# ISODISPLACE Workshop

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ISODISPLACE is a tool for exploring the structural distortion modes of crystalline materials. It provides a user-friendly interface to many of the algorithms used by the Isotropy Software Suite, allowing one to generate and explore distortion modes induced by irreducible representations of the parent space-group symmetry. It also provides a Java applet for visualizing and interactively manipulating the free parameters associated with these modes. ISODISPLACE was developed by Harold T. Stokes, Branton J. Campbell, and Dorian M. Hatch.

## Preparation for the workshop

Before coming to this workshop, you should test your version of Java. Direct your internet browser to stokes.byu.edu/bilbao/test.htm. If graphics appears on the screen, your version of Java is fine. If not, then you need to update your version of Java. For Windows, go to java.com/getjava. For Macs, use the update utility.

Also, create a new folder on your desktop (or wherever you want) and name it *isodisplace*. Download the zip file at stokes.byu.edu/bilbao/cif.zip and extract the files into the *isodisplace* folder.

## Part 1. Introduction to the Java applet

(a) $CaTiO_3$ (stokes.byu.edu/bilbao/CaTiO3.htm)

(b) $LaMnO_3$ (stokes.byu.edu/bilbao/LaMnO3.htm)

(c) $WO_3$ (stokes.byu.edu/bilbao/WO3.htm)

(d) $LiAlO_2$ (stokes.byu.edu/bilbao/LiAlO2.htm)

## Part 2. Using ISODISPLACE: Method 4

Mode decomposition of a distorted structure

If you know the structure of a distorted crystal and the structure of its undistorted parent (either from a phase at higher temperature or simply derived from the distorted structure), you can use method 4 to find the distortion and decompose it into symmetry-adapted modes of the parent. We will apply this method to $CaTiO_3$.

The structure of $CaTiO_3$ is reported in S. Sasaki, C. T. Prewitt, J. D. Bass and W. A. Schulze, "Orthorhombic Perovskite $CaTiO_3$ and $CdTiO_3$: Structure and Space Group," *Acta Cryst.* (1987), C**43**, 1668–1674.

Space Group: #62 *Pnma* (orthorhombic)
$a = 5.4423$, $b = 7.6401$, $c = 5.3796$
Ca (4c) 0.03602, 1/4, −0.00676
Ti (4b) 0, 0, 1/2

O(1) (4c) 0.4838, 1/4, 0.0714
O(2) (8d) 0.2888, 0.0371, 0.7108

This structure is a distortion of the cubic perovskite structure (as will be seen):

Space Group: #221 $Pm\bar{3}m$ (cubic)
Ca (1b) 1/2, 1/2, 1/2
Ti (1a) 0, 0, 0
O (3d) 1/2, 0, 0

We can obtain the lattice parameter of the cubic structure by requiring that the volume per formula unit be the same as in the orthorhombic structure. The cubic unit cell contains one formula unit (one Ca, one Ti, and three O). The orthorhombic unit cell contains four formula units. Thus, the volume of the orthorhombic unit cell must be four times as large as the volume of the cubic unit cell. The volume of the orthorhombic unit cell is $abc = (5.4423)(7.6401)(5.3796) = 223.68$. Thus the volume of the cubic unit cell will be $(223.68)/4 = 55.921$ and the lattice parameter $a = (55.921)^{1/3} = 3.8241$.

We will find the distortions that take the cubic structure into the orthorhombic structure using ISODISPLACE.

Go to the ISODISPLACE home page (stokes.byu.edu/isodisplace.html). Make a bookmark for this page. We will return to it several times during this workshop.

We have prepared CIF structure files for both the cubic and orthorhombic structures of $CaTiO_3$, so click on *Import parent structure from a CIF structure file.*

**Parent structure (CIF)**: Use the *Browse* button to find the file, *CaTiO cubic.cif* and click on *Upload*.

**Space-group preferences**: You can choose space-group settings here. The default is usually fine. Also, this page displays the preprocessed CIF file with everything removed except for the information ISODISPLACE needs. You can edit the CIF file here if you want. Click on *OK*.

**Search**: Click on the *View parent* button near the top of the page.

**View parent structure**: You should see a graphical rendering of the cubic perovskite structure.
If the graphics is too large for your window, you can change the size of the graphics by entering a smaller number like 720 into the *Applet width* box near the *View parent* button on the *search* page.
You can rotate the structure by dragging the mouse across it.
Close this window.

**Search**: We will use *Method 4: Mode decomposition of a distorted structure.*
Scroll down the window to *Method 4* and click on *OK* for *Option 1: Upload CIF file.*

**Upload distorted structure (CIF)**: Use the *Browse* button to find the file, *CaTiO3 orthorhombic.cif* and then click on *Upload*.

**Review distorted structure (CIF)**: This displays the preprocessed CIF file.
Click on *OK*.

**Distorted structure (basis)**: Here we must enter how the conventional lattice vectors of the cubic and orthorhombic structures are related. You can either enter the transformation by hand (option 2) or select one the guesses contained in drop-down menu (option 1).
Use the drop-down menu to select *(1,0,-1),(0,2,0),(1,0,1)* and click on *OK*.

**Distortion**: The program now fits the orthorhombic structure to the cubic structure, determines how the cubic structure is distorted, and decomposes the distortion into symmetry-adapted modes. The result is displayed in this *distortion* page. This page contains a lot of information.

Near the top of the *distortion* page, there are a number of buttons. By default, the button for *view distortion* is selected.
Click on *OK*.

**View distortion**: You should see a graphical rendering of the orthorhombic structure. If the graphics is too large for your window, you can change the size of the graphics by entering a smaller number like 720 into the *Applet width* box near the bottom of the *distortion* page.
Close window.

**Distortion**: Now select the *View diffraction* button.
Click on *OK*.

**View diffraction**: Here we see a single-crystal diffraction pattern that you would observe from this distorted structure. Move one of the slider bars to see how the amplitude of the distortion affects the diffraction pattern.
Select the *Powder* button at the bottom of the page. Now you see a power-diffraction pattern from this distorted structure.

**Exercise**: Start over at the ISODISPLACE home page and repeat the decomposition of $CaTiO_3$ described above.

# Part 3. Using ISODISPLACE: Method 1
Search over all special $k$ points

This method gives you quick access to all distortions due to a single irrep at a special $k$ point. These are the distortions listed in H. T. Stokes and D. M. Hatch, *Isotropy Subgroups of the 230 Crystallographic Space Groups* (World Scientific, Singapore, 1988), sometimes known as the "Green" book. We will apply this method to $LaMnO_3$.

The structure of various phases of $LaMnO_3$ is reported in J. Rodriguez-Carvajal, M. Hennion, F. Moussa, A. H. Moudden, L. Pinsard and A. Revcolevschi, "Neutron Diffraction Study of the Jahn-Teller transition in stoichiometric $LaMnO_3$," *Phys. Rev.* (1998), B**57**, R3189. The structures are all distorted cubic perovskites. One of the structures mentioned has the space-group symmetry 167 $R\bar{3}c$.

Go to the ISODISPLACE home page. Click on *Import parent structure from a CIF structure file.*

**Parent structure (CIF)**: Use the *Browse* button to find the file, *LaMnO3 cubic.cif* and click on *Upload*.

**Space-group preferences**: Click on *OK*.

**Search**: Note all of the different restrictions you can put on search method 1. We will simply look for space group 167. In the drop-down menu for *space-group symmetry*, select *167 R-3c D3d-6* and click on *OK*.

**Order parameter direction**: The drop-down menu shows all of the results of the search. In this case, there are three choices. The value of the size $s$ of the primitive unit cell of the distorted structure relative to that of the parent tells us that the first choice has cell doubling ($s = 2$) and the other two choices have a cell eight times larger ($s = 8$). Often, the correct choice is the one with the smaller cell size. Also, you may recall that the irrep $R4+$ played a predominant role in the orthorhombic structure we viewed earlier. This would be another reason to select the first choice.
Select the first choice, *R4+ P3(a,a,a) 167 R-3c. . .* and click on *OK*.

**Distortion**: *View distortion* is already selected. Click on *OK*.

**View distortion**: Move the slider bar for the $R4+$ oxygen mode and select *animate* at the bottom of the page. By viewing the structure from different directions, you can see that this mode rotates the $MnO_6$ octahedra about the rhombohedral $c$ axis, half of them in one direction and the other half in the other direction.

# Part 4. Using ISODISPLACE: Method 2
General method—search over specific $k$ points

This method lets you view the distortion caused by specified irreps. It also lets you search for the irrep that causes the kind of distortion you are interested in. It lets you choose more than one irrep at a time, so that you can see what happens when the irreps are simultaneously applied. The choice of $k$ vectors is not restricted to special $k$ points, as was the case in method 1. You can even select $k$ vectors with irrational components, leading to distortions which are incommensurate with respect to the the parent. We will apply method 2 to PZT, $Pb(Zr_{1-x}Ti_x)O_3$.

PZT is a ferroelectric. Its structure in various phases is reported in B. Noheda, J. A. Gonzalo, L. E. Cross, R. Guo, S.-E. Park, D. E. Cox, and G. Shirane. "Tetragonal-to-Monoclinic Phase Transition in a Ferroelectric Perovskite: The Structure of $PbZr_{0.52}Ti_{0.48}O_3$," *Phys. Rev.* (2000), B**61**, 8687–8694. PZT is a cubic perovskite above 600–700 K, depending on its composition. We will use method 2 to find the space-group symmetries of the ferroelectric phases.

Go to the ISODISPLACE home page. Click on *Import parent structure from a CIF structure file.*

**Parent structure (CIF)**: Use the *Browse* button to find the file, *PZT cubic.cif* and click on *Upload*.

**Space-group preferences**: Click on *OK*.

**Search**: Under *Method 2*, we can see that we must first select a $k$ point. Ferroelectric distortions always belong to *GM* irreps ($k = 0$), so use the *select k point* drop-down menu and select *GM, k12 (0,0,0)* and click on *OK*.

**Irreducible representation**: Now we must select an irrep. The drop-down menu give fives choices. Since we don't know which irrep(s) result in ferroelectric distortions, we must try each of them.

First, select *GM1+* and click on *OK*.
Click on *OK* on the next two pages too, until you arrive at the *view distortion* page.
We see that none of the slider bars gives atomic displacements. Close the last two windows and go back to the *irreducible representation* page.
Choose another irrep and repeat what we did for *GM1+*.
You will find that *GM3+* and *GM5+* also do not have displacement modes.
*GM4-* does have a displacement mode, and it's ferroelectric. The displacements are along the $z$ axis, so you will need to rotate the figure to see them.
*GM5-* also has a displacement mode, but it is not ferroelectric. In this mode, half of the oxygens move one way, and the other half move the other way. In a ferroelectric mode, all of the atoms move in the same direction.

Return to the *irreducible representation* page and select *GM4-* from the drop-down menu and click on *OK*.

**Order parameter direction**: The drop-down menu shows six different distorted structures that can arise from the *GM4-* irrep. *GM4-* is a 3-dimensional irrep and each of its dimensions causes a different distortion. The way these distortions are mixed is given by the order parameter. Note that each choice in the drop-down menu begins with a symbol (like P1) and a 3-dimensional vector, which is the order parameter. The six choices are given by the order parameters $(a, 0, 0)$, $(a, a, 0)$, etc.

In PZT, the structures for $(a, 0, 0)$ *P4mm*, $(a, a, a)$ *R3m*, and $(a, a, b)$ *Cm* have been observed.

# Part 5. Using ISODISPLACE: Method 3
Search over arbitrary $k$ points for specified point group and lattice

This method lets us search for distortions given the lattice and point group of the distorted structure. From diffraction data, we can easily determine the lattice of the distorted structure. Often, we can also know something about its space-group symmetry. This method gives you a list of possible distorted structures consistent with this information. You can then try to fit each distorted structure to your data.

As an example, suppose that we know that one of the phases of $LaMnO_3$ is a distorted cubic perovskite with space group 62 *Pnma* and lattice (2,0,0), (0,1,1), $(0, -1, 1)$. What are the possible distorted structures?

Go to the ISODISPLACE home page. Click on *Import parent structure from a CIF structure file*.

**Parent structure (CIF)**: Use the *Browse* button to find the file, *PZT cubic.cif* and click on *Upload*.

**Space-group preferences**: Click on *OK*.

**Search**: Under *Method 3*, enter the representative basis,
$a' = 2a$
$b' = b + c$
$c' = -b + c$
and then click on *OK*.
Note that we used the default selection, *primitive real-space superlattice* since the lattice of *Pnma* is not centered.

**Distorted structure: point group**: The drop-down menu shows the possible point groups of the distorted structure, given the chosen lattice. Select *Orthorhombic: mmm D2h* and click on *OK*.

**Distorted structure: subgroup**: Now the drop-down menu contains all of the distorted structures with the chosen lattice and point group. You will find four choices for *Pnma*. Unless you had further information, you would need to try to fit your data to each of these four structures to determine which is correct.

# Part 6. Exercises

**Method 1**: $YMnO_3$ is hexagonal with space group #194 $P6_3/mmc$ and undergoes a ferroelectric phase transition to space group #185 $P6_3cm$ with a unit cell triple in size. Find the irrep and order parameter that drives this phase transition. The file, *YMnO3 HT.cif*, contains the high-temperature undistorted parent structure.

**Method 2**: $LiAlO_2$ is tetragonal with space group #141 $I4_1/amd$. Find the irrep(s) that produce ferroelectric modes. The file, *LiAlO2 parent.cif*, contains the parent structure.

**Method 3**: Consider an order-disorder phase transition that takes an fcc crystal (space group #225 $Fm\bar{3}m$) into a bcc crystal (space group #229 $Im\bar{3}m$) with $a' = 2a$, $b' = 2b$ and $c' = 2c$. Find the irrep and order parameter that drives this phase transition. On the *search* page, be sure to select *Conventional real-space lattice with I centering*. The file, *fcc.cif*, contains the parent structure.

**Method 4**: $WO_3$ exhibits monoclinic structure, space group #14 $P2_1/n$, which is a distorted cubic structure. Use method 4 to decompose the distortion into symmetry-adapted modes of the cubic structure. Which irreps contribute modes involving atomic displacements? Which two irreps make the largest contribution to the distortion? The file, *WO3 monoclinic.cif*, contains the distorted structure, and the file, *WO3 cubic.cif*, contains the cubic structure derived from the monoclinic structure.