of a physical distortion can be described by a small number of symmetry-adapted distortion-mode amplitudes.

Relying purely on symmetry considerations, *ISODISPLACE* cannot take into account the physical parameters required to predict the actual distortion-mode amplitudes in a real material. Experimental (*e.g.* diffraction) data or *ab initio* calculations are generally required to obtain a realistic set of amplitudes that fully define a distortion. Of course, *ISODISPLACE* can be used to generate a candidate distortion model conveniently that can then be exported for further experimental or computational investigation.

Lattice vibrations can also be treated by thinking of distortions as frozen phonon modes. The phonon basis vectors at a given *k*-point are called polarization vectors or lattice normal modes and can also be assigned to a distortion symmetry. Phonon polarization vectors with a given distortion symmetry can, in principle, be decomposed over the symmetry-adapted distortion-mode basis of *ISODISPLACE* (Stokes, 1995). Once again, however, the details of the transformation will depend on physical parameters such as atomic masses, interatomic forces and thermodynamic state variables, which are not considered by *ISODISPLACE.*

4. Functionality

4.1. Distortion symmetry selection

Given the parent structure, the selection of a distortion symmetry involves three key decisions: a *k*-point in reciprocal space, an irrep of the parent space-group symmetry at that *k*-point, and an OPD in the carrier space of the irrep. At each step, *ISODISPLACE* computes the possible choices and presents them to the user in drop-down menus, so that all relevant possibilities can be explored without looking up obscure labels in lengthy tables. Several decision paths are currently available.

The general method requires the user to select the *k*-point, irrep, and OPD in sequence. This approach can be used at any commensurate *k*-point (expressed in terms of rational fractions), including special *k*-points, points located on *k*-lines and planes, and fully general *k*-points. For each type of *k*-point, there are a finite number of irreps available which are unique to that *k*-point. Similarly, each irrep has a finite number of OPDs which are unique to that irrep. While a given distortion symmetry may be associated with more than one irrep (as discussed below), two different OPD subspaces of the same irrep cannot lead to the same distortion symmetry. For a given parent space group, *k*-point and irrep, there may be more than one distortion symmetry that possesses the same supercell basis, or the same origin shift, or possibly the same space-group symmetry. However, the combination of supercell basis, origin shift and crystallographic space group identifies only one distortion symmetry, or rather identifies a specific domain of that distortion symmetry. To make domain differences more transparent, *ISODISPLACE* generates a complete list of the domains for a given distortion symmetry, along with other useful domain-specific information.

A convenient alternative to the general method allows the user to consider simultaneously all special *k*-points for relevant distortions involving a single irrep, while imposing practical restrictions on the final distortion symmetry, such as crystal family, space-group symmetry, or supercell shape. Because the set of distortion symmetries that can be obtained in this way is manageably finite, their irreps and OPDs have been precomputed and stored for rapid searching. This method is not available for non-special *k*-points simply because there are an infinite number of them. Another more flexible method allows the user to search over arbitrary commensurate *k*-points and coupled irreps while restricted to a user-specified space group and supercell or superlattice basis.

For distorted structures with experimentally determined atomic coordinates and cell parameters, *ISODISPLACE* also provides a mechanism for automatic mode decomposition: the process of transforming the superstructural atomic coordinates into the amplitudes of the symmetry-adapted distortion modes of the parent structure. This method requires the user to enter the parent structure and the superstructure separately, along with the superstructure basis.

4.2. Irrep and OPD labels

ISODISPLACE lists the following information in each drop-down menu that contains distortion symmetries: the space-group irrep label (from which the *k*-point can be inferred), the OPD label and vector, the conventional supercell basis, origin shift and size relative to the parent cell, and finally the subgroup index relative to the parent space-group symmetry. Like *ISOTROPY*, it uses the labels of Miller & Love (1967) for *k*-points and irreps. In this standard scheme, *k*-point labels consist of one or two capital letters. Space-group irrep labels begin with the *k*-point label, followed by a numeral and possibly a '+' or '−' sign. Where complex irreps must be combined in order to transform them to real form, the resulting physically reducible representation labels simply concatenate a pair of irrep labels (Bradley & Cracknell, 1972). Wyckoff site point-group irreps are also used by *ISODISPLACE*, which employs the conventional point-group irrep labels common to molecular spectroscopy (*e.g.* A_g, B_{1u}, T_{2g}, E, *etc.*).

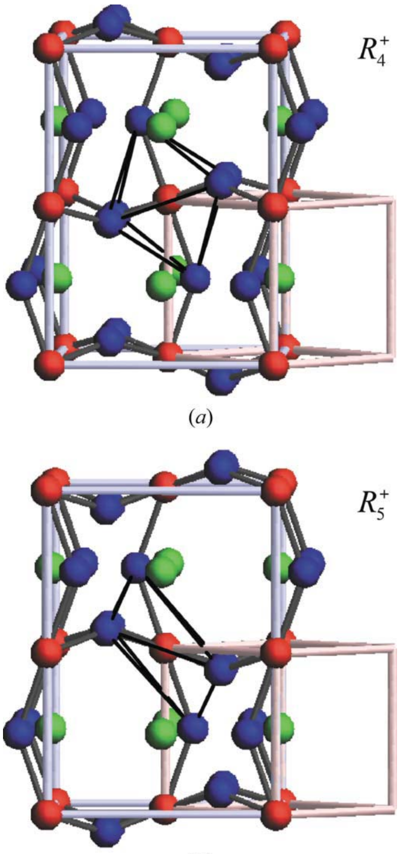
OPD labels follow the convention of Stokes & Hatch (1987), and begin with a capital letter or a numeral–letter combination that indicates the dimension of the OPD: P for one dimension, C for two dimensions and S for three dimensions, followed by the sequence $4D$, $6D$, $8D$, $12D$, $16D$, $24D$, $48D$. These labels are useful when space is limited, but do not contain as much information as complete OPD descriptions of the form $(a, -a, 0, b, c, 0)$. To avoid confusion, remember that the use of lowercase alphabet letters (*i.e.* a, b, c ...) in OPD and branch labels is not related to their use in Wyckoff point labels or as unit-cell parameters.

Note that one cannot generally expect a given *k*-point label to have comparable meanings within the contexts of two different parent space-group symmetries. The labels are defined independently within each parent space group. Similarly, it is not generally useful to compare the irrep labels amongst different k-points, or the OPD labels amongst different irreps. With experience, however, some useful trends do become apparent.

4.3. Primary and secondary order parameters

An order parameter is 'primary' if it energetically drives the phase transition. Similarly, the irrep by which the primary order parameter is induced is called the primary irrep. Any other order parameters (irreps) which are capable of cooperating with (*i.e.* coupling to) the primary order parameter (irrep) are called 'secondary'. *ISODISPLACE* assumes that the user-selected irrep is primary, and then calculates and displays all primary and secondary order parameters. For a given parent atom type, primary order-parameter components are always listed first, and can be identified by locating the primary irrep within their distortion-mode labels.

The distortion modes of primary order parameters are always sufficient for imposing the final distortion symmetry. Secondary order parameters, on the other hand, are usually not sufficient, *i.e.* they do not lower the symmetry enough by themselves. For example, any internal degrees of freedom permitted by the parent space-group symmetry will also exist in the superstructure as secondary order parameters. While the primary order parameters are sufficient for generating the final distortion symmetry, they are not sufficient for exploring the entire invariant subspace of distortion vectors that share that distortion symmetry. All primary and secondary order parameters must be coupled if one wishes to achieve a fully arbitrary distortion that utilizes all of the degrees of freedom available to the superstructure.



(*a*)

(*b*)

Figure 1
Two oxygen-displacement modes of cubic ABO_3 perovskite that belong to equi-symmetric irreps. Both result in a $2^{1/2} \times 2^{1/2} \times 2$ supercell and space-group symmetry *Imma*. Light-colored borders indicate the edges of the supercell and the smaller parent cell. (*a*) $R_4^+(a, a, 0)$ induces a tilting of the BO_6 octahedra, while (*b*) $R_5^+(a, a, 0)$ induces a distortion that flattens the BO_6 octahedra.

In some cases, secondary order parameters arise which prove sufficient to impose the final distortion symmetry by themselves. Let $\boldsymbol{\eta}_2$ be such a secondary order parameter. If $\boldsymbol{\eta}_1$ is selected as the primary order parameter, then $\boldsymbol{\eta}_2$ will couple as a secondary order parameter. Alternatively, if $\boldsymbol{\eta}_2$ is assumed to be the primary order parameter, then $\boldsymbol{\eta}_1$ will couple as a secondary order parameter. Thus, the respective distortion modes of this 'equi-symmetric' pair of order parameters, $\boldsymbol{\eta}_1$ and $\boldsymbol{\eta}_2$, can be very different, and yet lead to the same distortion symmetry. In practice, *ISODISPLACE* automatically couples all secondary order parameters so that both routes result in the same set of distortion modes.

The well known $a^-a^-c^0$ octahedral tilt pattern observed in many perovskites (Glazer, 1972; Hatch & Stokes, 1987; Howard & Stokes, 1998) is generated by an order parameter of $R_4^+(a, a, 0)$. The primary oxygen displacement mode produces the octahedral tilts, which are then accompanied by two secondary displacive modes of the equi-symmetric order parameter $R_5^+(a, a, 0)$ and three secondary strain modes (see Fig. 1). Strain modes are always associated with Γ-point irreps and usually appear as secondary order parameters in displacive transitions, though they must be primary in proper ferroelastic transitions.

4.4. Order-parameter selection

The distortion modes within a given distortion symmetry are grouped according to order parameter, where each order parameter corresponds to an instance of one of the irreps in the overall block-diagonal representation. Because multiple instances of an irrep can contribute to the same distortion, *ISODISPLACE* further classifies order parameters according to local atom-site considerations using the algorithm of Stokes *et al.* (1991). First, each unique atom in the parent cell can be associated with separate order parameters. Second, the modes of a given Wyckoff site can be classified according to the Wyckoff site point-group irreps that induce its local distortion.

A third level of classification is required for order parameters that share the same local point-group irrep. We call these common-local-irrep order parameters (CLIROPs) and distinguish them with an extra numeral in the mode label (*e.g.* 1, 2, 3 . . .). This 'order-parameter number' (OP#) is only displayed when there are at least two CLIROPs. As a simple example, the T-site sublattice of faujasite (a = 25 Å) has one Si atom at the general Wyckoff position i(0.941, 0.121, 0.0364) of space group $Fd\bar{3}m$. The distortion symmetry induced by $\Gamma_1^+(a)$ yields three one-dimensional CLIROPs associated with point-group irrep 'A'. They are [Si:i]A_1, [Si:i]A_2, and [Si:i]A_3. The corresponding distortions displace Si along the x, y and z directions, and appear to be breathing modes of the alpha-cage six-ring, the alpha-cage four-ring and the double-six-ring, respectively. Note that the structures of CLIROP modes are dependent on the irrep matrices used, which in the present case were taken from the *ISOTROPY* database. Another set of irrep matrices obtained by a similarity transform would mix the modes within a given set of CLIROPs, but could not mix modes from different k-points, atoms, space-group irreps, or local point-group irreps. Also note that *ISODISPLACE* CLIROP modes, while still independent, will not generally be mutually orthogonal when dealing with non-rectangular unit-cell shapes, though they can be easily orthogonalized if desired.

The individual distortion modes of multi-dimensional order parameters are further identified with the independent branches of their multi-dimensional OPD. For example, there are three octahedral-rotation modes of the three-dimensional order parameter $R_4^+(a,b,c)[\mathrm{O}:d]Eu$ of cubic $AB\mathrm{O}_3$ perovskite corresponding to branches '*a*', '*b*', and '*c*', respectively.

4.5. Order-parameter types and tensors

There are numerous distinct classes of physical order parameters (*e.g.* displacive, order–disorder, lattice strain, magnetic, *etc.*) that can be associated with isotropy subgroups of the parent space-group symmetry. These classes can be best described in terms of their tensorial properties. Atomic displacement modes, for example, have order parameters that transform like polar first-rank tensors under the matrix operations of the irrep, whereas macroscopic strain modes (*i.e.* lattice parameter changes) have polar symmetrized second-rank tensor order parameters, and order–disorder modes have scalar order parameters. While *ISODISPLACE* was originally intended only for the exploration of displacive transitions, the current version implements macroscopic strains and allows order–disorder transitions with some restrictions.

Because many distortion symmetries only have order parameters that are not of the displacive, strain, or order–disorder types, *ISODISPLACE* avoids time-consuming 'dead-end' searches by filtering out the irreps that induce them. When a particular *k*-point is considered, the program begins by checking each of the associated primary irreps individually and only returns those that are capable of atomic displacements, strains, or order–disorder. Later, when a specific distortion symmetry is selected, it identifies any secondary irreps capable of atomic displacements or strains, and outputs their respective distortion modes.

In contrast to the displacive and strain cases, *ISODISPLACE* does not classify order–disorder modes according to irrep, or even attempt to compute them at all. There are, for example, no 'site occupancy' slider bars. While these could be implemented, they would add complexity that does not seem necessary at the present time. Instead, *ISODISPLACE* provides a color scheme and a series of checkboxes that allow the user to individually highlight unique daughter sites in the low-symmetry phase which have split from the same parent site. In cubic $AB\mathrm{O}_3$ perovskite for example, $\Gamma_3^+(a,b)$ splits the parent oxygen site into three distinct daughter sites, any of which can be distinguished by using the appropriate checkbox. *ISODISPLACE* searches explicitly for irreps with order–disorder parameters in order to avoid missing transitions like this one which have no displacive modes.

Irrep subduction frequencies are used to determine whether or not an irrep can yield order parameters of a particular tensorial form. A detailed explanation of subduction frequencies can be found in the book by Bradley & Cracknell (1972). We will digress only briefly here to be concise regarding the method used. For microscopic atomic displacements, *ISODISPLACE* calculates the subduction frequency

$$n_{ijh} = \frac{1}{|H|}\sum_{x\in H}\chi^*[\Lambda_i^G(x)]\chi[\Lambda_j^H(x)],$$

where $\chi[\Lambda(x)]$ refers to the character of matrix $\Lambda(x)$ in the image of irrep Λ, Λ_i^G is the *i*th irrep of parent space group G, Λ_j^H is the *j*th irrep of the point group H of parent Wyckoff site h, $|H|$ indicates the order of the image of Λ_j^H, and x is summed over the elements of H. If there is an occupied Wyckoff site h in the parent structure with a point-group irrep Λ_j^H that has first-rank polar order parameters, then $n_{ijh} > 0$ implies that all isotropy subgroups induced by irrep Λ_i^G will have displacive order parameters. The requisite tensorial properties of the order parameters of point-group irreps are simply extracted from a pre-tabulated database.

For order–disorder parameters, Λ_j^H is replaced in the subduction frequency formula above by E^H, the identity irrep of point group H. If there is a Wyckoff site h in the parent structure such that $n_{ih} > 0$ and $\Lambda_i^G \neq E^H$, then all of the isotropy subgroups induced by irrep Λ_i^G will have order–disorder parameters.

Macroscopic strains, which can only be induced by Γ-point irreps of G, are treated somewhat differently. Any Γ-point irrep Γ_i^G that arises at a given *k*-point is tested directly for polar symmetrized second-rank tensor order parameters. If Γ_i^G is found to possess them, any isotropy subgroups induced by Γ_i^G will have strain order parameters.

Once the primary irreps that induce a specific isotropy subgroup S of G have been identified, *ISODISPLACE* identifies secondary irreps by calculating the following subduction frequency for each candidate:

$$n_j = \frac{1}{|S|}\sum_{x\in S}\chi[\Lambda_j^G(x)],$$

where x is summed over the distinct matrices in the image of Λ_j^G that belong to S. If $n_j > 0$, then Λ_j^G must be either a primary or secondary irrep of the transition that induces isotropy subgroup S. Secondary irreps identified in this way are then checked to make sure that they are capable of displacements, strains or order–disorder, as described above.

4.6. Coupled primary order parameters

Some distortions cannot be generated by a single primary order parameter, yet are still possible *via* the simultaneous application (*i.e.* 'coupling') of multiple primary order parameters. This process does not lead to new distortion modes, but rather combines existing distortion modes from different irreps to achieve more complex distortions. Because each contributing distortion mode is associated with a specific OPD and irrep, common expressions that arise include 'coupled modes', 'coupled order parameters' and 'coupled irreps'.

In *ISODISPLACE*, a user first specifies the primary irreps (including *k*-points) to be coupled, after which a drop-down menu appears with a list of possible OPD combinations, each of which identifies a distortion symmetry. Within a given distortion symmetry, the user can then manually couple the mode amplitudes from different irreps. Because coupled primary irreps involve a much larger parameter space, *ISODISPLACE* allows the user to enumerate all of the possibilities that might lead to a given supercell or space-group symmetry. Because *ISODISPLACE* automatically couples the primary irrep to any relevant secondary irreps, they do not need to be explicitly coupled in by the user.

Different domains of a single order parameter are energetically and physically equivalent, meaning that they are related by some operation of the parent space group (such as a rotation or inversion) that is lost in the transition. For example, a tetragonal strain can be oriented along any one of three equivalent cubic [100] directions. Rather than treating equivalent domains as distinct distortion symmetries, *ISODISPLACE* selects one representative domain in each case by internal convention, which may appear arbitrary to the user. In general, the choice of domain can be made using any reasonable convention without obviously changing the intrinsic appearance of the distortion modes. When a pair of order parameters are coupled, one domain must be selected from each of the contributing order parameters. In such cases, it is useful to realise that different combinations of the contributing domains may lead to entirely different final distortion symmetries.

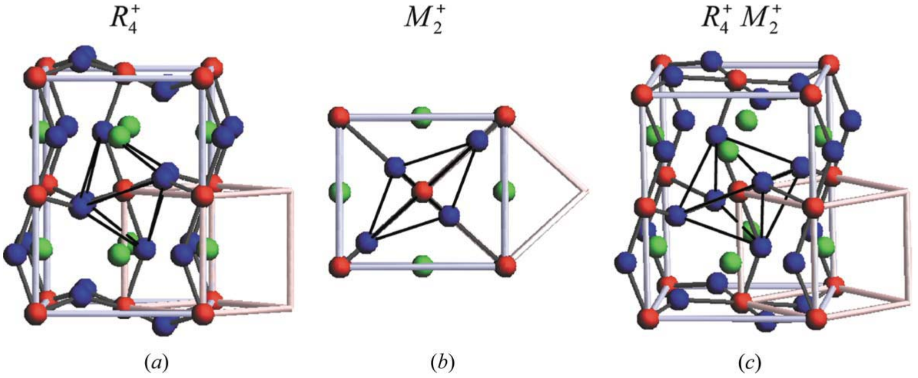


Figure 2
(*a*) Irrep R_4^+ of cubic ABO_3 perovskite induces a BO_6 octahedral tilt mode. (*b*) Irrep M_2^+ induces a Jahn–Teller octahedral stretch mode. Only oxygen-displacement modes are illustrated. (*c*) These two irreps couple to produce the well known *Pnma* phase with its $2^{1/2} \times 2^{1/2} \times 2$ supercell.

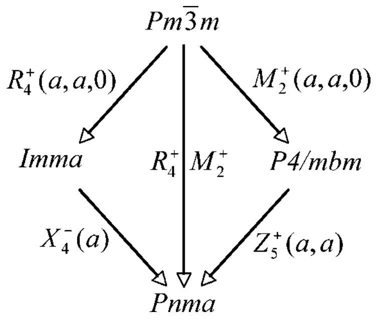


Figure 3
Symmetry map showing three routes to the *Pnma* tilted phase of cubic ABO_3 perovskite, one *via* directly coupled irreps, and two *via* multi-step routes.

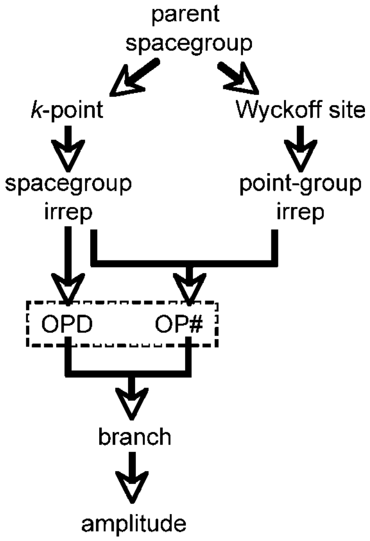


Figure 4
Dependency tree illustrating the classification of distortion modes. Nodes are choices to be made, while arrows indicate the dependence of each choice on previous choices. The dashed line indicates the point at which a symmetry-adapted order parameter has been specified. A branch of the order parameter further specifies an individual distortion mode.

Many distortions that require multiple primary irreps actually occur in multiple steps, where only one irrep is active in a given step. In *ISODISPLACE*, it is possible to implement those irreps independently in any order to obtain the same distortion symmetry. First, one irrep is applied, the resulting structure is saved and re-entered as the new parent structure, and then the second irrep is applied. This can be confusing because the second irrep must be defined relative to the intermediate distortion symmetry, so that its name and behavior may not be identical to those of the loosely corresponding irrep that is defined relative to the parent space group. Furthermore, the mode names and arrangements may be somewhat different depending on the route followed. Fortunately, with a little ingenuity, identical final distortions can always be achieved *via* different routes by appropriately adjusting the mode amplitudes. Patience and some experimentation are required whenever dealing with coupled primary irreps or multi-step transitions.

Perovskite $LaMnO_3$ exhibits a low-temperature phase transition at 750 K (Matsumoto, 1970) to an orthorhombic phase that accommodates both an out-of-plane octahedral tilt and a Jahn–Teller (JT) distortion. The tilt is induced by the irrep(OPD) combination $R_4^+(a, a, 0)$ yielding a $2^{1/2} \times 2^{1/2} \times 2$ supercell with *Imma* symmetry, while the JT distortion can be induced separately by $M_2^+(a, 0, 0)$ yielding a $2^{1/2} \times 2^{1/2} \times 1$ supercell with $P4/mbm$ symmetry. Together, these two distortions couple as $R_4^+ M_2^+(a, a, 0, 0, 0, b)$ to produce the well known *Pnma* phase in the larger $2(2^{1/2}) \times 2^{1/2} \times 2$ supercell, as illustrated in Fig. 2. Note that the in-plane octahedral rotation induced by equi-symmetric $M_3^+(a, 0, 0)$ is a prominent feature of this transition and more likely to be primary than $M_2^+(a, 0, 0)$. Experimentally, the irreps appear to couple directly, though the details are more complicated than this simple example suggests (Rodriquez-Carvajal *et al.*, 1998).

Now, for purely pedagogical reasons, consider a multi-step route to the *Pnma* phase in which two irreps are applied in sequence, as diagrammed in Fig. 3. One could first apply the $R_4^+(a, a, 0)$ distortion of $Pm\bar{3}m$ to obtain an intermediate *Imma* phase, followed by the $X_4^-(a)$ distortion of *Imma* to complete the descent to *Pnma*. In this case, the effect of $X_4^-(a)$ on the intermediate *Imma* phase is roughly analogous to that of $M_2^+(a, a, 0)$ on the $Pm\bar{3}m$ parent phase. Alternatively, one can first apply the $M_2^+(a, 0, 0)$ distortion of $Pm\bar{3}m$ to obtain an intermediate $P4/mbm$ phase, followed by the $Z_5^+(a, a)$ distortion of $P4/mbm$.

4.7. Distortion-mode classification

It is desirable to know the extent to which the distortion modes generated by *ISODISPLACE* are unique. It is also helpful to have unique labels with which to identify unique modes. These issues are explored here, along with a unified explanation of the various choices that identify a distinct mode. While many of these choices are managed behind the scenes by *ISODISPLACE*, some will find it useful to see how they are interrelated.

Distortion modes are classified by *ISODISPLACE* as illustrated by the dependency tree of Fig. 4. On the left-hand side of the dependency tree, the OPD (along with the choices leading up to it) specifies a distortion symmetry. On the right-hand side of the tree, the OP# (along with the choices leading up to it) specifies an order parameter. Combining an order parameter with a distortion symmetry (indicated by a dashed line in Fig. 4) adapts or restricts the order parameter to that distortion symmetry. Finally, each branch of the symmetry-adapted order parameter corresponds to a distinct distortion mode with its own amplitude. While an OPD branch can be considered independent of a specific order parameter, we find it helpful here to define the order parameter as a whole before splitting it up into branches. In practice, the user guides the selection of the distortion symmetry, after which *ISODISPLACE* generates and presents all available distortion modes for interactive exploration.

By combining global (parent space group) and local (Wyckoff site) information, *ISODISPLACE* provides a mode label that completely describes an arbitrary distortion mode of a parent structure. As an esoteric example that fully illustrates the label format, consider the following distortion of cubic $AB\mathrm{O}_3$ perovskite.

$$Pm\bar{3}m[\tfrac{1}{4},\tfrac{1}{4},0]SM1(a,a,b,-b,0,0,c,c,0,0,0,0)[O\!:\!d]Eu\_2(c)0.12$$

This label describes a $k = [\frac{1}{4}, \frac{1}{4}, 0]$ distortion along the S line of the parent space group $Pm\bar{3}m$. The 12-dimensional Σ_1 irrep and its three-dimensional OPD, $(a, a, b, -b, 0, 0, c, c, 0, 0, 0, 0)$ specify a distortion symmetry with a 4 × 4 × 4 supercell and space group $Ima2$. Parent Wyckoff site O:d, its point-group irrep Eu, and OP# 2 specify a symmetry-adapted order parameter. Branch (c) of the OPD then identifies a specific distortion mode belonging to the symmetry-adapted order parameter. The 0.12 Å amplitude indicates the magnitude of the largest displacement experienced by any of the atoms affected by the mode. This definition accounts for the fact that a single distortion mode can displace multiple unique atoms within the superstructure that have split from the same parent atom. In such cases, these unique atoms generally experience distinct displacements.

Placing an atom name next to the Wyckoff label links an abstract distortion mode to a physical atomic displacement pattern experienced by a specific parent crystal structure. When the atom name is removed, the mode label refers to a purely abstract distortion mode that could be applied to any parent structure with the specified space-group symmetry and occupied Wyckoff position.

For a given description of the parent crystal structure, there is a unique relationship between *ISODISPLACE* mode labels and physical atomic displacement patterns. However, if the parent structure has more than one equivalent description, distinct mode labels associated with different descriptions can refer to the same atomic displacement pattern. Cubic $AB\mathrm{O}_3$, for example, has unique atoms at Wyckoff positions A:$b(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, B:$a(0, 0, 0)$, and O:$d(\frac{1}{2}, 0, 0)$ of space group $Pm\bar{3}m$, but can be equivalently described by shifting the origin so as to place the atoms at positions A:$a(0, 0, 0)$, B:$b(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and O:$c(0, \frac{1}{2}, \frac{1}{2})$. As a result, $Pm\bar{3}m[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]R_4^+(a, a, 0)[\mathrm{O}\!:\!d]Eu(a)$ and $Pm\bar{3}m[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]R_5^-(a, a, 0)[\mathrm{O}\!:\!c]Eu(a)$ both describe the same octahedral tilt pattern. To avoid confusion, it is important always to refer to an explicit definition of the parent structure, including space-group settings and atomic coordinates, when communicating or interpreting mode labels.

In summary, the space of all possible distortions (consider all supercell shapes, sizes and orientations) of a parent structure is spanned by a basis of distortion modes that can be identified by their combination of k-point, space-group irrep, OPD, Wyckoff site, local point-group irrep, OP#, branch, and mode amplitude. While some aspects of *ISODISPLACE* output (*i.e.* OPD configurations and CLIROP modes) depend on the choice of irrep matrices used, the irrep matrices in the *ISOTROPY* database are convenient, self-consistent, and well tested, so that *ISODISPLACE* mode labels provide a robust means of communicating distortion-mode details.

4.8. The *xyz* basis

While the irrep basis of the parent space group is a very useful basis of the generalized vector space of all possible distortions, it is not the only one. For most applications (structural refinements, modeling, visualization, *etc.*), atomic displacements need to be described in the more familiar *xyz* basis, which is the set of all atomic x, y and z coordinates within the supercell. For a supercell with N atoms, there are $3N$ such coordinates, though only some of them will be independent degrees of freedom depending on the symmetry. *ISODISPLACE* uses the algorithm of Stokes *et al.* (1991), as contained within the *ISOTROPY* software, to compute the linear transformation from the irrep basis into the *xyz* basis. Naturally, the total number of degrees of freedom is independent of basis. Thus, if there are n free atomic coordinates in the low-symmetry phase, *ISODISPLACE* will provide n free order-parameter components.

As an example of the relationship between the irrep basis and the *xyz* basis, consider a hypothetical distortion of cubic $AB\mathrm{O}_3$ perovskite that doubles the cell size along the [100] axis. This would yield ten atoms in a 2 × 1 × 1 supercell and 30 potentially free atomic coordinates in the *xyz* basis. While no single irrep has a sufficiently high dimension to accommodate a 30-dimensional distortion space, a large block-diagonal representation can be constructed from a direct sum of each of the irreps capable of contributing to a distortion in the specified supercell. A given irrep subduces the reducible block-diagonal representation more than once depending on the number of parent cell atoms that it splits and other considerations. Some exploration reveals that there are five primary X-point irreps and two Γ-point irreps that can contribute: $X_1^+(a, 0, 0)\,\{2\}$, $X_5^+(a, b, 0, 0, 0, 0)\,\{2\}$, $X_3^-(a, 0, 0)\,\{2\}$, $X_4^-(a, 0, 0)\,\{1\}$, $X_5^-(a, b, 0, 0, 0, 0)\,\{3\}$, $\Gamma_4^-(a, b, c)\,\{4\}$ and $\Gamma_5^-(a, b, c)\,\{1\}$. The most general OPD leading to the 2 × 1 × 1 supercell is shown for each irrep, along with the number of order parameters per irrep (*i.e.* subduction frequency) in curly brackets.

The total number of independent distortion modes is then $1 \times 2 + 2 \times 2 + 1 \times 2 + 1 \times 1 + 2 \times 3 + 3 \times 4 + 3 \times 1 = 30$, as expected, which if all coupled simultaneously, will drive the space-group symmetry all the way down to $P1$. Whereas an *xyz* basis vector displaces only one coordinate of one atom within the supercell, a symmetry-adapted irrep mode displaces many atoms at once. However, each basis provides 30 independent degrees of freedom that span the same distortion space. Thus, any arrangement of the 30 atoms in the supercell can be achieved using either basis.

4.9. Limitations

Current limitations of *ISODISPLACE* include the following. (i) The order of the irreps required can be made arbitrarily large by choosing a sufficiently esoteric general k-point. When the irrep multiplication tables grow to tax or exceed the computer memory available, the computation may run indefinitely or crash. Coupled irreps leading to large supercells can have the same effect. (ii) Incommensurate k-points are being considered, but are not yet implemented.

5. Conclusions

The problem of describing the results of a displacive phase transition can be broken up into four steps: (i) determining the distortion symmetry, (ii) identifying the distortion modes, (iii) determining the individual mode amplitudes, and (iv) expressing the distorted structure in terms of the familiar *xyz* basis. Beginning with a parent crystal structure, *ISODISPLACE* employs drop-down menus to guide the user through the selection of any possible symmetry arising from parent space-group irreps at commensurate k-points in reciprocal space.

Once a distortion symmetry has been selected, the user is presented with an interactive Java applet containing a three-dimensional image of the resulting structure and a panel of controls that modify mouse behavior so as to permit arbitrary rotations, rotations about specific axes, specific view directions, zooming, continuous rotation, *etc.* In addition to atoms and bonds, the parent and supercell edges are both represented, making the relative basis transformation and origin shift apparent. Each distortion-mode amplitude can be independently adjusted *via* slider bars while observing its effect on the structure in real time. Once the individual amplitudes are chosen, the entire distortion can also be animated sinusoidally or saved to a structure file. Because each distortion symmetry can be explored interactively in the viewer, users can now explore a wide range of structural phase transitions without a thorough understanding of the group-theoretical concepts involved.

References

Bradley, C. J. & Cracknell, A. P. (1972). *The Mathematical Theory of Symmetry in Solids*. Oxford: Clarendon.

Capillas, C., Kroumova, E., Aroyo, M. I., Perez-Mato, J. M., Stokes, H. T. & Hatch, D. M. (2003). *J. Appl. Cryst.* **36**, 953–954.

Eyring, H., Walker, J. & Kimball, G. E. (1944). *Quantum Chemistry*, p. 371. New York: Wiley.

Glazer, A. M. (1972). *Acta Cryst.* B**28**, 3384–3392.

Hatch, D. M. & Stokes, H. T. (1987). *Phys. Rev. B*, **35**, 8509–8516. (Erratum published in *Phys. Rev. B*, **36**, 7185.)

Hatch, D. M. & Stokes H. T. (1991). *Phase Transit.* **34**, 53–67.

Howard, C. J. & Stokes, H. T. (1998). *Acta Cryst.* B**54**, 782–789.

Kopský, V. (2003). *Group Informatics (GI*KoBo-1)*. Dodrecht: Kluwer.

Kroumova, E., Aroyo, M. I., Perez Mato, J. M., Kirov, A., Capillas, C., Ivantchev, S. & Wondratschek, H. (2003). *Phase Transit.* **76**, 155–170. (*Bilbao Crystallographic Server*, http://www.cryst.ehu.es/.)

Landau, L. D. (1937). *Phys. Z. Sowjetunion.* **11**, 545–555.

Landau, L. D. & Lifshitz, E. M. (1980). *Statistical Physics*, 3rd ed., part 1, ch. XIV. New York: Pergamon.

Matsumoto, G. (1970). *J. Phys. Soc. Jpn*, **29**, 606–615.

Miller, S. C. & Love, W. F. (1967). *Tables of Irreducible Representations of Space Groups and Co-representations of Magnetic Space Groups*. Boulder: Pruett.

Rodriquez-Carvajal, J., Hennion, M., Moussa, F., Moudden, A. H., Pinsard, L. & Revcolevschi, A. (1998). *Phys. Rev. B*, **57**, R3198–R3192.

Stokes, H. T. (1995). *Ferroelectrics*, **164**, 183–188.

Stokes H. T. & Hatch, D. M. (1987). *Isotropy Subgroups of the 230 Crystallographic Space Groups*. Singapore: World Scientific.

Stokes, H. T. & Hatch D. M. (2000). *ISOTROPY Software*, Department of Physics and Astronomy, Brigham Young University, Utah, USA; http://stokes.byu.edu/isotropy.html.

Stokes, H. T., Hatch, D. M. & Wells, J. D. (1991). *Phys. Rev. B*, **43**, 11010(1–8).