

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. We refer to the basis functions of the irreducible representations (irreps) of a symmetry group as 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. The physical order parameters (e.g. atomic displacements, magnetic moments, site-occupancy variations, lattice strains, etc.) are comprised of sets of symmetry modes. If you really want to be technical, a distinct order parameter (possibly multi-dimensional) includes the modes from a single copy of a single irrep. Multiple order parameters can be superposed in a single distortion, as in multiferroics.

Many 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). Although it is common to refer to a distorted structure using only its space-group type and lattice basis, 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 Java applets for visualizing and interactively manipulating the distorted structure and its diffraction pattern. The various outputs types will also be explored in the following exercises.

Preparation

Download the tutorial files (get link from the presenter). Set your browser up so that new pages open in separate tabs of the same window rather than separate windows.

Double-click on each of the *visual.html files in the "visualization" directory to visually explore a variety of order-parameter types.

Make sure that you have a recent version of the Java run-time environment on your computer, which can either be installed manually from <http://java.com/en/download/> or automatically from within the Java Console (in Utilities folder in MacOSX, or in Control Panel -> Programs in Windows). For Linux, see http://www.java.com/en/download/help/enable_console_linux.xml. Regardless of the platform or the installation method, we recommend that you DON'T install any 3rd party helper tools (such as the "Ask Toolbar") that are sometimes packaged with Java by default -- you may actually have to uncheck a box to avoid them!

If you don't see a nice interactive crystal structure, then your Java installation has problems. Try one or more of the following solutions: (1) 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. (3) Use the "Security" tab in your Java Console to reduce the security settings to the lowest available level when using the applet. (4) If an error message appears in place of the applet within your browser window, try left or 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. (5) Always restart your browser after making a change in the Java Console. (6) Try more than one browser – note that Chrome will not work with Java applets.

If you see the interactive applet, but some of the controls are only partially visible, the problem may not be the installation. Here are a few troubleshooting options: (1) Reset the browser magnification to the standard setting. In most browsers, pressing "Control 0" will accomplish this. (2) Try resetting your computer's display resolution to the recommended setting if you have changed it recently. (3) Use the "Java" tab on your Java Console to add "-Dsun.java2d.d3d=false" (without the quotes) as a run-time parameter; and always restart your browser after making a change in the Java Console. (5) Try your luck with a different browser (e.g. Firefox, IE, Safari, Opera).

Go to the [home](http://iso.byu.edu) page of the ISOTROPY Suite at <http://iso.byu.edu>, and follow the link to the [home](#) page of ISODISTORT.

Exercise #1: Introduction to ISODISTORT (AFM LaMnO₃)

The objectives of this exercise are (1) become familiar with two of ISODISTORT's basic modes of operation (supercell search, and mode decomposition), and (2) to explore some of ISODISTORT's output options.

Above 750 K, LaMnO₃ has a cubic-perovskite structure ($Pm\bar{3}m$, #221). As reported by Rodriguez-Carvajal, Phys. Rev. (1998), B57, R3189, the room-temperature structure of LaMnO₃ 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, LaMnO₃ 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 was reported by Moussa et al. [Phys. Rev. (1995) B54, 15149-15155], which has magnetic-space-group #62.448 $Pn'ma'$.

- (a) **Parent structure (CIF):** Go to the ISODISTORT [home](#) page and find "**Import parent structure from a CIF structure file**". Click the **Browse** button and navigate to the [lamno3_cubic.cif](#) file. Then click **OK**, which takes you to the [search](#) page.
- (b) **Types of distortions:** Near the top of the [search](#) page, find the section called "**Types of distortions to be considered**." 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 atom-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.
- (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. Note that your 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 [subgroup](#) page.
- (e) **Subgroup:** 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). The first one happens to correspond to the published structure. Select it 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 present 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")). Symmetry modes are grouped together according to order parameters (one for each irrep). For

each order parameter, the details of the isotropy subgroup that would result from activating only this order parameter are given. Each symmetry mode is preceded by an editable field containing the amplitude of the mode.

- (g) **View distortion:** On the [distortion](#) page, select **View distortion** to open an interactive structure-viewing applet, with which you can manipulate and visualize the various modes available to this structure, and click **OK**. When the applet window opens, use the mouse to rotate (left-click) and translate (right-click) the crystal structure. Use the mode sliders in the panel to the right of the crystal structure to apply various combinations of symmetry modes, and 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 applet 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 the entire applet, 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 $mX5+$ is active in the experimentally observed structure. The $R4+$ and $M3+$ modes contribute distinct octahedral rotations to the displacive superstructure, while the $M2+$ mode contributes a Jahn-Teller stretch. Try superposing modest amplitudes for $R4+$, $M3+$, $M2+$ and $mX5+$ modes, and then “animate” the resulting distortion. Click the (?) button above the applet window to see more information about the applet features. Close the tab containing the applet window when finished.
- (h) **View diffraction:** On the [distortion](#) page, select **View-diffraction** to open an interactive applet, where you see how each symmetry mode affects the diffraction pattern, and click **OK**. The mode-slider controls here are identical to those of the interactive structure-viewing applet. But the controls at the bottom of the page are different. 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. Click the (?) button above the applet window to see more information about the applet features. Close the tab containing the applet window when finished.
- (i) **Other subgroups:** Close the browser tabs containing the [distortion](#) page, and return to the tab containing the [subgroup](#) page. Try one of the other candidate isotropy subgroups on the [subgroup](#) page with the same symmetry and basis as before, but a different supercell origin. Use the interactive applet to visualize the structure and observe that the expected modes from the published structure are NOT all available there. Reconcile in your own mind what it means for two completely different space-groups to have the same supercell basis and space-group type, but different origins. When we say “space-group” here, we obviously refer 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.
- (j) **Method 4 (mode decomposition):** Close the browser tabs containing the [distortion](#) and [subgroup](#) pages, and return to the tab containing the [search](#) page. Find the Method 4 section on the page, which allows us to perform a mode decomposition of a known distorted structure in terms of an undistorted parent structure. A symmetry-mode decomposition determines how much each parent symmetry mode contributes to the distorted child structure. Upload the anti-ferromagnetic room-temperature LaMnO_3 structure file called **lamno3_magnetic.cif**, and click **OK**, proceeding to next page.
- (k) **Basis and origin:** The drop-down menu of “**probable bases**” is the computer’s attempt to find supercells of the parent that are roughly consistent with the cell parameters of the distorted structure. There's only one to choose from. Keep the default options of “**automatic origin detection**” and **nearest-neighbor** atom matching; we only employ the slower and more “robust” method when the **nearest-neighbor** method fails. Click **OK** to proceed. The program automatically (1) matches the

atoms of the distorted and undistorted structures, (2) detects the isotropy subgroup and (3) performs the decomposition.

- (l) **Distortion page:** Unlike the case of Method 3, you will now see that each symmetry mode has a non-zero amplitude based on the decomposition (coordinate transformation) of an experimentally-determined structure.
- (m) **View distortion:** From the [distortion](#) page, open the interactive structure viewer to see the resulting distortion. Animate the distortion to see the strains, displacements, and magnetic moments that are active in the experimentally determined structure. Close the tab when finished.
- (n) **CIF output:** From the [distortion](#) page, view the [CIF-file](#) output and try to understand how the magnetic space group and the magnetic moments are described.
- (o) **Modes details:** From the [distortion](#) page, view 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. Note that this page only describes the contributions of each mode to the symmetry-unique atoms of the child structure, whereas the [complete-modes-details](#) page lists all of the atoms of the child structure separately.
- (p) **Refinement software output:** Symmetry modes can be directly refined within several important structure analysis software packages, including FULLPROF, GSAS-2 (alpha), JANA, and TOPAS. Output files for these packages can be exported from the [distortion](#) page. GSAS-2 reads symmetry-mode definitions from the CIF output file. TOPAS reads symmetry-mode definitions from the TOPAS.str output file. Both FULLPROF and JANA can read symmetry-mode definitions from the FULLPROF.pcr output file.
- (q) **Distortion file:** From the [distortion](#) page, save the current state of the LaMnO₃ structural distortion into a file called [lamno3_distortion.txt](#). When you import this file later, you will return immediately to this point for further exploration. To see how this works, close all tabs, return to the ISODISTORT [home](#) page, and upload this file using the “[Import an ISODISTORT distortion file](#)” link.

Exercise 2: Specify Irrep/OPD (ferroic perovskites)

The objectives of this exercise are (1) to become familiar with ISODISTORT’s most general mode of operation [Method 2: General search], which allows the user to specify the active irreps and OPDs, and (2) to emphasize that a multi-dimensional irrep can lead to any one of several distinct isotropy subgroups.

PZT (PbTiO₃-PbZrO₃) is a cubic perovskite (#221, $Pm\bar{3}m$) above 600-700 K, depending on its composition. Its structures in various low-temperature ferroelectric phases are reported in Noheda *et al.*, Phys. Rev. **B61**, 8687-8694 (2000). We’ll consider them and also their ferromagnetic analogues.

- (a) **Parent structure:** Rather than uploading a parent structure, follow the “[Get started quickly with a cubic perovskite example](#)” link on the ISODISTORT [home](#) page, which loads a predefined cubic SrTiO₃ 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. Just imagine your favorite metal ions on the respective A and B sites.

- (b) **Types of distortions:** Under "**Types of distortions**" near the top of the [search](#) page, deselect strain, and keep all of the displacements but none of the magnetic moments. Then click the **Change** button 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 (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 drop-down menu shows six different OPDs that can arise from the 3-dimensional GM4- irrep and their corresponding isotropy subgroups. Because GM4- is the only ferroelectric irrep, this list represents all of the possibilities. Each OPD vector is preceded by a short symbol (e.g. P1, P2, etc.) that can serve as an alternative OPD label. 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 (a,0,0), (a,a,a) and (a,a,b) OPDs yield space group types $P4mm$, $R3m$ and Cm , respectively, which correspond to well-known ferroelectric structures. Explore some of these options and view them in the interactive applet.
- (f) **Analogous magnetic structures:** We can do the same thing to obtain an analogous list of possible ferromagnetic orderings. Delete the browser tabs containing the interactive applet, the **distortion** page, and the **order-parameter-direction** page, and return to the **search** page. Now add magnetic moments to the Ti atom on the perovskite B site (obviously hypothetical) and deselect the strain and atomic displacements, and click the **Change** button 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 (a,a,b), which appears to be a linear combination of the OPDs of the tetragonal and rhombohedral OPDs, and use the interactive applet to visualize the result. Show that the $C2'/m'$ 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: Superposed Irreps (displacive WO_3)

The objectives of this exercise are (1) to emphasize that the symmetry-mode (irrep) description tends to be much more compact than the traditional description of a structural distortion because nature tends to activate only a relatively small fraction of the available symmetry-mode parameters, and (2) to reinforce the concept of symmetry-mode decomposition.

Though the temperature phase diagram of WO_3 is quite complicated, each observed phase can be viewed as a distortion of the same cubic aristotype (space group $Pm\bar{3}m$). At room temperature, the structure has a monoclinic $2 \times 2 \times 2$ supercell relative to the cubic parent, with 24 positional degrees of freedom in total – 8 atoms on general Wyckoff sites of space-group $P2_1/n$. The number of symmetry-mode parameters must then also be 24. Woodward et al. *J. Phys. Chem. Solids* **56**, 1305–1315 (1995); Howard et al., *J. Phys. Condens. Matter* **14**, 377–387 (2002). Note that $P2_1/n$ is an alternative setting of space group #14 $P2_1/c$

based on monoclinic cell choice 2. Though this non-magnetic example is more complicated than most magnetic cases, the principles involved are the same, and the increased generality is illuminating.

- (a) **Parent structure:** From the ISODISTORT [home](#) page, upload the hypothetical cubic parent structure ([wo3_cubic.cif](#)).
- (b) **Types of distortions:** Because all atoms are configured for displacive modes by default, you won't need to modify the distortion-type settings on the [search](#) page.
- (c) **Decomposition:** Employ Method 4 on the [search](#) page to upload to the room-temperature structure of WO_3 ([wo3_RTmono.cif](#)). On the [basis](#) page, choose (2,0,0)(0,2,0),(0,0,2) from the drop-down menu as the supercell basis. The default origin-search and Wyckoff-site matching strategies should be sufficient. When you reach the [distortion](#) page, you have decomposed the room-temperature structure into displacive symmetry-modes of the parent structure.
- (d) **Visualization:** Use the interactive applet from the [distortion](#) page to visualize the distortion. Consider that one mode can influence multiple symmetry-unique atoms and that one atom can be influenced by multiple modes.
- (e) **Simplification:** You should see that only 5 of 24 symmetry-mode parameters have substantially non-zero amplitudes – an impressive simplification that cannot be achieved using traditional coordinates! The three important oxygen modes are octahedral-rotation modes about different axes. See *Acta Cryst. A* **68**, 222-234 (2012) to see how the active modes can be identified without prior knowledge of the distorted structure, so as to simplify the structure determination.
- (f) **Modes details:** Use the [modes-details](#) output option from the [distortion](#) page to see detailed information about the distortion. This page contains traditional descriptions of the undistorted and distorted superstructures, as well as a textual listing of each of the distortion modes, and a summary of the various mode amplitudes. From the M3+ irrep details, observe the directions and relative magnitudes of the displacements of the six symmetry-unique oxygens. In the amplitude summary near the bottom, see that the six modes associated with the X5- irrep can be combined into a single amplitude. This is possible because the modes are all mutually orthogonal and because an amplitude represents the root-summed-squared displacement of the atoms affected by the mode. The A_S and A_P amplitudes sum over the supercell and parent-cell, respectively; either measure can be useful.
- (g) **Refinement-package output:** Use the [CIF-file](#), [TOPAS.str](#) and [FULLPROF.pcr](#) output options to generate refinement-package input files. For each file, take a moment to see how the symmetry-mode amplitudes are related to traditional atomic coordinates.

Exercise 4: Create/modify magCIFs with ISOCIF (Cr_2WO_6)

The objectives of this exercise are to explore the features of the ISOCIF tool for creating and manipulating CIF structure files. ISOCIF was originally created as a means of preparing input for ISODISTORT, but is now used by many for more general purposes. Start by selecting ISOCIF at <http://iso.byu.edu>. The example presented here is that of Cr_2WO_6 from Zhu *et al.*, PRL **113** 076406 (2014).

- (a) **Create a new magnetic CIF:** Select “[Create a new CIF](#)”. Choose magnetic space-group #58.395 ($Pn'mn$) from the drop-down menu. Choosing a magnetic space group trumps any non-magnetic space group that might also be selected. Enter cell parameter $a \approx b = 4.852 \text{ \AA}$ and $c = 8.870 \text{ \AA}$ (no need to enter the angles, which are assumed to be 90° for an orthorhombic metric). Indicate that there will

be 4 unique atoms in the structure. And set the alternative *ba-c* orthorhombic cell orientation as a space-group preference. Click **OK** at the bottom of the page to proceed. In this orientation, the MSG symbol is (*Pnn'm*).

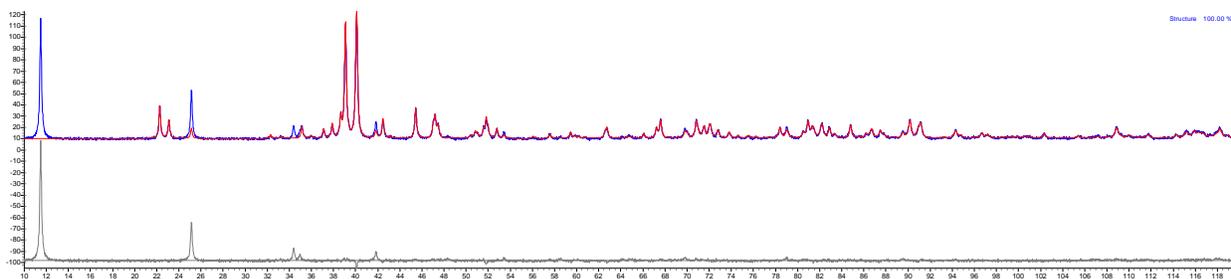
- (b) **Atomic coordinates:** Enter the coordinates and magnetic moments of each of the four atoms, which are Cr (0, 0, $z = 0.3345$), W (0, 0, 0), O1 ($x = y = 0.3030$), O2 ($x = y = 0.3060, z = 0.3400$). If you only enter the atom name, the type will be determined automatically. Each Wyckoff site is selected using a drop-down menu; use the numerical fields to give values to parameters that aren't fixed by symmetry. Leave each occupancy at the default value of 1.00. Only Cr atom needs gets a non-zero magnetic moment: ($m_x = 0, m_y = 1.0 \mu_B, m_z = 0$). Click **OK** at the bottom of the page to proceed.
- (c) **View structure:** Visualize the structure in the interactive applet by clicking the **View-structure** button. By selecting the **Axes** checkbox in the applet controls, you'll see that the Cr moments are oriented along the *y* axis (*x* is black, *y* is white, *z* is gray). Use the **Color** button to give all atoms of the same type the same color. Close the browser tab containing the applet with finished.
- (d) **Change setting:** Recall that you selected an alternative cell choice (orthorhombic *ba-c*). Use the **Change-setting** button to transform the structure to the standard BNS setting (*abc*), and use the interactive visualizer to verify that the moment directions change relative to the cell basis as expected. Once again, close the browser tab containing the applet when finished.
- (e) **Save** the structure as **Cr2WO6_magnetic.cif** (in the standard *abc* BNS setting) by clicking **Save-CIF-file** near the bottom of the page.
- (f) **Change lattice and origin:** Use the "**Change lattice and origin**" feature to shift the origin of your structure by $\mathbf{v} = (1/2, 0, 0)$, and use the interactive applet to visualize the result. Because this feature only permits transformations that leave the form of the symmetry operators invariant, few interesting basis transformations are possible. You could try changing the signs of the **a** and **b** vectors, which flips all of the moments. Use your browser's Back button a few times to return to the original setting just to see that you can undo past steps.
- (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. Visualize the structure again to make sure that nothing intrinsic has changed. Then click **Find-actual-symmetry** to auto-detect the unrepresented symmetries possessed by the structure. If the symmetry had been incorrect to begin with, this feature would have corrected it. Observe that detecting the symmetry from scratch takes the structure to the standard BNS setting: orthorhombic cell choice *abc* rather than *ba-c*.
- (h) **Remove magnetic moments:** Select this option to zero all magnetic moments, which results in non-magnetic space-group 58 (*Pnnm*). Save this parent structure as **Cr2WO6_parent.cif**.
- (i) **Irreps analysis:** In ISODISTORT, import the parent structure in **Cr2WO6_parent.cif**, make Cr magnetic, use Method 4 to decompose the magnetic structure in **Cr2WO6_magnetic.cif**, and visualize the result in the interactive applet. You should find that the mGM3- irrep is responsible for this magnetic structure.
- (j) See the **MAGNDATA** entry for magnetic Cr₂WO₆ on the Bilbao Crystallographic Server site (<http://webbdcristal.ehu.es/magnadata/index.php?index=0.75>), from which this example was prepared.
- (k) As another example, download the magnetic structure for MgCr₂O₄ (MAGNDATA entry 3.4), import it into ISOCIF to automatically convert it to a standard setting, save the result as **MgCr2O4_magnetic.cif**, remove all magnetic moments, save the result as **MgCr2O4_parent.cif**,

import the parent structure into ISODISTORT, and use Method 4 decompose the magnetic child into symmetry modes of the parent. This time, you'll see a rich variety of different irrep contributions!

Exercise 5: Symmetry-mode refinement (TOPAS, LaMnO₃)

The objectives of this exercises are to (1) illustrate the refinement of a magnetic structure, and (2) to illustrate a direct symmetry-mode refinement in TOPAS. This exercise depends on your completion of the earlier exercise on antiferromagnetic LaMnO₃. It assumes that you have an active installation of TOPAS Academic license (version 5x higher) and the jEdit editor.

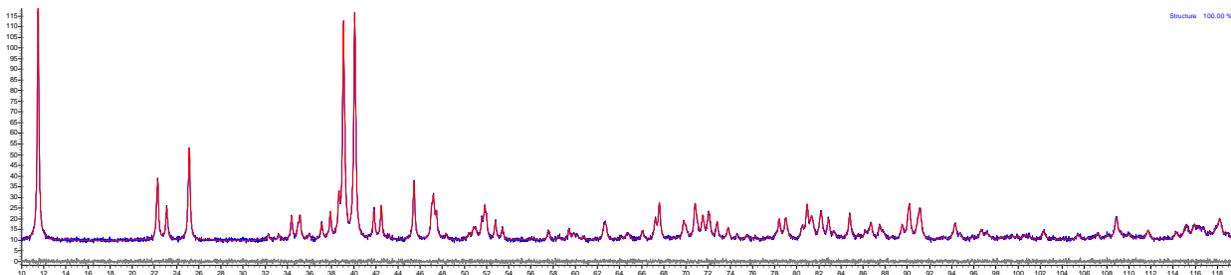
(a) Open the **lamno3_nonmagnetic.inp** in the jEdit ascii-text editor and submit it to TOPAS for a few least-squares cycles. This model has already been fit to the corresponding simulated magnetic-neutron diffraction dataset, and should converge immediately. You will see that there are a number of magnetic peaks that have not been accounted for in this fit.



(b) In the .inp file replace “space_group 62” with “mag_space_group 62.448”, and add the following two lines immediately after the line containing “site Mn”.

```
mlx @ 1.0 mly @ 0 mlz @ 0  
MM_CrystalAxis_Display(0.00000, 0.00000, 0.00000)
```

These first of these two lines enables the refinement of a Mn magnetic moment and gives it a kick start, while the second line displays the moment in Bohr-magneton (μ_B) units. Run a few more convergence cycles to obtain a good fit to the entire pattern. The x -component of the Mn moment should now be approximately $3.87 \mu_B$. Save the resulting file as **lamno3_magnetic.inp**. You have completed a magnetic model refinement!



(c) Starting over -- from the ISODISTORT [home](#) page, upload the magnetic LaMnO₃ distortion file that you save previously (**lamno3_distortion.txt**), which takes you directly to a previously saved [distortion](#) page. Then export a TOPAS.str output file called **lamno3_sm-mag.str** from the [distortion](#) page.

(d) Copy/paste the symmetry-mode model from **lamno3_sm-mag.str** over the top of the fitted traditional-coordinate model within **lamno3_nonmagnetic.inp**, and save the result as **lamno3_sm-mag.inp**. Take care not to delete the last few lines containing the scale factor and powder profile shape. To save time, copy the refined cell parameters and isotropic-thermal parameters from the old non-magnetic model back

into the appropriate locations within the new magnetic symmetry-mode model, and resave the .inp file (**lamno3_sm-mag.inp**). Because the initial mode amplitudes from the earlier decomposition are pretty good, and because the displacive and magnetic symmetry-mode parameters are all fixed, the refinement should converge immediately. But proceed to free up all of the magnetic and displacive symmetry-mode amplitudes, and run a few more convergence cycles to obtain a very good symmetry-mode fit.

(e) Fix the cell, peak-profile, background, and isotropic thermal parameters, which are already good enough. Disable the displacive and magnetic modes. Zero both the displacive and magnetic symmetry-mode amplitudes, which yields the simple-cubic perovskite parent structure. Run a convergence cycle to verify that the fit neglects all magnetic and non-magnetic superlattice peaks. Enable all of these displacive and magnetic modes again, and using simulated annealing, recover a good model of both the displacive and magnetic superstructures. It should be clear that the magnetic mX5+ mode is dominant, and that the mGM4+ and mR4+ modes contribute little if anything to the magnetic structure.

Exercise 6: Incommensurate magnetic structure (DyMn₆Ge₆)

The objective of this exercise is to generate and explore an incommensurate magnetic structure, while simultaneously employing magnetic superspace symmetry and representational (symmetry-mode) analysis.

Hexagonal DyMn₆Ge₆ has non-magnetic parent space-group *P6/mmm* (#191). Its magnetic structure below $T_N = 420$ K is an incommensurate circular spiral with a single temperature-dependent incommensurate wavevector $(0, 0, k_z \approx 0.17)$, which has magnetic-superspace-group symmetry $P6221'(0,0,g)h00s$. A second magnetic phase transition occurs at 100 K, below which a ferromagnetic contribution appears at $k = (0,0,0)$, resulting in a conical spiral with magnetic-superspace-group $P62'2'(0,0,g)h00$. Schobinger-Papamantellos *et al.*, *J. Alloys and Compounds* **215**, 111 (1994); *J. Magn. Magn. Materials* **150**, 311 (1995).

- MAGNDATA:** Go to the Bilbao Crystallographic Server, and select the MAGNDATA site. Do an element search for “Dy Mn Ge”, for which there is only the correct entry. Select DyMn₆Ge₆, and click on the “view in Jmol” link to visualize the structure in three dimensions. Observe the counter-rotating conical spirals on the Dy and Mn sites, and their anti-parallel *c*-axis moment projections.
- Parent structure:** From the ISODISTORT [home](#) page, upload the hexagonal parent structure (**DyMn6Ge6_parent.cif**).
- Types of distortions:** Under “**Types of distortions**” near the top of the [search](#) page, deselect each of the atomic displacements, and make Dy and Mn magnetic. Then click the **Change** button to update the page with updated menus.
- k* point:** In the Method 2 section of the [search](#) page, indicate that you want to superpose two irreps; then click the adjacent **Change** button to generate additional data fields for the second irrep. Two irreps are needed to achieve the low-temperature conical-spiral structure. Choose the GM $(0,0,0)$ as the first wavevector, and choose DT $(0,0,g = 0.167)$ with 1 incommensurate modulation as the second wavevector. Click **OK** to proceed.
- Irreducible representation:** Choose mGM2+ ($m\Gamma_2^+$) and mDT6 ($m\Delta_6$) from the [irreducible-representation](#) page. The *m* at the beginning of an irrep label means “magnetic”. Click **OK** to proceed.
- Order parameter direction:** When superposing two irreps (i.e. making them both primary), contributions from different irreps are separated by a vertical-bar (“|”) in the joint-OPD symbol. Each OPD leads to an inequivalent isotropy subgroup, which then has a distinct combination of magnetic

superspace-group, basis, and origin. Select the first and simplest OPD, $(a|b,0,0,0)$ – the MSSG is $P62'2'(0,0,g)h00$, where the last three symbols are the phase shifts associated with the three generators in the symbol. The h indicates that the six-fold rotation must be combined with a modulation-phase shift of $\pi/3$ to leave the structure invariant. Click **OK** to proceed. If the next page fails to generate completely (due to a subtle memory-allocation bug), simply refresh the page in your browser to proceed.

- (g) **Visualize:** Use the interactive applet to visualize the magnetic structure. You should find that mGM2+ contributes one ferromagnetic parameter to each of Dy and Mn, while mDT6 contributes one transverse magnetic mode to Dy and four transverse modes to Mn. The ferromagnetic components of the Dy and Mn moments should point in opposite directions. Observe that the Dy mDT6 mode is simple circular magnetic spiral. Explore the Mn mDT6 modes to find a combination that produces a spiral to rotates in the opposite direction. Write down the set of mode amplitudes that produces a structure that appears to be a likely candidate.
- (h) **CIF output:** On the **distortion** page, enter the mode amplitudes that you wrote down in the previous step, and save the structure to a magnetic CIF file. Because we have not yet implemented incommensurate magnetic symmetry-mode details for magCIF output, only the traditional Fourier amplitudes will be included. Examine the CIF output, and see that the Fourier amplitudes are restricted by symmetry, and that only the Fourier amplitudes of symmetry-unique atoms are given – the rest can be calculated using MSSG operators. One can load this file into JANA to refine the magnetic parameters against magnetic neutron-diffraction data.
- (i) **Future plans:** Future efforts will include (1) symmetry-mode details in incommensurate magCIF output, (2) send incommensurate symmetry-mode parameters directly to JANA, (3) domain output for incommensurate structures, (4) decomposition of incommensurate structures.

Exercise 7: Incommensurate magnetic structure (TbMnO₃)

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

TbMnO₃ 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, TbMnO₃ 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 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 mSM2 and mSM3. The mSM2 Mn moments are directed along the z-axis and are 90 degrees out of phase with the mSM3 y-axis Mn moments, so that the LTI magnetic structure is cycloidal. Remarkably, the isotropy subgroup that results has no center of inversion and couples to secondary ferroelectric irrep (GM4-). 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.

- (a) **Parent structure:** Upload **tbmno3_pbnm.cif** as the parent structure.

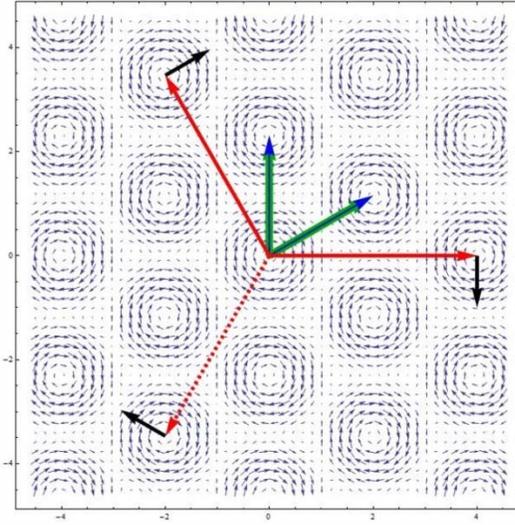
- (b) **Types of distortions:** On the [distortion](#) page, keep strains and atomic displacements, and add magnetic moments to Mn. Click the [Change](#) button to update the page.
- (c) **Space-group preferences:** Near the bottom of the [search](#) page, select the "ba-c" permutation of orthorhombic 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 the [Change](#) button to update the page.
- (d) **k point:** Under Method 2 on the [search](#) page, indicate that you want to superpose two irreps, click the [Change](#) button, and then 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.
- (e) **Irreducible representation:** Select mSM3 and mSM2 as the two irreps.
- (f) **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.
- (g) **View distortion:** On the [distortion](#) page, near the bottom of the page, set the "**Maximum bond length**" to 2.25 Angstroms (makes the structure look nicer). Then open the interactive structure viewer. 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 "i" on your keyboard) and give roughly equal numerical amplitudes to 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 x and antiferromagnetic along z. 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.
- (h) **Full k -star:** Consider that the coupling of the cycloidal magnetic modes to a ferroelectric secondary mode make TbMnO₃ 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 k vector at a time. ISODISTORT simultaneously treats all symmetry-related arms of the star of k , which includes both $+k$ and $-k$ 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.
- (i) **Incommensurate CIF file:** From the [distortion](#) page, save the incommensurately-modulated TbMnO₃ structure to a CIF file called **tbmno3_incommensurate.cif**. Then open the file in an ascii text editor and explore its magCIF structure.
- (j) **Distortion file:** From the [distortion](#) page, use the [distortion-file](#) option save the current state into a file called **tbmno3_distortion.txt**. When this file is imported again, you return immediately to this point.

Exercise 8: (3+d)D incommensurate magnetic structures

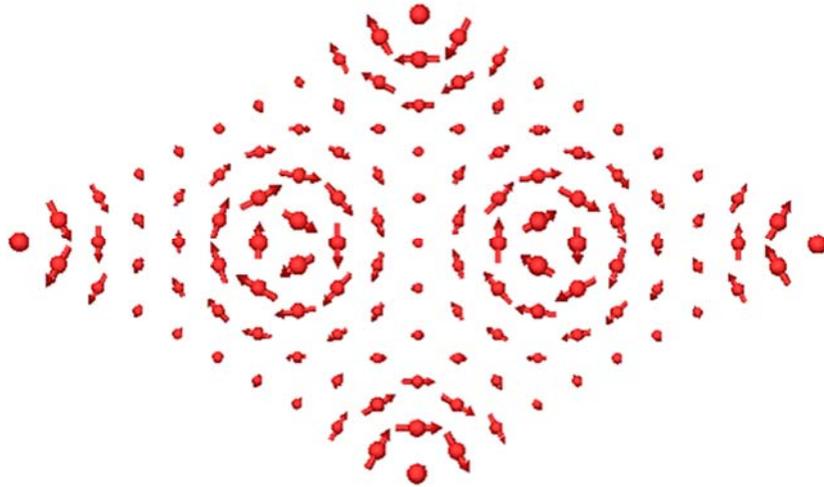
The objective of this exercise is to discover the power of combining a fully-general representational (symmetry-mode) analysis with (3+d)-dimensional superspace-symmetry. For more information, see Stokes and Campbell, *Acta Cryst A*, Jan 2017.

A skyrmion is a whirlpool-like rotational pattern of magnetic moments that is topologically protected from minor perturbations -- it tends to keep its shape when poked or prodded. Hexagonal lattices of skyrmions 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)].

- (a) **Parent structure (CIF):** Upload the **Fe_monolayer.cif** file as your parent structure.
- (b) **Types of distortions:** On the **search** page, add magnetic and occupational modes to the Fe atom, and click the **Change** button 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. Click **OK** to proceed to the next page. Note that 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 $k_1 = (-q, -q, 0)$, $k_2 = (2q, -q, 0)$, and $k_3 = (-q, 2q, 0)$. Since $k_1 + k_2 + k_3 = 0$, only two of these directions are linearly independent.



- (d) **Irreducible representation:** Choose the mLD3 irrep from the drop-down menu. This irrep is responsible for 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 modulation 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. Click **OK** to proceed to the next page. If the next page fails to generate completely, simply refresh the page in your browser.
- (f) **View distortion:** From the **distortion** page, open the interactive structure viewer. Uncheck the **Bonds** button in the applet to simplify the appearance of the structure. Observe that in addition to the primary magnetic order parameter, that secondary displacive and strain modes are also available to this distortion; or in other words, they are also allowed by the symmetry of the isotropy subgroup. Drag the magnetic-mode amplitude to its maximum value to see the skyrmion lattice of identically-oriented magnetic whirlpools. Animate the distortion. Then mix in the secondary displacive and occupancy modes just to see what they do.



- (g) **CIF output:** Based on what seem like reasonable magnetic and displacive mode amplitudes in the interactive applet, enter amplitude values into the appropriate fields on the [distortion](#) page. Then generate a CIF output file, and examine its contents. The symmetry operators comprise a (3+2)D magnetic superspace group (MSSG). Because there are no secondary order parameters at commensurate k vectors, the undistorted and distorted versions of the basic cell will be the same. But you should be able to identify the wave-vectors and the modulation amplitudes and phases of the magnetic and displacive waves of the structure. Note that because such groups have been partially classified, but not fully tabulated, the last character of the MSSG number is given as "?". One should, in principle, be able to import this structure into the latest version of the JANA 2006 program.
- (h) **Further exploration:** 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 try the other simple OPDs (i.e. those with only one variable) of mLD3 and possibly mLD2, which should have very different magnetic patterns.