ISODISTORT Tutorial Exercises

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Introduction

ISODISTORT is a tool for generating, exploring, and exporting distorted crystal structures in terms of the symmetry modes of the irreducible representations of the parent space-group symmetry. A distorted (child) structure can be described as a symmetry-lowering deviation from some undistorted reference (parent) structure. These physical order parameters (e.g. atomic displacements, magnetic moments, site-occupancy variations, lattice strains, etc.) can be classified as basis functions of the irreducible representations (irreps) of the parent symmetry group. Multiple order parameters can be superposed in a single distortion -- consider multiferroics. An irreducible representation can contribute more than one multi-dimensional order parameter to a structure (sometimes referred to as separate “instances” of the order parameter). The individual degrees of freedom provided by an instance of a multi-dimensional order parameters are called symmetry modes. The symmetry modes of the parent space group are important because they provide a natural and custom-tailored parameter set for describing distortions of the parent structure.

Some of the symmetry elements of the parent space group are lost when a distortion arises. The symmetries that remain (i.e. the space group of the child structure) comprise an isotropy subgroup of the parent space group. The isotropy subgroup of a distortion is uniquely identified (to within a domain), by its combination of space-group type (one of 230 crystallographic space-group types), lattice basis (supercell size/shape) and supercell origin (relative to the origin of the parent cell). In addition to the space-group type and lattice basis, it is less well understood that the origin is also essential to an unambiguous description.

The full collection of new structural parameters that arise in a structural distortion (e.g. the x,y,z vector components of atomic displacements and magnetic moments, and the scalar site-occupancy deviations) can be arranged into one large-dimensional vector in the vector space of all possible distortions. [In the context of frozen phonons, this vector is often referred to as the "polarization vector".] The collection of all irrep symmetry-mode amplitudes represents the same distortion vector, but in a different coordinate system. Thus, the number of independent structural degrees of freedom in the traditional and symmetry-mode coordinate systems must be the same. Because each structural parameter in the traditional coordinate system can be expressed as a linear combination of symmetry-mode amplitudes, and vice versa, the transformation between the traditional basis and the symmetry-mode basis is an invertible square matrix. When the user chooses an isotropy subgroup of the parent symmetry, ISODISTORT automatically calculates this transformation matrix using group representation theory.

There are an infinite number of ways to distort any crystal structure, provided that one allows an arbitrarily large supercell. ISODISTORT allows one to perform a filtered search for a isotropy subgroup of a given parent structure that has certain user-specified properties. We will explore each of four different search methods. Once an isotropy subgroup has been selected, and the resulting symmetry-modes calculated, ISODISTORT provides a variety of outputs, including tools for visualizing and interactively manipulating the distorted structure and its diffraction pattern. The various outputs types will also be explored in the following exercises.

Installation and Preparation

Start by downloading and unzipping the **isotutorials.zip** file provided by the workshop organizers.

Next, go the home page of the ISOTROPY Software Suite (either at http://iso.byu.edu or at the local URL provided by the workshop organizers). Because the software suite consists mainly of server-side internet-based tools, it is not necessary to install them. Rather you interact with each program through a web browser. We recommend that you set your browser up so that new pages open in separate tabs of the same window rather than in separate windows. Any widely-used web browser should work with ISODISTORT, though we prefer Firefox over Chrome for downloading data files due its option to open the files directly.

The ISODISTORT program interacts with the user primarily via simple html and php web pages and the upload/download of ascii text files, which can be done on any computer or mobile device without special preparations. Because numerical output can sometimes be hard to digest, ISODISTORT is accompanied by two stand-alone applications, ISOVIZ and ISOVIZQ (computers only, not for mobile devices), which allow the user to interactively visualize the effect of symmetry modes on the crystal and its diffraction pattern. There are two options (A and B) for installing them.

Option A: Install stand-alone ISOVIZ/ISOVIZQ applications

Installation: Find the appropriate ISOVIZ and ISOVIZQ installers (MacOS or Windows, not Linux or mobile-OS devices), either from the ISOVIZ page of the ISOTROPY Software Suite or from the **installers** folder provided by the workshop organizers, and execute them to install these applications on your computer. In Windows, the programs are installed in C:\Program Files\Isoviz, whereas in MacOS, you must drag the program into the **Applications** folder. When you run either application, it opens a window that allows you to browse your file system for an input file; choose one of the **visual_*.isoviz** files in the **visualizations** folder.

Operating system file extensions: You may find it convenient to associate .isoviz files on your computer with the ISOVIZ application, so that merely clicking on the data files will open the correct application. In **Windows**, right-click on an .isoviz data file to open the contextual menu, choose "Properties", click the "Change" button adjacent to "Opens with" to open a file browser, browse to Isoviz.exe (in C:/Program Files/Isoviz), click "OK" twice to close the file browser and the "Properties" window. This also adds the program to the contextual menu. Test the new association by double-clicking on one of the .isoviz files in the **visualizations** folder. In **MacOS**, the associations should be set automatically. But if they aren't, right-click on a .isoviz file to open a contextual menu, mouse-over the "Open With" option, choose "Other, choose to "Enable All Applications" (not just the recommended ones), and select ISOVIZ from the list of installed apps. The same procedures apply for associating ISOVIZQ with .isovizq files.

Browser file associations: Any widely-used web browser should work with ISODISTORT, though we prefer Firefox and Edge over Chrome because they can be conveniently configured to "Always Ask" whether to directly open or save a file, what application to open it with, and where to save it. It can be convenient to open a text file (including CIF files) or an ISOVIZ or ISOVIZQ file directly without the extra step of saving and opening the data file. Edge automatically uses the OS file extensions, making it especially convenient. In Firefox, to configure the "Open with" file associations, select "Options" in the menu (an icon with three horizontal bars), find the "Files and Applications" section, select the Downloads action to "Always ask you where to save files", and set the "Applications" action to "Always ask" for both "TXT", "CIF", and "Firefox HTML Document" files. Because .isoviz .isovizq are not standard extensions, they do not appear in Firefox's association list. Next, browse to the ISODISTORT home page, click the "Get started quickly with a distorted perovskite example" link, select the "Save interactive distortion" option on the next page, and click the adjacent "OK" button. Firefox should then open a dialogue box that allows you to either save or open the resulting .isoviz file. Choose the "Other" option at the bottom of the "Open with" drop-down menu, browse to the ISOVIZ executable/app on your computer. It's best not to check the "Do this automatically for files like this from now on" box, because you will sometimes want to save the file instead; but if you do, it's easy to reset the action back to "Always ask" (look for "Firefox HTML Document" in the associations list). To verify the association, close ISOVIZ, return to ISODISTORT, and generate the .isoviz file again; you should now see ISOVIZ conveniently among the options listed in Firefox's "Open with" drop-down menu. Update: In Windows 10, as of Firefox 69.x, ISOVIZ files seem to automatically download rather than open, regardless of the settings described above.

Ascii text editor: You can also choose to open isoviz/isovizq files in an ascii-text editor; but if you open them directly from Firefox without saving them first, be sure to use an editor that automatically converts Linux line endings to those of your operating system; otherwise all of the lines will run together. If you don't already have a favorite, we recommend Notepad++ (not Notepad or Wordpad) for **Windows**, and recommend TextEdit in **MacOS** (set Preferences → New Document → Format to "Plain text"). Editing the parameters near the top of the isoviz/isovizq file allows one to modify the visualization after it has been generated (rarely necessary). Increasing the "appletwidth" parameter, for example, will change the size of the visualization window (e.g. smaller is better for a small laptop screen). The isoviz and isovizq file formats are almost the same, but have been optimized a bit differently for historical reasons; one can use either application can use either file type; their formats, and possibly the apps themselves, will merged in the future.

Option B: Install JDK and run ISOVIZ/ISOVIZQ Jar files from command line

Alternatively, both ISOVIZ and ISOVIZQ can be run from the command line on any non-mobile operating system (including Linux) using the **isoviz.jar** and **isovizq.jar** files. This requires that the Java run-time environment (JRE) be installed on your computer. You can download a specific older version from https://www.oracle.com/technetwork/java/javase/downloads/, or the latest version from http://java.com/en/download/. The jar files should work with the latest subversions of JRE Versions 8, 9, and 10, but not for versions 11 or beyond. After installation, you may want to become familiar with the Java Console (Mac: System Preferences → Java Windows: Control Panel → Java, Linux: http://www.java.com/en/download/help/enable_console_linux.xml). From a new terminal window, type "java –version" to verify that Java is installed correctly. If this fails, try adding your JRE's **bin** folder to your PATH or pointing the JAVA_HOME environment variable to this folder.

ISOVIZ and ISOVIZQ can be opened from the command line as shown below, where "yourpath" is the location of the jar files on your computer's file system, and "yourdata" is the name of your input file. If you don't provide an input file, the application will open a file-browser window to assist you in locating the desired input file.

```
java -cp yourpath/isoviz.jar isoapps.Isoviz yourdata.isoviz
java -cp yourpath/isovizq.jar isoapps.IsovizQ yourdata.isovizq
```

If you try to view an exceptionally large input file, you may need to increase the run-time memory allocated to the JRE by adding -Xmx256m as a run-time setting in your Java control (increases allocation to 256 megabytes). Also, if you find that the application controls are not all fully visible, it may help to add -Dsun.java2d.d3d=false as an additional run-time setting.

If you don't see an interactive crystal structure after launching the jar file, then your Java installation has problems. Try one or more of the following solutions: (1) If your Java installation is old, use the "Update" tab in your Java Console to update your java installation. (2) Use the "Java" tab in your Java Console to ensure that you have only one version of Java installed (at least no more versions that necessary for whatever you use Java for). (3) Use the "Security" tab in your Java Console to see if the security settings are reasonable. The JAR file has been signed with a commercial RSA-certified key. (4) If an error message appears in place of the name of the JAR file, try right clicking the error message for more information. You can also use the "Advanced" tab in the Java Console to "Show console", which sometimes gives more information about Java errors.

Exercise 1: Antiferromagnetic $LaMnO_3$ supercell search

The objectives of this exercise are to (1) become familiar with ISODISTORT's supercell-search method of generating a magnetic-structure model, and (2) explore some of ISODISTORT's output options.

As reported by Rodriguez-Carvajal *et al*. [*Phys. Rev. B* **57**, R3189 (1998)], the room-temperature structure of $LaMnO_3$ is a distorted perovskite with space-group type *Pnma* (#62) and a supercell with lattice basis = {(1,0,-1), (0,2,0), (1,0,1)}. Below 139.5 K, $LaMnO_3$ develops a layered magnetic structure: with ferromagnetic layers of Mn spins (along a cubic 110 direction normal to the long supercell axis) that alternate antiferromagnetically from layer to layer. The magnetic structure at 1.4 K has been reported by Moussa et al. [*Phys. Rev. B* **54** (1995), 15149-15155] and proves to have magnetic space-group #62.448 *Pn'ma'* with no change in the size of the supercell.

(a) **Parent structure (CIF)**: Go the ISODISTORT home page and click on "Import parent structure from a CIF structure file". Click the "Browse" button and navigate to the **lamno3-cubic.cif** file in the **exercises** folder. Then click "OK", which takes you to the "search" page.

(b) **Types of distortions**: Near the top of the "search" page, you need to specify the types of order parameters that you want to include in your distortion. Lattice strains and atomic displacements are included by default. Check the "Magnetic" box for the Mn atom in order to permit magnetic Mn moments. We are not interested in atomic site-occupancy ("order") modes in this case. It is important to click on the adjacent "Change" button after making this change, which updates the whole page to include new content based on your choices.

(c) **Space-group preferences**: The space-group preferences at the bottom of the "search" page determine the space-group settings of any distortions that you generate in subsequent steps (they don't affect the interpretation of the parent structure). Just keep the default preferences for this exercise.

(d) **Method 3 (supercell search)**: Under Method 3 on the "search" page, select #62 *Pnma* as the space-group symmetry, which filters the possible distortions so as to include only magnetic structures based on non-magnetic space-group #62. Enter the relative supercell basis as {(1,1,0),(-1,1,0),(0,0,2)}, which indicates a $\sqrt{2} \times \sqrt{2} \times 2$supercell. The orientation of the supercell doesn't matter since the cubic 100, 010 and 001 axes are equivalent; and the unit cells of candidate distortions are automatically rotated to match your preferred space-group setting anyway. The basis must be right-handed (determinant = +1). By default, the radio-button provided indicates that your basis specifies a "real-space sublattice of the parent lattice" with "Default" centering. Click "OK" to proceed to the "distorted structure subgroup" page.

(e) **Isotropy subgroups**: Your list of candidate isotropy subgroups includes 30 entries, four of which possess the desired supercell basis and magnetic space-group symmetry #62.448 *Pn'ma'*, but which have different supercell origins (relative to the parent cell in parent-cell coordinates). We need to figure out which of the four corresponds to the published structure. Try the first and click "OK" to proceed to the "distortion" page.

(f) **Distortion page**: The "distortion" page displays a list of all of the symmetry modes available to the child structure corresponding to this isotropy subgroup, grouped by irrep, along with basic information about each irrep and mode. At this point, the key group-theoretical calculations have already been performed, and you now have the opportunity to choose between several different types of output. The page header information summarizes the choices and preferences that led you to the present scenario, as well as the details of the resulting isotropy subgroup (cell parameters, atomic positions, space-group type, basis, origin, child/parent primitive-cell-size ratio (given as "s"), and parent/child symmetry density (given as "i"). For each symmetry mode, the details of the isotropy subgroup that would result from activating only this order parameter are given, preceded by an editable field containing the amplitude of the mode. The editable parameters at the bottom of the "distortion" page primarily influence the visualization of the structure, though some parameters affect the CIF output instead.

(g) **Save interactive distortion (ISOVIZ)**: On the "distortion" page, select the "Save interactive distortion" radio button and click “OK” to save an isoviz file to your computer. Then use the ISOVIZ application to open the file, where you can interactively manipulate the various symmetry modes available to the child structure. Use the mouse (with and without a right-click) to rotate and translate the crystal structure. Use the mode sliders in the panel to the right of the crystal structure to apply various combinations of symmetry modes. Check the Wyckoff-site boxes above the mode sliders of each parent atom to identify unique Wyckoff sites of the child structure. Try other radio-button and check-box controls near the bottom of the ISOVIZ window. To zero all of the modes, press “z” on the keyboard. To reset all modes to their original values (if non-zero), press “i” on the keyboard. To reset everything, press "r" on the keyboard. Use the mode sliders to explore all three magnetic modes to see that they are different. All of these modes are allowed by the magnetic space-group symmetry. But only mX_5^+ is active in the experimentally observed structure. The R_4^+, and M_3^+ modes contribute distinct octahedral rotations to the displacive superstructure, while the M_2^+ mode contributes a Jahn-Teller stretch. Try superposing modest amplitudes for R_4^+, M_3^+, M_2^+ and mX_5^+ modes, and then "animate" the resulting distortion. Close the interactive window when finished, which will end the ISOVIZ session.

(h) **Save interactive diffraction (ISOVIZQ)**: On the "distortion" page, select the "Save interactive diffraction" radio button and click “OK” to save an isovizq file to your computer. Then use the ISOVIZQ application to open the file, where you can interactively manipulate the same symmetry modes as before. But this time, you’ll see how the diffraction pattern varies in response to the amplitude of each mode. The controls at the bottom of the window are a bit different from those of ISOVIZ. Try both single-crystal and powder diffraction modes. Verify that the magnetic modes influence the pattern in "neutron" mode but not "x-ray" mode. Change the orientation and range of the single-crystal pattern, and change the horizontal units and range of the powder pattern. Close the interactive window when finished, which will end the ISOVIZQ session.

(i) **Other subgroups**: Close the browser tabs containing the "distortion" page, and return to the tab containing the "distorted structure subgroup" page. Try one of the other candidate isotropy subgroups listed as having the same magnetic space group (#62.448 *Pn'ma'*) and supercell shape ($\sqrt{2} \times \sqrt{2} \times 2$) as before, but a different supercell origin. Visualize the structure and observe that some but NOT ALL of the expected modes ($R_4^+, M_3^+, M_2^+, mX_5^+$) are all available. Reconcile in your own mind what it means for two completely different subgroups to have the same supercell and space-group type, but different origins. The choice of subgroup refers not only to the space-group type (in the range 1-230), which dictates the symmetry elements contained within the group, but also to their actual locations within the crystal.

Exercise 2: Ferroic perovskites

The objectives of this exercise are (1) to become familiar with ISODISTORT's most general mode of operation (Method 2: General search), and (2) to emphasize that a multi-dimensional irrep can lead to a variety of different isotropy subgroups.

PZT is a cubic perovskite (space group #221 Pm-3m) above 600-700 K, depending on its composition. Its structures in various low-temperature ferroelectric phases are reported in Noheda *et al*. [*Phys. Rev. B* **61**, 8687-8694 (2000)].

(a) **Parent structure**: Rather than importing a parent structure, follow the "Get started quickly with a cubic perovskite example" link on the ISODISTORT home page, which loads a predefined cubic $SrTiO_3$ perovskite parent structure, and takes us directly to the "search" page. Since we are primarily exploring symmetry in this example, it doesn't matter what atom types we use. Instead of being offended by magnetic Ti, just imagine your favorite metal ion in its place.

(b) **Types of distortions**: Under "Types of distortions" near the top of the "distortion" page, deselect strain, and keep all of the displacements selected. Then click "Change" to update the page with updated menus.

(c) ***k* point**: Method 2 lets you view the distortions caused by specified irreps. One can select special or non-special ***k*** points, and even irrational modulation vectors that produce incommensurate structures. You can also choose more than one irrep at a time in order to see what happens when they are simultaneously applied. But this example is relatively simple. Ferroelectric distortions always belong to gamma irreps, which are defined at the gamma [i.e. ***k*** = (0,0,0)] point at the center of the Brillouin zone. Under method 2, use the "Select k point" drop-down menu to select "GM, k12 (0,0,0)" and click "OK" to proceed to the "irreducible representation page".

(d) **Irreducible representation**: The drop-down menu lists all of the gamma-point irreps of the parent symmetry that are consistent with the distortion types that we selected. There are only two. Try "GM4-" and click "OK" to proceed to the "order-parameter direction" page.

(e) **Order parameter direction**: The OPD vector has the same dimension as the irrep matrices (3 in this case); but the number of free parameters in the OPD can be as small as 1. The drop-down menu shows six different OPDs that can arise from the 3-dimensional GM4- irrep and their corresponding isotropy subgroups. Each OPD vector is preceded by a short symbol (e.g. *P*1) that can serve as an alternative OPD label. Because GM4- is the only ferroelectric irrep, this list represents all of the ferroelectric possibilities. The $(a, 0,0)$, (a, a, a) and (a, a, b) OPDs yield space group types *P*4*mm*, *R*3*m* and *Cm*, respectively, which correspond to well-known ferroelectric structures. One can tell at a glance from the OPDs that the *Cm* structure allows the *P*4*mm* and *R*3*m* structures as special cases (it's a common subgroup of both). Explore some of these options and explore them in ISOVIZ.

(f) **Analogous magnetic structures**: We can do the same thing to obtain an analogous list of possible ferromagnetic orderings. Close ISOVIZ, delete the browser tab containing the "distortion" and "order-parameter direction" pages, and return to the "search" page. In the order-parameter types section, select magnetic moments for the Ti atom (obviously hypothetical) and deselect the strain and atomic displacements for all atoms; then click "Change" to update the page. Take the steps necessary to select the magnetic mGM4+ irrep via Method 2. You should find that there are six possible ferromagnetic OPDs, each with a different magnetic space-group symmetry. Select OPD (a, a, b) and visualize the result. Show that the *C*2'/*m*' magnetic space-group allows you to smoothly vary the magnetic moment between the 100 (tetragonal) and 111 (rhombohedral) axes of the parent structure.

Exercise 3: Symmetry-mode decompositions

The objectives of this exercise are to practice mode decomposition and to gain a better understanding of how modes from multiple irreps contribute to a given structure with a given isotropy subgroup. This feature of ISODISTORT (Method 4) only works with commensurate child structures at present, but will work with incommensurate child structures at some point in the future.

CASE 1: ANTIFERROMAGNETIC $LaMnO_3$

Here, we continue an analysis of LaMnO3. The objectives of this exercise are to (1) become familiar with ISODISTORT's "symmetry-mode decomposition" feature, and (2) explore more of ISODISTORT's output options. Symmetry-mode decomposition compares a known distorted crystal structure (the child) to some higher-symmetry parent structure; it quantifies precisely how much each symmetry mode of the parent structure contributes to the distorted child structure.

(a) **Getting started**: If you still have your browser open from the previous exercise, close the browser tabs containing the "distortion" and "subgroup" pages, and return to the tab containing the "search" page. Otherwise, repeat the first three steps of that exercise: go to the ISODISTORT home page, import parent-structure file **lamno3-cubic.cif** from the **exercises** folder, add magnetic order parameters to the Mn atom, and keep the default space-group preferences.

(b) **Method 4 (mode decomposition)**: In the Method 4 section of the "search" page, upload the antiferromagnetic room-temperature $LaMnO_3$ structure file (**lamno3-magchild.cif**) and proceed to next page.

(c) **Supercell basis**: On the "basis" page, a mode decomposition requires that we know how the unit cells of the parent and child are related. The drop-down menu containing "probable bases" shows the result of ISODISTORTs effort to guess the answer. It can usually find the correct relative basis if the lattice strains are not too great; otherwise, the user must "specify" the basis explicitly In this example, ISODISTORT correctly guesses the basis to be {(1,0,-1),(0,2,0),(1,0,1)}, which implies a $\sqrt{2} \times 2 \times \sqrt{2}$ supercell.

(d) **Supercell origin**: Also on the "basis" page, choose the default option of "automatic origin detection". An isotropy subgroup is defined by a combination of space-group type, relative lattice basis, and relative origin. The location of the child-cell origin within the parent cell is critical to determining which parent symmetry operations are retained by the child and which are lost. When the user-provided distorted structure is truly a child of the parent, ISODISTORT usually finds the correct origin automatically. But if the automatic routine fails, you must specify the origin explicitly.

(e) **Atom matching**: Using the parent structure, the child basis and origin provided by the user, and the space-group type from the child CIF, ISODISTORT creates an "undistorted child structure", which is really just the parent structure presented in the setting of the child structure. Next, ISODISTORT must establish a one-to-one relationship between the atoms of this undistorted child structure and the atoms in the child CIF, which is very difficult when the atomic displacements are large compared to nearest-neighbor distances. For this exercise, choose the "nearest-neighbor" atom-matching routine. But in general, if this routine fails, we can employ the slower and more "robust" atom-matching method. The atom matching and origin-shift routines are actually integrated so that atom matching is attempted for each candidate origin. Click "OK" to proceed.

(f) **Distortion page**: When you arrive at the "distortion" page, the mode decomposition is already complete, and each symmetry-mode amplitude is shown to have a non-zero amplitude. Recall that in the previous supercell-search exercise, these fields were all zero initially. Of the three magnetic irreps capable of contributing to antiferromagnetic $LaMnO_3$, observe that only mX_5^+ $(a,a;0,0;0,0)$ actually contributes – it provides a 3.87 μ_B moment. Perhaps the other two magnetic irreps also make contributions that are simply too small to be readily detected by experiment.

(g) **Save interactive distortion**: save an interactive distortion and open it with ISOVIZ to see the resulting symmetry modes. Animate the distortion to see the strains, displacements, and magnetic moments that are active in the experimentally determined structure. Close the tab when finished.

(h) **CIF output**: From the “distortion” page, view the “CIF file” output, and take a few minutes to better understand how the magnetic space group and the magnetic moments are described using magCIF tags.

(i) **Modes details**: From the “distortion” page, the “Modes details” option provides a human-friendly description of the magnetic structure and the symmetry modes of the system. The mode-amplitude summary that follow each mode list is particularly informative. Following descriptions of the undistorted and distorted child structures, a detailed description of each symmetry-mode is presented, showing how each mode changes the atomic coordinate or magnetic moment of each symmetry-unique atom. Note that the amplitude of each mode is defined as the root-summed-squared value of its local order parameter over all supercell atoms (not just the symmetry-unique ones) descending from the effected parent atom – each parent atom has its own modes. The local order parameter can be an atomic displacement (Å units), magnetic moment (μ_B units), occupancy change (unitless), or rotational moment (radian units). When a given irrep contributes multiple modes (e.g. R_5^+ in this example), observe that their amplitudes add in quadrature to give an aggregate amplitude for the irrep as a whole; the aggregate irrep amplitudes also add in quadrature to give a total amplitude for each type of order parameters.

(j) **Complete modes details**: From the “distortion” page, the “Complete modes details" option is very similar to the “Modes details” page, except that the description of each symmetry mode shows the effect on every atom in the supercell rather than focusing only on the symmetry-unique atoms.

(k) **Refinement software output**: Symmetry-mode amplitudes can be directly refined within several important structure analysis software packages. Any of these packages can read the traditional-coordinate information from a CIF file. But reading symmetry-mode information is another matter. GSAS-2 reads symmetry-mode definitions from ISODISTORT’s CIF output file. TOPAS and PDFgui read symmetry-mode definitions from the TOPAS.str output file. FULLPROF reads symmetry-mode definitions from the FULLPROF.pcr output file. JANA has a feature for sending symmetry-mode queries directly to ISODISTORT over the internet rather than importing a file.

(l) **Distortion file**: From the "distortion" page, use the “Distortion file” option to save the current state of the distortion page to your computer (call it **lamno3-magchild-distortion.txt**), so that you can return quickly to this page later for further exploration. To test it, close all browser tabs, return to the ISODISTORT home page, and import the recently-saved distortion file using the “Import an ISODISTORT distortion file” link. You should find all of the details of the distortion page to exactly as they were before. This feature is especially helpful for distortions that are complicated or time consuming to generate.

(m) **Subgroup tree**: From the “distortion” page, use the “Subgroup tree” option to obtain a list of the intermediate subgroups that lie between the parent and child structures. For the magnetic $LaMnO_3$ structure, there should be a total of 29 subgroups including parent and child. Each entry in the subgroup indicates a unique isotropy subgroup (space-group type, relative basis, relative origin), the maximal subgroups that descend from it, and the irreps that can contribute to its order parameters. A separate structure file will be generated for each subgroup if the appropriate “Generate TOPAS.STR output for subgroup tree” box is checked near the bottom of the distortion page (save as **lamno3-magchild-tree.zip**).

CASE 2: DISPLACIVE SUPERSTRUCTURE OF WO_3

The room temperature crystal structure of WO_3 has space-group symmetry $P2_1/n$ (#14) and a $2 \times 2 \times 2$ supercell relative to its hypothetical cubic parent structure of $Pm\bar{3}m$ (#221) symmetry. See Woodward *et al.*, *J. Phys. Chem. Solids* **56**, 1305-1315 (1995). The four atoms per parent unit cell multiply to yield 32 atoms per supercell, all on general positions, and 96 atomic coordinates. Because the child point group has four operators, the number of free displacive parameters in the child structure is reduced to 24. Of the 24 symmetry modes available to the child structure, only 5 have significant mode amplitudes, rendering the symmetry-mode description highly compact. See C. J. Howard *et al.*, *J. Phys*. C **14**, 377-387 (2002); B. J. Campbell, J. S. O. Evans, F. Perselli, H. T. Stokes, *IUCr Comp. Comm.* 8, 81-95 (2007); Kerman *et al.*, *Acta. Cryst* A 68, 222-234 (2012).

(a) Use ISODISTORT to upload a (hypothetical) cubic WO_3 parent structure (**wo3-cubic.cif**) from the **exercises** folder. Use the default space-group preferences and default order-parameter types (i.e. only displacements for each atom) on the "search" page.

(b) Use Method 4 to decompose the room-temperature structure of WO_3 (**wo3-RTmono.cif**) relative to the cubic parent structure. The basis required for this decomposition is {(2,0,0),(0,2,0),(0,0,2)}, which should already be in the drop-down menu of "probable bases". Use the default options for automatic origin detection and Wyckoff-site matching. Verify that the space-group type is as expected (#14) and that the relative origin of the supercell is (1/2,0,1/2) in parent-cell coordinates. Notice that the size index is $s = 8$, as expected for a $2 \times 2 \times 2$ supercell, and that the symmetry index is $i = 8 * 12 = 96$, where 12 is the index of the point group $2/m$ in parent point group $m\bar{3}m$. Overall, only 1 out of ever 96 parent space-group operations are retained by the child.

(c) Use ISOVIZ to visualize the distorted WO_3 structure and its symmetry modes. Remarkably, when described using the irrep-mode coordinate system, only 5 of 24 symmetry-mode parameters have substantially non-zero amplitudes – an impressive simplification. See that only 5 of the 24 sliders are substantially different from zero. The smaller parameters are important, though one can obtain a reasonably nice fit to a powder x-ray diffraction dataset with only the five largest modes. The three large-amplitude oxygen displacements correspond to octahedral WO_6 rotations around various crystal axes.

(d) From the distortion page, use the "TOPAS.STR" output option and save the resulting file as **wo3-RTmono.str** in the **exercises** folder This could be used for structural refinement against experimental diffraction data using the TOPAS Academic program.

(e) Open **wo3-RTmono.str** with an ascii-text editor. After the cell parameters and space-group symmetry are specified, the names and amplitudes of the 24 symmetry-mode amplitudes are listed. The name of each mode includes the parent space-group symmetry, the k vector, the space-group irrep and OPD, details of the parent Wyckoff site and type of order parameter, the irrep of the Wyckoff-site point group, and finally, a specific branch of the space-group irrep. Because the OPD of $X_5^-(0,0;a,0;0,b)$ has only two non-zero branches, each order parameter of this irrep has two symmetry modes, a and b. In fact, if you look through the entire list, you'll see that X_5^- contributes three order parameters to the distortion, one for W and two for O, each of which has two non-zero modes. The star of the X point has three k vectors: [0,1/2,0], [1/2,0,0], and [0,0,1/2]. The semicolons in X_5^- $(0,0;a,0;0,b)$ separate contributions from distinct arms of the star, so that the [1/2,0,0] and [0,0,1/2] are clearly active capable of producing diffraction satellites, but not [0,1/2,0]. In contrast, the R point at k = [1/2,1/2,1/2] has only one arm because each symmetry-equivalent k vector differs from the first by a reciprocal lattice vector; for example, $k - (-k) = [1,1,1]$. Multi-k order parameters (i.e. cases with more than one active k arm) like that of X_5^- in WO_3 are less common for magnetic structures, but very common for displacive distortions. The MAGNDATA collection on the Bilbao Crystallographic Server lists several multi-k magnetic structures.

(f) In the “mode-amplitude to delta transformation” section of the .str file, you’ll see the dependence of each atomic-coordinate shift on each of the symmetry modes. The square invertible matrix of coefficients is the primary result of any ISODISTORT calculation, though there are many output formats for presenting it, including the graphical isoviz format. Can you see that simply turning off the non-contributing symmetry modes (i.e. setting them to zero) is a very elegant form of structural constraint?

(g) The “distorted parameters” section of the .str file shows how the parameters of each symmetry-unique child atom are computed from the sum of their original undistorted values and their shifts. Finally, the “mode-dependent sites” section of the .str file contains every structural detail to be passed onto to a structure-factor calculations. From the sections above, one can see that each of these parameters is either a constant or a function of symmetry-mode amplitudes. In this way, one can directly refine symmetry-mode amplitudes against experimental diffraction data.

CASE 3: CREATE YOUR OWN EXAMPLE

(a) Use one of your own structures, or possibly download a commensurate structure from the MAGNDATA database (Bilbao Crystallographic Server), or. If possible, choose something a bit complicated. Upload the file into ISOCIF to ensure a that the structure is presented in a standard (or at least a typical “alternative”) setting, verify that the symmetry group is correct, just to be safe, and save the resulting CIF file in the **exercises** folder as **myexample-child.cif**.

(b) Create a non-magnetic parent structure (if you don’t already have one). One way to do this is to import the child structure into ISOCIF, remove any magnetic moments, and use fairly loose displacive tolerances in order to detect a higher symmetry space group. Name your parent structure as **myexample-parent.cif** in the **exercises** folder.

(c) Import your parent structure (**myexample-parent.cif**) into ISODISTORT. If your child structure is magnetic, turn on magnetic moments for the relevant magnetic atoms on the search page.

(d) Use Method 4 to upload **myexample-child.cif** as the child structure. Ideally, ISODISTORT will guess the basis and auto-detect the origin shift automatically. If you have trouble with this step, ask for help. If your decomposition is successful, go to the next step.

(e) View the ISOVIZ, Modes details, CIF, FullProf.pcr, and TOPAS.STR outputs to compare their presentations of the symmetry-mode information. Check to see how many symmetry modes are available to the child structure, and which ones actually contribute.

Exercise 4: Building structures with ISOCIF

The objectives of these exercises are to explore the features of the ISOCIF tool for manipulating CIF structure files. It was originally developed for preparing CIF input for ISODISTORT, but tends to be used by others for a variety of other purposes. Start by finding a link to the ISOCIF home page on the ISOTROPY Software Suite home page. ISOCIF currently only works with commensurate structures, though most of the infrastructure for incommensurate structures in place and should be released soon.

CASE 1: ANTIFERROMAGNETIC MnO

Magnetic space group: BNS 15.90 C_c2/c or OG 12.8.73 $C_{2c}2/m'$
Cell parameters: a =5.44522, $b = 3.14380$, $c = 6.28759$, $\beta = 125.26439$
Atomic coordinates: Mn at (0, 0, 0) and O at (0, 1/2, 3/4).
Mn moment in crystal-axis coordinates: (-5.65832, 0, 0.00000) μ_B

(a) **Select "Create new CIF file"**: Choose the BNS magnetic space-group (shown above) by either selecting it from the drop-down menu or by simply typing the BNS number into the adjacent text field; note that choosing a magnetic space group trumps any non-magnetic space group that might also be selected. Then enter the cell parameters (shown above); it's not necessary to enter the parameters that are fixed by the crystal family or that are related by symmetry to a previous parameter in the list. Indicate that there are 2 unique atoms in the structure. Keep the default space-group preferences. Click "OK" to proceed. On the next page, enter the atomic coordinates;

(b) **Atom coordinates**: Enter the atom names and atomic coordinates. If the atom name begins with a standard element name, the element name will be extracted automatically – no need to enter it separately. Choose each Wyckoff position from the drop-down menu. Because both atoms are on fully fixed positions, there is no need to type their numerical values -- only type in parameters that are not fixed by symmetry.

(c) **Magnetic moments**: Enter the magnetic moments in crystal-axis coordinates (μ_B units), where each component indicates the moment along one of the unit-cell edge directions.

(d) **View/Save result**: Set the "Max bond length" to 2.5 Å, and use ISOVIZ to visualize the result before saving the structure to CIF format (**mno-magnetic.cif**) in the **exercises** folder.

(e) **Alternative MSG settings**: Explore several different monoclinic cell choices and special axes, and click "Change setting" after each selection to see how the cell parameters and atomic coordinates and moments change. Now return to the original setting (special *b* axis and monoclinic cell choice 1), and enter a new origin of (1/2,1/2,0) and click "Change lattice and origin" to see the atomic coordinates change. If you attempt an arbitrary change, you'll find that this latter feature is restricted to transformations that do not change the form of the MSG operators (arbitrary transformations tend to make the operators look different).

(f) **Non-standard MSG setting:** return to the ISOCIF home page, select "Modify existing CIF", and upload the **mno-magnetic.cif** file that you saved a few minutes previous; this ensures that you have returned to the original setting. Now check the "Use alternate (possibly nonstandard) setting in CIF file" box under the "Save CIF" button, and enter the following (seemingly arbitrary) setting transformation: $\{(0,2,1),(0,-2,1),(2,0,1)\}$ with an origin shift of $(0,0,-1)$. Click "Save CIF" to save the file as **mno-nonstandard.cif**, and then open the file in an ascii-text editor to examine the new form of the symmetry operators and the atomic coordinates and magnetic moments. This non-standard setting is used for MnO in the MAGNDATA database (entry #1.31) on the Bilbao Crystallographic Server. You might want to use the VESTA program to view the magnetic structure in this setting.

(g) **Detect symmetry**: Click "Reduce symmetry to $P1$" to drop the symmetry of this magnetic structure to $P1$, which greatly increases the number of independent atoms and moments. Next, click "Find actual symmetry", which employs the FINDSYM tool to detect the magnetic symmetry group. You should find that the original MSG and setting have been recovered**.**

(h) Click "**Remove magnetic moments**" to delete the magnetic moments from the Mn atoms, and observe that the resulting symmetry group ($C2/m$) is non-magnetic. Then go a step further by clicking "Find actual symmetry" to see that the atomic coordinates possessed a higher symmetry all along – only the magnetic structure was responsible for the monoclinic supercell. This sort of thing tends to happen when magneto-structural coupling is weak, though the atomic displacements and occupancies can also contribute to the loss of symmetry at a magnetic phase transition.

Case 2: ANTIFERROMAGNETIC $LaMnO_3$

(a) **Auto-detect symmetry**: Return to the ISOCIF home page and choose "Modify an existing CIF", and upload **lamno3-magchild.cif** (the same file used in a previous exercise). Choose to "Reduce the symmetry to $P1$" and save the result to a CIF called **lamno3-magchild-P1.cif**. Return to the ISOCIF home page to upload the $P1$-symmetry CIF that you just created, and observe that the orthorhombic magnetic space group is detected automatically, but not enforced automatically. You must go a step further and click the "Find actual symmetry" button in ISOCIF to apply the detected symmetry group. Note that ISOCIF always performs a symmetry-detection check when importing any structure.

(b) **Remove magnetic moments**: use the "Remove magnetic moments" button to delete the magnetic moments from each magnetic atom. The resulting non-magnetic structure should have space-group *Pnma* (#62). Save the result to a CIF called **lamno3-nonmagchild.cif**. This feature is useful for preparing the non-magnetic parent of a magnetic structure (particularly for type-IV magnetic structures).

(c) **Reintroduce the moments**. In ISODISTORT, import non-magnetic **lamno3-nonmagchild.cif** as the parent structure. On the "search" page, add magnetic order parameters to the Mn atom. Because the orthorhombic parent and magnetic cells are the same size in this case, we are specifically interested irreps at the gamma (GM or Γ) point, i.e. at $\boldsymbol{k} = (0,0,0)$. Using Method 2, test different magnetic Γ-point irreps and simple OPDs until you identify the one that produces the correct magnetic space group (#62.448 *Pn'ma'*). Then explore the magnetic symmetry modes of this model in ISOVIZ to see if the magnetic structure can be arranged as you remember it from previous exercises. Two of the modes look very similar; which is correct? You might need to open **lamno3-magchild.cif** again in ISOCIF to see how the magnetic moments and octahedral MnO_6 rotations are supposed to be mutually oriented.

Exercise 5: Incommensurate magnetic DyMn6Ge6

The objectives of this exercise are (1) to use ISODISTORT's general-search mode to generate an interesting incommensurately-modulated structure, and (2) to demonstrate FINDSYM's ability to detect and apply the superspace-group symmetry of modulated structures containing displacive, magnetic, occupational, and or/rotational modulations (excludes composite structures).

The high-temperature nuclear parent structure of $DyMn_6Ge_6$ is $P6/mmm$ (#191). Below $T_N = 420$ K, an incommensurate magnetic modulation arises with a wave vector of the form $(0, 0, k_z)$, where k_z decreases steadily from above 0.21 at room temperature to approximately 0.16 at 100 K, and then remains steady below 100 K. The structure consists of several flat magnetic spiral patterns of the same chirality (one large-amplitude spiral from Dy and multiple small-amplitude spirals from Mn). Below 11 K, a ferromagnetic order parameter arises along the modulation direction, such that each spiral pattern becomes strongly conical [P. Schobinger-Papamantellos *et al.*, *J. Alloys and Compounds* **215**, 111 (1994); *J. Magn. Magn. Mat.* **150**, 311 (1995)]. The structural parameters used in this example were taken from MAGNDATA entry #1.1.10 of the Bilbao Crystallographic Server.

(a) **Parent structure**: Upload **dymn6ge6-parent.cif** as the parent structure.

(b) **Types of distortions:** On the "search" page, turn off atomic displacements for each atom, and also turn on magnetic moments for Dy and Mn. Click the adjacent "Change" button to update the page.

(c) **Space-group preferences**: Simply use the default space-group preferences.

(d) ***k* point**: Under Method 2 on the "search" page, indicate that you want to superpose two irreps and click the adjacent "Change" button. Select GM(0,0,0) as the first *k* point, and select DT(0,0,g) as the second *k* point with a value of $g = 0.1650$ and $d = 1$ modulation.

(e) **Irreducible representation**: Select mGM2+ and mDT6 as the two irreps.

(f) **Order parameter direction**: Choose the OPD of the form (a|b,0,0,0), which should be the first one listed; it combines mGM2+(a) and mDT6(a,0,0,0) with independent amplitudes. The resulting magnetic superspace-group symmetry should be 177.1.24.2.m153.1 P62'2'(0,0,g)h00.

(g) **Mode amplitudes**: This low-temperature magnetic structure has both a commensurate ferromagnetic contribution from mGM2+ (one Dy mode and one Mn mode) and an incommensurate conical magnetic contribution from mDT6 (one Dy mode and four Mn modes). On the distortion page, manually enter the mode amplitudes (in μ_B units) as follows:

```
mGM2+[Dy1]A2g(a) -3.93200
mGM2+[Mn1]A2(a)   2.81446
mDT6[Dy1]E1g(a)   6.19555
mDT6[Mn1]B2_1(a)  2.89018
mDT6[Mn1]B2_2(a)  1.08973
mDT6[Mn1]B1_1(a)  1.08897
mDT6[Mn1]B1_2(a) -2.88980
```

(h) **Distortion file**: Use the "Distortion file" option to save your work as **dymn6ge6-distortion.txt**, so that you can return quickly to this point from the ISODISTORT home page in the future, if needed.

(i) **Save interactive distortion**: From the "distortion" page, save an interactive distortion and open it with ISOVIZ. In ISOVIZ, check the "Color" box to make all parent atoms of the same type have the same color. Orient the structure so the modulation direction (the long direction) runs approximately into the page. It may help to zoom in (click "Zoom", zoom with mouse, click "Normal", continue to reorient). You should now be able to discern the conical magnetic progressions of both Mn and Dy, which have different phases.

(j) **Modes details**: From the "distortion" page, generate and inspect the human-readable "Modes details" output. This page includes the nuclear parent structure, the child symmetry group, the wave vectors, the undistorted child structure (all order parameters set to zero), and the distorted child structure, with its commensurate and incommensurate order parameters (modulations described using amplitude and phase rather than cosine and sine components). Next, the symmetry modes of the child are presented, grouped according to order parameter type (displacive, magnetic, occupational, rotational, strain). Only magnetic moments and strains are presented here because we turned all other order parameters off in a previous step. Each magnetic symmetry mode is defined in terms of its effect on the symmetry-unique atoms of the basic unit cell, followed by a summary of the magnetic mode amplitudes. An aggregate root-summed-squared moment is also computed for each irrep, and for the entire structure. See the exercise below on quantitative symmetry-mode amplitudes for more information.

(k) **CIF output**: From the "distortion" page, save a CIF file containing the incommensurate structure that you generated as **dymn6ge6-modulated.cif**. Then open this CIF with an ascii text editor and examine the overall structure of the file. Search through the file to identify the operators of the magnetic superspace group, the propagation vector, the atom coordinates and magnetic moments of the basic unit cell, and the magnetic modulation amplitudes. Also consider the custom _iso* tags that identify the symmetry modes and their amplitudes, the symmetry-unique traditional parameters, and the sparse matrix (square and invertible) that relates them.

(l) **FINDSSG**: Keep **dymn6ge6-modulated.cif** open in your asci-text editor; temporarily delete the integer index preceding each symmetry operator in the _space_group_symop_magn_ssg_operation.id loop. Close all browser tabs. From the ISOTROPY-suite home page, open the FINDSSG program. Copy/paste the magnetic superspace-group operators from the CIF into the "Symmetry operators" field of FINDSSG, check the "magnetic" box, and click "OK". On the resulting output page, you should find that the correct magnetic superspace group [177.1.24.2.m153.1 P62'2'(0,0,g)h00] has been detected and presented, along with the superspace transformation from the canonical setting of the ISOTROPY suite to the setting of the user-provided operators. The JANA2006 software communicates with FINDSSG to obtain this information. The related TRANSFORMSSG tool is also of interest for transforming the operators from one superspace-group setting to another.

(m) **FINDSYM**: Close all ISODISTORT tabs. From the ISOTROPY-suite home page, select the FINDSYM program and use it to import the modulated structure in **dymn6ge6-modulated.cif**. FINDSYM automatically reduces the symmetry of the structure to *P*1 superspace symmetry (the top portion of the output), and then proceeds to detect from scratch any symmetries or pseudo-symmetries (within tolerance) present in the structure (the bottom portion of the output). Observe that the original magnetic superspace-group is detected and applied to the structure. This is an exciting and long-sought capability that has only very recently been developed. If detecting the symmetry-group already provided in the input file seems like sleight of hand, try instead to detect the true symmetry of a structure which is clearly presented in *P*1 (find the pre-prepared **dymn6ge6-modulated-P1.cif** file). You should get the same result as before. Additional features (e.g. user-set modulation-amplitude tolerances for incommensurate pseudo-symmetry detection, the option to zero or eliminate the modulations, and arbitrary superspace transformations of modulated structures) are planned for FINDSYM in the near future.

Exercise 6: Incommensurate multiferroic distortion

The objectives of this exercise are (1) to use ISODISTORT's general-search mode to examine an important incommensurate magnetic modulation that couples to a polar moment, and (2) to emphasize that all secondary order parameters are automatically generated in ISODISTORT output.

$TbMnO_3$ provides an interesting example involving an incommensurate magnetic order parameter that results in multiferroic behavior, as reported by Kenzelmann *et al.* [*Phys. Rev. Lett.* **95**, 087206 (2005)]. At high-temperatures, $TbMnO_3$ exhibits the well-known orthorhombic $Pbnm$ (#62) displacive superstructure. At lower temperatures, it exhibits two different magnetic phases. The high-temperature insulating (HTI) phase appears below 35K and is described by magnetic irrep $m\Sigma_3$ (mSM3), which gives rise to two z-component modes for Tb and one mode for Mn in each of the x, y and z directions. Experiments suggest that only the y-axis Mn mode is active. In the LTI phase below 28K, the best fit to the magnetic neutron diffraction data was provided by superposing $m\Sigma_2$ and $m\Sigma_3$. The $m\Sigma_2$ Mn moments are directed along the z-axis and are 90 degrees out of phase with the $m\Sigma_3$ y-axis Mn moments, so that the LTI magnetic structure is cycloidal. Remarkably, the isotropy subgroup that results has no center of inversion due to coupling to secondary ferroelectric irrep (Γ_4^-). By manipulating the magnetic structure with an external magnetic field, the ferroelectric moment can be reversed. The ***k*** vector (0,b,0) varies slightly with temperature throughout the range below 35K, starting at b=0.27 at 35K. A Tb moment is noticeable only well below the HTI-LTI transition.

(n) **Parent structure**: Upload **tbmno3-pbnm.cif** as the parent structure.

(o) **Types of distortions**: On the "search" page, keep strains and atomic displacements on, and also turn on magnetic moments for Mn. Click "Change" to update the page.

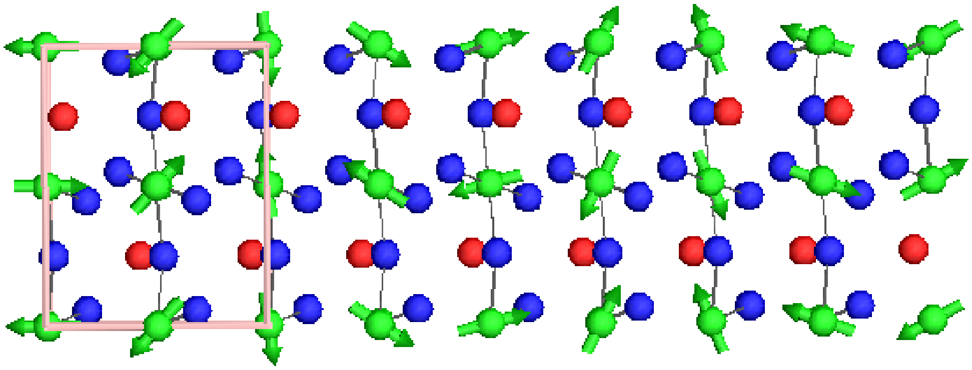
(p) **Space-group preferences**: Near the bottom of the "search" page, select the "ba-c" permutation of orthorhombic axes so that the axes of the distorted structure will match those of the *Pbnm* parent. Set the "Superspace-group setting" option to "basic (IT-A)" to indicate that we want default settings from the International Tables Vol. A rather than from the superspace-group tables in Vol. C. These settings make interpreting the distorted structure easier. Click "Change" to update the page.

(q) ***k*** **point**: Under Method 2 on the "search" page, indicate that you want to superpose two irreps, and select SM(0,a,0) as the ***k*** point for each one, with a = 0.27 for the value and *d* = 1 for the number of incommensurate modulations.

(r) **Irreducible representation**: Select mSM3 and mSM2 as the two irreps.

(s) **Order parameter direction**: There will be three OPDs to choose from, the last of which (the kernel) includes all parameters from the first two. Choose the OPD (a,0;b,0), which has the desired relative phase between the mSM3 and mSM2 waves.

(t) **Save interactive distortion**: On the "distortion" page, near the bottom of the page, set the "Maximum bond length" to 2.3 Angstroms (makes the structure look nicer). Then save an interactive distortion and open it with ISOVIZ. Orient the structure so the modulation direction (the long direction) runs from left to right. Check the "Color" box to make all parent atoms of the same type have the same color. Explore each of the magnetic Mn modes; then zero all amplitudes (type "z" [zero] or "i" [initialize] on your keyboard) and give roughly equal numerical amplitudes (e.g. 4.0 μ_B) to both the mSM3[Mn:b]Ag_1 and mSM2[Mn:b]Ag_2 modes. Can you see the cycloid pattern of spins progress along the modulation direction? You should also see that perpendicular to the modulation direction, the configuration is ferromagnetic along the parent *x* direction and antiferromagnetic along the parent *z* direction; you can use the “Axes” button to see the crystal axes (short = parent, long = child, x = black, y = white, z = grey). Finally, use the ferroelectric GM4- modes to displace the Tb and Mn atoms in the opposite direction as the O atoms (make the effect slight but noticeable), and animate the result. Whether or not cycloidal $TbMnO_3$ is ferroelectric was once a great controversy. ISODISTORT definitively demonstrates that the ferroelectric moment (separation of positive and negative charges) is a secondary order parameter of the primary magnetic cycloidal order parameter.



(u) **Consider** that the coupling of the cycloidal magnetic modes to a ferroelectric secondary mode make $TbMnO_3$ an important multiferroic material. This coupling has been the subject of intense research activity during the past decade, and was not well illuminated by irrep-based tools that treat only a single $\boldsymbol{k}$ vector at a time. ISODISTORT simultaneously treats all symmetry-related arms of the star of $\boldsymbol{k}$, which includes both $+\boldsymbol{k}$ and $-\boldsymbol{k}$ in this case, and also automatically generates all secondary order parameters consistent with the symmetry of the primary order parameters. It’s the combination of these two important general capabilities that reveal an otherwise elusive multiferroic tendency.

(v) **Distortion file**: Write down on paper the numerical values of the mode amplitudes used to obtain a nice cycloidal moment. Close ISOVIZ and return to the “distortion” page, where you should type these numerical mode amplitudes into the respective text fields. Then save everything to a "distortion file" called **tbmno3-distortion.txt**, so that you can return quickly to this point if necessary.

(w) **CIF output**: Save a CIF file containing the incommensurate structure that you generated (call it **tbmno3-modulated.cif**). Then open this CIF with an ascii text editor and examine the overall structure of the file. Try to identify the superspace-group name and operators, the propagation vector, the atom coordinates in the basic unit cell, the magnetic modulation amplitudes. Also consider the custom _iso_* tags that identify the symmetry modes and their amplitudes, the symmetry-unique traditional parameters, and the sparse matrix (square and invertible) that relates them.

Exercise 7: 2D vortex lattice on Fe monolayer

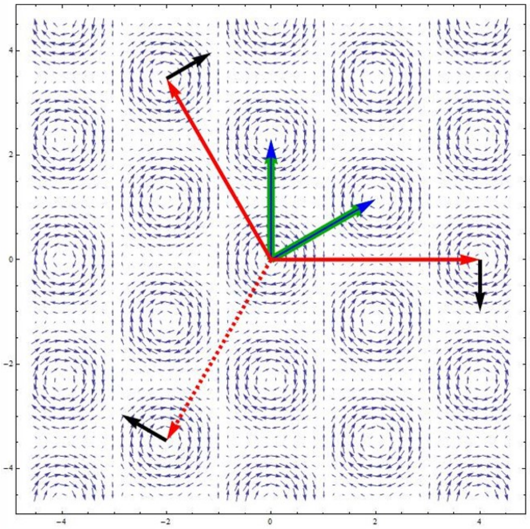
Hexagonal lattices of skyrmion were first discovered in manganese silicide [Mühlbauer *et al.*, *Science* **323**, 915-919 (2009)], and have now been observed in a variety of different systems, including a 2D Fe monolayer on an Ir(111) substrate [Heinze *et al.*, *Nature Physics* **7**, 713-718, (2011)].

The objective of this exercise is to discover the power of combining a fully-general irrep-mode analysis with $(3+d)$-dimensional superspace-symmetry. This new capability of ISODISTORT was released in May 2014.

(a) **Parent structure (CIF)**: Upload the **skyrmion-parent.cif** file as your parent structure.

(b) **Types of distortions**: On the "search" page, add occupational and magnetic order parameters to the Fe atom, and click "Change" to update the page.

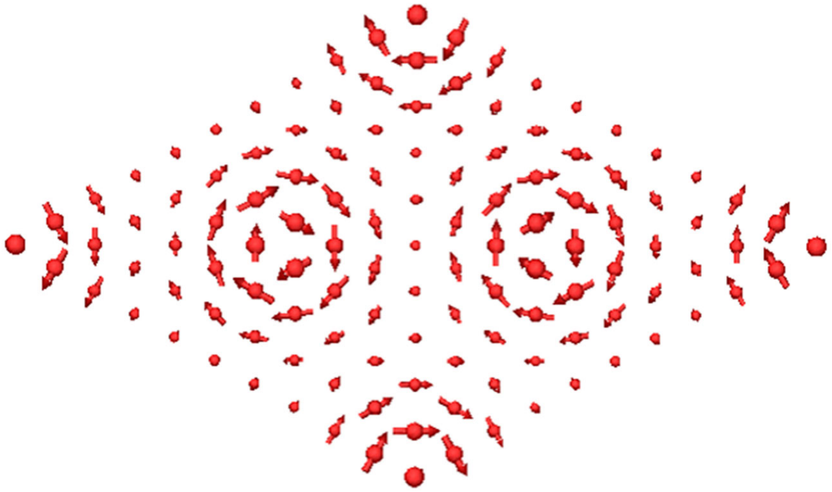
(c) ***k* point**: Under Method 2, use the "Select k point" drop-down menu to choose "LD(a,a,0)" for the irrep/OPD, with $a = 0.1$ for the value. This time, select $d = 2$ for the number of independent incommensurate modulations. We are looking for a distortion with modulation waves along each of the three in-plane (1,1,0) type directions in hexagonal reciprocal space, which are k1 = (-q,-q,0), k2 = (2q,-q,0), and k3 = (-q,2q,0).



(d) **Irreducible representation**: Choose the $m\Lambda_3$ (mLD3) irrep from the drop-down menu. This irrep is responsible for the in-plane (vortex) part of the skyrmionic order parameter in this system. Click 'OK" to proceed to the next page.

(e) **Order parameter direction**: Choose (a,0;a,0;a,0) for the OPD. This choice keeps the three modulations waves in phase with one another, and thereby preserves the symmetry relationship amongst them. Due to the residual symmetry relationships amongst the three modulation vectors, the point-group symmetry is still hexagonal. Because $k1+k2+k3 = 0$, it is clear that only two of the three vectors are independent. This means that structure can be described fully in a (3+2)-dimensional superspace -- see that the magnetic superspace-group number has a "2" rather than a "3" in the second position.

(f) **Save interactive distortion**: From the "distortion" page, save an interactive structure distortion, and open it in ISOVIZ. Uncheck the "Bonds" button to simplify the appearance of the structure. Observe that in addition to the primary magnetic order parameter, we have enabled secondary displacive, occupational, and strain modes. Turn the magnetic $m\Lambda_3$ mode slider to its maximum amplitude to see the skyrmion lattice of identically-oriented magnetic vortices. Animate the distortion. Then, just for amusement, mix in the secondary occupational and displacive modes. Record the approximate numerical mode amplitudes that generate an image like the one below.



(g) **CIF output**: Return to ISODISTORT and enter the numerical values from the previous step into the corresponding fields on the "distortion" page. Then generate and save a CIF output file and examine its contents with an ascii text editor. The symmetry operators comprise a (3+2)D magnetic superspace group (MSSG). Because there are no secondary order parameters at commensurate ***k*** vectors in this example, you should see that the undistorted and distorted versions of the "basic unit cell" will be the same. Search through the CIF to identify the wave-vectors and the modulation amplitudes of each type of order parameter. Such a CIF is ready for import into the latest version of the JANA 2006 program, and refinement against experimental data.

(h) **Further exploration #1**: Close the tab containing the "distortion" page and return to the "order parameter direction" page. Now choose a different OPD: (a,0;a,0;0,a), and use ISOVIZ to explore how it differs from the 2D skyrmion lattice. For example, you see pairs of counter-rotating whirlpools, which could annihilate in principle if brought together.

(i) **Further exploration #2**: Return to the “search” page and close any other browser tabs. Under Method 2, indicate that you want to superpose two irreps and click the adjacent “Change” button. For both k points, choose “LD(a,a,0)" with a value of $a = 0.1$ and $d = 2$ modulations. On the irrep page, choose irreps mLD3 and mLD4. On the OPD page, choose the OPD of the form (a,0;a,0;a,0 | b,0;b,0;b,0), which effectively assigns the same OPD to each irrep, but with independent amplitudes. The resulting magnetic superspace group should be 177.2.83.6.m153.1 P62'2'(a,a,0)000(-2a,a,0)000. On the “distortion” page, increase the “Maximum magnetic moment per mode” parameter to 6.0 magnetons. Save a “Distortion file” (**skyrmion-distortion.txt**) so that this work need not be repeated in the future. Then use ISOVIZ to see how the out-of-plane contribution from mLD4 removes the discontinuity at the center of each skyrmion vortex, so that the overall skyrmionic order parameter is continuous everywhere.

(j) **Further exploration #3**: Close the tab containing the "distortion" page, return to the "order parameter direction" page, and use your browser's "Back" button to return to the "irreducible representation" page. Now choose irrep $m\Lambda_2$ (mLD2) and OPD (a,0;a,0;a,0) and see how the resulting distortion differs from that of the skyrmion lattice.

Exercise 8: Quantitative symmetry-mode amplitudes

This exercise will reuse the LaMnO3 work done previously. The objective is to understand how quantitative symmetry-mode amplitudes are computed from the atomistic details of a distortion.

(a) From the main page of ISODISTORT, use the "Import an ISODISTORT distortion file" option to upload **lamno3-magchild-distortion.txt**, which you created in the previous exercise on symmetry-mode decompositions. If you didn't complete that exercise, complete the first five steps now to arrive at the same point, and also the complete the step of saving the distortion file.

(b) On the "distortion" page, save and open the structure in ISOVIZ, and verify that there are 4 Mn and 12 O atoms in the supercell. Use one of the checkboxes just above the oxygen-atom sliders to differentiate the O1 and O2 descendants of the parent O atom. Use the "s" key on the keyboard to toggle off all of the gray irrep-specific master sliders (near the bottom of the slider panel). Then turn them back on one irrep at a time. Study the octahedral rotation belonging to R_4^+, and the magnetic structure belonging to mX_5^+. It's interesting that R_4^+ affects both O1 and O2. In general, a single symmetry-mode can affect multiple symmetry-distinct child atoms descending from the same parent atom. Keep the ISOVIZ window open throughout the remainder of the exercise.

(c) Return to the "distortion" page and go to the "Complete modes details" output. The "Displacive mode definitions" section of the output shows the displacement (d_x, d_y, d_z) of each oxygen atom in the supercell affected by the R_4^+ mode. Verify that there are 8 O2 atoms and 4 O1 atoms, and that R_4^+ affects both.

(d) The Cartesian components of the displacement of an O2 atom are computed as $\boldsymbol{d} = \boldsymbol{B} \cdot (A\, n\, \boldsymbol{p})$, where $A = 1.25554$ Å is the mode amplitude, $\boldsymbol{p} = (0, \pm½, 0)$ is the pretty form of the displacement vector, $n = 0.06344$ Å^{-1} is the mode-normalization factor that makes $\boldsymbol{p}$ less pretty but more realistic, and $\boldsymbol{B}$ is the transformation from lattice coordinates to Cartesian coordinates, which for an orthorhombic lattice is simply the diagonal matrix $\{(a,0,0),(0,b,0),(0,0,c)\}$, where $a = 5.57313$, $b = 7.88160$, and $c = 5.57313$ Å are the unit-cell parameters. The magnitude of the displacement, which has only one non-zero component, is then $d(\mathrm{O}_2) = A\, n\, ½\, b = 0.31389$ Å. Similarly, the displacement of the O_1 atom is computed as $d(\mathrm{O}_1) = A\, n\, 1\, c = 0.44390$ Å. The "Displacive mode amplitudes" section of the "Complete modes details" output confirms that the largest displacement affected by R_4^+ is 0.44390 Å.

(e) The mode amplitude of the root-summed-squared displacement of all supercell atoms affected by the mode, so that $A(R_4^+) = \sqrt{4\, d(\mathrm{O}_1)^2 + 8\, d(\mathrm{O}_2)^2} = 1.25554$ Å, as expected. The mode normalization was designed to ensure this outcome.

(f) The Cartesian components of the magnetic moment of a Mn atom are computed as $\boldsymbol{m} = \boldsymbol{B} \cdot (A\, n\, \boldsymbol{p})$, where $A = 7.50701\, \mu_B$ is the mode amplitude, $\boldsymbol{p} = (\pm 1,0,0)$ is the pretty form of the displacement vector, $n = 0.08972$ Å^{-1} is the mode-normalization factor, and $\boldsymbol{B}$ is the same as before. Thus, the magnitude of the moment is simply $m(\mathrm{Mn}) = A\, n\, 1\, a = 3.75366\, \mu_B$. And the mode amplitude is $A(mX_5^+) = \sqrt{4\, m(\mathrm{Mn})^2} = 2\, m(\mathrm{Mn}) = 7.50731\, \mu_B$. These numbers suffer from a little round-off error due to the finite precision of the numbers used.

Exercise 9: Domains and primary order parameters

The object of this exercise is to become acquainted with primary and secondary order parameters, and also domains of the order parameter.

(a) From the main ISODISTORT page, upload the lamno3_cubic.cif parent structure. On the "search" page, add magnetic order parameters to Mn while keeping the default displacive and strain order parameters

(b) In Method 2, change the number of superposed IRs to 2 (and press the adjacent OK button). Choose to superpose the X[0,1/2,0] and GM[0,0,0] points. Then, on the "irreducible representation" page, choose the antiferromagnetic mX_5^+ and ferroelectric Γ_4^- irreps. Finally, on the "order parameter direction" page, choose (0,a;0,0;0,0|0,b,0) as the OPD, which yields magnetic space group #26.73 P_cmc2_1, a supercell that doubles along the child 001 axis relative to the cubic parent, and a relative origin shift of zero. The point group drops from $m\bar{3}m$ to $mm2$, for a point-symmetry index of $48/4 = 12$. Given the size index of 2, the total symmetry index is $2 * 12 = 24$.

(c) From the distortion page, save and view the distorted structure in ISOVIZ. See that the mX_5^+ magnetic moments are parallel to the child 100 axis while the ferroelectric Γ_5^- displacements of each atom are parallel to the long child 001 axis. Also see that $\Gamma_1^+(a)$ and $\Gamma_3^+(a,b)$ irreps contribute only lattice strains. Keep the ISOVIZ window open.

(d) From the "distortion" page, choose the "primary order parameters" output option. This page lists each of the irreps (five in all) at the user-selected k points (X and Γ) that are capable of generating order parameters of the user-selected types (lattice strains, any atomic displacements, Mn magnetic moments). Further down, we also see which order parameters or combinations or order parameters are mathematically "primary", meaning that they are capable of generating the isotropy subgroup without assistance from other order parameters. In this case, though no one order parameter is primary by itself, there are two primary combinations: $mX_5^+ + \Gamma_4^-$ and $mX_5^+ + \Gamma_5^-$. Let's assume (for simplicity) that ferroelectric $\Gamma_4^-(0,a,0)$ has a signficant amplitude while antiferroelectric $\Gamma_5^-(0,0,a)$ has a negligible amplitude, so that Γ_4^- is clearly primary and Γ_5^- is "secondary". A secondary order parameter can be active without further lowering the symmetry, but is not capable of generating the isotropy subgroup by itself. For example, on the "distortion" page, we can see that if secondary $\Gamma_5^-(0,0,a)$ acts by itself, the resulting isotropy subgroup would be 115.284 $P\bar{4}m21'$ on the parent basis and origin (symmetry index of 6). Because two primary order parameters must be superposed to achieve this isotropy subgroup, even $m\mathrm{X}_5^+$ can't generate it alone, but instead results in magnetic space group #51.298 P_amma in a doubled supercell, which has a higher point symmetry (mmm) that also includes the spatial inversion ($\bar{1}$). The ferroelectric Γ_4^- irrep is needed to further break the inversion symmetry.

(e) From the distortion page, choose the "domains" output option. This page lists a representative parent-symmetry operation for each coset of the isotropy subgroup. Each of these cosets corresponds to a domain of the primary order parameter(s) of the child structure. The number of domains is equal to the symmetry index of the subgroup. Three integers in the output identify each domain; in this case, there are 6 lattice-orientation domains, 2 internal-orientation domains, and 2 translational domains result in a total of 24 domains, which must be equal to the symmetry index of the subgroup. Starting with a cubic space group, any of the parent 100, 010, or 001 axes can be chosen as the cell-doubled axis of the child; and once this choice is made, there are still two choices for the mX_5^+ magnetic moments (confirm this visually in the ISOVIZ window); this explains why the child has $3 * 2 = 6$ possible lattice orientations relative to the parent. Furthermore, because the orthorhombic child lattice possesses the inversion symmetry, while the subgroup does not, applying the parent inversion symmetry reverses the direction of the ferroelectric Γ_4^- displacements without changing the lattice orientation; this explains why there are two internal-orientation domains. Because the child cell is doubled relative to the parent, there are obviously two translation domains; shifting the child structure by one parent cell along the double axis obviously results in a different domain.

(f) The relative basis and origin of the child structure are $\{(-1,0,0), (0,0,1), (0,2,0)\}$ and $(0,0,0)$ respectively. Together with magnetic space-group $P_a mma$, these details define the reference domain. Find the domain indexed by the integers "2 1 1", which corresponds to the external-orientation domain generated by a 3-fold rotation around the 111 cubic axis: (y, z, x); observe its effect on the supercell basis. Find the domain indexed by the integers "1 2 1", which corresponds to the other internal-orientation domain; the representative operation given is a two-fold rotation around the parent/child 100 axis (not retained in the subgroup): $(x, -y, -z)$; the inversion could also have been used since it belongs to the same coset. Find the domain indexed by the integers "1 1 2", which corresponds to the other translation domain: $(x, y + 1, z)$; notice how this translates the origin of the supercell by one parent cell along the cell-doubled direction. Then observe how these three simple operations work together in the other domains.

(g) For each domain, observe the effect on the OPD. Recall that the semicolons in the OPD separate contributions from different arms of the star of *k*, and that the vertical bar separates the *k* stars of different irreps. Each lattice-orientation clearly changes the active arms of the stars of both primary irreps, whereas the effects of internal orientation and translation are more subtle: the internal orientation reverses the direction of the ferroelectric Γ_4^- order parameter (displacements) and the translation reverses the direction of the mX_5^+ order parameter (magnetic moments).

(h) In summary, any parent symmetry operation that is not retained in the child will result in a different domain when applied to the child; in fact, it will permute the full set of domains. Because any one of these domains could be presented as the child structure in a literature source, it is useful to understand how they are related and how to transform one presentation into another.