ISOTROPY

Tutorial

September 2021

Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell
Department of Physics and Astronomy
Brigham Young University

with a contribution by
Christopher J. Howard
University of Newcastle, Australia

Contents

Session 1: Introduction and Space Groups

This tutorial guide is intended to help you learn how to use ISOTROPY. All of the features of ISOTROPY are not shown here. For more details, see the descriptions of the commands in the user's manual.

Start ISOTROPY by typing `iso`. The following message will appear on the screen:

```
Isotropy, Version 9.0, August 2007
Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell
Brigham Young University
Current setting is International (new ed.) with conventional basis vectors.
*
```

The asterisk `*` is a prompt, telling you that ISOTROPY is waiting for a command. Let's begin with an example. Let us display the elements of space group #24 $I2_12_12_1$ (D_2^9). We suggest that you work through these examples at the computer terminal with ISOTROPY running.

```
*VALUE PARENT 24
*SHOW PARENT
*SHOW ELEMENTS
*DISPLAY PARENT
Parent        Elements
24 I2_12_12_1 (E|0,0,0), (C2x|0,0,1/2), (C2y|1/2,0,0), (C2z|0,1/2,0)
*
```

Commands are composed of keywords (`VALUE`, `PARENT`, `SHOW`, and `ELEMENTS` in the example above) and parameters (`24`, in the example above). Different keywords and parameters are separated by space characters in the command. All keywords may be entered using either upper or lower case letters. All keywords may be abbreviated to the first one or more characters, depending on the ambiguity of different keywords that start with the same letter(s). For example, we could have typed `V PA 24` instead of `VALUE PARENT 24`. However, if we type

```
*V P 24
Ambiguous command: P
*
```

we find that the keyword `P` is ambiguous, since there is another keyword, `POINTGROUP`, also beginning with `P`, and ISOTROPY doesn't know which you mean. ISOTROPY returns an error message and does not try to execute the command. In our examples, we will always enter the keywords spelled out in full and in upper-case letters. If you misspell a keyword,

```
*VALUE PARRENT
Syntax error: PARRENT
*
```

ISOTROPY tells you which word is misspelled and does not try to execute the command. If you enter extra keywords or parameters at the end of a command,

```
*SHOW PARENT VALUE
Warning: Extra parameters ignored: VALUE
*
```

ISOTROPY executes the valid part of the command `SHOW PARENT` and then issues a warning about the extra keyword or parameter at the end. Let us return to our example:

```
*VALUE PARENT 24
*SHOW PARENT
*SHOW ELEMENTS
*DISPLAY PARENT
Parent        Elements
24 I2_12_12_1 (E|0,0,0), (C2x|0,0,1/2), (C2y|1/2,0,0), (C2z|0,1/2,0)
*
```

`DISPLAY` commands cause output to be generated. In this case, `DISPLAY PARENT` causes information about space groups to be displayed. The `VALUE` command selects which space group to display. The `SHOW` commands control what information about each space group is to be displayed. In this case, `VALUE PARENT 24` selects space group #24. `SHOW PARENT` and `SHOW ELEMENTS` causes the symbol for the space group and the elements of the space group to be displayed (actually, the coset representatives with respect to the translational subgroup of the space group). The program recognizes the international and Schoenflies symbols for the space group as well. For example, we could have typed `VALUE PARENT I2_12_12_1` or `VALUE PARENT D2-9`. We can also control which kind of space-group symbols are to be displayed.

```
*VALUE PARENT 24
*SHOW PARENT
*SHOW ELEMENTS
*LABEL SPACEGROUP SCHOENFLIES
*DISPLAY PARENT
Parent  Elements
24 D2-9 (E|0,0,0), (C2x|0,0,1/2), (C2y|1/2,0,0), (C2z|0,1/2,0)
*LABEL SPACEGROUP INTERNATIONAL
*DISPLAY PARENT
Parent        Elements
24 I2_12_12_1 (E|0,0,0), (C2x|0,0,1/2), (C2y|1/2,0,0), (C2z|0,1/2,0)
*
```

See the description of the command, `LABEL SPACEGROUP`, in the user's manual for more information. We can also control the way space-group elements are displayed.

```
*LABEL ELEMENTS INTERNATIONAL
*DISPLAY PARENT
Parent        Elements
24 I2_12_12_1 (x,y,z), (x,-y,-z+1/2), (-x+1/2,y,-z), (-x,-y+1/2,z)
```

```
*LABEL ELEMENTS BRADLEY-CRACKNELL
*DISPLAY PARENT
Parent        Elements
24 I2_12_12_1 (E|0,0,0), (C2x|0,0,1/2), (C2y|1/2,0,0), (C2z|0,1/2,0)
*
```

See the description of the command, `LABEL ELEMENTS`, in the user's manual for more information. We can also use different settings of space groups. For example, the space-group setting (choice of origin and axes) for this space group is chosen different by Bradley and Cracknell.

```
*SETTING BRADLEY-CRACKNELL
*DISPLAY PARENT
Parent        Elements
24 I2_12_12_1 (E|0,0,0), (C2y|0,0,1/2), (C2x|0,1/2,0), (C2z|1/2,0,0)
*
```

Sometimes it is useful to see the vectors in terms of primitive lattice vectors instead of conventional lattice vectors.

```
*LABEL VECTOR PRIMITIVE
*DISPLAY PARENT
Parent        Elements
24 I2_12_12_1 (E|0,0,0), (C2y|1/2,1/2,0), (C2x|0,1/2,1/2), (C2z|1/2,0,1/2)
*
```

By the way, we can always find out which setting and form of vectors are being used:

```
*DISPLAY SETTING
Current setting is Bradley-Cracknell with primitive basis vectors.
*
```

For that matter, we can always find out which `VALUE` and `SHOW` commands are in effect:

```
*DISPLAY VALUE
The following VALUE commands are in effect:
PARENT 24
*DISPLAY SHOW
The following SHOW commands are in effect:
ELEMENT, PARENT
*
```

We can also display information using different settings in *International Tables*. For example, there are two choices of origin for space group #48. By default, the program uses the second choice, where the the origin is at the point of inversion.

```
*VALUE PARENT 48
*LABEL VECTOR CONVENTIONAL
*SETTING INTERNATIONAL
*DISPLAY PARENT
```

```
Parent  Elements
48 Pnnn (E|0,0,0), (C2x|0,1/2,1/2), (C2y|1/2,0,1/2), (C2z|1/2,1/2,0), (I|0,0,0),
        (SGx|0,1/2,1/2), (SGy|1/2,0,1/2), (SGz|1/2,1/2,0)
*SETTING INTERNATIONAL ALL ORIGIN 1
*DISPLAY PARENT
Parent  Elements
48 Pnnn (E|0,0,0), (C2x|0,0,0), (C2y|0,0,0), (C2z|0,0,0), (I|1/2,1/2,1/2),
        (SGx|1/2,1/2,1/2), (SGy|1/2,1/2,1/2), (SGz|1/2,1/2,1/2)
*
```

The different settings for monoclinic and rhombohedral space groups are also available. See the command, `SETTING INTERNATIONAL` in the user's manual for more information. The settings and forms of symbols that you prefer can be written into the file, iso.ini, which the program will read and execute when it starts. For example, suppose that you want elements to be displayed using the notation of *International Tables* and that you want to always use the first origin choice. Then you would create a file, iso.ini, with the following lines:

```
LABEL ELEMENT INTERNATIONAL
SETTING INTERNATIONAL ALL ORIGIN 1
```

and when the program starts it would read and execute those commands:

```
Isotropy, Version 8.0.2, October 2003
Harold T. Stokes and Dorian M. Hatch
Brigham Young University
Commands from iso.ini:
*LABEL ELEMENT INTERNATIONAL
*SETTING INTERNATIONAL ALL ORIGIN 1
End of commands from iso.ini.
Current setting is International (new ed.) with conventional basis vectors.
*
```

Now let us examine some of the other options for the `DISPLAY PARENT` command. We can select space groups with a monoclinic base-centered lattice:

```
*CANCEL SHOW ALL
*CANCEL VALUE ALL
*SHOW PARENT
*VALUE LATTICE MC
*DISPLAY PARENT
Parent
5 C2
8 Cm
9 Cc
12 C2/m
```

```
15 C2/c
*
```

Note that the CANCEL command can remove SHOW and VALUE commands that have been previously executed. See the description for the command, VALUE LATTICE, in the user's manual for a list of symbols for the the lattices. We can also select space groups with crystal class $2/m$:

```
*CANCEL VALUE LATTICE
*VALUE POINTGROUP 2/M
*DISPLAY PARENT
Parent
10 P2/m
11 P2_1/m
12 C2/m
13 P2/c
14 P2_1/c
15 C2/c
*
```

See the description for the command, VALUE POINTGROUP, in the user's manual for a list of symbols for the point groups. We can display the generating elements of the space group:

```
*CANCEL VALUE POINTGROUP
*VALUE PARENT 24
*SHOW GENERATORS
*DISPLAY PARENT
Parent        Generators
24 I2_12_12_1 (C2z|0,1/2,0), (C2x|0,0,1/2)
*
```

We can display the Wyckoff positions:

```
*CANCEL SHOW GENERATORS
*SHOW WYCKOFF VECTOR
*DISPLAY PARENT
Parent        Wyckoff Points
24 I2_12_12_1 a (x,0,1/4), b (1/4,y,0), c (0,1/4,z), d (x,y,z)
*
```

We can also display all of the points for each position:

```
*SHOW WYCKOFF VECTOR ALL
*DISPLAY PARENT
Parent        Wyckoff Points Coordinates
24 I2_12_12_1 a              (x,0,1/4), (-x+1/2,0,-1/4)
              b              (1/4,y,0), (1/4,-y,1/2)
              c              (0,1/4,z), (0,-1/4,-z+1/2)
```

```
              d               (x,y,z), (x,-y,-z+1/2), (-x+1/2,y,-z),
                              (-x,-y+1/2,z)
*
```

We can select a particular position:

```
*CANCEL SHOW WYCKOFF VECTOR ALL
*VALUE WYCKOFF A
*DISPLAY PARENT
Parent        Wyckoff Points
24 I2_12_12_1 a (x,0,1/4)
*
```

We can show the point group of the position:

```
*SHOW WYCKOFF POINTGROUP
*DISPLAY PARENT
Parent        Wyckoff Points, Point Groups
24 I2_12_12_1 a (x,0,1/4) C2
*
```

C_2 is the Schoenflies symbol for the point group. If we want the international symbol 2 to be displayed,

```
*LABEL POINTGROUP INTERNATIONAL
*DISPLAY PARENT
Parent        Wyckoff Points, Point Groups
24 I2_12_12_1 a (x,0,1/4) 2
*
```

We can also show the elements of the point group:

```
*SHOW WYCKOFF ELEMENTS
*DISPLAY PARENT
Parent        Wyckoff Points Point Group Elements
24 I2_12_12_1 a (x,0,1/4)    2           (E|0,0,0), (C2x|0,0,1/2)
*
```

We can select values for the parameters x, y, z in the Wyckoff positions and display the atomic coordinates:

```
*CANCEL SHOW WYCKOFF POINTGROUP
*CANCEL SHOW WYCKOFF ELEMENTS
*VALUE WYCKOFF XYZ 0.245 0 0
*SHOW WYCKOFF VECTOR ALL
*DISPLAY PARENT
Parent        Wyckoff Points Coordinates
24 I2_12_12_1 a              (0.24500, 0.00000, 0.25000)
                             (0.25500, 0.00000, -0.25000)
*
```

Note that values must be selected for y and z, even though they are not used in the Wyckoff position. If we select values for the lattice parameters, $a, b, c, \alpha, \beta, \gamma$ (α is the angle between $\vec{b}$ and $\vec{c}$, etc.), then we can display the coordinates in cartesian coordinates:

```
*VALUE LATTICE PARAMETER 7.62 8.43 9.79 90 90 90
*SHOW CARTESIAN
*DISPLAY PARENT
Parent        Wyckoff Points Coordinates
24 I2_12_12_1 a              (1.86690, 0.00000, 2.44750)
                             (1.94310, 0.00000, -2.44750)
*
```

See the description for the command, `SHOW WYCKOFF` in the user's manual for more information. There is a limited amount of on-line help available. The keyword `?` displays the valid keywords that could possibly be inserted at that position. For example,

```
*SETTING ?
Valid Keywords: BRADLEY-CRACKNELL, INTERNATIONAL, KOVALEV, MILLER-LOVE,
ZAK, MAGNETIC, NOMAGNETIC
*
```

This is the end of this tutorial. You may exit the program:

```
*QUIT
```

If you have been running ISOTROPY, quit the program and start it again.

We can display the $\vec{k}$ vectors in the first Brillouin zone. Let us do this for space group #225 $Fm\bar{3}m$ (O_h^5):

```
*VALUE PARENT 225
*SETTING MILLER-LOVE
*SHOW KPOINT
*SHOW KDEGREE
*DISPLAY KPOINT
    k vector              k degree
GM  (0,0,0)               0
DT  (0,2a,0)              1
LD  (a,a,a)               1
SM  (2a,2a,0)             1
L   (1/2,1/2,1/2)         0
X   (0,1,0)               0
W   (1/2,1,0)             0
Q   (1/2,-2a+1,2a)        1
V   (2a,1,0)              1
C   (b,b,2a-b)           2
A   (-2a+2b,2a,0)         2
GP  (-a+b+c,a-b+c,a+b-c) 3
*
```

These symbols for the $\vec{k}$ vectors follow the convention of Miller and Love. Greek letters are represented with pairs of letters (GM = Γ, DT = Δ, LD = Λ, SM = Σ). GP is the general point. The symbols a,b,c represent the parameters defining the $\vec{k}$ vector when it is along a line, or in a plane, or at a general point. (Miller and Love use symbols α, β, γ.) The degrees of freedom is equal to the number of parameters which define each $\vec{k}$ vector. $\vec{k}$ vectors with zero degrees of freedom are called $\vec{k}$ points of symmetry. Those with one degree are $\vec{k}$ lines of symmetry. Those with two degrees are $\vec{k}$ planes of symmetry. The general point always has three degrees of freedom. The coordinates are given in terms of the conventional reciprocal lattice vectors, which in this case are $(2\pi/a)\hat{\mathbf{i}}$, $(2\pi/a)\hat{\mathbf{j}}$, $(2\pi/a)\hat{\mathbf{k}}$, where a is the lattice parameter. For example, the actual cartesian coordinates for the W point are $(\pi/a, 2\pi/a, 0)$. In terms of the primitive reciprocal lattice vectors,

```
*CANCEL SHOW KDEGREE
*LABEL VECTOR PRIMITIVE
*DISPLAY KPOINT
    k vector
GM  (0,0,0)
DT  (a,0,a)
LD  (a,a,a)
SM  (a,a,2a)
```

```
L   (1/2,1/2,1/2)
X   (1/2,0,1/2)
W   (1/2,1/4,3/4)
Q   (1/2,a+1/4,-a+3/4)
V   (1/2,a,a+1/2)
C   (a,a,b)
A   (a,-a+b,b)
GP  (a,b,c)
*
```

We can select a particular $\vec{k}$ point and display its star:

```
*LABEL VECTOR CONVENTIONAL
*VALUE KPOINT X
*SHOW STAR
*DISPLAY KPOINT
   k vector Star of k
X  (0,1,0)  (0,1,0), (1,0,0), (0,0,1)
*
```

Irreducible representations (irreps) are associated with $\vec{k}$ vectors. For example, the irreps at the Γ point are

```
*CANCEL SHOW ALL
*VALUE KPOINT GM
*SHOW IRREP
*DISPLAY IRREP
Irrep (ML)
GM1+
GM2+
GM3+
GM4+
GM5+
GM1-
GM2-
GM3-
GM4-
GM5-
*
```

These irrep symbols following the convention of Miller and Love and denote the irreps Γ_1^+, Γ_2^+, etc. We can display the corresponding symbols for other settings:

```
*SHOW IRREP KOVALEV
*D IRREP
Irrep (ML) Irrep (Kov)
GM1+       k11t1
GM2+       k11t3
```

```
GM3+       k11t5
GM4+       k11t9
GM5+       k11t7
GM1-       k11t2
GM2-       k11t4
GM3-       k11t6
GM4-       k11t10
GM5-       k11t8
*
```

where the symbols denote irreps of Kovalev ($k_{11}\hat{\tau}^1$, $k_{11}\hat{\tau}^3$, etc.) For irreps at $\vec{k} = 0$ (Γ point), the symbols for point-group irreps are often used. We can also display these:

```
*CANCEL SHOW IRREP KOVALEV
*SHOW IRREP POINTGROUP
*DISPLAY IRREP
Irrep (ML)
GM1+       A1g
GM2+       A2g
GM3+       Eg
GM4+       T1g
GM5+       T2g
GM1-       A1u
GM2-       A2u
GM3-       Eu
GM4-       T1u
GM5-       T2u
*
```

where the symbols denote A_{1g}, A_{2g}, etc. Irreps map elements of the space group onto matrices. The character is the trace of the matrix. We can display the character and/or matrix for any element of the space group.

```
*CANCEL SHOW IRREP POINTGROUP
*VALUE IRREP GM4-
*SHOW CHARACTER
*SHOW MATRIX
*VALUE ELEMENT C2X 0 0 0
*DISPLAY IRREP
Irrep (ML) Element     Char   Matrix
GM4-       (C2x|0,0,0) -1.000   1  0  0
                                0 -1  0
                                0  0 -1

*
```

Here is an example for an irrep with a large dimension:

```
*VALUE IRREP W5
*VALUE ELEMENT SGX 1/2 1/2 0
*DISPLAY IRREP
Irrep (ML) Element         Char  Matrix
W5         (SGx|1/2,1/2,0) 0.000  -1  0  0  0  0  0  0  0  0  0  0  0
                                   0  1  0  0  0  0  0  0  0  0  0  0
                                   0  0  0  1  0  0  0  0  0  0  0  0
                                   0  0 -1  0  0  0  0  0  0  0  0  0
                                   0  0  0  0  0  0  0  0  0  0  0  1
                                   0  0  0  0  0  0  0  0  0  0  1  0
                                   0  0  0  0  0  0  1  0  0  0  0  0
                                   0  0  0  0  0  0  0 -1  0  0  0  0
                                   0  0  0  0  0  0  0  0  0 -1  0  0
                                   0  0  0  0  0  0  0  0  1  0  0  0
                                   0  0  0  0  0  1  0  0  0  0  0  0
                                   0  0  0  0  1  0  0  0  0  0  0  0
*
```

The set of matrices onto which the irrep maps elements of the space group is called the image of the irrep. Among the irreps for $\vec{k}$ points of symmetry, there are only 132 distinct images. These have been identified and labeled by Stokes and Hatch. For example, the image onto which the irrep W_5 maps space group elements is

```
*CANCEL SHOW ALL
*SHOW IRREP
*SHOW IMAGE
*DISPLAY IRREP
Irrep (ML) Image
W5         G1536a
*
```

The letter at the beginning of the symbol indicates the dimension of the image (G for 12-dimensional image). The numbers represent the number of distinct matrices in the image (in this case, 1536 matrices), and the trailing letter distinguishes the different 12-dimensional images with 1536 matrices. Among the 132 images, there are actually four of these, $G1536a$, $G1536b$, $G1536c$, and $G1536d$. We can display all of the matrices in an image. Let us display one with four two-dimensional matrices:

```
*VALUE IMAGE B4A
*CANCEL SHOW IRREP
*SHOW ELEMENTS
*DISPLAY IMAGE
```

```
Image Elements
B4a     1  0
        0  1

       -1  0
        0 -1

        0 -1
        1  0

        0  1
       -1  0
*
```

We can also show the generating matrices of an image:

```
*CANCEL SHOW ELEMENTS
*SHOW GENERATORS
*DISPLAY IMAGE
Image Generators
B4a     0  1
       -1  0
*
```

For irreps at non $\vec{k}$ points of symmetry, one or more of the parameters, α, β, γ (denoted by `a,b,c` in the program), must be selected. For example, the irrep Δ_1 is on a $\vec{k}$ line of symmetry and requires a value for α. We select the value $\alpha = \frac{1}{4}$ using `VALUE KVALUE 1,1/4`. The `1` in front of the `1/4` tells ISOTROPY that the value for one parameter will follow.

```
*CANCEL SHOW ALL
*CANCEL VALUE IMAGE
*VALUE IRREP DT1
*VALUE KVALUE 1,1/4
*SHOW MATRIX
*VALUE ELEMENT C4Z+ 0 0 0
*DISPLAY IRREP
Element      Matrix
(C4z+|0,0,0)   0  0  1  0  0  0
               0  0  0  1  0  0
               1  0  0  0  0  0
               0 -1  0  0  0  0
               0  0  0  0  1  0
               0  0  0  0  0  1
*
```

Compatibility relations can also be shown. For example,

```
*CANCEL SHOW ALL
*VALUE KPOINT GM
*VALUE COMPATIBILITY DT
*SHOW COMPATIBILITY
*DISPLAY IRREP
Compat (ML)
GM1+: DT1
GM2+: DT2
GM3+: DT1 DT2
GM4+: DT4 DT5
GM5+: DT3 DT5
GM1-: DT4
GM2-: DT3
GM3-: DT3 DT4
GM4-: DT1 DT5
GM5-: DT2 DT5
*
```

These relations show what happens as the $\vec{k}$ vector moves along the Δ line to the Γ point: each Δ irrep becomes a Γ representation which can be decomposed into one or more Γ irreps. For example, the six-dimensional Δ_1 irrep at the Γ point can be decomposed into the one-dimensional Γ_1^+ irrep, the two-dimensional Γ_3^+ irrep, and the three-dimensional Γ_4- irrep. These same relations show what happens to the irreps of the "little group of $\vec{k}$" as the $\vec{k}$ vector moves from the Γ point along the Δ line: each Γ irrep of the little group becomes a Δ representation of the little group which can be decomposed into one or more Δ irreps of the little group. For example, the three-dimensional Γ_4^- irrep of the little group splits into the one-dimensional Δ_3 irrep of the little group and the two-dimensional Δ_5 irrep of the little group. These compatibility relations are useful when labeling phonon dispersion curves and electron band structures.

Irreps are classified as type 1, type 2, and type 3. A type-1 irrep can be brought to real form by a similarity transformation. A type-2 irrep cannot be brought to real form, but it can be brought to its complex conjugate by a similarity transformation. A type-2 irrep is equivalent to its own complex conjugate. Its characters are real. A type-3 irrep cannot be brought to real form and cannot be brought to its complex conjugate. Some of its characters are complex. In phase transformation theory, we use real matrices. For type-2 and -3 irreps, we form real matrices by forming the direct sum of the matrix with its complex conjugate and then bringing the resulting matrix to real form by a similarity transformation. This resulting reducible representation is said to be *physically* irreducible, i.e., irreducible with respect to real numbers. For example, there are three irreps at the H point for space group #184: H_1, H_2 are type 3, and H_3 is type 2. H_2 is the complex conjugate of H_1, and H_3 is equivalent to its own complex conjugate.

```
*VALUE PARENT 184
*VALUE KPOINT H
```

```
*CANCEL SHOW ALL
*SHOW IRREP
*SHOW TYPE
*DISPLAY IRREP
Irrep (ML) Type
H1H2       3
H3H3       2
*
```

The program lists the physically irreducible representations, $H_1 \oplus H_2$ and $H_3 \oplus H_3$. The program displays the matrices of these representations in real form:

```
*CANCEL VALUE KVALUE
*VALUE IRREP H1H2
*VALUE ELEMENT SGV1 0 0 1/2
*SHOW MATRIX
*DISPLAY IRREP
Irrep (ML) Type Element        Matrix
H1H2       3    (SGv1|0,0,1/2)   0.000  0.000  0.500  0.866
                                 0.000  0.000  0.866 -0.500
                                -0.500 -0.866  0.000  0.000
                                -0.866  0.500  0.000  0.000
*
```

This is the end of this tutorial. You may exit the program.

```
*QUIT
```

If you have been running ISOTROPY, quit the program and start it again.

A great majority of solid-solid phase transitions can be described by the Landau theory of phase transitions. In this theory, the free energy of a crystal is expanded in powers of the order parameter, an n-dimensional vector in representation space. A phase transition takes place when the minimum of the free energy occurs at a nonzero value of the order parameter. Symmetry is lost in the transition, and the space-group symmetry is now a subgroup of the parent group and consists of all space-group elements which leave the order parameter invariant. This is called an isotropy subgroup.
As an example, let us consider the isotropy subgroups for the Γ_4^- irrep of space group #221 $Pm\bar{3}m$ (O_h^1).

```
*VALUE PARENT 221
*VALUE IRREP GM4-
*SHOW SUBGROUP
*SHOW BASIS
*SHOW ORIGIN
*DISPLAY ISOTROPY
Subgroup Basis Vectors              Origin
99 P4mm  (0,1,0),(0,0,1),(1,0,0)    (0,0,0)
38 Amm2  (0,0,1),(1,-1,0),(1,1,0)   (0,0,0)
160 R3m  (1,-1,0),(0,1,-1),(1,1,1)  (0,0,0)
6 Pm     (0,1,0),(0,0,1),(1,0,0)    (0,0,0)
8 Cm     (1,1,0),(-1,1,0),(0,0,1)   (0,0,0)
1 P1     (1,0,0),(0,1,0),(0,0,1)    (0,0,0)
*
```

The coordinates of the origin as well as each basis vector of the lattice are given in terms of the basis vectors of the lattice of the parent space group. For example, the basis vectors $\vec{a}_i'$ of the lattice of the isotropy subgroup $R3m$ are given by

$$\vec{a}_1' = \vec{a}_1 - \vec{a}_2\,,$$
$$\vec{a}_2' = \vec{a}_2 - \vec{a}_3\,,$$
$$\vec{a}_3' = \vec{a}_1 + \vec{a}_2 + \vec{a}_3\,,$$

where $\vec{a}_i$ are basis vectors of the lattice of the parent space group $Pm\bar{3}m$. The irrep Γ_4^- is three dimensional so that in this case the order parameter is a three-dimensional vector. We can display the direction of the order parameter for each isotropy subgroup:

```
*CANCEL SHOW BASIS
*CANCEL SHOW ORIGIN
*SHOW DIRECTION VECTOR
*DISPLAY ISOTROPY
```

```
 Subgroup Dir
99 P4mm  P1  (a,0,0)
38 Amm2  P2  (a,a,0)
160 R3m  P3  (a,a,a)
6 Pm     C1  (a,b,0)
8 Cm     C2  (a,a,b)
1 P1     S1  (a,b,c)
*
```

The symbols, `P3,P1,P3,C2,C1,S1`, for the directions of the order parameters were chosen by Stokes and Hatch. The symbols, `a,b,c`, in the components of the order parameters represent arbitrary real numbers. Let us consider the isotropy subgroup $P4mm$. We can select this subgroup with either the `VALUE SUBGROUP 99` or the `VALUE DIRECTION P1` command. Let us display the elements of the subgroup:

```
*VALUE DIRECTION P1
*SHOW ELEMENTS
*DISPLAY ISOTROPY
Subgroup Dir         Elements
99 P4mm  P1  (a,0,0) (E|0,0,0), (C2x|0,0,0), (C4x+|0,0,0), (C4x-|0,0,0),
                     (SGy|0,0,0), (SGz|0,0,0), (SGdf|0,0,0), (SGdd|0,0,0)
*
```

These are elements of the parent space group $Pm\bar{3}m$ which belong to the isotropy subgroup $P4mm$. We see that the four-fold rotation axis points in the cubic x direction, the same direction as the third basis vector of the lattice of $P4mm$ (see above, where we displayed the basis vectors). In the setting of $P4mm$, these both become the z direction.

The irrep Γ_4^- maps each element of the space group onto a three-dimensional matrix. An element operates on an order parameter via multiplication by these matrices. The elements in the subgroup $P4mm$ are mapped onto matrices which leave the order parameter $(a,0,0)$ invariant. For example, the matrix for $\{C_{4x}^+|0,0,0\}$ is

```
*SHOW MATRIX
*VALUE ELEMENT C4X+ 0 0 0
*DISPLAY IRREP
Element      Matrix
(C4x+|0,0,0)   1  0  0
               0  0 -1
               0  1  0
*
```

Thus, when $\{C_{4x}^+|0,0,0\}$ operates on $(a,0,0)$, we obtain

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} ,$$

and, as we can see, the order parameter is left invariant by this operation. We can also show the generating elements of the subgroup:

```
*CANCEL SHOW MATRIX
*CANCEL SHOW ELEMENT
*SHOW GENERATOR
*DISPLAY ISOTROPY
Subgroup Dir         Generators
99 P4mm  P1  (a,0,0) (C4x+|0,0,0), (SGy|0,0,0)
*
```

It is sometimes useful to obtain a mapping of points in the parent group to points in the subgroup:

```
*CANCEL SHOW GENERATOR
*SHOW XYZ
*DISPLAY ISOTROPY
Subgroup Dir         New xyz
99 P4mm  P1  (a,0,0) (y,z,x)
*
```

This means that a point (x, y, z) in $Pm\bar{3}m$ becomes (y, z, x) in $P4mm$. For example, an atom at $(0.681, \frac{1}{2}, 0)$ in $Pm\bar{3}m$ is at $(\frac{1}{2}, 0, 0.681)$ in $P4mm$. Perhaps an even more useful function of ISOTROPY is to identify the Wyckoff positions in the subgroup. For example, in $Pm\bar{3}m$, an atom at $(0.681, \frac{1}{2}, 0)$ is at Wyckoff position h $(x, \frac{1}{2}, 0)$ with $x = 0.681$.

```
*CANCEL SHOW XYZ
*SHOW WYCKOFF SUBGROUP
*VALUE WYCKOFF H
*SHOW WYCKOFF VECTOR ALL
*DISPLAY PARENT
Wyckoff Points Coordinates
h              (x,1/2,0), (-x,1/2,0), (1/2,0,x), (1/2,0,-x), (0,x,1/2),
               (0,-x,-1/2), (-1/2,-x,0), (-1/2,x,0), (-x,0,-1/2), (x,0,1/2),
               (0,-1/2,-x), (0,1/2,x)
*DISPLAY ISOTROPY
Subgroup Dir         Wyckoff New Wyckoff
99 P4mm  P1  (a,0,0) h       c, z'=x
                             c, z'=-x
                             e, x'=-x, z'=1/2
                             f, x'=x, z'=0
*VALUE PARENT 99
*VALUE WYCKOFF C
*DISPLAY PARENT
Wyckoff Points Coordinates
c              (1/2,0,z), (0,1/2,z)
*VALUE WYCKOFF E
```

```
*DISPLAY PARENT
Wyckoff Points Coordinates
e              (x,0,z), (-x,0,z), (0,x,z), (0,-x,z)
*VALUE WYCKOFF F
*DISPLAY PARENT
Wyckoff Points Coordinates
f              (x,1/2,z), (-x,-1/2,z), (-1/2,x,z), (1/2,-x,z)
*VALUE PARENT 221
*
```

We see that the 12 atoms at Wyckoff position h in $Pm\bar{3}m$ become, in $P4mm$, 2 atoms at Wyckoff position c, 2 more atoms at a different Wyckoff position c, 4 atoms at Wyckoff position e, and 4 atoms at Wyckoff position f. The symbols x', z' above denote variables in the Wyckoff positions in $P4mm$. For example, the Wyckoff position c in $P4mm$ is $(\frac{1}{2}, 0, z')$. Since $x = 0.681$ in our example, the atom is at $(\frac{1}{2}, 0, 0.681)$ in $P4mm$, the same atom we mapped above using (y, z, x).

Now let us show some additional information about each subgroup. For this purpose, we look at the isotropy subgroups for the irrep X_1^+.

```
*CANCEL SHOW WYCKOFF SUBGROUP
*VALUE IRREP X1+
*SHOW SIZE
*SHOW INDEX
*SHOW MAXIMAL
*CANCEL VALUE DIRECTION
*DISPLAY ISOTROPY
Subgroup   Max Index Size Dir
123 P4/mmm yes 6     2    P1  (a,0,0)
123 P4/mmm yes 12    4    P2  (a,a,0)
221 Pm-3m  yes 8     8    P3  (a,a,a)
47 Pmmm    no  24    4    C1  (a,b,0)
123 P4/mmm no  24    8    C2  (a,a,b)
47 Pmmm    no  48    8    S1  (a,b,c)
*
```

In the column labeled "Max" we find out whether or not the subgroup is maximal with respect to the other isotropy subgroups for this irrep. (A maximal isotropy subgroup is not a subgroup of any of the other isotropy subgroups.)

In the column labeled "Size" is given the size of the primitive unit cell of the subgroup relative to the size of the primitive unit cell of the parent group. For example, consider the subgroup $P4/mmm$ in direction P1. Its lattice vectors are given by:

```
*VALUE DIRECTION P1
*SHOW BASIS
*DISPLAY ISOTROPY
```

```
Subgroup   Max Index Size Dir         Basis Vectors
123 P4/mmm yes 6     2    P1  (a,0,0) (0,0,1),(1,0,0),(0,2,0)
*
```

i.e., $\vec{a}'_1 = \vec{a}_3$, $\vec{a}'_2 = \vec{a}_1$, and $\vec{a}'_3 = 2\vec{a}_2$. The size of the unit cell of $Pm\bar{3}m$ is a^3, where a is the lattice parameter. The size of the unit cell of $P4/mmm$ is $2a^3$, twice as large.

In the column labeled "Index" is given the index of the subgroup with respect to the parent group. For example, the index of subgroup $P4/mmm$ in direction P1 is 6. The point group of $Pm\bar{3}m$ is $m\bar{3}m$, which contains 48 elements. The point group of $P4/mmm$ is $4/mmm$, which contains 16 elements. There are 3 times as many elements in $m\bar{3}m$ as there are in $4/mmm$. Also, as shown above, the size of the unit cell in $P4/mmm$ is 2 times as large as the unit cell in $Pm\bar{3}m$. Thus the index is $3 \times 2 = 6$.

Since the size of the unit cell in $P4/mmm$ is twice as large as the unit cell in $Pm\bar{3}m$, half of the lattice points in $Pm\bar{3}m$ are no longer lattice points in $P4/mmm$. We can obtain a list of these points:

```
*CANCEL SHOW BASIS
*CANCEL SHOW MAXIMAL
*CANCEL SHOW INDEX
*SHOW NEWFRACTIONAL
*SHOW XYZ
*DISPLAY ISOTROPY
Subgroup   Size Dir         New xyz    New Fractionals
123 P4/mmm 2    P1  (a,0,0) (z,x,1/2y) (0,0,0), (0,1,0)
*
```

In the column labeled "New Fractionals" are given points in the unit cell of $P4/mmm$ which were lattice points in $Pm\bar{3}m$. The coordinates of these points are given in terms of the basis vectors of the lattice of $Pm\bar{3}m$. For example, the lattice point $(0, 1, 0)$ in $Pm\bar{3}m$ becomes a non-lattice point $(0, 0, \frac{1}{2})$ in $P4/mmm$.

We can obtain information about the nature of the possible phase transitions.

```
*CANCEL SHOW SIZE
*CANCEL SHOW XYZ
*CANCEL SHOW NEWFRACTIONAL
*CANCEL VALUE DIRECTION
*SHOW LANDAU
*SHOW LIFSHITZ
*SHOW ACTIVE
*SHOW CONTINUOUS
*DISPLAY ISOTROPY
Subgroup   Cont Active Lan Lif Dir
123 P4/mmm RG   yes    0   0   P1  (a,0,0)
123 P4/mmm no   yes    0   0   P2  (a,a,0)
```

```
221 Pm-3m  RG    yes   0   0   P3  (a,a,a)
47 Pmmm    no    yes   0   0   C1  (a,b,0)
123 P4/mmm no    yes   0   0   C2  (a,a,b)
47 Pmmm    no    yes   0   0   S1  (a,b,c)
*
```

In the column labeled "Lan" is shown the number of independent third-degree invariant polynomials in the free energy expansion for this irrep. If this number is not zero, the phase transition cannot be continuous. This is called the Landau condition.

In the column labeled "Lif" is shown the number of times that the vector representation is contained in the antisymmetrized cube of the irrep. If this number is not zero, the phase transition cannot be continuous. This is called the Lifshitz condition.

If both the Landau and Lifshitz conditions are met, the irrep is said to be active, as shown in the column labeled "active".

Finally, in Landau theory, a phase transition can be continuous only if it is possible for the minimum of the free energy expanded to fourth degree to occur at the direction of the order parameter. This is indicated by yes or no in the column labeled "Cont". RG indicates that the transition is allowed to be continuous in renormalization-group theory, as well as in Landau theory. In the case above, when we minimize the free energy expanded to fourth degree, we find that, depending on the value of the coefficients in the expansion, the minimum can occur only at $(a, 0, 0)$ or (a, a, a). Thus, a phase transition from $Pm\bar{3}m$ to $P4/mmm$ in direction P1 or to $Pm\bar{3}m$ in direction P3 may be continuous, but a phase transition to any of the other isotropy subgroups cannot be continuous.

Searches for isotropy subgroups with particular properties are facilitated by various `VALUE` commands: `VALUE CONTINUOUS`, `VALUE PARENT`, `VALUE SUBGROUP`, `VALUE LATTICE`, `VALUE LATTICE PARENT`, `VALUE POINTGROUP`, `VALUE IRREP`, `VALUE KPOINT`, `VALUE IMAGE`, `VALUE DIMENSION`, `VALUE ACTIVE`, `VALUE CONTINUOUS`, `VALUE LANDAU`, `VALUE LIFSHITZ`, `VALUE DIRECTION`, `VALUE SIZE`, `VALUE MAXIMAL`. You can read more about them in the user's manual.

In a phase transition where symmetry is lost, the crystal often becomes divided into domains, each with the same space-group symmetry of the subgroup but oriented in different directions. As an example, we generate the domains for the isotropy subgroup in direction P1 for irrep Γ_4^- of space group $Pm\bar{3}m$.

```
*CANCEL SHOW ALL
*CANCEL VALUE ALL
*VALUE PARENT 221
*VALUE IRREP GM4-
*VALUE DIRECTION P1
*SHOW SUBGROUP
*SHOW DIRECTION VECTOR
*SHOW GENERATOR
*SHOW DOMAIN
*SHOW DOMAIN GENERATOR
```

```
*SHOW DISTINCT
*DISPLAY ISOTROPY
Domain Distinct Gen          Subgroup Dir          Generators
1      1        (E|0,0,0)    99 P4mm  P1  (a,0,0)  (C4x+|0,0,0), (SGy|0,0,0)
2      1        (C2y|0,0,0)  99 P4mm      (-a,0,0) (C4x-|0,0,0), (SGy|0,0,0)
3      2        (C31-|0,0,0) 99 P4mm      (0,0,a)  (C4z+|0,0,0), (SGx|0,0,0)
4      2        (C32-|0,0,0) 99 P4mm      (0,0,-a) (C4z-|0,0,0), (SGx|0,0,0)
5      3        (C31+|0,0,0) 99 P4mm      (0,a,0)  (C4y+|0,0,0), (SGz|0,0,0)
6      3        (C34+|0,0,0) 99 P4mm      (0,-a,0) (C4y-|0,0,0), (SGz|0,0,0)
*
```

We see six domains, numbered 1 through 6, each with a domain generator (in the column labeled "Gen"). Let g_i, $\vec{\eta}_i$, and G_i denote the generator, order parameter, and isotropy subgroup, respectively, of the ith domain. We then have $\vec{\eta}_i = g_i\vec{\eta}_1$ and $G_i = g_i G_i g_i^{-1}$. For example, $\{C_{31}^-|0,0,0\}$ generates the third domain by operating on the first domain. Since $\{C_{4x}^+|0,0,0\}$ is one of the elements of the isotropy subgroup in the first domain, $\{C_{4z}^+|0,0,0\} = \{C_{31}^-|0,0,0\}\{C_{4x}^+|0,0,0\}\{C_{31}^-|0,0,0\}^{-1}$ is an element of the isotropy subgroup in the third domain. The irrep Γ_4^- maps $\{C_{31}^-|0,0,0\}$ onto the matrix:

```
*VALUE ELEMENT C31- 0 0 0
*SHOW MATRIX
*DISPLAY IRREP
Generators                                Element      Matrix
(C31+|0,0,0), (C4x+|0,0,0), (I|0,0,0) (C31-|0,0,0)   0  1  0
                                                     0  0  1
                                                     1  0  0
*
```

so that,

$$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ a \end{pmatrix}$$

is the direction of the order parameter in the third domain. We can see that some of the domains are not distinct. For example, the isotropy subgroups in domains 1 and 2 have the same elements. In the column labeled "Distinct" is shown a numbering of distinct isotropy subgroups. Since both domains 1 and 2 are numbered 1 in the "Distinct" column, their isotropy subgroups contain the same elements.

See the tutorial on domains to learn more about additional features in ISOTROPY that deal with domains.

There are primary and secondary order parameters associated with any phase transition. The distortions due to the primary order parameter completely determine the space-group symmetry of the subgroup. The distortions due to the secondary order parameters are consistent with that space-group symmetry but usually exhibit higher symmetry. For example, we list the secondary order parameters associated with the isotropy subgroup in direction P2 for the irrep X_1^+ of space group $Pm\bar{3}m$.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 221
*VALUE IRREP X1+
*VALUE DIRECTION C1
*SHOW SUBGROUP
*SHOW DIRECTION VECTOR
*SHOW FREQUENCY DIRECTION
*DISPLAY ISOTROPY
Subgroup Dir         Frequency
47 Pmmm  C1  (a,b,0) 1 GM1+ P1(1), 1 GM2+ P1(1), 2 GM3+ C1(1), 2 X1+ C1(1), 2
                     X2+ C1(1), 1 M1+ P1(3), 1 M2+ P1(3)
*
```

Technically speaking, we see here all of the irreps which subduce $Pmmm$. The number in front of the irrep symbol is the subduction frequency. Following the irrep symbol is direction of the order parameter for the isotropy subgroup (and domain) which is a supergroup of $Pmmm$. As an example, consider the third domain of the isotropy subgroup with direction P1 for irrep M_1^+.

```
*CANCEL SHOW FREQUENCY
*SHOW BASIS
*SHOW GENERATOR
*DISPLAY ISOTROPY
Subgroup Dir         Basis Vectors           Generators
47 Pmmm  C1  (a,b,0) (1,0,0),(0,2,0),(0,0,2) (C2z|0,0,0), (C2x|0,0,0), (I|0,0,0)
*VALUE IRREP M1+
*VALUE DIRECTION P1
*VALUE DOMAIN 3
*DISPLAY ISOTROPY
Domain Subgroup   Dir         Basis Vectors            Generators
3      123 P4/mmm P1  (0,a,0) (0,1,1),(0,-1,1),(1,0,0) (C4x+|0,0,0),
                                                       (C2d|0,0,0), (I|0,0,0)
*
```

We can see that $P4/mmm$ is a supergroup of $Pmmm$. Every element of $Pmmm$ is also an element of $P4/mmm$, including the translations. A distortion with $P4/mmm$ symmetry may be present without changing the symmetry $Pmmm$ of the crystal. The order parameter $(a, b, 0)$ for irrep X_1^+ is the primary order parameter. It determines the symmetry $Pmmm$ of the crystal. The order parameter $(0, a, 0)$ for irrep M_1^+ is a secondary order parameter. It is allowed to be present in a crystal with $Pmmm$ symmetry. The same is true of all of the other secondary order parameters listed in the column labeled "Frequency". Note that the primary order parameter, `X1+ C1(1)`, is also listed for completeness. Any space group is its own supergroup.

The data base which ISOTROPY uses contains isotropy subgroups only for irreps at $\vec{k}$ points of symmetry. Isotropy subgroups for other irreps must be calculated as needed. As an example, consider an irrep along the Δ line in the first Brillouin zone.

```
*CANCEL SHOW ALL
*CANCEL VALUE ALL
*VALUE PARENT 221
*SHOW KPOINT
*DISPLAY KPOINT
    k vector
GM  (0,0,0)
DT  (0,a,0)
LD  (a,a,a)
SM  (a,a,0)
R   (1/2,1/2,1/2)
X   (0,1/2,0)
M   (1/2,1/2,0)
S   (a,1/2,a)
T   (1/2,1/2,a)
Z   (a,1/2,0)
C   (a,a,b)
A   (a,b,0)
B   (a,1/2,b)
GP  (a,b,c)
*
```

We see that points on the Δ line (abbreviated `DT`) are given by $(2\pi/a)(0, \alpha, 0)$. Let $\alpha = \frac{1}{4}$, a point half-way to the X point.

```
*VALUE KPOINT DT
*SHOW IRREP
*DISPLAY IRREP
Irrep (ML) k vector
DT1        (0,a,0)
DT2        (0,a,0)
DT3        (0,a,0)
DT4        (0,a,0)
DT5        (0,a,0)
*
```

There are five irreps. Let's choose Δ_1 (`DT1`) and display the isotropy subgroups.

```
*VALUE IRREP DT1
*VALUE KVALUE 1,1/4
*CANCEL SHOW KPOINT
*CANCEL SHOW IRREP
*SHOW SUBGROUP
```

```
*SHOW DIRECTION VECTOR
*DISPLAY ISOTROPY
 You have requested information about isotropy subgroups for:
      irrep: DT1      space group: Oh-1
 The data base for these isotropy subgroups cannot be found.
 Should the data base be added?
 Enter RETURN to continue.  Enter any character to stop

 Adding data base...
Subgroup   Dir
123 P4/mmm P1  (a,0,0,0,0,0)
123 P4/mmm P2  (a,-a,0,0,0,0)
123 P4/mmm P3  (a,0,a,0,0,0)
123 P4/mmm P4  (a,-a,a,-a,0,0)
221 Pm-3m  P5  (a,0,a,0,a,0)
221 Pm-3m  P6  (a,-a,a,-a,a,-a)
99 P4mm    C1  (a,b,0,0,0,0)
47 Pmmm    C2  (a,0,b,0,0,0)
47 Pmmm    C3  (a,-a,b,0,0,0)
47 Pmmm    C4  (a,-a,b,-b,0,0)
38 Amm2    C5  (a,b,a,-b,0,0)
123 P4/mmm C6  (a,0,a,0,b,0)
123 P4/mmm C7  (a,0,a,0,b,-b)
123 P4/mmm C8  (a,-a,a,-a,b,0)
123 P4/mmm C9  (a,-a,a,-a,b,-b)
160 R3m    C10 (a,b,a,b,a,b)
25 Pmm2    S1  (a,b,c,0,0,0)
25 Pmm2    S2  (a,b,c,-c,0,0)
47 Pmmm    S3  (a,0,b,0,c,0)
47 Pmmm    S4  (a,0,b,0,c,-c)
47 Pmmm    S5  (a,-a,b,0,c,-c)
47 Pmmm    S6  (a,-a,b,-b,c,-c)
 Enter RETURN to continue.  Enter any character to stop.X
Quit display
*
```

ISOTROPY assumes that the height of the screen is 22 lines. So, after displaying 22 lines, it pauses and waits for the user to indicate whether or not to display the next screen of data. We terminated the display by entering an X instead of a return. The number of lines to be displayed at a time can be changed with the `PAGE` command. Also, this feature can be turned off with the `PAGE NOBREAK` command.

Some of the features available for isotropy subgroups for irreps at $\vec{k}$ points of symmetry are not presently implemented for those at non $\vec{k}$ points of symmetry. Also note that the labeling of order parameter directions are arbitrary here. For example, the meaning of P1 here is different than its meaning for the six-dimensional images already in the data base.

The labels for the directions are merely given for convenience so that we can refer to a particular isotropy subgroup using it.

```
*VALUE DIRECTION P6
*DISPLAY ISOTROPY
Subgroup  Dir
221 Pm-3m P6  (a,-a,a,-a,a,-a)
*
```

Sometimes, the list of isotropy subgroups for a particular irrep may be very long and may require an unreasonable amount of time for ISOTROPY to calculate them. A shorter list can be generated by using only one arm of the star. You can do that by using `VALUE DIRECTION ONEARM`. Sometimes only the kernel is needed. (The kernel is the isotropy subgroup for a general direction of the order parameter.) This can be generated using `VALUE DIRECTION KERNEL`.

ISOTROPY also generates isotropy subgroups for coupled order parameters. For example, consider the coupling of order parameters for the M_3^+ and R_4^+ irreps of space group $Pm\bar{3}m$.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 221
*VALUE IRREP M3+ R4+
*SHOW SUBGROUP
*SHOW DIRECTION VECTOR
*SHOW IRREP
*DISPLAY ISOTROPY COUPLED
Data base for these coupled subgroups does not exist
Should the data base be added?
 Enter RETURN to continue.  Enter any character to stop.
Adding coupled isotropy subgroups...
Irrep (ML) Subgroup     Dir
M3+R4+     148 R-3      P3(1)P3(1) (a,a,a,b,b,b)
M3+R4+     127 P4/mbm   P1(1)P1(1) (a,0,0,b,0,0)
M3+R4+     63 Cmcm      P1(1)P1(2) (a,0,0,0,0,b)
M3+R4+     137 P4_2/nmc P2(1)P1(2) (a,a,0,0,0,b)
M3+R4+     59 Pmmn      S1(1)P1(1) (a,b,c,d,0,0)
M3+R4+     62 Pnma      P1(1)P2(5) (a,0,0,0,b,b)
M3+R4+     63 Cmcm      P2(1)P2(1) (a,a,0,b,b,0)
M3+R4+     14 P2_1/c    P1(1)C2(9) (a,0,0,c,b,b)
M3+R4+     15 C2/c      P2(1)C2(1) (a,a,0,b,b,c)
M3+R4+     12 C2/m      P1(1)C1(1) (a,0,0,b,c,0)
M3+R4+     11 P2_1/m    P1(1)C1(5) (a,0,0,0,b,c)
M3+R4+     11 P2_1/m    S1(1)C1(1) (a,b,c,d,e,0)
M3+R4+     2 P-1        P1(1)S1(1) (a,0,0,b,c,d)
M3+R4+     2 P-1        S1(1)S1(1) (a,b,c,d,e,f)
```

```
*
```

ISOTROPY generates a file containing information about these isotropy subgroups. In this case, the file was named `s4550_01.iso`. In the future, when we ask about these subgroups, ISOTROPY will find this file and will not need to generate the data again.

These isotropy subgroups actually belong to the six-dimensional reducible representation $M_3^+ \oplus R_4^+$, the direct sum of M_3^+ and R_4^+. The first three components of the order parameter belong to M_3^+ and the last three components belong to R_4^+. For example, the first subgroup in the list contains all of the elements that keep the direction (a, a, a) of the order parameter for M_3^+ invariant, and, at the same time, keep the direction (b, b, b) of the order parameter for R_4^+ invariant. It is actually the intersection of the isotropy subgroup in direction P3 for M_3^+ and the isotropy subgroup in direction P3 for R_4^+. That is the meaning of the symbol for the direction: P3(1)P3(1). The numbers in parentheses refer to domains. In this case, the two isotropy subgroups are those of the first domain. The third subgroup in the list, however, is an intersection of the first domain $(a, 0, 0)$ of the isotropy subgroup in direction P1 for M_3^+ and the second domain $(0, 0, b)$ of the isotropy subgroup in direction P1 for R_4^+. We can select one of these isotropy subgroups using the symbol for the direction of the order parameter exactly as it appears in the list.

```
*VALUE DIRECTION P1(1)P1(2)
*DISPLAY ISOTROPY COUPLED
Irrep (ML) Subgroup Dir
M3+R4+     63 Cmcm  P1(1)P1(2) (a,0,0,0,0,b)
*
```

What do you do if you know the structure of the subgroup but do not know which irrep drives the transition? ISOTROPY has a very useful feature for finding the primary and secondary order parameters if the group-subgroup relation is known.

As an example, consider a monoclinic subgroup of $Pm\bar{3}m$. Suppose that we know its space-group symmetry is $P2/m$, the basis vectors of its lattice is $(1, \bar{1}, 1)$, $(1, 1, 0)$, $(0, 0, 1)$, and its origin is at the same point as the origin of the parent group $Pm\bar{3}m$.

```
*VALUE SUBGROUP 10
*VALUE BASIS 1,-1,1 1,1,0 0,0,1
*VALUE ORIGIN 0,0,0
*SHOW KPOINT
*DISPLAY DIRECTION
Irrep (ML) k vector    Dir             Subgroup   Size
GM1+       (0,0,0)     (a)             221 Pm-3m  1
GM3+       (0,0,0)     (a,0)           123 P4/mmm 1
GM4+       (0,0,0)     (a,a,0)         12 C2/m    1
GM5+       (0,0,0)     (a,b,-b)        12 C2/m    1
M1+        (1/2,1/2,0) (a,0,0)         123 P4/mmm 2
M4+        (1/2,1/2,0) (a,0,0)         123 P4/mmm 2
M5+        (1/2,1/2,0) (a,a,0,0,-a,a) 53 Pmna    2
```

This is a complete list of order parameters that drive this phase transition,
along with the isotropy subgroup for each order parameter.
The primary order parameter completely determines the symmetry $P2/m$
of the subgroup. As we can see, none of the order parameters in the above list completely
determines the $P2/m$ symmetry of the subgroup. There is no single primary
order parameter in this case. There must be a coupled primary order parameter.

```
*CANCEL VALUE SUBGROUP
*CANCEL VALUE DIRECTION
*VALUE IRREP M1+ M5+
*SHOW IRREP
*DISPLAY ISOTROPY COUPLED
Data base for these coupled subgroups does not exist
Should the data base be added?
 Enter RETURN to continue.  Enter any character to stop.
Adding coupled isotropy subgroups...
Irrep (ML) Subgroup   Dir
M1+M5+     12 C2/m    P1(1)P2(1)  (a,0,0,b,b,0,0,0,0)
M1+M5+     74 Imma    P1(1)P2(3)  (a,0,0,0,0,b,b,0,0)
M1+M5+     10 P2/m    P1(1)P10(1) (a,0,0,b,b,0,0,b,-b)
M1+M5+     2 P-1      P1(1)C13(1) (a,0,0,b,b,0,0,c,-c)
M1+M5+     166 R-3m   P3(1)P6(1)  (a,a,a,b,0,b,0,b,0)
M1+M5+     69 Fmmm    P1(1)P1(3)  (a,0,0,0,0,b,0,0,0)
M1+M5+     140 I4/mcm P1(1)P9(2)  (a,0,0,b,-b,0,0,b,b)
M1+M5+     69 Fmmm    C2(1)P9(3)  (a,a,b,0,0,c,c,c,-c)
M1+M5+     87 I4/m    C2(1)P9(6)  (a,a,b,0,0,-c,-c,c,-c)
M1+M5+     148 R-3    P3(1)C23(1) (a,a,a,b,c,b,c,b,c)
M1+M5+     12 C2/m    P1(1)C1(3)  (a,0,0,0,0,b,c,0,0)
M1+M5+     72 Ibam    P1(1)C12(2) (a,0,0,c,-c,0,0,b,b)
M1+M5+     12 C2/m    S1(1)C12(1) (a,b,c,d,d,e,-e,0,0)
M1+M5+     12 C2/m    C2(1)S12(9) (a,a,b,e,0,c,d,c,-d)
M1+M5+     15 C2/c    P1(1)4D3(5) (a,0,0,d,e,b,b,c,c)
M1+M5+     2 P-1      S1(1)6D1(1) (a,b,c,d,e,f,g,h,i)
*CANCEL SHOW DIRECTION
*SHOW BASIS
*SHOW ORIGIN
*VALUE SUBGROUP 10
*DISPLAY ISOTROPY COUPLED
Irrep (ML) Subgroup Dir         Basis Vectors            Origin
M1+M5+     10 P2/m  P1(1)P10(1) (1,1,0),(-1,1,0),(0,0,1) (0,0,0)
*CANCEL SHOW BASIS
*CANCEL SHOW ORIGIN
*CANCEL VALUE SUBGROUP
*SHOW DIRECTION VECTOR
```

```
*VALUE IRREP M4+ M5+
*DISPLAY ISOTROPY COUPLED
Data base for these coupled subgroups does not exist
Should the data base be added?
 Enter RETURN to continue.  Enter any character to stop.
Adding coupled isotropy subgroups...
Irrep (ML) Subgroup   Dir
M4+M5+     12 C2/m    P1(1)P2(1)  (a,0,0,b,b,0,0,0,0)
M4+M5+     74 Imma    P1(1)P2(2)  (a,0,0,0,0,0,0,b,b)
M4+M5+     10 P2/m    P1(1)P10(1) (a,0,0,b,b,0,0,b,-b)
M4+M5+     2 P-1      P1(1)C13(1) (a,0,0,b,b,0,0,c,-c)
M4+M5+     166 R-3m   P3(1)P6(1)  (a,a,a,b,0,b,0,b,0)
M4+M5+     140 I4/mcm P1(1)P1(3)  (a,0,0,0,0,b,0,0,0)
M4+M5+     69 Fmmm    C2(1)P1(1)  (a,a,b,c,0,0,0,0,0)
M4+M5+     87 I4/m    C2(1)P1(4)  (a,a,b,0,c,0,0,0,0)
M4+M5+     69 Fmmm    P1(1)P9(2)  (a,0,0,b,-b,0,0,b,b)
M4+M5+     148 R-3    P3(1)C23(1) (a,a,a,b,c,b,c,b,c)
M4+M5+     72 Ibam    P1(1)C1(3)  (a,0,0,0,0,b,c,0,0)
M4+M5+     12 C2/m    S1(1)C1(1)  (a,b,c,d,e,0,0,0,0)
M4+M5+     12 C2/m    P1(1)C12(2) (a,0,0,c,-c,0,0,b,b)
M4+M5+     12 C2/m    C2(1)S12(9) (a,a,b,e,0,c,d,c,-d)
M4+M5+     15 C2/c    P1(1)4D3(3) (a,0,0,c,c,d,e,b,b)
M4+M5+     2 P-1      S1(1)6D1(1) (a,b,c,d,e,f,g,h,i)
*CANCEL SHOW DIRECTION
*SHOW BASIS
*SHOW ORIGIN
*VALUE SUBGROUP 10
*DISPLAY ISOTROPY COUPLED
Irrep (ML) Subgroup Basis Vectors            Origin
M4+M5+     10 P2/m  (1,1,0),(-1,1,0),(0,0,1) (0,0,0)
*
```

We see that M_5^+ may couple with either M_1^+ or M_4^+ to produce the $P2/m$ symmetry. This result would have been rather difficult to obtain without this very useful `DISPLAY DIRECTION` feature of ISOTROPY.

This is the end of this tutorial. You may exit the program.

```
*QUIT
```

If you have been running ISOTROPY, quit the program and start it again.

There are two different kinds of distortions in a crystal: macroscopic and microscopic. Macroscopic distortions are tensor quantities like strain which involve the crystal as a whole. Microscopic distortions involve individual atoms. They include atomic displacements and molecular rotations.

Macroscopic distortions are always associated with irreps at $\vec{k} = 0$ (Γ irreps). We will consider here the most common type of macroscopic distortion: strain, which is a symmetrized tensor of rank 2. We specify this kind of tensor with the command, `RANK [12]`. (See the description of the `VALUE RANK` command in the user's manual for more information.) For example, let us look at the possible macroscopic strains in a cubic crystal.

```
*VALUE PARENT 221
*VALUE KPOINT GM
*VALUE RANK [12]
*SHOW MACROSCOPIC
*SHOW IRREP
*DISPLAY DISTORTION
Irrep (ML) Basis Functions
GM1+       xx+yy+zz
GM3+       xx+yy-2zz,1.732xx-1.732yy
GM5+       xy,yz,xz
*
```

We see here that $\epsilon_{11} + \epsilon_{22} + \epsilon_{33}$ transforms like the basis function of the one-dimensional irrep Γ_1^+, that $\epsilon_{11} + \epsilon_{22} - 2\epsilon_{33}$ and $\sqrt{3}\epsilon_{11} - \sqrt{3}\epsilon_{22}$ transform like basis functions of the two-dimensional irrep Γ_3^+, and that ϵ_{12}, ϵ_{23}, ϵ_{13} transform like basis functions of the three-dimensional irrep Γ_5^+.

Suppose there is a phase transition which results in the isotropy subgroup in the direction P1 for irrep X_1^+.

```
*VALUE IRREP X1+
*VALUE DIRECTION P1
*SHOW FREQUENCY GAMMA
*SHOW FREQUENCY DIRECTION
*SHOW SUBGROUP
*DISPLAY ISOTROPY
Irrep (ML) Subgroup   Frequency
X1+        123 P4/mmm 1 GM1+ P1(1), 1 GM3+ P1(2)
*CANCEL SHOW FREQUENCY
*SHOW GENERATOR
*DISPLAY ISOTROPY
```

```
Irrep (ML) Subgroup   Generators
X1+        123 P4/mmm (C4y+|0,0,0), (C2z|0,0,0), (I|0,0,0)
*
```

We see that both P1 (domain 1) for irrep Γ_1^+ and P1 (domain 2) for irrep Γ_3^+ are secondary order parameters. Both of these irreps allow strains. The irrep Γ_1^+ allows a strain where $\epsilon_{11} = \epsilon_{22} = \epsilon_{33}$. This is simply a change in volume of the crystal. For the irrep Γ_3^+, we have

```
*VALUE IRREP GM3+
*VALUE DOMAIN 2
*DISPLAY DISTORTION
Irrep (ML) Domain Basis Functions
GM3+       2      xx-2yy+zz
*
```

which is a strain where $\epsilon_{11} = -2\epsilon_{22} = \epsilon_{33}$. This is a tetrahedral strain where the sides of the unit cell in the cubic x and z directions remain equal. This is consistent with the tetrahedral space group symmetry $P4/mmm$ with the four-fold axis in the cubic y direction. The direction of the order parameter P1 in the second domain is given by:

```
*CANCEL SHOW GENERATOR
*SHOW DIRECTION VECTOR
*DISPLAY ISOTROPY
Irrep (ML) Domain Subgroup   Dir
GM3+       2      123 P4/mmm P1  (-0.500a,0.866a)
*
```

The distortion is obtained by a dot product of the order parameter and the basis functions: $-\frac{1}{2}a(xx + yy - 2zz) + \frac{1}{2}\sqrt{3}a(\sqrt{3}xx - \sqrt{3}yy) = a(xx - 2yy + zz)$. This result was automatically calculated when we displayed the distortion because we had selected the direction and domain. Let's do one more example:

```
*VALUE IRREP M5-
*VALUE DIRECTION C15
*CANCEL VALUE DOMAIN
*CANCEL SHOW DOMAIN
*SHOW GENERATOR
*DISPLAY ISOTROPY
Irrep (ML) Subgroup Dir                Generators
M5-        12 C2/m  C15 (a,b,a,-b,0,0) (C2f|0,1,1), (I|0,1,1)
*CANCEL SHOW DIRECTION
*CANCEL SHOW GENERATOR
*SHOW FREQUENCY GAMMA
*SHOW FREQUENCY DIRECTION
*DISPLAY ISOTROPY
```

```
Irrep (ML) Subgroup Frequency
M5-        12 C2/m  1 GM1+ P1(1), 1 GM3+ P1(3), 1 GM4+ P2(11), 2 GM5+ C2(5)
*VALUE IRREP GM5+
*VALUE DIRECTION C2
*VALUE DOMAIN 5
*DISPLAY DISTORTION
Irrep (ML) Dir Domain Basis Functions
GM5+       C2  5      xy+xz,yz
*CANCEL SHOW FREQUENCY
*SHOW DIRECTION VECTOR
*SHOW GENERATOR
*DISPLAY ISOTROPY
Irrep (ML) Domain Subgroup Dir         Generators
GM5+       5      12 C2/m  C2  (a,b,a) (C2f|0,0,0), (I|0,0,0)
*
```

Note that in this case, the secondary order parameter for irrep Γ_5^+ is in the direction (a, b, a), so that the distortion is given by $axy + byz + axz = a(xy + xz) + byz$. Since a, b are arbitrary parameters in the order parameter, there are two independent distortions, $xy + xz$ and yz.

Now let us consider microscopic distortions. ISOTROPY can display information about distortions in a very general way. (Fortunately, for our convenience, ISOTROPY also implements three specific kinds of distortions which we also describe below.) A global distortion is induced from a local distortion about a particular Wyckoff position in the crystal. As an example, consider Wyckoff position c in cubic space group $Pm\bar{3}m$. The point group symmetry of that position is $4/mmm$.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 221
*VALUE WYCKOFF C
*SHOW WYCKOFF POINTGROUP
*LABEL POINTGROUP INTERNATIONAL
*DISPLAY PARENT
Wyckoff Points, Point Groups
c 4/mmm
*
```

The irreps of the point group $4/mmm$ are the same as the irreps of the space group $P4/mmm$ at the Γ point. We can make a list of them. By using the command, `SHOW IRREP POINTGROUP`, we can also obtain the labeling of these point-group irreps, which is different from their labeling in the space group.

```
*VALUE PARENT P4/MMM
*SHOW IRREP POINTGROUP
*VALUE KPOINT GM
```

```
*DISPLAY IRREP
Irrep (ML)
GM1+       A1g
GM2+       B1g
GM3+       A2g
GM4+       B2g
GM5+       Eg
GM1-       A1u
GM2-       B1u
GM3-       A2u
GM4-       B2u
GM5-       Eu
*
```

Suppose we are considering the space group irrep X_1^+. We want to obtain global distortions that belong to this irrep. We can induce such distortions from local distortions that belong to point group irreps of the Wyckoff c position.

```
*VALUE PARENT 221
*VALUE IRREP X1+
*SHOW FREQUENCY
*DISPLAY IRREP
Irrep (ML) Frequency
X1+        c 1 A1g, 1 Eu
*
```

We see here that at Wyckoff position c, only local distortions that belong to point group irreps, A_{1g} and E_u, will induce global distortions that belong to the space group irrep X_1^+. Let us consider a local distortion that belongs to E_u.

```
*VALUE WYCKOFF IRREP EU
*SHOW MICROSCOPIC
*DISPLAY DISTORTION
Irrep (ML) Wyckoff Point       Operation    Projected Basis Functions
X1+        c       (0,1/2,1/2) (E|0,0,0)    f1+f2, -f1+f2, 0
                   (0,1/2,3/2) (E|0,0,1)    f1+f2, f1-f2, 0
                   (0,3/2,1/2) (E|0,1,0)    -f1-f2, -f1+f2, 0
                   (0,3/2,3/2) (E|0,1,1)    -f1-f2, f1-f2, 0
                   (1,1/2,1/2) (E|1,0,0)    f1+f2, -f1+f2, 0
                   (1,1/2,3/2) (E|1,0,1)    f1+f2, f1-f2, 0
                   (1,3/2,1/2) (E|1,1,0)    -f1-f2, -f1+f2, 0
                   (1,3/2,3/2) (E|1,1,1)    -f1-f2, f1-f2, 0
                   (1/2,1/2,0) (C31-|0,0,0) -f1+f2, 0, f1+f2
                   (1/2,1/2,1) (C31-|0,0,1) -f1+f2, 0, f1+f2
                   (1/2,3/2,0) (C31-|0,1,0) f1-f2, 0, f1+f2
                   (1/2,3/2,1) (C31-|0,1,1) f1-f2, 0, f1+f2
                   (3/2,1/2,0) (C31-|1,0,0) -f1+f2, 0, -f1-f2
```

```
                    (3/2,1/2,1) (C31-|1,0,1) -f1+f2, 0, -f1-f2
                    (3/2,3/2,0) (C31-|1,1,0) f1-f2, 0, -f1-f2
                    (3/2,3/2,1) (C31-|1,1,1) f1-f2, 0, -f1-f2
                    (1/2,0,1/2) (C31+|0,0,0) 0, f1+f2, -f1+f2
                    (1/2,0,3/2) (C31+|0,0,1) 0, -f1-f2, -f1+f2
                    (1/2,1,1/2) (C31+|0,1,0) 0, f1+f2, -f1+f2
                    (1/2,1,3/2) (C31+|0,1,1) 0, -f1-f2, -f1+f2
                    (3/2,0,1/2) (C31+|1,0,0) 0, f1+f2, f1-f2
                    (3/2,0,3/2) (C31+|1,0,1) 0, -f1-f2, f1-f2
                    (3/2,1,1/2) (C31+|1,1,0) 0, f1+f2, f1-f2
                    (3/2,1,3/2) (C31+|1,1,1) 0, -f1-f2, f1-f2
*
```

In the column labeled "Point" are the positions of the atoms inside the unit cell of the kernel of X_1^+. f_1 and f_2 are local distortions at $(0, \frac{1}{2}, \frac{1}{2})$ which transform like the basis functions of the two-dimensional point group irrep E_u. The projected basis functions are the global distortions at each point that transform like the basis functions of the three-dimensional space-group irrep X_1^+. In the column labeled "Operation" are elements of the space group which take the first point $(0, \frac{1}{2}, \frac{1}{2})$ to the point on the corresponding row. For example, $\{C_{31}^+|0,1,0\}(0, \frac{1}{2}, \frac{1}{2}) = (\frac{1}{2}, 1, \frac{1}{2})$. Each local distortion in the projected basis functions must be operated on by the point operator in that element. For example, the projected basis functions at $(\frac{1}{2}, 1, \frac{1}{2})$ are actually $0, C_{31}^+(f_1 + f_2), C_{31}^+(-f_1 + f_2)$.

If we want the distortions specific to a particular isotropy subgroup, we simply take the dot product of the order parameter with the projected basis functions. ISOTROPY does this for us.

```
*VALUE DIRECTION P1
*DISPLAY DISTORTION
Irrep (ML) Wyckoff Point       Operation    Projected Basis Functions
X1+        c       (0,1/2,1/2) (E|0,0,0)    f1+f2
                   (0,3/2,1/2) (E|0,1,0)    -f1-f2
                   (1/2,1/2,0) (C31-|0,0,0) -f1+f2
                   (1/2,3/2,0) (C31-|0,1,0) f1-f2
                   (1/2,0,1/2) (C31+|0,0,0) 0
                   (1/2,1,1/2) (C31+|0,1,0) 0
*
```

Since the direction P1 is $(a, 0, 0)$, the global distortions are simply the first basis function for each point. Also, only points inside the unit cell for the isotropy subgroup in direction P1 are listed.

Now let us treat specific kinds of microscopic distortions. First of all, we consider the most common type: atomic displacements. These can occur in a phase transition. They also occur in vibrational modes. ISOTROPY can be very useful for putting the dynamical matrix into block-diagonal form.

As an example of atomic displacements, consider a phase transition in a perovskite crystal. The parent space group is the cubic $Pm\bar{3}m$, and the irrep is Γ_4^-. The atoms are at Wyckoff positions a, b, c. The direction of the order parameter is P2.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 221
*VALUE IRREP GM4-
*VALUE DIR P2
*VALUE WYCKOFF A B C
*SHOW DIRECTION VECTOR
*SHOW SUBGROUP
*SHOW BASIS
*DISPLAY ISOTROPY
Subgroup Dir         Basis Vectors
38 Amm2  P2  (a,a,0) (0,0,1),(1,-1,0),(1,1,0)
*SHOW WYCKOFF
*SHOW MICROSCOPIC VECTOR
*DISPLAY DISTORTION
Dir Wyckoff Point         Projected Vectors
P2  a       (0,0,0)       (1,1,0)
P2  b       (1/2,1/2,1/2) (1,1,0)
P2  c       (0,1/2,1/2)   (1,0,0)
            (1/2,1/2,0)   (0,0,0)
            (1/2,0,1/2)   (0,1,0)
P2  c       (0,1/2,1/2)   (0,2,0)
            (1/2,1/2,0)   (2,2,0)
            (1/2,0,1/2)   (2,0,0)
*
```

The isotropy subgroup is orthorhombic. Global distortions are induced by a local distortion at Wyckoff position a and at position b and by two different local distortions at position c. We do not need to specify the point group irreps. ISOTROPY tries all of them and finds the ones that induce global distortions that belong to Γ_4^-. We can also display the atomic positions and displacements in cartesian coordinates:

```
*VALUE LATTICE PARAMETER 3.88 3.88 3.88 90 90 90
*VALUE WYCKOFF XYZ 0 0 0
*SHOW CARTESIAN
*DISPLAY DISTORTION
Dir Wyckoff Point                       Projected Vectors
P2  a       (0.00000, 0.00000, 0.00000) (3.88000, 3.88000, 0.00000)
P2  b       (1.94000, 1.94000, 1.94000) (3.88000, 3.88000, 0.00000)
P2  c       (0.00000, 1.94000, 1.94000) (3.88000, 0.00000, 0.00000)
            (1.94000, 1.94000, 0.00000) (0.00000, 0.00000, 0.00000)
            (1.94000, 0.00000, 1.94000) (0.00000, 3.88000, 0.00000)
```

```
P2  c       (0.00000, 1.94000, 1.94000) (0.00000, 7.76000, 0.00000)
            (1.94000, 1.94000, 0.00000) (7.76000, 7.76000, 0.00000)
            (1.94000, 0.00000, 1.94000) (7.76000, 0.00000, 0.00000)
*
```

These are atomic displacements due to the primary order parameter. Let us look for atomic displacements due to secondary order parameters.

```
*CANCEL SHOW CARTESIAN
*CANCEL VALUE WYCKOFF XYZ
*CANCEL SHOW BASIS
*SHOW FREQUENCY DIRECTION
*DISPLAY ISOTROPY
Subgroup Dir         Frequency
38 Amm2  P2  (a,a,0) 1 GM1+ P1(1), 1 GM3+ P1(1), 1 GM5+ P1(1), 1 GM4- P2(1), 1
                     GM5- P2(10)
*VALUE IRREP GM1+
*VALUE DIRECTION P1
*DISPLAY DISTORTION
*VALUE IRREP GM3+
*DISPLAY DISTORTION
*VALUE IRREP GM5+
*DISPLAY DISTORTION
*VALUE IRREP GM5-
*VALUE DIRECTION P2
*VALUE DOMAIN 10
*DISPLAY DISTORTION
Dir Domain Wyckoff Point       Projected Vectors
P2  10     c       (0,1/2,1/2) (0,-2,0)
                   (1/2,1/2,0) (2,2,0)
                   (1/2,0,1/2) (-2,0,0)
*
```

We first find that secondary order parameters occur for irreps Γ_1^+, Γ_3^+, Γ_5^+, Γ_5^-. We try them one at a time. If there is no data displayed in response to the `DISPLAY DISTORTION` command, then no local atomic displacements can induce a global distortion for that space group irrep. We see that the only secondary order parameter that produces atomic displacement distortions is P2 (domain 10) for irrep Γ_5^-. This global distortion involves only displacements of the atoms at Wyckoff position *c*.

The collection of primary and secondary modes is called a "bush" of modes. We can display the entire bush with one command.

```
*VALUE IRREP GM4-
*VALUE DIRECTION P2
*CANCEL VALUE DOMAIN
*SHOW MODES
```

```
*DISPLAY BUSH
Irrep (ML) Dir(dom) Wyckoff Point         Displacement
GM4-       P2(1)    a       (0,0,0)       (1,1,0)
GM4-       P2(1)    b       (1/2,1/2,1/2) (1,1,0)
GM4-       P2(1)    c       (0,1/2,1/2)   (1,0,0), (0,2,0)
                            (1/2,1/2,0)   (0,0,0), (2,2,0)
                            (1/2,0,1/2)   (0,1,0), (2,0,0)
GM5-       P2(10)   c       (0,1/2,1/2)   (0,-2,0)
                            (1/2,1/2,0)   (2,2,0)
                            (1/2,0,1/2)   (-2,0,0)
*
```

We can illustrate some additional features available by considering an atom at Wyckoff position e and the order parameter P1 for irrep M_1^+.

```
*VALUE IRREP M1+
*VALUE DIRECTION P1
*VALUE WYCKOFF E
*SHOW BASIS
*CANCEL SHOW DOMAIN
*CANCEL SHOW FREQUENCY
*DISPLAY ISOTROPY
Subgroup   Dir         Basis Vectors
123 P4/mmm P1  (a,0,0) (1,1,0),(-1,1,0),(0,0,1)
*DISPLAY DISTORTION
Dir Wyckoff Point      Projected Vectors
P1  e       (x,0,0)    (1,0,0)
            (x,1,0)    (-1,0,0)
            (-x,0,0)   (-1,0,0)
            (-x,1,0)   (1,0,0)
            (0,0,x)    (0,0,0)
            (0,1,x)    (0,0,0)
            (0,0,-x)   (0,0,0)
            (0,1,-x)   (0,0,0)
            (0,x,0)    (0,1,0)
            (0,x+1,0)  (0,-1,0)
            (0,-x,0)   (0,-1,0)
            (0,-x+1,0) (0,1,0)
P1  e       (x,0,0)    (0,0,0)
            (x,1,0)    (0,0,0)
            (-x,0,0)   (0,0,0)
            (-x,1,0)   (0,0,0)
            (0,0,x)    (0,0,1)
            (0,1,x)    (0,0,-1)
            (0,0,-x)   (0,0,-1)
            (0,1,-x)   (0,0,1)
```

```
            (0,x,0)    (0,0,0)
            (0,x+1,0)  (0,0,0)
            (0,-x,0)   (0,0,0)
            (0,-x+1,0) (0,0,0)
*
```

We note that there are two sets of projected vectors. Each corresponds to a different global distortion. These arise from different local distortions that belong to the same point group irrep. Also, we can assign a value to the parameter x in Wyckoff position.

```
*VALUE WYCKOFF XYZ 0.156 0 0
*DISPLAY DISTORTION
Dir Wyckoff Point                          Projected Vectors
P1  e       (0.15600, 0.00000, 0.00000)  (1,0,0)
            (0.15600, 1.00000, 0.00000)  (-1,0,0)
            (-0.15600, 0.00000, 0.00000) (-1,0,0)
            (-0.15600, 1.00000, 0.00000) (1,0,0)
            (0.00000, 0.00000, 0.15600)  (0,0,0)
            (0.00000, 1.00000, 0.15600)  (0,0,0)
            (0.00000, 0.00000, -0.15600) (0,0,0)
            (0.00000, 1.00000, -0.15600) (0,0,0)
            (0.00000, 0.15600, 0.00000)  (0,1,0)
            (0.00000, 1.15600, 0.00000)  (0,-1,0)
            (0.00000, -0.15600, 0.00000) (0,-1,0)
            (0.00000, 0.84400, 0.00000)  (0,1,0)
P1  e       (0.15600, 0.00000, 0.00000)  (0,0,0)
            (0.15600, 1.00000, 0.00000)  (0,0,0)
            (-0.15600, 0.00000, 0.00000) (0,0,0)
            (-0.15600, 1.00000, 0.00000) (0,0,0)
            (0.00000, 0.00000, 0.15600)  (0,0,1)
            (0.00000, 1.00000, 0.15600)  (0,0,-1)
            (0.00000, 0.00000, -0.15600) (0,0,-1)
            (0.00000, 1.00000, -0.15600) (0,0,1)
            (0.00000, 0.15600, 0.00000)  (0,0,0)
            (0.00000, 1.15600, 0.00000)  (0,0,0)
            (0.00000, -0.15600, 0.00000) (0,0,0)
            (0.00000, 0.84400, 0.00000)  (0,0,0)
*
```

Next, consider an atom at Wyckoff position c.

```
*CANCEL VALUE WYCKOFF XYZ
*VALUE WYCKOFF C
*DISPLAY DISTORTION
Dir Wyckoff Point       Projected Vectors
P1  c       (0,1/2,1/2) (0,2,0)
            (0,3/2,1/2) (0,-2,0)
```

```
            (1/2,1/2,0) (0,0,0)
            (1/2,3/2,0) (0,0,0)
            (1/2,0,1/2) (2,0,0)
            (1/2,1,1/2) (-2,0,0)
*
```

We can control which points are displayed. By default, the points inside the unit cell of the isotropy subgroup are displayed. All other points can be obtained by translations using lattice vectors of the isotropy subgroup. It may sometimes be more convenient, though, to display more points. We can define a cell containing the points to be displayed.

```
*VALUE CELL 2,0,0 0,2,0 0,0,2
*DISPLAY DISTORTION
Dir Wyckoff Point       Projected Vectors
P1  c       (0,1/2,1/2) (0,2,0)
            (0,1/2,3/2) (0,2,0)
            (0,3/2,1/2) (0,-2,0)
            (0,3/2,3/2) (0,-2,0)
            (1,1/2,1/2) (0,-2,0)
            (1,1/2,3/2) (0,-2,0)
            (1,3/2,1/2) (0,2,0)
            (1,3/2,3/2) (0,2,0)
            (1/2,1/2,0) (0,0,0)
            (1/2,1/2,1) (0,0,0)
            (1/2,3/2,0) (0,0,0)
            (1/2,3/2,1) (0,0,0)
            (3/2,1/2,0) (0,0,0)
            (3/2,1/2,1) (0,0,0)
            (3/2,3/2,0) (0,0,0)
            (3/2,3/2,1) (0,0,0)
            (1/2,0,1/2) (2,0,0)
            (1/2,0,3/2) (2,0,0)
            (1/2,1,1/2) (-2,0,0)
            (1/2,1,3/2) (-2,0,0)
            (3/2,0,1/2) (-2,0,0)
            (3/2,0,3/2) (-2,0,0)
            (3/2,1,1/2) (2,0,0)
            (3/2,1,3/2) (2,0,0)
*
```

Now let us consider another kind of microscopic distortion: rotations. These are pseudovectors. Consider the order parameter P1 for irrep R_5^- and atoms at Wyckoff positions a, b, c. The atomic displacements are

```
*CANCEL VALUE CELL
*VALUE IRREP R5-
```

```
*VALUE DIRECTION P1
*VALUE WYCKOFF A B C
*DISPLAY DISTORTION
Dir Wyckoff Point       Projected Vectors
P1  c       (0,1/2,1/2) (0,2,0)
            (0,1/2,3/2) (0,-2,0)
            (1/2,1/2,0) (0,0,0)
            (1/2,1/2,1) (0,0,0)
            (1/2,0,1/2) (-2,0,0)
            (1/2,0,3/2) (2,0,0)
```

These displacements can be view as a rotation of octahedra about Wyckoff position b.

```
*SHOW MICROSCOPIC VECTOR PSEUDO
*DISPLAY DISTORTION
Dir Wyckoff Point         Projected Pseudo Vectors
P1  b       (1/2,1/2,1/2) (0,0,1)
            (1/2,1/2,3/2) (0,0,-1)
*
```

Indeed this is a simpler way of viewing it: rotations about the z axis which alternate in sign as we move along the z axis.

The last type of microscopic distortion featured in ISOTROPY is order-disorder. Consider an alloy on a bcc lattice. An order-disorder phase transition could occur which causes the occupation at center of the cubic unit cell to be different from that at the corners. The parent space group is $Im\bar{3}m$. The order parameter is P1 of irrep H_1^+.

```
*VALUE PARENT 229
*VALUE IRREP H1+
*VALUE DIRECITON P1
*DISPLAY ISOTROPY
Subgroup  Dir     Basis Vectors
221 Pm-3m P1  (a) (1,0,0),(0,1,0),(0,0,1)
*VALUE WYCKOFF A
*SHOW MICROSCOPIC SCALAR
*DISPLAY DISTORTION
Dir Wyckoff Point         Projected Order Functions
P1  a       (0,0,0)       f
            (1/2,1/2,1/2) -f
*
```

We see that the ordering at $(0,0,0)$ is opposite to the ordering at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, as expected.

This is the end of this tutorial. You may exit the program.

```
*QUIT
```

If you have been running ISOTROPY, quit the program and start it again.

In the Landau theory of phase transitions, the free energy of a crystal is expanded in terms of components of the order parameter. From symmetry, certain monomials in this expansion can be shown to vanish. Similarly, certain monomials can be combined to form invariant polynomials.

As an example, consider the irrep Γ_4^- of space group $Pm\bar{3}m$.

```
*VALUE PARENT 221
*VALUE IRREP GM4-
*DISPLAY INVARIANT
Deg Invariants
2   n1^2 +n2^2 +n3^2
4   n1^4 +2n1^2n2^2 +2n1^2n3^2 +n2^4 +2n2^2n3^2 +n3^4
4   n1^4 +n2^4 +n3^4
*
```

There is a second-degree invariant polynomial $(\eta_1^2 + \eta_2^2 + \eta_3^2) \equiv \eta^2$ and two fourth-degree invariant polynomials, η^4 and $(\eta_1^4 + \eta_2^4 + \eta_3^4)$. Since ISOTROPY did not display any first-degree or third-degree invariant polynomials, there are none. By default, ISOTROPY displays invariant polynomials up to fourth degree. However, we can override the default:

```
*VALUE DEGREE 1 6
*DISPLAY INVARIANT
Deg Invariants
2   n1^2 +n2^2 +n3^2
4   n1^4 +2n1^2n2^2 +2n1^2n3^2 +n2^4 +2n2^2n3^2 +n3^4
4   n1^4 +n2^4 +n3^4
6   n1^6 +3n1^4n2^2 +3n1^4n3^2 +3n1^2n2^4 +6n1^2n2^2n3^2 +3n1^2n3^4 +n2^6
    +3n2^4n3^2 +3n2^2n3^4 +n3^6
6   n1^4n2^2 +n1^4n3^2 +n1^2n2^4 +3n1^2n2^2n3^2 +n1^2n3^4 +n2^4n3^2 +n2^2n3^4
6   n1^6 +n2^6 +n3^6
*
```

and we can also display invariant polynomials for a single degree:

```
*VALUE DEGREE 6
*DISPLAY INVARIANT
Deg Invariants
6   n1^6 +3n1^4n2^2 +3n1^4n3^2 +3n1^2n2^4 +6n1^2n2^2n3^2 +3n1^2n3^4 +n2^6
    +3n2^4n3^2 +3n2^2n3^4 +n3^6
6   n1^4n2^2 +n1^4n3^2 +n1^2n2^4 +3n1^2n2^2n3^2 +n1^2n3^4 +n2^4n3^2 +n2^2n3^4
6   n1^6 +n2^6 +n3^6
*
```

We can display invariant polynomials for coupled order parameters as well:

```
*VALUE DEGREE 1 4
*VALUE IRREP GM5- GM4-
*SHOW IRREP
*DISPLAY INVARIANT
Irrep (ML) Deg Invariants
GM5-,GM4-  2   n1^2 +n2^2 +n3^2
           2   n4^2 +n5^2 +n6^2
           4   n1^4 +2n1^2n2^2 +2n1^2n3^2 +n2^4 +2n2^2n3^2 +n3^4
           4   n1^4 +n2^4 +n3^4
           4   n1^2n2n4 -n1^2n3n5 -n1n2^2n6 +n1n3^2n6 +n2^2n3n5 -n2n3^2n4
           4   n1^2n4^2 +n1^2n5^2 +n1^2n6^2 +n2^2n4^2 +n2^2n5^2 +n2^2n6^2
               +n3^2n4^2 +n3^2n5^2 +n3^2n6^2
           4   n1^2n4^2 +n1^2n5^2 +n2^2n5^2 +n2^2n6^2 +n3^2n4^2 +n3^2n6^2
           4   n1n2n4n6 +n1n3n5n6 +n2n3n4n5
           4   n1n4^2n6 -n1n5^2n6 +n2n4n5^2 -n2n4n6^2 -n3n4^2n5 +n3n5n6^2
           4   n4^4 +2n4^2n5^2 +2n4^2n6^2 +n5^4 +2n5^2n6^2 +n6^4
           4   n4^4 +n5^4 +n6^4
```

Here the order parameter for Γ_5^- is (η_1, η_2, η_3) and
the order parameter for Γ_4^- is (η_4, η_5, η_6)

ISOTROPYčan display invariant polynomials containing spatial derivatives. For example, consider the irrep M_1 of space group $P4/n$. Its Lifshitz frequency is 1, so there exists a single second-degree invariant polynomial containing first derivatives with respect to x, y, z.

```
*VALUE PARENT 85
*VALUE IRREP M1
*VALUE GRADIENT 1
*VALUE DEGREE 2
*DISPLAY INVARIANT
Irrep (ML) Deg Invariants
M1         2   n1n2z -n2n1z
*
```

The invariant polynomial is $\eta_1(\partial\eta_2/\partial z) - \eta_2(\partial\eta_1/\partial z)$.

ISOTROPY can evaluate invariant polynomials at a certain direction of the order parameter. As an example, consider the irrep X_5^- of space group $Pm\bar{3}m$. This is a six-dimensional irrep. There are five invariant polynomials of fourth-degree. If we evaluate these polynomials at order parameter direction C1, $\vec{\eta} = (a, b, 0, 0, 0, 0)$, we obtain polynomials with only two variables (a, b, which we rename η_1, η_2). We find that

these five polynomials are now no longer independent. ISOTROPY automatically removes the polynomials that are not independent.

```
*VALUE PARENT 221
*VALUE IRREP X5-
*CANCEL VALUE GRADIENT
*VALUE DEGREE 1 4
*CANCEL SHOW IRREP
*DISPLAY INVARIANT
Deg Invariants
2   n1^2 +n2^2 +n3^2 +n4^2 +n5^2 +n6^2
4   n1^4 +2n1^2n2^2 +2n1^2n3^2 +2n1^2n4^2 +2n1^2n5^2 +2n1^2n6^2 +n2^4 +2n2^2n3^2
    +2n2^2n4^2 +2n2^2n5^2 +2n2^2n6^2 +n3^4 +2n3^2n4^2 +2n3^2n5^2 +2n3^2n6^2
    +n4^4 +2n4^2n5^2 +2n4^2n6^2 +n5^4 +2n5^2n6^2 +n6^4
4   n1^4 +n2^4 +n3^4 +n4^4 +n5^4 +n6^4
4   n1^2n2^2 +n3^2n4^2 +n5^2n6^2
4   n1^2n3n4 -n1^2n5n6 -n1n2n3^2 -n1n2n4^2 +n1n2n5^2 +n1n2n6^2 +n2^2n3n4
    -n2^2n5n6 +n3^2n5n6 -n3n4n5^2 -n3n4n6^2 +n4^2n5n6
4   n1n2n3n4 +n1n2n5n6 +n3n4n5n6
*VALUE DIRECTION C1
*DISPLAY INVARIANT
Deg Invariants
2   n1^2 +n2^2
4   n1^4 +2n1^2n2^2 +n2^4
4   n1^4 +n2^4
*
```

We can also display invariant polynomials associated with a bush of vibrational modes. These polynomials would be terms in the potential energy. Consider a primary order parameter P2 for irrep Γ_4^-, space group $Pm\bar{3}m$.

```
*VALUE IRREP GM4-
*VALUE DIRECTION P2
*VALUE WYCKOFF C
*SHOW MODES
*SHOW INVARIANT
*DISPLAY BUSH
Irrep (ML) Dir(dom) Wyckoff Point       Displacement
GM4-       P2(1)    c       (0,1/2,1/2) (1,0,0), (0,2,0)
                            (1/2,1/2,0) (0,0,0), (2,2,0)
                            (1/2,0,1/2) (0,1,0), (2,0,0)
GM5-       P2(10)   c       (0,1/2,1/2) (0,-2,0)
                            (1/2,1/2,0) (2,2,0)
                            (1/2,0,1/2) (-2,0,0)
Irrep (ML) Dir(dom) Wyckoff Mode Variables
GM4-       P2(1)    c       n1,n2
```

```
GM5-       P2(10)   c       n3
Deg Invariants
2   n1^2
2   n1n2
2   n2^2
2   n3^2
4   n1^4
4   n1^3n2
4   n1^2n2^2
4   n1n2^3
4   n2^4
4   n1^2n3^2
4   n1n2n3^2
4   n2^2n3^2
4   n3^4
4   n1^3n3
4   n1^2n2n3
4   n1n2^2n3
4   n1n3^3
4   n2^3n3
4   n2n3^3
*
```

There are three modes, two for irrep Γ_4^- (primary order parameter or root mode) and one for Γ_5^- (secondary order parameter or secondary mode).

This is the end of this tutorial. You may exit the program.

```
*QUIT
```

If you have been running ISOTROPY, quit the program and start it again.
When a crystal undergoes a phase transition, a collection of coherent domains usually appear. These domains are symmetrically and energetically equivalent structures differing only in their orientation and possibly position.

More details about domain pairs and twins and their symmetry groups can be found in:
D. M. Hatch and W. Cao, "Determination of Domain and Domain Wall Formation at Ferroic Transitions," *Ferroelectrics* **222**, 1–10 (1999).
R. A. Hatt and D. M. Hatch, "Order-Parameter Profiles in Ferroic Phase Transitions," *Ferroelectrics* **226**, 61–78 (1999).
D. M. Hatch, W. Cao, and A. Saxena, "Orientational Twins in an Improper Ferroelectric Phase Transition Driven by the M_5^- Zone-Boundary Phonon in $R\mathrm{Ag}_{1-x}\mathrm{In}_x$," *Physical Review B* **65**, 094110–1–11 (2002).

In the first part of this session, we consider as an example the space group $R\bar{3}m$ and subgroup $P2_1/c$. This subgroup is obtained from irrep F_2^+ with order parameter direction P1.

```
*VALUE PARENT 166
*VALUE IRREP F2+
*VALUE DIRECTION P1
*SHOW SUBGROUP
*SHOW BASIS
*SHOW ELEMENTS
*DISPLAY ISOTROPY
Subgroup  Basis Vectors                              Elements
14 P2_1/c (-1/3,-2/3,1/3),(1,0,0),(1/3,2/3,2/3) (E|0,0,0), (C21''|2/3,1/3,1/3),
                                                    (I|0,0,0), (SGv1|2/3,1/3,1/3)
*
```

There are six single domain states (SDS's) that occur at this transition, and they correspond to the cosets in $R\bar{3}m$ which can be formed with respect to $P2_1/c$. The prototype of the transition shown above is always chosen to be the first domain state, and the symmetry group elements that leave that domain invariant are given above. To obtain the SDS's, $R\bar{3}m$ is decomposed into cosets with respect to the subgroup $P2_1/c$ of the first domain. In this case, there are six cosets. The elements of the ith coset take the first domain state into the ith domain state. One element from each coset is chosen to be a domain state generator. The symmetry elements of the ith domain state are $F_i = g_i F_1 g_i^{-1}$, where g_i is the generator, and F_i is the set of space group elements for the ith domain. We obtain the generators for each domain state and the elements of each symmetry group below.

```
*CANCEL SHOW SUBGROUP
*CANCEL SHOW BASIS
*SHOW DOMAIN GENERATOR
*DISPLAY ISOTROPY
```

```
Domain Gen                 Elements
1      (E|0,0,0)           (E|0,0,0), (C21''|2/3,1/3,1/3), (I|0,0,0),
                           (SGv1|2/3,1/3,1/3)
2      (C3+|0,0,0)         (E|0,0,0), (C22''|-1/3,1/3,1/3), (I|0,0,0),
                           (SGv2|-1/3,1/3,1/3)
3      (C3-|0,0,0)         (E|0,0,0), (C23''|-1/3,-2/3,1/3), (I|0,0,0),
                           (SGv3|-1/3,-2/3,1/3)
4      (E|2/3,1/3,1/3)     (E|0,0,0), (C21''|1,1,1), (I|4/3,2/3,2/3),
                           (SGv1|5/3,1/3,1/3)
5      (C3+|-1/3,1/3,1/3)  (E|0,0,0), (C22''|-1,0,1), (I|-2/3,2/3,2/3),
                           (SGv2|-1/3,4/3,1/3)
6      (C3-|-1/3,-2/3,1/3) (E|0,0,0), (C23''|0,-1,1), (I|-2/3,-4/3,2/3),
                           (SGv3|-4/3,-5/3,1/3)
*
```

Note that the space group symmetry of each domain is $P2_1/c$. Only the orientation and/or position of its origin is different.

```
*CANCEL SHOW DOMAIN GENERATORS
*CANCEL SHOW ELEMENTS
*SHOW SUBGROUP
*SHOW BASIS
*SHOW ORIGIN
*DISPLAY ISOTROPY
Domain Subgroup  Basis Vectors                              Origin
1      14 P2_1/c (-1/3,-2/3,1/3),(1,0,0),(1/3,2/3,2/3)   (0,0,0)
2      14 P2_1/c (2/3,1/3,1/3),(0,1,0),(-2/3,-1/3,2/3)   (0,0,0)
3      14 P2_1/c (-1/3,1/3,1/3),(-1,-1,0),(1/3,-1/3,2/3) (0,0,0)
4      14 P2_1/c (-1/3,-2/3,1/3),(1,0,0),(1/3,2/3,2/3)   (2/3,1/3,1/3)
5      14 P2_1/c (2/3,1/3,1/3),(0,1,0),(-2/3,-1/3,2/3)   (-1/3,1/3,1/3)
6      14 P2_1/c (-1/3,1/3,1/3),(-1,-1,0),(1/3,-1/3,2/3) (-1/3,-2/3,1/3)
*
```

In the above list, we see that domains 1 and 4 both have the same basis vectors but a different origin. These two domains do have, in fact, the same space group elements. This can be seen from the directions of the order parameters in each domain.

```
*CANCEL SHOW BASIS
*CANCEL SHOW ORIGIN
*SHOW DIRECTION VECTOR
*DISPLAY ISOTROPY
Domain Subgroup  Dir
1      14 P2_1/c P1  (a,0,0)
2      14 P2_1/c     (0,a,0)
3      14 P2_1/c     (0,0,a)
4      14 P2_1/c     (-a,0,0)
5      14 P2_1/c     (0,-a,0)
6      14 P2_1/c     (0,0,-a)
```

```
*
```

Since the value of a in the order parameter is arbitrary, $(a,0,0)$ and $(-a,0,0)$ are actually identical directions. Similarly, domains 2 and 5 have the same space group elements, and domains 3 and 6 do also. There are three distinct domains for this transition. The distinct domains can be shown explicitly.

```
*SHOW DISTINCT
*DISPLAY ISOTROPY
Domain Distinct Subgroup  Dir
1      1        14 P2_1/c P1  (a,0,0)
2      2        14 P2_1/c     (0,a,0)
3      3        14 P2_1/c     (0,0,a)
4      1        14 P2_1/c     (-a,0,0)
5      2        14 P2_1/c     (0,-a,0)
6      3        14 P2_1/c     (0,0,-a)
*
```

The next simplest structure to consider is a domain pair. This is an idealization of two superimposed single domains in the same space but otherwise not interacting. The entire set of possible pairs (S_i, S_j) is $6^2 = 36$ pairs. Pairs are equivalent if there is some element g of the parent group such that $(S_i, S_j) = g(S_k, S_l) \equiv (gS_k, gS_l)$. In our example this reduces the number of distinct classes of domain pairs to 3. ISOTROPY shows us which pairs $(1, j)$ [shorthand for (S_1, S_j)] are equivalent, along with operators g which connect them.

```
*CANCEL SHOW DISTINCT
*CANCEL SHOW SUBGROUP
*CANCEL SHOW DIRECTION
*SHOW PAIRS
*DISPLAY ISOTROPY
Domain Pairs Equiv ops
1      1     (E|0,0,0)
2      3     (E|0,0,0)
3      3     (C21''|0,-1,1)
4      2     (E|0,0,0)
5      3     (E|-1,0,1)
6      3     (C21''|-1/3,-5/3,4/3)
*
```

Here we see 3 distinct classes of domain pairs (the number in the column labeled `Pairs`). Domain pair (1,1) is in a class by itself (which we call class 1), domain pair (1,4) is also in a class by itself (class 2), and domain pairs (1,2), (1,3), (1,5), and (1,6) are all equivalent and are in class 3. Also, in this class, we have $\{C''_{21}|0,-1,1\}(1,2) = (1,3)$, $\{E|-1,0,1\}(1,2) = (1,5)$, and $\{C''_{21}|-\frac{1}{3},-\frac{5}{3},\frac{4}{3}\}(1,2) = (1,6)$.

The pair symmetry group consists of two types of operations that leave the domain pair invariant: (1) operations that simultaneously leave both SDS's unchanged and

(2) operations, if they exist, that interchange (switch) the two SDS's. We can write this symmetry group as

$$J_{ij} = F_{(i)} \cap F_{(j)} + j'_{ij} F_{(i)} \cap F_{(j)},$$

where $F_{(i)}$ is the space group of the ith domain and j'_{ij} is an element that switches the two SDS's. The first term, $F_{(i)} \cap F_{(j)}$, is called the pair intersection group. For example, we obtain the pair intersection group for the domain pair (1,2):

```
*VALUE DOMAIN PAIR 1 2
*SHOW PAIRS INTERSECT
*DISPLAY ISOTROPY
Domain Pairs Pair intersect
(1,2)        S1
*
```

The pair intersection group is always one of the other isotropy subgroups. In this case, it is the isotropy subgroup with the order parameter in the direction S1. We display the elements, basis vectors of the lattice, and origin of this pair intersection group:

```
*CANCEL SHOW ALL
*VALUE DIRECTION S1
*SHOW SUBGROUP
*SHOW ELEMENTS
*DISPLAY ISOTROPY
Subgroup Elements
2 P-1    (E|0,0,0), (I|0,0,0)
*CANCEL SHOW ELEMENTS
*SHOW BASIS
*SHOW ORIGIN
*DISPLAY ISOTROPY
Subgroup Basis Vectors                                    Origin
2 P-1    (-4/3,-2/3,1/3),(2/3,-2/3,1/3),(2/3,4/3,1/3) (0,0,0)
*
```

We can also obtain the element j'_{12} that switches the two SDS's.

```
*CANCEL SHOW ALL
*VALUE DIRECTION P1
*VALUE DOMAIN PAIR 1 2
*SHOW PAIRS SWITCH
*DISPLAY ISOTROPY
Domain Pairs Pair switch
(1,2)        (C23''|-1/3,1/3,1/3)
*
```

Finally, we obtain the pair group:

```
*CANCEL SHOW PAIRS SWITCH
*SHOW PAIRS GROUP
```

```
*SHOW PAIRS ELEMENTS
*DISPLAY ISOTROPY
Domain Pairs Pair group Elements
(1,2)        12 C2/m    (E|0,0,0), (C23''|-1/3,1/3,1/3), (I|2/3,4/3,1/3),
                        (SGv3|1,1,0)
*CANCEL SHOW PAIRS ELEMENTS
*SHOW PAIRS BASIS
*SHOW PAIRS ORIGIN
*DISPLAY ISOTROPY
Domain Pairs Pair group Basis                              Origin
(1,2)        12 C2/m    (-2/3,2/3,2/3),(2,2,0),(0,0,-1) (1/3,2/3,1/6)
*
```

The next more complicated structure to be considered is a domain twin. A domain twin can be viewed as two domains, each occupying a half space separated by a specified plane wall. The wall is specified by a direction $\hat{n}$ normal to the wall and a point $\vec{P}$ through which the wall passes. The symmetry group of the twin group consists of four parts and can be denoted as

$$\bar{J}_{ij} = \hat{F}_{ij} + \underline{t}'_{ij}\hat{F}_{ij} + \underline{r}_{ij}\hat{F}_{ij} + s'_{ij}\hat{F}_{ij}.$$

All four parts leave $\vec{P}$ invariant. In addition, (1) $\hat{F}_{ij}$ contains those elements that leave S_i, S_j, and $\hat{n}$ invariant (we refer to $\hat{F}_{ij}$ as the twin intersection group), (2) $\underline{t}'_{ij}\hat{F}_{ij}$ contains those elements that interchange S_i and S_j and reverses $\hat{n}$ (we refer to $\underline{t}'_{ij}$ as the switch both element), (3) $\underline{r}_{ij}\hat{F}_{ij}$ contains those elements that leave S_i and S_j invariant and reverses $\hat{n}$ (we refer to $\underline{r}_{ij}$ as the switch normal element), (4) $s'_{ij}\hat{F}_{ij}$ contains those elements that interchange S_i and S_j and leave $\hat{n}$ invariant (we refer to s'_{ij} as the switch side element). Note that both the twin intersection group $\hat{F}_{ij}$ and the twin group $\bar{J}_{ij}$ are diperiodic space groups. The lattice for these groups is two-dimensional, and therefore only two basis vectors of the lattice are given.

As an example, we consider a domain wall between S_1 and S_2 with position $\vec{P} = (0, 0, 0)$ and Miller indices (1,1,0). First, we obtain the twin intersection group $\hat{F}_{12}$.

```
*CANCEL SHOW ALL
*VALUE DOMAIN PAIR 1 2
*VALUE POSITION 0 0 0
*VALUE NORMAL 1 1 0
*SHOW TWIN INTERSECT GROUP
*SHOW TWIN INTERSECT BASIS
*SHOW TWIN INTERSECT ORIGIN
*SHOW TWIN INTERSECT ELEMENTS
*DISPLAY ISOTROPY
Domain Pairs Twin intersect Basis                    Origin  Elements
(1,2)        1 P1           (-2/3,2/3,-1/3),(0,0,-1) (0,0,0) (E|0,0,0)
*
```

We also obtain the switch normal element $\underline{r}_{12}$, the switch side element s'_{12}, and the switch both element $\underline{t}'_{12}$.

```
*CANCEL SHOW TWIN
*SHOW TWIN SWITCH NORMAL
*SHOW TWIN SWITCH SIDE
*SHOW TWIN SWITCH BOTH
*DISPLAY ISOTROPY
Domain Pairs Twin switch normal Twin switch side     Twin switch both
(1,2)        (I|-2/3,2/3,2/3)   (C23''|-1/3,1/3,1/3) (SGv3|-1/3,1/3,1/3)
*
```

And finally we obtain the twin symmetry group $\bar{J}_{12}$. Notice that it is a diperiodic space group.

```
*CANCEL SHOW TWIN
*SHOW TWIN GROUP
*SHOW TWIN ELEMENTS
*DISPLAY ISOTROPY
Domain Pairs Twin group Elements
(1,2)        7 P2/b11   (E|0,0,0), (C23''|-1/3,1/3,-2/3), (I|0,0,0),
                        (SGv3|-1/3,1/3,-2/3)
*CANCEL SHOW TWIN ELEMENTS
*SHOW TWIN BASIS
*SHOW TWIN ORIGIN
*DISPLAY ISOTROPY
Domain Pairs Twin group Basis                             Origin
(1,2)        7 P2/b11   (-2/3,2/3,-1/3),(-2/3,2/3,-4/3) (0,0,0)
*
```

Of course, if the position or orientation of the domain wall is changed, the twin group will change. Physical properties of materials such as fatigue, polarization switching voltage, etc. depend on domain wall formation, i.e., placement and orientation.

We now consider the average symmetry of a crystal when more than one domain is present. We consider as an example a ferroelectric phase transition in a pervoskite crystal from the cubic space group $Pm\bar{3}m$ to the tetragonal subgroup $P4mm$ (order parameter P1, irrep Γ_4^-). There are six domain states associated with this phase transition.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 221
*VALUE IRREP GM4-
*VALUE DIRECTION P1
*SHOW DOMAINS
*SHOW DIRECTION VECTOR
*DISPLAY ISOTROPY
```

```
 Domain Dir
1      P1  (a,0,0)
2          (-a,0,0)
3          (0,0,a)
4          (0,0,-a)
5          (0,a,0)
6          (0,-a,0)
*
```

We now obtain the possible multidomain structures and their average symmetries.

```
*CANCEL SHOW DOMAINS
*CANCEL SHOW DIRECTION
*SHOW DOMAIN SETS
*SHOW DOMAIN SETS GROUP
*SHOW DOMAIN SETS BASIS
*SHOW DOMAIN SETS ORIGIN
*DISPLAY ISOTROPY
Class Set           Sets Group Basis                          Origin
1     (1,2,3,4,5,6) 221 Pm-3m  (0,-1,0),(-1,0,0),(0,0,-1)    (0,0,0)
2     (1,2,5,6)     123 P4/mmm (-1,0,0),(0,-1,0),(0,0,1)     (0,0,0)
3     (3,4)         123 P4/mmm (-1,0,0),(0,-1,0),(0,0,1)     (0,0,0)
4     (1,2),(3,4)   47 Pmmm    (-1,0,0),(0,0,1),(0,1,0)      (0,0,0)
5     (3)           99 P4mm    (-1,0,0),(0,-1,0),(0,0,1)     (0,0,0)
6     (1,3,5)       160 R3m    (-1,0,1),(0,1,-1),(-1,-1,-1) (0,0,0)
7     (1,2),(5)     25 Pmm2    (-1,0,0),(0,0,1),(0,1,0)      (0,0,0)
8     (3,6)         38 Amm2    (-1,0,0),(0,-1,-1),(0,-1,1)   (0,0,0)
9     (3),(5)       6 Pm       (0,0,-1),(-1,0,0),(0,1,0)     (0,0,0)
10    (1,5),(3)     8 Cm       (-1,-1,0),(-1,1,0),(0,0,-1)   (0,0,0)
11    (1),(3),(5)   1 P1       (-1,0,0),(0,1,0),(0,0,-1)     (0,0,0)
*
```

The symbol for each set displays domain states enclosed in parentheses. The domain states enclosed within a single set of parentheses are present in equal equal amounts in the crystal. For example, the set (1,2,3,4,5,6) represents a crystal with all six domains present in equal amounts. The average symmetry is the full cubic symmetry $Pm\bar{3}m$ of the parent group. The set (1,2,5,6) represents a crystal with domain states 1,2,5,6 present in equal amounts. Domain states 3 and 4 are not present. The average symmetry consists of operators which permute the domain states 1,2,5,6.

Domain states enclosed within different sets of parentheses are not present in equal amounts. For example, the set (1,2),(3,4) represents a crystal with domain states 1,2,3,4 present. Domain states 1 and 2 are present in equal amounts, and domain states 3 and 4 are present in equal amounts, but domain states 1 and 3 are present in unequal amounts, etc. The average symmetry consists of operators which permute the domain states 1,2 and also permute the domain states 3,4, but do not mix 1 or 2 with 3 or 4.

We can select a single multidomain structure.

```
*VALUE DOMAIN SETS CLASS 4
*DISPLAY ISOTROPY
Class Set         Sets Group Basis                     Origin
4     (1,2),(3,4) 47 Pmmm    (-1,0,0),(0,0,1),(0,1,0) (0,0,0)
*
```

Besides the basis vectors and origin of the symmetry group, we can also display the generators and the elements.

```
*CANCEL SHOW DOMAIN SETS BASIS
*CANCEL SHOW DOMAIN SETS ORIGIN
*SHOW DOMAIN SETS GENERATORS
*DISPLAY ISOTROPY
Class Set         Sets Group Generators
4     (1,2),(3,4) 47 Pmmm    (C2y|0,0,0), (C2x|0,0,0), (I|0,0,0)
*CANCEL SHOW DOMAIN SETS GENERATORS
*SHOW DOMAIN SETS ELEMENTS
*DISPLAY ISOTROPY
Class Set         Sets Group Elements
4     (1,2),(3,4) 47 Pmmm    (E|0,0,0), (C2x|0,0,0), (C2z|0,0,0), (C2y|0,0,0),
                             (I|0,0,0), (SGx|0,0,0), (SGz|0,0,0), (SGy|0,0,0)
*
```

The lists above shows only nonequivalent multidomain structures. We can also display equivalent structures.

```
*CANCEL SHOW DOMAIN SETS ELEMENTS
*SHOW DOMAIN SETS ALL
*SHOW DOMAIN SETS EQUIVALENT
*DISPLAY ISOTROPY
Class Set         Equiv op     Sets Group
4     (1,2),(3,4) (E|0,0,0)    47 Pmmm
4     (3,4),(5,6) (C31-|0,0,0) 47 Pmmm
4     (5,6),(1,2) (C31+|0,0,0) 47 Pmmm
4     (5,6),(3,4) (C2b|0,0,0)  47 Pmmm
4     (1,2),(5,6) (C2f|0,0,0)  47 Pmmm
4     (3,4),(1,2) (C2e|0,0,0)  47 Pmmm
*
```

The equivalence operators shows us how each multidomain structure is related to the first one on the list. Note that you view equivalent structures only if a class has been selected.

Let us represent multidomain structures with a six-dimensional vector $\vec{s}$. The components of $\vec{s}$ represent the relative amounts each domain state is present in a crystal. To find the most general domain structure associated with a given symmetry, we simply find the most general form of $\vec{s}$ which is invariant under each operator in the symmetry group. Let us illustrate this with the present example.

```
*SHOW DOMAIN SETS DIRECTION
*DISPLAY ISOTROPY
Dir Domain Sets Dir Sets Group
1   (a,a,a,a,a,a)   221 Pm-3m
2   (a,a,b,b,a,a)   123 P4/mmm
3   (a,a,b,b,c,c)   47 Pmmm
4   (a,a,b,c,a,a)   99 P4mm
5   (a,b,a,b,a,b)   160 R3m
6   (a,a,b,b,c,d)   25 Pmm2
7   (a,a,b,c,c,b)   38 Amm2
8   (a,b,c,c,d,d)   3 P2
9   (a,b,c,c,b,a)   5 C2
10  (a,a,b,c,d,e)   6 Pm
11  (a,b,c,d,a,b)   8 Cm
12  (a,b,c,d,e,f)   1 P1
*
```

The first entry $\vec{s} = (a, a, a, a, a, a)$ is the structure with all domain states present in equal amounts: (1,2,3,4,5,6). The second entry is a structure with domain states 1,2,5,6 present in equal amounts and domain states 3,4 present in equal amounts, i.e., (1,2,5,6),(3,4). Its symmetry is $P4/mmm$. It turns out that the symmetry of (1,2,5,6) alone ($b = 0$) is also $P4/mmm$ and that of (3,4) alone ($a = 0$) is $P4/mmm$. Therefore we list (1,2,5,6) and (3,4) separately as domain structures. For brevity, we do not list (1,2,5,6),(3,4). We list only the minimal sets of domain states required for each symmetry.

The list above shows only nonequivalent vectors $\vec{s}$. To see equivalent vectors, we select one of the directions. Note that `SHOW DOMAIN SETS ALL` and `SHOW DOMAIN SETS EQUIVALENT` are still in effect. Note that `VALUE DOMAIN SETS CLASS` only has effect when viewing classes of sets, whereas `VALUE DOMAIN SETS DIRECTION` only has effect when viewing directions of $\vec{s}$.

```
*VALUE DOMAIN SETS DIRECTION 6
*DISPLAY ISOTROPY
Dir Domain Sets Dir Equiv op     Sets Group
6   (a,a,b,b,c,d)   (E|0,0,0)    25 Pmm2
6   (a,a,b,c,d,d)   (C31-|0,0,0) 25 Pmm2
6   (a,b,c,c,d,d)   (C31+|0,0,0) 25 Pmm2
*
```

This is the end of this tutorial. You may exit the program.

```
*QUIT
```

Case Study 1: Octahedral Tilting in Perovskites

This case study explains how ISOTROPY was used in the research which resulted in the publication, Christopher J. Howard and Harold T. Stokes, "Group Theoretical Analysis of Octahedral Tilting in Perovskites," *Acta Cryst. B*, **54**, 782–789 (1998).

The perovskites ABX_3 have a cubic structure: space group #221 $Pm\bar{3}m$ with atom A at Wyckoff position b, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, atom B at Wyckoff position a, (0,0,0), and atom X at Wyckoff position d, $(\frac{1}{2},0,0)$, $(0,\frac{1}{2},0)$, $(0,0,\frac{1}{2})$. The X atoms lie on vertices of octahedra BX_6, centered about each B atom. These octahedral are linked, since each X atom is at the vertex of two adjacent octahedra. We want to find possible phase transitions which involve tilting of these octahedra.

There are two constraints on this problem. The first constraint is due to the linking of the octahedra. If the octahedron centered at (0,0,0) tilts about the x axis, then neighboring octahedra at $(0,\pm1,0)$ and $(0,0,\pm1)$ must also tilt about the x axis, but in the opposite direction. In fact, every octahedron in the yz plane must be tilted about the x axis, half of them in one direction and the other half in the other direction. There is a similar constraint for tilting about the y and z axes.

The other constraint is one of our own making in order to restrict the scope of our search. If the octahedron centered at (0,0,0) tilts about the x axis, then, as we saw above, the tilting of every octahedron in the yz plane is determined. However, we have the freedom to choose the tilting of octahedra about the x axis in adjacent yz planes. We will consider two different tilt patterns: (1) the tilting about the x axis in adjacent yz planes is the same, and (2) the tilting about the x axis in adjacent yz planes is opposite. Thus, as we move along the x axis, we find tilt patterns which are either $+++++++\ldots$ or $+-+-+-\ldots$ We use a similar constraint for tilting about the y and z axes as well.

Now let us first find the irreps for which these tilt patterns are basis functions. We find all possible distortions caused by tilts (pseudovectors) at Wyckoff position a. We consider only irreps at $\vec{k}$ points of symmetry.

```
*VALUE PARENT 221
*VALUE WYCKOFF A
*VALUE KDEGREE 0
*VALUE CELL 2,0,0 0,2,0 0,0,2
*SHOW IRREP
*SHOW MICROSCOPIC VECTOR PSEUDO
*DISPLAY DISTORTION
Irrep (ML) Point   Projected Pseudo Vectors
GM4+       (0,0,0) (1,0,0), (0,1,0), (0,0,1)
           (0,0,1) (1,0,0), (0,1,0), (0,0,1)
           (0,1,0) (1,0,0), (0,1,0), (0,0,1)
           (0,1,1) (1,0,0), (0,1,0), (0,0,1)
           (1,0,0) (1,0,0), (0,1,0), (0,0,1)
           (1,0,1) (1,0,0), (0,1,0), (0,0,1)
```

```
          (1,1,0) (1,0,0), (0,1,0), (0,0,1)
          (1,1,1) (1,0,0), (0,1,0), (0,0,1)
R4+       (0,0,0) (0,0,1), (1,0,0), (0,1,0)
          (0,0,1) (0,0,-1), (-1,0,0), (0,-1,0)
          (0,1,0) (0,0,-1), (-1,0,0), (0,-1,0)
          (0,1,1) (0,0,1), (1,0,0), (0,1,0)
          (1,0,0) (0,0,-1), (-1,0,0), (0,-1,0)
          (1,0,1) (0,0,1), (1,0,0), (0,1,0)
          (1,1,0) (0,0,1), (1,0,0), (0,1,0)
          (1,1,1) (0,0,-1), (-1,0,0), (0,-1,0)
X3+       (0,0,0) (0,-1,0), (0,0,-1), (1,0,0)
          (0,0,1) (0,-1,0), (0,0,1), (1,0,0)
          (0,1,0) (0,1,0), (0,0,-1), (1,0,0)
          (0,1,1) (0,1,0), (0,0,1), (1,0,0)
          (1,0,0) (0,-1,0), (0,0,-1), (-1,0,0)
          (1,0,1) (0,-1,0), (0,0,1), (-1,0,0)
          (1,1,0) (0,1,0), (0,0,-1), (-1,0,0)
          (1,1,1) (0,1,0), (0,0,1), (-1,0,0)
X5+       (0,0,0) (1,0,1), (1,0,-1), (1,1,0), (-1,1,0), (0,1,1), (0,-1,1)
          (0,0,1) (1,0,1), (1,0,-1), (-1,-1,0), (1,-1,0), (0,1,1), (0,-1,1)
          (0,1,0) (-1,0,-1), (-1,0,1), (1,1,0), (-1,1,0), (0,1,1), (0,-1,1)
          (0,1,1) (-1,0,-1), (-1,0,1), (-1,-1,0), (1,-1,0), (0,1,1), (0,-1,1)
          (1,0,0) (1,0,1), (1,0,-1), (1,1,0), (-1,1,0), (0,-1,-1), (0,1,-1)
          (1,0,1) (1,0,1), (1,0,-1), (-1,-1,0), (1,-1,0), (0,-1,-1), (0,1,-1)
          (1,1,0) (-1,0,-1), (-1,0,1), (1,1,0), (-1,1,0), (0,-1,-1), (0,1,-1)
          (1,1,1) (-1,0,-1), (-1,0,1), (-1,-1,0), (1,-1,0), (0,-1,-1), (0,1,-1)
M3+       (0,0,0) (0,0,1), (1,0,0), (0,1,0)
          (0,0,1) (0,0,1), (-1,0,0), (0,-1,0)
          (0,1,0) (0,0,-1), (-1,0,0), (0,1,0)
          (0,1,1) (0,0,-1), (1,0,0), (0,-1,0)
          (1,0,0) (0,0,-1), (1,0,0), (0,-1,0)
          (1,0,1) (0,0,-1), (-1,0,0), (0,1,0)
          (1,1,0) (0,0,1), (-1,0,0), (0,-1,0)
          (1,1,1) (0,0,1), (1,0,0), (0,1,0)
M5+       (0,0,0) (1,0,-1), (1,0,1), (-1,1,0), (1,1,0), (0,-1,1), (0,1,1)
          (0,0,1) (1,0,1), (1,0,-1), (1,-1,0), (-1,-1,0), (0,-1,-1), (0,1,-1)
          (0,1,0) (-1,0,1), (-1,0,-1), (-1,-1,0), (1,-1,0), (0,1,1), (0,-1,1)
          (0,1,1) (-1,0,-1), (-1,0,1), (1,1,0), (-1,1,0), (0,1,-1), (0,-1,-1)
          (1,0,0) (-1,0,-1), (-1,0,1), (1,1,0), (-1,1,0), (0,1,-1), (0,-1,-1)
          (1,0,1) (-1,0,1), (-1,0,-1), (-1,-1,0), (1,-1,0), (0,1,1), (0,-1,1)
          (1,1,0) (1,0,1), (1,0,-1), (1,-1,0), (-1,-1,0), (0,-1,-1), (0,1,-1)
          (1,1,1) (1,0,-1), (1,0,1), (-1,1,0), (1,1,0), (0,-1,1), (0,1,1)
*
```

We find 24 tilt patterns, three from each of the three-dimensional irreps, Γ_4^+, R_4^+, X_3^+, M_3^+ and six from each of the six-dimensional irreps, X_5^+, M_5^+. Most of these tilt patterns violate the constraint due to linking of the octahedra. We find the tilt patterns of interest by inspection of the projected pseudo vectors above. The $+++++++\ldots$ pattern belongs to M_3^+, and the $+-+-+-\ldots$ pattern belongs to R_4^+. These are both three-dimensional irreps. By inspection, we also see that the tilts for the three basis functions are about the z, x, and y axes, respectively.

Now we find the isotropy subgroups. First of all, we find the subgroups for the uncoupled order parameters.

```
*SHOW DIRECTION VECTOR
*SHOW BASIS
*SHOW ORIGIN
*SHOW SUBGROUP
*VALUE IRREP M3+
*DISPLAY ISOTROPY
Irrep (ML) Subgroup   Dir          Basis Vectors             Origin
M3+        127 P4/mbm P1  (a,0,0) (1,1,0),(-1,1,0),(0,0,1) (0,0,0)
M3+        204 Im-3   P3  (a,a,a) (2,0,0),(0,2,0),(0,0,2)  (1/2,1/2,1/2)
M3+        139 I4/mmm P2  (a,a,0) (0,0,2),(2,0,0),(0,2,0)  (3/2,1/2,1/2)
M3+        71 Immm    S1  (a,b,c) (2,0,0),(0,2,0),(0,0,2)  (1/2,1/2,1/2)
*VALUE IRREP R4+
*DISPLAY ISOTROPY
Irrep (ML) Subgroup   Dir          Basis Vectors               Origin
R4+        167 R-3c   P3  (a,a,a) (-1,1,0),(0,-1,1),(2,2,2)  (0,0,0)
R4+        140 I4/mcm P1  (a,0,0) (1,1,0),(-1,1,0),(0,0,2)   (0,0,0)
R4+        74 Imma    P2  (a,a,0) (1,0,1),(0,2,0),(-1,0,1)   (0,0,0)
R4+        15 C2/c    C2  (a,a,b) (-1,2,-1),(-1,0,1),(1,0,1) (0,1/2,1/2)
R4+        12 C2/m    C1  (a,b,0) (0,0,-2),(0,2,0),(1,0,1)   (0,1/2,1/2)
R4+        2 P-1      S1  (a,b,c) (0,1,1),(1,0,1),(1,1,0)    (0,0,0)
*
```

Let us consider the interpretation of this data. The subgroup in direction P1 $(a,0,0)$ involves tilting about the z axis only. The subgroup in direction P2 $(a,a,0)$ involves tilting about both the z and x axes. Since the first two components of the order parameter $\vec{\eta}$ are equal, the tilts about the z and x axes are equal. On the other hand, the subgroup in direction C1 $(a,b,0)$ involves tilts about the z and x axes that are unequal.

Let us next find the isotropy subgroups for the coupled order parameters.

```
*VALUE IRREP M3+ R4+
*CANCEL SHOW IRREP
*DISPLAY ISOTROPY COUPLED
Subgroup     Dir                      Basis Vectors             Origin
148 R-3      P3(1)P3(1) (a,a,a,b,b,b) (-2,0,2),(2,-2,0),(2,2,2) (0,0,0)
127 P4/mbm   P1(1)P1(1) (a,0,0,b,0,0) (1,1,0),(-1,1,0),(0,0,2)  (0,0,0)
```

```
63 Cmcm      P1(1)P1(2) (a,0,0,0,0,b) (2,0,0),(0,2,0),(0,0,2)   (1/2,-1/2,0)
137 P4_2/nmc P2(1)P1(2) (a,a,0,0,0,b) (0,0,2),(2,0,0),(0,2,0)   (0,-1,0)
59 Pmmn      S1(1)P1(1) (a,b,c,d,0,0) (2,0,0),(0,2,0),(0,0,2)   (0,0,0)
62 Pnma      P1(1)P2(5) (a,0,0,0,b,b) (1,1,0),(0,0,2),(1,-1,0)  (0,0,0)
63 Cmcm      P2(1)P2(1) (a,a,0,b,b,0) (2,0,2),(2,0,-2),(0,2,0)  (0,0,0)
14 P2_1/c    P1(1)C2(9) (a,0,0,c,b,b) (0,0,2),(1,-1,0),(1,1,0)  (0,0,0)
15 C2/c      P2(1)C2(1) (a,a,0,b,b,c) (2,0,2),(-2,0,2),(0,-2,0) (0,0,0)
12 C2/m      P1(1)C1(1) (a,0,0,b,c,0) (2,0,0),(0,2,0),(0,0,2)   (1/2,1/2,0)
11 P2_1/m    P1(1)C1(5) (a,0,0,0,b,c) (-1,1,0),(0,0,2),(1,1,0)  (0,0,0)
11 P2_1/m    S1(1)C1(1) (a,b,c,d,e,0) (2,0,0),(0,2,0),(0,0,2)   (0,0,0)
2 P-1        P1(1)S1(1) (a,0,0,b,c,d) (0,0,2),(1,1,0),(-1,1,0)  (0,0,0)
2 P-1        S1(1)S1(1) (a,b,c,d,e,f) (0,0,2),(0,2,0),(-2,0,0)  (0,0,0)
*
```

We now use our second constraint to eliminate some of these. A superposition of a $+++++++\ldots$ and a $+-+-+-+-\ldots$ tilt pattern (around the same axis) yields a pattern where adjacent planes contain tilts which are neither the same nor opposite. These are tilt patterns beyond the scope of our present interest. This means that if any component of the order parameter for M_3^+ is nonzero, then that component of the order parameter for R_4^+ must be zero, and vice versa. We thus obtain the following list of allowable isotropy subgroups for the coupled order parameters:

```
Subgroup     Dir                      Basis Vectors              Origin
63 Cmcm      P1(1)P1(2) (a,0,0,0,0,b) (2,0,0),(0,2,0),(0,0,2)   (1/2,-1/2,0)
137 P4_2/nmc P2(1)P1(2) (a,a,0,0,0,b) (0,0,2),(2,0,0),(0,2,0)   (0,-1,0)
62 Pnma      P1(1)P2(5) (a,0,0,0,b,b) (1,1,0),(0,0,2),(1,-1,0)  (0,0,0)
11 P2_1/m    P1(1)C1(5) (a,0,0,0,b,c) (-1,1,0),(0,0,2),(1,1,0)  (0,0,0)
```

As an example of how to interpret these tilt patterns, we see that the subgroup in direction P1(1)P1(2) involves tilting about the z axis with the $+++++++\ldots$ pattern superimposed on tilting about the y axis with the $+-+-+-+-\ldots$ pattern.

This is the end of this case study. You may exit the program:

```
*QUIT
```

Case Study 2: Ferroelectric Phase Transition in $BaAl_2O_4$

$BaAl_2O_4$ belongs to the family of stuffed tridymites. Corner-sharing AlO_4 tetrahedra form a three-dimensional network with hexagonal channels filled with Ba atoms. $BaAl_2O_4$ exhibits a ferroelectric phase transition at 396 K. The structure of the high-temperature paraelectric phase was proposed by Abakumov *et al.*, *Phase Transitions* **71**, 143 (2000) to be #182 $P6_322$. The structure of the ferroelectric phase was known to be #173 $P6_3$. In the transition, the dimensions of the unit cell are doubled in the *ab* plane. We will first find this phase transition in the data base. We search for all phase transitions from space group #182 to space group #173 with a unit cell that increases in size by a factor of four.

```
*VALUE PARENT 182
*VALUE SUBGROUP 173
*VALUE SIZE 4
*SHOW IRREP
*SHOW DIRECTION VECTOR
*SHOW SUBGROUP
*SHOW BASIS
*SHOW ORIGIN
*DISPLAY ISOTROPY
Irrep (ML) Subgroup Dir         Basis Vectors           Origin
M2         173 P6_3 P3  (a,a,a) (2,0,0),(0,2,0),(0,0,1) (0,0,0)
*
```

We found one, and we see from the basis vectors that the value of a doubles in size, in agreement with known facts. The direction of the order parameter is (a, a, a), denoted by our symbol P3. This order parameter, which belongs to the irrep M_2, is the primary order parameter. It completely determines the symmetry of the ferroelectric phase. We now find the secondary order parameters.

```
*CANCEL SHOW DIRECTION
*CANCEL SHOW BASIS
*CANCEL SHOW ORIGIN
*SHOW FREQUENCY DIRECTION
*DISPLAY ISOTROPY
Irrep (ML) Subgroup Frequency
M2         173 P6_3 1 GM1 P1(1), 1 GM2 P1(1), 1 M1 P3(1), 1 M2 P3(1)
*
```

The secondary order parameters belong to the irreps M_1, Γ_2, and Γ_1. We find the symmetry of the isotropy subgroups determined by these order parameters.

```
*CANCEL SHOW FREQUENCY
*CANCEL VALUE SUBGROUP
*CANCEL VALUE SIZE
*SHOW BASIS
*SHOW ORIGIN
```

```
*VALUE IRREP M1
*VALUE DIRECTION P3
*DISPLAY ISOTROPY
Irrep (ML) Subgroup   Basis Vectors           Origin
M1         182 P6_322 (2,0,0),(0,2,0),(0,0,1) (0,0,0)
*VALUE IRREP GM2
*VALUE DIRECTION P1
*DISPLAY ISOTROPY
Irrep (ML) Subgroup Basis Vectors           Origin
GM2        173 P6_3 (1,0,0),(0,1,0),(0,0,1) (0,0,0)
*VALUE IRREP GM1
*DISPLAY ISOTROPY
Irrep (ML) Subgroup   Basis Vectors           Origin
GM1        182 P6_322 (1,0,0),(0,1,0),(0,0,1) (0,0,0)
*
```

Next, we find the mapping of the atomic positions in the paraelectric phase to positions in the ferroelectric phase. In the paraelectric phase, the Ba atoms are at Wyckoff position b, the Al atoms are at f ($z \approx 0.058$), and the O atoms are at c and g ($x \approx 0.352$).

```
*CANCEL SHOW BASIS
*CANCEL SHOW ORIGIN
*VALUE WYCKOFF B F C G
*SHOW WYCKOFF SUBGROUP
*VALUE IRREP M2
*VALUE DIRECTION P3
*DISPLAY ISOTROPY
Irrep (ML) Subgroup Wyckoff New Wyckoff
M2         173 P6_3 b       a, z'=1/4
                            c, x'=0, y'=1/2, z'=1/4
                    f       c, x'=1/6, y'=1/3, z'=z
                            c, x'=5/6, y'=2/3, z'=-z
                            b, z'=1/2+z
                            b, z'=-z
                    c       c, x'=1/6, y'=1/3, z'=1/4
                            b, z'=3/4
                    g       c, x'=1/2x, y'=0, z'=0
                            c, x'=1/2x, y'=1/2, z'=0
                            c, x'=1/2x, y'=1/2+1/2x, z'=1/2
                            c, x'=0, y'=1/2+1/2x, z'=0
*
```

Finally, we find the distortions allowed by each of the order parameters.

```
*SHOW WYCKOFF
*SHOW MICROSCOPIC VECTOR
*DISPLAY DISTORTION
```

Irrep (ML)	Wyckoff	Point	Projected Vectors
M2	b	(0,0,1/4)	(0,0,3)
		(0,1,1/4)	(0,0,-1)
		(1,0,1/4)	(0,0,-1)
		(1,1,1/4)	(0,0,-1)
		(0,0,3/4)	(0,0,3)
		(0,1,3/4)	(0,0,-1)
		(1,0,3/4)	(0,0,-1)
		(1,1,3/4)	(0,0,-1)
M2	b	(0,0,1/4)	(0,0,0)
		(0,1,1/4)	(0,-2,0)
		(1,0,1/4)	(-2,0,0)
		(1,1,1/4)	(2,2,0)
		(0,0,3/4)	(0,0,0)
		(0,1,3/4)	(0,2,0)
		(1,0,3/4)	(2,0,0)
		(1,1,3/4)	(-2,-2,0)
M2	c	(1/3,2/3,1/4)	(0,0,1)
		(1/3,5/3,1/4)	(0,0,1)
		(4/3,2/3,1/4)	(0,0,-3)
		(4/3,5/3,1/4)	(0,0,1)
		(-1/3,1/3,3/4)	(0,0,1)
		(-1/3,4/3,3/4)	(0,0,1)
		(2/3,1/3,3/4)	(0,0,1)
		(2/3,4/3,3/4)	(0,0,-3)
M2	c	(1/3,2/3,1/4)	(2,0,0)
		(1/3,5/3,1/4)	(-2,-2,0)
		(4/3,2/3,1/4)	(0,0,0)
		(4/3,5/3,1/4)	(0,2,0)
		(-1/3,1/3,3/4)	(2,2,0)
		(-1/3,4/3,3/4)	(-2,0,0)
		(2/3,1/3,3/4)	(0,-2,0)
		(2/3,4/3,3/4)	(0,0,0)
M2	f	(1/3,2/3,z)	(0,0,1)
		(1/3,5/3,z)	(0,0,1)
		(4/3,2/3,z)	(0,0,-3)
		(4/3,5/3,z)	(0,0,1)
		(-1/3,1/3,z+1/2)	(0,0,1)
		(-1/3,4/3,z+1/2)	(0,0,1)
		(2/3,1/3,z+1/2)	(0,0,1)
		(2/3,4/3,z+1/2)	(0,0,-3)
		(-1/3,-2/3,-z)	(0,0,1)
		(-1/3,1/3,-z)	(0,0,1)
		(2/3,-2/3,-z)	(0,0,-3)
		(2/3,1/3,-z)	(0,0,1)

```
                  (1/3,-1/3,-z+1/2) (0,0,1)
                  (1/3,2/3,-z+1/2)  (0,0,1)
                  (4/3,-1/3,-z+1/2) (0,0,1)
                  (4/3,2/3,-z+1/2)  (0,0,-3)
M2          f     (1/3,2/3,z)       (2,2,0)
                  (1/3,5/3,z)       (0,-2,0)
                  (4/3,2/3,z)       (0,0,0)
                  (4/3,5/3,z)       (-2,0,0)
                  (-1/3,1/3,z+1/2)  (0,2,0)
                  (-1/3,4/3,z+1/2)  (-2,-2,0)
                  (2/3,1/3,z+1/2)   (2,0,0)
                  (2/3,4/3,z+1/2)   (0,0,0)
                  (-1/3,-2/3,-z)    (0,2,0)
                  (-1/3,1/3,-z)     (2,0,0)
                  (2/3,-2/3,-z)     (0,0,0)
                  (2/3,1/3,-z)      (-2,-2,0)
                  (1/3,-1/3,-z+1/2) (-2,0,0)
                  (1/3,2/3,-z+1/2)  (0,-2,0)
                  (4/3,-1/3,-z+1/2) (2,2,0)
                  (4/3,2/3,-z+1/2)  (0,0,0)
M2          f     (1/3,2/3,z)       (0,-2,0)
                  (1/3,5/3,z)       (-2,0,0)
                  (4/3,2/3,z)       (0,0,0)
                  (4/3,5/3,z)       (2,2,0)
                  (-1/3,1/3,z+1/2)  (2,0,0)
                  (-1/3,4/3,z+1/2)  (0,2,0)
                  (2/3,1/3,z+1/2)   (-2,-2,0)
                  (2/3,4/3,z+1/2)   (0,0,0)
                  (-1/3,-2/3,-z)    (-2,-2,0)
                  (-1/3,1/3,-z)     (0,2,0)
                  (2/3,-2/3,-z)     (0,0,0)
                  (2/3,1/3,-z)      (2,0,0)
                  (1/3,-1/3,-z+1/2) (0,-2,0)
                  (1/3,2/3,-z+1/2)  (2,2,0)
                  (4/3,-1/3,-z+1/2) (-2,0,0)
                  (4/3,2/3,-z+1/2)  (0,0,0)
M2          g     (x,0,0)           (0,0,0)
                  (x,1,0)           (2,0,0)
                  (x+1,0,0)         (0,0,0)
                  (x+1,1,0)         (-2,0,0)
                  (x,x,1/2)         (0,0,0)
                  (x,x+1,1/2)       (-2,-2,0)
                  (x+1,x,1/2)       (2,2,0)
                  (x+1,x+1,1/2)     (0,0,0)
                  (0,x,0)           (0,0,0)
```

		(0,x+1,0)	(0,0,0)
		(1,x,0)	(0,-2,0)
		(1,x+1,0)	(0,2,0)
		(-x,0,1/2)	(0,0,0)
		(-x,1,1/2)	(-2,0,0)
		(-x+1,0,1/2)	(0,0,0)
		(-x+1,1,1/2)	(2,0,0)
		(-x,-x,0)	(0,0,0)
		(-x,-x+1,0)	(2,2,0)
		(-x+1,-x,0)	(-2,-2,0)
		(-x+1,-x+1,0)	(0,0,0)
		(0,-x,1/2)	(0,0,0)
		(0,-x+1,1/2)	(0,0,0)
		(1,-x,1/2)	(0,2,0)
		(1,-x+1,1/2)	(0,-2,0)
M2	g	(x,0,0)	(1.155,2.309,0)
		(x,1,0)	(0,0,0)
		(x+1,0,0)	(-1.155,-2.309,0)
		(x+1,1,0)	(0,0,0)
		(x,x,1/2)	(-1.155,1.155,0)
		(x,x+1,1/2)	(0,0,0)
		(x+1,x,1/2)	(0,0,0)
		(x+1,x+1,1/2)	(1.155,-1.155,0)
		(0,x,0)	(-2.309,-1.155,0)
		(0,x+1,0)	(2.309,1.155,0)
		(1,x,0)	(0,0,0)
		(1,x+1,0)	(0,0,0)
		(-x,0,1/2)	(-1.155,-2.309,0)
		(-x,1,1/2)	(0,0,0)
		(-x+1,0,1/2)	(1.155,2.309,0)
		(-x+1,1,1/2)	(0,0,0)
		(-x,-x,0)	(1.155,-1.155,0)
		(-x,-x+1,0)	(0,0,0)
		(-x+1,-x,0)	(0,0,0)
		(-x+1,-x+1,0)	(-1.155,1.155,0)
		(0,-x,1/2)	(2.309,1.155,0)
		(0,-x+1,1/2)	(-2.309,-1.155,0)
		(1,-x,1/2)	(0,0,0)
		(1,-x+1,1/2)	(0,0,0)
M2	g	(x,0,0)	(0.577,1.155,0)
		(x,1,0)	(-0.577,-1.155,0)
		(x+1,0,0)	(0.577,1.155,0)
		(x+1,1,0)	(-0.577,-1.155,0)
		(x,x,1/2)	(-0.577,0.577,0)
		(x,x+1,1/2)	(0.577,-0.577,0)

		(x+1,x,1/2)	(0.577,-0.577,0)
		(x+1,x+1,1/2)	(-0.577,0.577,0)
		(0,x,0)	(-1.155,-0.577,0)
		(0,x+1,0)	(-1.155,-0.577,0)
		(1,x,0)	(1.155,0.577,0)
		(1,x+1,0)	(1.155,0.577,0)
		(-x,0,1/2)	(-0.577,-1.155,0)
		(-x,1,1/2)	(0.577,1.155,0)
		(-x+1,0,1/2)	(-0.577,-1.155,0)
		(-x+1,1,1/2)	(0.577,1.155,0)
		(-x,-x,0)	(0.577,-0.577,0)
		(-x,-x+1,0)	(-0.577,0.577,0)
		(-x+1,-x,0)	(-0.577,0.577,0)
		(-x+1,-x+1,0)	(0.577,-0.577,0)
		(0,-x,1/2)	(1.155,0.577,0)
		(0,-x+1,1/2)	(1.155,0.577,0)
		(1,-x,1/2)	(-1.155,-0.577,0)
		(1,-x+1,1/2)	(-1.155,-0.577,0)
M2	g	(x,0,0)	(0,0,2)
		(x,1,0)	(0,0,0)
		(x+1,0,0)	(0,0,-2)
		(x+1,1,0)	(0,0,0)
		(x,x,1/2)	(0,0,2)
		(x,x+1,1/2)	(0,0,0)
		(x+1,x,1/2)	(0,0,0)
		(x+1,x+1,1/2)	(0,0,-2)
		(0,x,0)	(0,0,2)
		(0,x+1,0)	(0,0,-2)
		(1,x,0)	(0,0,0)
		(1,x+1,0)	(0,0,0)
		(-x,0,1/2)	(0,0,2)
		(-x,1,1/2)	(0,0,0)
		(-x+1,0,1/2)	(0,0,-2)
		(-x+1,1,1/2)	(0,0,0)
		(-x,-x,0)	(0,0,2)
		(-x,-x+1,0)	(0,0,0)
		(-x+1,-x,0)	(0,0,0)
		(-x+1,-x+1,0)	(0,0,-2)
		(0,-x,1/2)	(0,0,2)
		(0,-x+1,1/2)	(0,0,-2)
		(1,-x,1/2)	(0,0,0)
		(1,-x+1,1/2)	(0,0,0)
M2	g	(x,0,0)	(0,0,1)
		(x,1,0)	(0,0,-1)
		(x+1,0,0)	(0,0,1)

```
                    (x+1,1,0)          (0,0,-1)
                    (x,x,1/2)          (0,0,1)
                    (x,x+1,1/2)        (0,0,-1)
                    (x+1,x,1/2)        (0,0,-1)
                    (x+1,x+1,1/2)      (0,0,1)
                    (0,x,0)            (0,0,1)
                    (0,x+1,0)          (0,0,1)
                    (1,x,0)            (0,0,-1)
                    (1,x+1,0)          (0,0,-1)
                    (-x,0,1/2)         (0,0,1)
                    (-x,1,1/2)         (0,0,-1)
                    (-x+1,0,1/2)       (0,0,1)
                    (-x+1,1,1/2)       (0,0,-1)
                    (-x,-x,0)          (0,0,1)
                    (-x,-x+1,0)        (0,0,-1)
                    (-x+1,-x,0)        (0,0,-1)
                    (-x+1,-x+1,0)      (0,0,1)
                    (0,-x,1/2)         (0,0,1)
                    (0,-x+1,1/2)       (0,0,1)
                    (1,-x,1/2)         (0,0,-1)
                    (1,-x+1,1/2)       (0,0,-1)
*VALUE IRREP M1
*DISPLAY DISTORTION
Irrep (ML) Wyckoff Point              Projected Vectors
M1         b       (0,0,1/4)          (0,0,0)
                   (0,1,1/4)          (2.309,1.155,0)
                   (1,0,1/4)          (-1.155,-2.309,0)
                   (1,1,1/4)          (-1.155,1.155,0)
                   (0,0,3/4)          (0,0,0)
                   (0,1,3/4)          (-2.309,-1.155,0)
                   (1,0,3/4)          (1.155,2.309,0)
                   (1,1,3/4)          (1.155,-1.155,0)
M1         c       (1/3,2/3,1/4)      (1.155,2.309,0)
                   (1/3,5/3,1/4)      (1.155,-1.155,0)
                   (4/3,2/3,1/4)      (0,0,0)
                   (4/3,5/3,1/4)      (-2.309,-1.155,0)
                   (-1/3,1/3,3/4)     (-1.155,1.155,0)
                   (-1/3,4/3,3/4)     (-1.155,-2.309,0)
                   (2/3,1/3,3/4)      (2.309,1.155,0)
                   (2/3,4/3,3/4)      (0,0,0)
M1         f       (1/3,2/3,z)        (0,0,1)
                   (1/3,5/3,z)        (0,0,1)
                   (4/3,2/3,z)        (0,0,-3)
                   (4/3,5/3,z)        (0,0,1)
                   (-1/3,1/3,z+1/2)   (0,0,1)
```

```
                (-1/3,4/3,z+1/2)  (0,0,1)
                (2/3,1/3,z+1/2)   (0,0,1)
                (2/3,4/3,z+1/2)   (0,0,-3)
                (-1/3,-2/3,-z)    (0,0,-1)
                (-1/3,1/3,-z)     (0,0,-1)
                (2/3,-2/3,-z)     (0,0,3)
                (2/3,1/3,-z)      (0,0,-1)
                (1/3,-1/3,-z+1/2) (0,0,-1)
                (1/3,2/3,-z+1/2)  (0,0,-1)
                (4/3,-1/3,-z+1/2) (0,0,-1)
                (4/3,2/3,-z+1/2)  (0,0,3)
M1        f     (1/3,2/3,z)       (2,2,0)
                (1/3,5/3,z)       (0,-2,0)
                (4/3,2/3,z)       (0,0,0)
                (4/3,5/3,z)       (-2,0,0)
                (-1/3,1/3,z+1/2)  (0,2,0)
                (-1/3,4/3,z+1/2)  (-2,-2,0)
                (2/3,1/3,z+1/2)   (2,0,0)
                (2/3,4/3,z+1/2)   (0,0,0)
                (-1/3,-2/3,-z)    (0,-2,0)
                (-1/3,1/3,-z)     (-2,0,0)
                (2/3,-2/3,-z)     (0,0,0)
                (2/3,1/3,-z)      (2,2,0)
                (1/3,-1/3,-z+1/2) (2,0,0)
                (1/3,2/3,-z+1/2)  (0,2,0)
                (4/3,-1/3,-z+1/2) (-2,-2,0)
                (4/3,2/3,-z+1/2)  (0,0,0)
M1        f     (1/3,2/3,z)       (0,-2,0)
                (1/3,5/3,z)       (-2,0,0)
                (4/3,2/3,z)       (0,0,0)
                (4/3,5/3,z)       (2,2,0)
                (-1/3,1/3,z+1/2)  (2,0,0)
                (-1/3,4/3,z+1/2)  (0,2,0)
                (2/3,1/3,z+1/2)   (-2,-2,0)
                (2/3,4/3,z+1/2)   (0,0,0)
                (-1/3,-2/3,-z)    (2,2,0)
                (-1/3,1/3,-z)     (0,-2,0)
                (2/3,-2/3,-z)     (0,0,0)
                (2/3,1/3,-z)      (-2,0,0)
                (1/3,-1/3,-z+1/2) (0,2,0)
                (1/3,2/3,-z+1/2)  (-2,-2,0)
                (4/3,-1/3,-z+1/2) (2,0,0)
                (4/3,2/3,-z+1/2)  (0,0,0)
M1        g     (x,0,0)           (2,0,0)
                (x,1,0)           (0,0,0)
```

		(x+1,0,0)	(-2,0,0)
		(x+1,1,0)	(0,0,0)
		(x,x,1/2)	(2,2,0)
		(x,x+1,1/2)	(0,0,0)
		(x+1,x,1/2)	(0,0,0)
		(x+1,x+1,1/2)	(-2,-2,0)
		(0,x,0)	(0,2,0)
		(0,x+1,0)	(0,-2,0)
		(1,x,0)	(0,0,0)
		(1,x+1,0)	(0,0,0)
		(-x,0,1/2)	(-2,0,0)
		(-x,1,1/2)	(0,0,0)
		(-x+1,0,1/2)	(2,0,0)
		(-x+1,1,1/2)	(0,0,0)
		(-x,-x,0)	(-2,-2,0)
		(-x,-x+1,0)	(0,0,0)
		(-x+1,-x,0)	(0,0,0)
		(-x+1,-x+1,0)	(2,2,0)
		(0,-x,1/2)	(0,-2,0)
		(0,-x+1,1/2)	(0,2,0)
		(1,-x,1/2)	(0,0,0)
		(1,-x+1,1/2)	(0,0,0)
M1	g	(x,0,0)	(1,0,0)
		(x,1,0)	(-1,0,0)
		(x+1,0,0)	(1,0,0)
		(x+1,1,0)	(-1,0,0)
		(x,x,1/2)	(1,1,0)
		(x,x+1,1/2)	(-1,-1,0)
		(x+1,x,1/2)	(-1,-1,0)
		(x+1,x+1,1/2)	(1,1,0)
		(0,x,0)	(0,1,0)
		(0,x+1,0)	(0,1,0)
		(1,x,0)	(0,-1,0)
		(1,x+1,0)	(0,-1,0)
		(-x,0,1/2)	(-1,0,0)
		(-x,1,1/2)	(1,0,0)
		(-x+1,0,1/2)	(-1,0,0)
		(-x+1,1,1/2)	(1,0,0)
		(-x,-x,0)	(-1,-1,0)
		(-x,-x+1,0)	(1,1,0)
		(-x+1,-x,0)	(1,1,0)
		(-x+1,-x+1,0)	(-1,-1,0)
		(0,-x,1/2)	(0,-1,0)
		(0,-x+1,1/2)	(0,-1,0)
		(1,-x,1/2)	(0,1,0)

		(1,-x+1,1/2)	(0,1,0)
M1	g	(x,0,0)	(0,0,0)
		(x,1,0)	(1.155,2.309,0)
		(x+1,0,0)	(0,0,0)
		(x+1,1,0)	(-1.155,-2.309,0)
		(x,x,1/2)	(0,0,0)
		(x,x+1,1/2)	(1.155,-1.155,0)
		(x+1,x,1/2)	(-1.155,1.155,0)
		(x+1,x+1,1/2)	(0,0,0)
		(0,x,0)	(0,0,0)
		(0,x+1,0)	(0,0,0)
		(1,x,0)	(2.309,1.155,0)
		(1,x+1,0)	(-2.309,-1.155,0)
		(-x,0,1/2)	(0,0,0)
		(-x,1,1/2)	(-1.155,-2.309,0)
		(-x+1,0,1/2)	(0,0,0)
		(-x+1,1,1/2)	(1.155,2.309,0)
		(-x,-x,0)	(0,0,0)
		(-x,-x+1,0)	(-1.155,1.155,0)
		(-x+1,-x,0)	(1.155,-1.155,0)
		(-x+1,-x+1,0)	(0,0,0)
		(0,-x,1/2)	(0,0,0)
		(0,-x+1,1/2)	(0,0,0)
		(1,-x,1/2)	(-2.309,-1.155,0)
		(1,-x+1,1/2)	(2.309,1.155,0)
M1	g	(x,0,0)	(0,0,0)
		(x,1,0)	(0,0,2)
		(x+1,0,0)	(0,0,0)
		(x+1,1,0)	(0,0,-2)
		(x,x,1/2)	(0,0,0)
		(x,x+1,1/2)	(0,0,-2)
		(x+1,x,1/2)	(0,0,2)
		(x+1,x+1,1/2)	(0,0,0)
		(0,x,0)	(0,0,0)
		(0,x+1,0)	(0,0,0)
		(1,x,0)	(0,0,-2)
		(1,x+1,0)	(0,0,2)
		(-x,0,1/2)	(0,0,0)
		(-x,1,1/2)	(0,0,2)
		(-x+1,0,1/2)	(0,0,0)
		(-x+1,1,1/2)	(0,0,-2)
		(-x,-x,0)	(0,0,0)
		(-x,-x+1,0)	(0,0,-2)
		(-x+1,-x,0)	(0,0,2)
		(-x+1,-x+1,0)	(0,0,0)

```
                    (0,-x,1/2)          (0,0,0)
                    (0,-x+1,1/2)        (0,0,0)
                    (1,-x,1/2)          (0,0,-2)
                    (1,-x+1,1/2)        (0,0,2)
*VALUE IRREP GM2
*VALUE DIRECTION P1
*DISPLAY DISTORTION
Irrep (ML) Wyckoff Point               Projected Vectors
GM2        b       (0,0,1/4)           (0,0,1)
                   (0,0,3/4)           (0,0,1)
GM2        c       (1/3,2/3,1/4)       (0,0,1)
                   (-1/3,1/3,3/4)      (0,0,1)
GM2        f       (1/3,2/3,z)         (0,0,1)
                   (-1/3,1/3,z+1/2)    (0,0,1)
                   (-1/3,-2/3,-z)      (0,0,1)
                   (1/3,-1/3,-z+1/2)   (0,0,1)
GM2        g       (x,0,0)             (0.577,1.155,0)
                   (x,x,1/2)           (-0.577,0.577,0)
                   (0,x,0)             (-1.155,-0.577,0)
                   (-x,0,1/2)          (-0.577,-1.155,0)
                   (-x,-x,0)           (0.577,-0.577,0)
                   (0,-x,1/2)          (1.155,0.577,0)
GM2        g       (x,0,0)             (0,0,1)
                   (x,x,1/2)           (0,0,1)
                   (0,x,0)             (0,0,1)
                   (-x,0,1/2)          (0,0,1)
                   (-x,-x,0)           (0,0,1)
                   (0,-x,1/2)          (0,0,1)
*VALUE IRREP GM1
*DISPLAY DISTORTION
Irrep (ML) Wyckoff Point               Projected Vectors
GM1        f       (1/3,2/3,z)         (0,0,1)
                   (-1/3,1/3,z+1/2)    (0,0,1)
                   (-1/3,-2/3,-z)      (0,0,-1)
                   (1/3,-1/3,-z+1/2)   (0,0,-1)
GM1        g       (x,0,0)             (1,0,0)
                   (x,x,1/2)           (1,1,0)
                   (0,x,0)             (0,1,0)
                   (-x,0,1/2)          (-1,0,0)
                   (-x,-x,0)           (-1,-1,0)
                   (0,-x,1/2)          (0,-1,0)
*
```

We see that there are 12 M_2 distortions, 9 M_1 distortions, 5 Γ_2 distortions, and 2 Γ_1 distortions. The net distortion that takes place in the phase transition is some linear combination of these distortions.

Note that four of the Γ_2 distortions are simply translations of the atoms along the c axis. A linear combination of these will generally result in a net electric dipole moment in the unit cell, causing a spontaneous polarization field characteristic of a ferroelectric phase.

The two Γ_1 distortions preserve the symmetry of the paraelectric phase. They simply change the values of the z parameter of the Al atoms in the f position and the x parameter of the O atoms in the g position.

Finally, we obtain invariant polynomials up to fourth degree in the order parameters. We include polynomials which contain contributions from more than a single irrep.

```
*VALUE IRREP M2 M1 GM1 GM2
*VALUE DIRECTION P3 P3 P1 P1
*DISPLAY INVARIANT
Irrep (ML)            Deg Invariants
M2P3,M1P3,GM2P1,GM1P1 1   n4
                      2   n4^2
                      2   n1^2
                      2   n2^2
                      2   n3^2
                      3   n4^3
                      3   n1^2n4
                      3   n2^2n4
                      3   n3^2n4
                      3   n1^2n2
                      3   n1n2n3
                      3   n2^3
                      4   n4^4
                      4   n1^2n4^2
                      4   n1^4
                      4   n2^2n4^2
                      4   n1^2n2^2
                      4   n2^4
                      4   n3^2n4^2
                      4   n1^2n3^2
                      4   n2^2n3^2
                      4   n3^4
                      4   n1^2n2n4
                      4   n1n2n3n4
                      4   n2^3n4
                      4   n1^3n3
                      4   n1n2^2n3
*
```

In the above results, $\eta_1, \eta_2, \eta_3, \eta_4$ refer to the order parameter (η_1, η_1, η_1) for M_2 (direction P3), the order parameter (η_2, η_2, η_2) for M_1 (direction P3), the order parameter (η_3) for Γ_2, and the order parameter (η_4) for Γ_1, respectively. The form of the Landau free energy expanded in powers of the order parameters is simply a linear combination of the above polynomials.

This is the end of this case study. You may exit the program:

```
*QUIT
```

Case Study 3: Reconstructive Phase Transition in NaCl

At ≈ 30 GPa, NaCl undergoes a phase transition from its usual fcc structure (space group $G_1 = Fm\bar{3}m$) to a CsCl-like structure (space group $G_2 = Pm\bar{3}m$). This phase transition takes place via an intermediate unstable structure with symmetry G which is a subgroup of both G_1 and G_2. The crystalline structure evolves from G_1 to G_2 along some path with symmetry G.

Group theoretically, we treat G_1 like the parent phase. At the transition, distortions (strains and atomic displacements) appear which lower the symmetry to G. These distortions evolve along the path from G_1 to G_2 until they reach some particular values where the symmetry suddenly increases to G_2.

The distortions that take the crystal from G_1 to G can, as usual, be decomposed into parts that belong to different irreps. The goal of this case study is to obtain this decomposition.

First, we will gather some general information which will save us time and effort later. Strains are rank-two symmetric tensors. They always belong to irreps at the Γ point. We find which irreps are associated with strains:

```
*VALUE PARENT 225
*VALUE RANK [12]
*VALUE KPOINT GM
*SHOW MACROSCOPIC
*SHOW IRREP
*DISPLAY DISTORTION
Irrep (ML)  Basis Functions
GM1+        xx+yy+zz
GM3+        xx+yy-2zz,1.732xx-1.732yy
GM5+        xy,yz,xz
*
```

We see that only the irreps Γ_1^+, Γ_3^+, Γ_5^+ are associated with strains. Using the notation $e = (x^2, y^2, z^2, xy, yz, zx)$ for the strain tensor elements, we see that the strains associated with these irreps are

$$\begin{aligned}
\Gamma_1^+ :&\quad (1,1,1,0,0,0),\\
\Gamma_3^+ :&\quad (1,1,-2,0,0,0),\ (\sqrt{3},-\sqrt{3},0,0,0,0),\\
\Gamma_5^+ :&\quad (0,0,0,1,0,0),\ (0,0,0,0,1,0),\ (0,0,0,0,0,1).
\end{aligned}$$

Next we find which irreps are associated with atomic displacements. The Na and Cl atoms are at Wyckoff positions (a) and (b), respectively, in $G_1 = Fm\bar{3}m$. We first look at the Γ irreps.

```
*VALUE WYCKOFF A B
*SHOW WYCKOFF
*SHOW MICROSCOPIC VECTOR
```

```
*DISPLAY DISTORTION
Irrep (ML) Wyckoff Point         Projected Vectors
GM4-       a       (0,0,0)       (1,0,0), (0,1,0), (0,0,1)
GM4-       b       (1/2,1/2,1/2) (1,0,0), (0,1,0), (0,0,1)
*
```

Only the Γ_4^- irrep allows atomic displacements Each site has a point-group symmetry consisting of all space-group operators that leave that site fixed. We find the point-group irreps for the Wyckoff (a) and (b) sites that allow atomic displacements.

```
*VALUE IRREP GM4-
*SHOW FREQUENCY
*DISPLAY IRREP
Irrep (ML) Frequency
GM4-       a 1 T1u
           b 1 T1u
*
```

In both cases, atomic displacements are only allowed by the point group irrep T_{1u}. A space-group irrep of $Fm\bar{3}m$ will allow atomic displacements if and only if its decomposition, when restricted to elements of a site point group, contains the point-group irrep T_{1u} (nonzero subduction frequency). We make a list of such space-group irreps. We restrict the list to irreps at $\mathbf{k}$ points of symmetry, since these are the only ones we are likely to encounter in this case study. Note that we have edited the following output from ISOTROPY. We have removed space-group irreps which do not contain T_{1u}.

```
*CANCEL VALUE IRREP
*VALUE KDEGREE 0
*DISPLAY IRREP
Irrep (ML) Frequency
GM4-       a 1 T1u
           b 1 T1u
L1+        a 1 A1g, 1 T2g
           b 1 A2u, 1 T1u
L3+        a 1 Eg, 1 T2g, 1 T1g
           b 1 Eu, 1 T2u, 1 T1u
L2-        a 1 A2u, 1 T1u
           b 1 A1g, 1 T2g
L3-        a 1 Eu, 1 T2u, 1 T1u
           b 1 Eg, 1 T2g, 1 T1g
X3-        a 1 T1u
           b 1 T1u
X5-        a 1 T2u, 1 T1u
           b 1 T2u, 1 T1u
W1         a 1 A1g, 1 Eg, 1 T2u
           b 1 A2g, 1 Eg, 1 T1u
W2         a 1 A2g, 1 Eg, 1 T1u
```

```
           b 1 A1g, 1 Eg, 1 T2u
W5         a 1 T2g, 1 T1g, 1 T2u, 1 T1u
           b 1 T2g, 1 T1g, 1 T2u, 1 T1u
*
```

We see that only irreps Γ_4^-, L_1^+, L_3^+, L_2^-, L_3^-, X_3^-, X_5^-, W_1, W_2, W_5 allow atomic displacements in NaCl.

$R\bar{3}m$ Path

Buerger proposed a path with space group symmetry $G = R\bar{3}m$. In terms of the orthogonal lattice vectors of G_1, the hexagonal lattice vectors of G are given by

$$(\tfrac{1}{2}, 0, \tfrac{1}{2}), (0, \tfrac{1}{2}, \tfrac{\bar{1}}{2}), (\bar{1}, 1, 1).$$

In the hexagonal unit cell of $R\bar{3}m$, the Na atoms are at the Wyckoff (a) position, (0,0,0), and the Cl atoms are at the Wyckoff (b) position, $(0, 0, \frac{1}{2})$. Since there is a Na atom at the origin in both G_1 and G, we can choose the origins of both G_1 and G to be at the same point. We first find the irreps and order parameters associated with the transition $G_1 \to G$.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 225
*VALUE SUBGROUP 166
*VALUE BASIS 1/2,0,1/2 0,1/2,-1/2 -1,1,1
*VALUE ORIGIN 0,0,0
*DISPLAY DIRECTION
Irrep (ML) Dir
GM1+       (a)
GM5+       (a,-a,a)
*
```

There are two irreps involved, Γ_1^+ and Γ_5^+. They both allow strain. Neither one allows atomic displacements. There are no atomic displacements with respect to the unit cell in the transition along the $R\bar{3}m$ path, only strain. The strains are

$$\begin{aligned} \Gamma_1^+ : &\quad (a, a, a, 0, 0, 0), \\ \Gamma_5^+ : &\quad (0, 0, 0, a, \bar{a}, a). \end{aligned}$$

$P2_1/m$ path

This is a modification of the $R\bar{3}m$ path where more distortion is allowed along the path. In terms of the orthogonal lattice vectors of G_1, the monoclinic lattice vectors of G are given by

$$(\tfrac{1}{2}, 1, \tfrac{\bar{1}}{2}), (\tfrac{\bar{1}}{2}, 0, \tfrac{\bar{1}}{2}), (\tfrac{\bar{1}}{2}, 0, \tfrac{1}{2}).$$

In the monoclinic unit cell of $P2_1/m$, the Na atoms are at the Wyckoff (e) position, $(\frac{1}{4}, \frac{1}{4}, 0)$, and the Cl atoms are at the Wyckoff (e) position, $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$. The orthogonal coordinates of the Na atom are

$$\tfrac{1}{4}(\tfrac{1}{2}, 1, \tfrac{\bar{1}}{2}) + \tfrac{1}{4}(\tfrac{\bar{1}}{2}, 0, \tfrac{\bar{1}}{2}) = (0, \tfrac{1}{4}, \tfrac{\bar{1}}{4}),$$

so the origin of G with respect to G_1 can be chosen to be at $(0, \frac{\bar{1}}{4}, \frac{1}{4})$. We find the irreps and order parameters associated with the transition to $P2_1/m$.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 225
*VALUE SUBGROUP 11
*VALUE BASIS 1/2,1,-1/2 -1/2,0,-1/2 -1/2,0,1/2
*VALUE ORIGIN 0,-1/4,1/4
*DISPLAY DIRECTION
Irrep (ML) Dir
GM1+       (a)
GM3+       (a,-1.732a)
GM4+       (a,0,a)
GM5+       (a,-a,b)
X2-        (a,0,0)
X3-        (a,0,0)
X5-        (a,0,0,0,0,0)
*
```

The irreps Γ_1^+, Γ_3^+, Γ_5^+ allow strain. We obtain

$$\begin{aligned}
\Gamma_1^+ &: \quad (a, a, a, 0, 0, 0), \\
\Gamma_3^+ &: \quad a(1, 1, -2, 0, 0, 0) - \sqrt{3}a(\sqrt{3}, -\sqrt{3}, 0, 0, 0, 0) = (2\bar{a}, 4a, 2\bar{a}, 0, 0, 0), \\
\Gamma_5^+ &: \quad (0, 0, 0, a, \bar{a}, b).
\end{aligned}$$

The irreps X_3^- and X_5^- allow atomic displacements. To find the displacements, we need to first find the order parameters in the data base. We edit the output of ISOTROPY below, leaving only the line containing the order parameter we are looking for.

```
*CANCEL VALUE SUBGROUP
*SHOW IRREP
*SHOW SUBGROUP
*SHOW DIRECTION VECTOR
*VALUE IRREP X3-
*DISPLAY ISOTROPY
Irrep (ML) Subgroup     Dir
X3-        129 P4/nmm   P1  (a,0,0)
*VALUE IRREP X5-
*DISPLAY ISOTROPY
```

```
Irrep (ML) Subgroup      Dir
X5-        59 Pmmn       P1  (a,0,0,0,0,0)
*
```

We see that the order parameter for X_3^- and X_5^- are both labeled P1 in the data base. We now obtain the atomic displacements.

```
*VALUE WYCKOFF A B
*SHOW MICROSCOPIC VECTOR
*SHOW WYCKOFF
*VALUE IRREP X3-
*VALUE DIRECTION P1
*DISPLAY DISTORTION
Irrep (ML) Dir Wyckoff Point         Projected Vectors
X3-        P1  a       (0,0,0)       (0,1,0)
                       (0,1/2,1/2)   (0,-1,0)
X3-        P1  b       (1/2,1/2,1/2) (0,1,0)
                       (1/2,1,1)     (0,-1,0)
*VALUE IRREP X5-
*DISPLAY DISTORTION
Irrep (ML) Dir Wyckoff Point         Projected Vectors
X5-        P1  a       (0,0,0)       (1,0,-1)
                       (0,1/2,1/2)   (-1,0,1)
X5-        P1  b       (1/2,1/2,1/2) (1,0,-1)
                       (1/2,1,1)     (-1,0,1)
*
```

$Pmmn$ Path

Watanabe proposed a path with space group symmetry $G = Pmmn$. In terms of the orthogonal lattice vectors of G_1, the orthorhombic lattice vectors of G are given by

$$(1,0,0), (0, \tfrac{1}{2}, \tfrac{\bar{1}}{2}), (0, \tfrac{1}{2}, \tfrac{1}{2}).$$

In the orthorhombic unit cell of $Pmmn$, the Na atoms are at the Wyckoff (a) position, $(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$, and the Cl atoms are at the Wyckoff (b) position, $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$. The orthogonal coordinates of the Na atom are

$$\tfrac{1}{4}(1,0,0) + \tfrac{1}{4}(0, \tfrac{1}{2}, \tfrac{\bar{1}}{2}) + \tfrac{3}{4}(0, \tfrac{1}{2}, \tfrac{1}{2}) = (\tfrac{1}{4}, \tfrac{1}{2}, \tfrac{1}{4}),$$

so the origin of G with respect to G_1 can be chosen to be at $(\frac{\bar{1}}{4}, \frac{\bar{1}}{2}, \frac{\bar{1}}{4})$. We find the irreps and order parameters associated with the transition to $Pmmn$. Note that the atomic positions in $Pmmn$ are given for the space group setting with origin choice 2, which is the default setting in ISOTROPY.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 225
```

```
*VALUE SUBGROUP 59
*VALUE BASIS 1,0,0 0,1/2,-1/2 0,1/2,1/2
*VALUE ORIGIN -1/4,-1/2,-1/4
*DISPLAY DIRECTION
Irrep (ML) Dir
GM1+       (a)
GM3+       (a,1.732a)
GM5+       (0,a,0)
X5-        (0,0,0,0,0,a)
*
```

The irreps Γ_1^+, Γ_3^+, Γ_5^+ allow strain. We obtain

$$\begin{aligned}
\Gamma_1^+ :&\quad (a,a,a,0,0,0),\\
\Gamma_3^+ :&\quad a(1,1,-2,0,0,0)+\sqrt{3}a(\sqrt{3},-\sqrt{3},0,0,0,0)=(4a,2\bar{a},2\bar{a},0,0,0),\\
\Gamma_5^+ :&\quad (0,0,0,0,a,0).
\end{aligned}$$

The irrep X_5^- allows atomic displacements. To find the displacements, we need to first find the order parameter in the data base. Since the order parameter only contains one variable a, we edit the following output of ISOTROPY and show only those order parameters that contain one variable.

```
*CANCEL VALUE SUBGROUP
*SHOW IRREP
*SHOW SUBGROUP
*SHOW DIRECTION VECTOR
*VALUE IRREP X5-
*DISPLAY ISOTROPY
Irrep (ML) Subgroup      Dir
X5-        59 Pmmn       P1  (a,0,0,0,0,0)
X5-        63 Cmcm       P2  (a,a,0,0,0,0)
X5-        155 R32       P6  (a,0,a,0,a,0)
X5-        160 R3m       P7  (0,a,0,a,0,a)
X5-        129 P4/nmm    P9  (a,a,a,-a,0,0)
X5-        136 P4_2/mnm  P10 (a,a,0,0,a,-a)
X5-        198 P2_13     P11 (a,a,a,a,a,a)
*
```

We do not find $(0,0,0,0,0,a)$ in the above output. We must look at domains. Let us first try the direction P1. We edit the following output of ISOTROPY, showing only the line with the order parameter we are looking for.

```
*VALUE DIRECTION P1
*SHOW DOMAINS
*DISPLAY ISOTROPY
Irrep (ML) Domain Subgroup Dir
```

```
X5-        10     59 Pmmn  P1  (0,0,0,0,0,a)
*
```

We see that the order parameter belongs to the 10th domain of P1. We now obtain the atomic displacements.

```
*CANCEL SHOW DOMAINS
*VALUE WYCKOFF A B
*SHOW MICROSCOPIC VECTOR
*SHOW WYCKOFF
*VALUE IRREP X5-
*VALUE DOMAIN 10
*DISPLAY DISTORTION
Irrep (ML) Dir Domain Wyckoff Point         Projected Vectors
X5-        P1  10     a       (0,0,0)       (0,1,1)
                             (-1/2,1/2,0)  (0,-1,-1)
X5-        P1  10     b       (1/2,1/2,1/2) (0,1,1)
                             (0,1,1/2)     (0,-1,-1)
*
```

$C2$ Path

This path is not as energetically favorable as those proposed by Buerger and Watanabe. We include it as an example of a more complex situation. In terms of the orthogonal lattice vectors of G_1, the monoclinic lattice vectors of $G = C2$ are given by

$$(\tfrac{1}{2}, \bar{1}, \bar{\tfrac{1}{2}}), (\tfrac{1}{2}, 0, \tfrac{1}{2}), (\bar{\tfrac{1}{2}}, \bar{1}, \tfrac{1}{2}).$$

In the monoclinic unit cell of $C2$, the Na atoms are at the Wyckoff (a) position $(0, 0, 0)$ and the Wyckoff (b) position $(0, \frac{1}{2}, \frac{1}{2})$, and the Cl atoms are at the Wyckoff (c) position $(\frac{1}{4}, \frac{1}{2}, \frac{3}{4})$. Since there is a Na atom at the origin in both G_1 and G, we can choose the origins of both G_1 and G to be at the same point. We find the irreps and order parameters associated with the transition to $C2$. Note that the lattice vectors and atomic positions in $C2$ are given for the space group setting with unique axis b and cell choice 1, which is the default setting in ISOTROPY.

```
*CANCEL VALUE ALL
*CANCEL SHOW ALL
*VALUE PARENT 225
*VALUE SUBGROUP 5
*VALUE BASIS 1/2,-1,-1/2 1/2,0,1/2 -1/2,-1,1/2
*VALUE ORIGIN 0,0,0
*DISPLAY DIRECTION
Irrep (ML) Dir
GM1+       (a)
GM3+       (a,-1.732a)
GM4+       (a,0,a)
GM5+       (a,-a,b)
```

```
GM1-       (a)
GM3-       (a,0.577a)
GM4-       (a,0,a)
GM5-       (a,-a,b)
L1+        (0,a,0,0)
L3+        (0,0,a,-0.268a,0,0,0,0)
L1-        (0,a,0,0)
L3-        (0,0,a,3.732a,0,0,0,0)
*
```

The irreps Γ_1^+, Γ_3^+, Γ_5^+ allow strain. We obtain

$$\begin{aligned}
\Gamma_1^+ :&\quad (a,a,a,0,0,0),\\
\Gamma_3^+ :&\quad a(1,1,-2,0,0,0) - \sqrt{3}a(\sqrt{3},-\sqrt{3},0,0,0,0) = (2\bar{a},4a,2\bar{a},0,0,0),\\
\Gamma_5^+ :&\quad (0,0,0,a,\bar{a},b).
\end{aligned}$$

The irreps Γ_4^-, L_1^+, L_3^+, L_3^- allow atomic displacements. To find the displacements, we need to first find the order parameter in the data base. Since each of these order parameters only contains one variable a, we edit the following output of ISOTROPY and show only those order parameters that contain one variable. First, we consider Γ_4^-.

```
*CANCEL VALUE SUBGROUP
*SHOW IRREP
*SHOW SUBGROUP
*SHOW DIRECTION VECTOR
*VALUE IRREP GM4-
*DISPLAY ISOTROPY
Irrep (ML) Subgroup Dir
GM4-       107 I4mm P1  (a,0,0)
GM4-       44 Imm2  P2  (a,a,0)
GM4-       160 R3m  P3  (a,a,a)
*
```

The order parameter $(a,0,a)$ is not in the list. As before, we look at domains. We first try P2, since it looks similar to $(a,0,a)$. We edit the following output of ISOTROPY, showing only the line with the order parameter we are looking for.

```
*VALUE DIRECTION P2
*SHOW DOMAINS
*DISPLAY ISOTROPY
Irrep (ML) Domain Subgroup Dir
GM4-       5      44 Imm2  P2  (a,0,a)
*
```

The order parameter belongs to the 5th domain of P5. Next we consider L_1^+.

```
*CANCEL SHOW DOMAINS
```

```
*CANCEL VALUE DIRECTION
*VALUE IRREP L1+
*DISPLAY ISOTROPY
Irrep (ML) Subgroup  Dir
L1+        166 R-3m  P1  (a,0,0,0)
L1+        65 Cmmm   P3  (a,a,0,0)
L1+        225 Fm-3m P11 (a,a,a,a)
L1+        227 Fd-3m P12 (a,a,a,-a)
*VALUE DIRECTION P1
*SHOW DOMAINS
*DISPLAY ISOTROPY
Irrep (ML) Domain Subgroup Dir
L1+        4      166 R-3m P1  (0,a,0,0)
*
```

The order parameter belongs to the 4th domain of P1. Next we consider L_3^+.

```
*CANCEL SHOW DOMAINS
*CANCEL VALUE DIRECTION
*VALUE IRREP L3+
*DISPLAY ISOTROPY
Irrep (ML) Subgroup     Dir
L3+        12 C2/m      P2  (a,a,0,0,0,0,0,0)
L3+        15 C2/c      P7  (a,-a,0,0,0,0,0,0)
L3+        65 Cmmm      P8  (a,a,a,a,0,0,0,0)
L3+        67 Cmma      P14 (a,-a,a,-a,0,0,0,0)
L3+        139 I4/mmm   P15 (a,a,a,a,a,a,a,a)
L3+        141 I4_1/amd P16 (a,a,a,a,a,a,-a,-a)
L3+        140 I4/mcm   P19 (a,-a,a,-a,a,-a,a,-a)
L3+        142 I4_1/acd P20 (a,-a,a,-a,a,-a,-a,a)
L3+        167 R-3c     P21 (a,3.732a,3.732a,a,2.732a,-2.732a,0,0)
L3+        166 R-3m     P22 (a,a,0,0,1.366a,-0.366a,0.366a,-1.366a)
*VALUE DIRECTION P2
*SHOW DOMAINS
*DISPLAY ISOTROPY
Irrep (ML) Domain Subgroup Dir
L3+        20     12 C2/m  P2  (0,0,1.366a,-0.366a,0,0,0,0)
*
```

We find for the 20th domain,
$(0, 0, 1.366a, -0.366a, 0, 0, 0, 0) = 1.366(0, 0, a, -0.268a, 0, 0, 0, 0)$, which is same as the one we are looking for, to within an arbitrary multiplier. Next we consider L_3^-.

```
*CANCEL SHOW DOMAINS
*CANCEL VALUE DIRECTION
*VALUE IRREP L3-
*DISPLAY ISOTROPY
```

```
Irrep (ML) Subgroup     Dir
L3-        12 C2/m      P2  (a,a,0,0,0,0,0,0)
L3-        15 C2/c      P7  (a,-a,0,0,0,0,0,0)
L3-        65 Cmmm      P8  (a,a,a,a,0,0,0,0)
L3-        67 Cmma      P14 (a,-a,a,-a,0,0,0,0)
L3-        139 I4/mmm   P15 (a,a,a,a,a,a,a,a)
L3-        141 I4_1/amd P16 (a,a,a,a,a,a,-a,-a)
L3-        140 I4/mcm   P19 (a,-a,a,-a,a,-a,a,-a)
L3-        142 I4_1/acd P20 (a,-a,a,-a,a,-a,-a,a)
L3-        167 R-3c     P21 (a,3.732a,3.732a,a,2.732a,-2.732a,0,0)
L3-        166 R-3m     P22 (a,a,0,0,1.366a,-0.366a,0.366a,-1.366a)
*VALUE DIRECTION P2
*SHOW DOMAINS
*DISPLAY ISOTROPY
Irrep (ML) Domain Subgroup Dir
L3-        1      12 C2/m  P2  (a,a,0,0,0,0,0,0)
           2      12 C2/m      (0,0,0,0,a,a,0,0)
           3      12 C2/m      (0,0,0,0,0,0,a,a)
           4      12 C2/m      (0,0,a,a,0,0,0,0)
           5      12 C2/m      (-1.366a,0.366a,0,0,0,0,0,0)
           6      12 C2/m      (0,0,0,0,-1.366a,0.366a,0,0)
           7      12 C2/m      (0,0,0,0,0,0,-1.366a,0.366a)
           8      12 C2/m      (0,0,-1.366a,0.366a,0,0,0,0)
           9      12 C2/m      (0.366a,-1.366a,0,0,0,0,0,0)
           10     12 C2/m      (0,0,0,0,0.366a,-1.366a,0,0)
           11     12 C2/m      (0,0,0,0,0,0,0.366a,-1.366a)
           12     12 C2/m      (0,0,0.366a,-1.366a,0,0,0,0)
           13     12 C2/m      (-a,-a,0,0,0,0,0,0)
           14     12 C2/m      (0,0,0,0,-a,-a,0,0)
           15     12 C2/m      (0,0,0,0,0,0,-a,-a)
           16     12 C2/m      (0,0,-a,-a,0,0,0,0)
           17     12 C2/m      (1.366a,-0.366a,0,0,0,0,0,0)
           18     12 C2/m      (0,0,0,0,1.366a,-0.366a,0,0)
           19     12 C2/m      (0,0,0,0,0,0,1.366a,-0.366a)
           20     12 C2/m      (0,0,1.366a,-0.366a,0,0,0,0)
           21     12 C2/m      (-0.366a,1.366a,0,0,0,0,0,0)
           22     12 C2/m      (0,0,0,0,-0.366a,1.366a,0,0)
           23     12 C2/m      (0,0,0,0,0,0,-0.366a,1.366a)
           24     12 C2/m      (0,0,-0.366a,1.366a,0,0,0,0)
*VALUE DIRECTION P7
*DISPLAY ISOTROPY
Irrep (ML) Domain Subgroup Dir
L3-        8      15 C2/c  P7  (0,0,0.366a,1.366a,0,0,0,0)
*
```

We could not find the order parameter among the domains of P2. Instead, we found it in the 8th domain of P7. Now we can find the atomic displacements.

```
*CANCEL SHOW DOMAINS
*VALUE WYCKOFF A B
*SHOW MICROSCOPIC VECTOR
*SHOW WYCKOFF
*VALUE IRREP GM4-
*VALUE DIRECTION P2
*VALUE DOMAIN 5
*DISPLAY DISTORTION
Irrep (ML) Dir Domain Wyckoff Point         Projected Vectors
GM4-       P2  5      a       (0,0,0)       (1,0,1)
GM4-       P2  5      b       (1/2,1/2,1/2) (1,0,1)
*VALUE IRREP L1+
*VALUE DIRECTION P1
*VALUE DOMAIN 4
*DISPLAY DISTORTION
Irrep (ML) Dir Domain Wyckoff Point           Projected Vectors
L1+        P1  4      b       (1/2,1/2,1/2)   (-1,-1,1)
                             (-1/2,-1/2,3/2) (1,1,-1)
*VALUE IRREP L3+
*VALUE DIRECTION P2
*VALUE DOMAIN 20
*DISPLAY DISTORTION
Irrep (ML) Dir Domain Wyckoff Point         Projected Vectors
L3+        P2  20     b       (1/2,1/2,1/2) (-0.732,1.464,0.732)
                             (0,0,1/2)     (0.732,-1.464,-0.732)
*VALUE IRREP L3-
*VALUE DIRECTION P7
*VALUE DOMAIN 8
*DISPLAY DISTORTION
Irrep (ML) Dir Domain Wyckoff Point         Projected Vectors
L3-        P7  8      a       (0,0,0)       (1.268,0,1.268)
                             (-1/2,-1/2,0) (-1.268,0,-1.268)
*
```

This is the end of this case study. You may exit the program:

```
*QUIT
```

Case Study 4: Spin Reorientation Transitions in $FePO_4$ and Fe_3O_4
Contribution by Christopher J. Howard, University of Newcastle, Australia

This case study concerns the application of ISOTROPY to examine the magnetic structures and magnetic phase transitions in iron phosphate, $FePO_4$, and hematite, α-Fe_2O_3. Both these compounds crystallize in the trigonal system.

Below about 950 K, hematite is antiferromagnetic (actually, weakly ferromagnetic), and at room temperature the magnetic moments are thought to lie, at least approximately, in the "basal" plane, *i.e.*, the plane perpendicular to the three-fold axis. Within a given plane, the moments on the Fe^{3+} are parallel, but essentially antiparallel to moments in adjacent planes. A spin reorientation, known as the Morin transition [F. J. Morin, *Phys. Rev.* **78**, 819–820 (1950)] occurs at about 265 K. Below this temperature the moments are perpendicular to the basal plane.

Iron phosphate is not magnetically ordered at room temperature, but at 24 K, it becomes antiferromagnetic with moments lying in the basal plane, and at 17 K, it then shows a spin reorientation akin to the Morin transition. Below 17 K, the moments are perpendicular to the basal plane.

First we consider the case of $FePO_4$. The space group for the room temperature structure is No. 152 $P3_121$ and the magnetic Fe^{3+} ion is at Wyckoff position $3a$. At the onset of magnetic ordering, the unit cell is doubled along the direction of the three-fold axis [Battle *et al.*, *J, Phys. C* **15**, L919-L924 (1982)], so we look for irreps at $\mathbf{k} = 0, 0, \frac{1}{2}$.

```
*VALUE PARENT 152
*SHOW KPOINT
*DISPLAY KPOINT
    k vector
GM  (0,0,0)
DT  (0,0,a)
LD  (a,a,0)
SM  (a,0,0)
A   (0,0,1/2)
H   (1/3,1/3,1/2)
K   (1/3,1/3,0)
L   (1/2,0,1/2)
M   (1/2,0,0)
P   (1/3,1/3,a)
Q   (a,a,1/2)
R   (a,0,1/2)
U   (1/2,0,a)
B   (a,b,0)
C   (a,a,b)
D   (a,0,b)
E   (a,b,1/2)
GP  (a,b,g)
```

*

From the above, we identify $\mathbf{k} = 0, 0, \frac{1}{2}$ as the A-point of the Brillouin zone. Accordingly, we look for the magnetic ordering induced by irreps at the A-point. Note that magnetic moment is an axial or pseudo vector.

```
*CANCEL SHOW KPOINT
*VALUE KPOINT A
*VALUE WYCKOFF A
*SHOW IRREP
*SHOW MICROSCOPIC VECTOR PSEUDO
*DISPLAY DISTORTION
Irrep (ML) Point     Projected Pseudo Vectors
A1         (x,0,1/3) (1,0,0)
           (x,0,4/3) (-1,0,0)
           (0,x,2/3) (0,-1,0)
           (0,x,5/3) (0,1,0)
           (-x,-x,1) (-1,-1,0)
           (-x,-x,2) (1,1,0)
A2         (x,0,1/3) (0.577,1.155,0)
           (x,0,4/3) (-0.577,-1.155,0)
           (0,x,2/3) (1.155,0.577,0)
           (0,x,5/3) (-1.155,-0.577,0)
           (-x,-x,1) (0.577,-0.577,0)
           (-x,-x,2) (-0.577,0.577,0)
A2         (x,0,1/3) (0,0,1)
           (x,0,4/3) (0,0,-1)
           (0,x,2/3) (0,0,-1)
           (0,x,5/3) (0,0,1)
           (-x,-x,1) (0,0,1)
           (-x,-x,2) (0,0,-1)
A3         (x,0,1/3) (1,0,0), (0,0,0)
           (x,0,4/3) (-1,0,0), (0,0,0)
           (0,x,2/3) (0,0.500,0), (0,-0.866,0)
           (0,x,5/3) (0,-0.500,0), (0,0.866,0)
           (-x,-x,1) (0.500,0.500,0), (0.866,0.866,0)
           (-x,-x,2) (-0.500,-0.500,0), (-0.866,-0.866,0)
A3         (x,0,1/3) (0,0,0), (0.577,1.155,0)
           (x,0,4/3) (0,0,0), (-0.577,-1.155,0)
           (0,x,2/3) (-1,-0.500,0), (-0.577,-0.289,0)
           (0,x,5/3) (1,0.500,0), (0.577,0.289,0)
           (-x,-x,1) (0.500,-0.500,0), (-0.289,0.289,0)
           (-x,-x,2) (-0.500,0.500,0), (0.289,-0.289,0)
A3         (x,0,1/3) (0,0,0), (0,0,1)
           (x,0,4/3) (0,0,0), (0,0,-1)
           (0,x,2/3) (0,0,0.866), (0,0,0.500)
```

```
(0,x,5/3) (0,0,-0.866), (0,0,-0.500)
(-x,-x,1) (0,0,0.866), (0,0,-0.500)
(-x,-x,2) (0,0,-0.866), (0,0,0.500)
```

*

We examine the magnetic ordering associated with each of the irreps shown above. The magnetic structures are best understood by sorting the "projected pseudo vectors" (*i.e.*, magnetic moments) in order of increasing z coordinate, *i.e.*, $z = \frac{1}{3}, \frac{2}{3}, 1, \frac{4}{3}, \frac{5}{3}, 2$, so that we can see by inspection the direction of the magnetic moments in adjacent basal planes.

For irrep A1, the moments so sorted are $(1,0,0)$, $(0,-1,0)$, $(-1,-1,0)$, $(-1,0,0)$, $(0,1,0)$, $(1,1,0)$. Bearing in mind that these vectors are given in hexagonal coordinates (the parent is trigonal), we find that these moments lie in the basal plane and are rotated by $-60°$ between adjacent layers. This does not correspond to any known structure of $FePO_4$.

For irrep A2, there are two independent modes. (A2 appears twice in the irrep column of the output.) The sequence in the second of these is $(0,0,1)$, $(0,0,-1)$, $(0,0,1)$, $(0,0,-1)$, $(0,0,1)$, $(0,0,-1)$. This is an arrangement with moments aligned along the three-fold axis, the moments in adjacent layers pointing in opposite directions. This matches the description of the structure of $FePO_4$ below 17 K. The sequence in the first mode is (1,2,0), (2,1,0), $(1,-1,0)$, $(-1,-2,0)$, $(-2,-1,0)$, $(-1,1,0)$ (removing a common factor of 0.577). This is identical to the arrangement produced by A1, rotated by 90°. In principle, A2 leads to a superposition of these two modes, so that the moments are not constrained by symmetry to lie along the three-fold axis as described. However, it is often argued that the form of the exchange interaction favors parallel or antiparallel arrangement of spins, in which case the second mode would be most strongly favored.

The irrep A3 is two-dimensional and generates three independent modes. First we will set the order parameter to (a,0), direction P1, so that we need consider only the first component of each mode. The sequences for the three modes are as follows:

z	mode 1	mode 2	mode 3
1/3	$(1,0,0)$	$(0,0,0)$	$(0,0,0)$
2/3	$(0,1/2,0)$	$(-1,-1/2,0)$	$(0,0,\sqrt{3}/2)$
1	$(1/2,1/2,0)$	$(1/2,-1/2,0)$	$(0,0,\sqrt{3}/2)$
4/3	$(-1,0,0)$	$(0,0,0)$	$(0,0,0)$
5/3	$(0,-1/2,0)$	$(1,1/2,0)$	$(0,0,-\sqrt{3}/2)$
2	$(-1/2,-1/2,0)$	$(-1/2,1/2,0)$	$(0,0,-\sqrt{3}/2)$

In mode 1, the moments at $z = 1/3$ and $z = 4/3$ are constrained to lie parallel and antiparallel to the a axis, and there is no contribution here from the other modes. It will be seen later that this constraint is due to the fact that these moments lie along a two-fold axis. The moments at other z-values are not so constrained by symmetry. It is worth noting however that a 1:1 combination of modes 1 and 2 will lead to the sequence (1,0,0), $(-1,0,0)$, (1,0,0), $(-1,0,0)$, (1,0,0), $(-1,0,0)$ which may be favored by the

physics of the situation and which is in accord with the structure suggested for the range 17–24 K.

If we set the order parameter to $(0, a)$, direction P2, there are no longer any moments constrained by lying on two-fold axes. However a 1:1 combination of modes 1 and 2 will give another alternating sequence (1,2,0), $(-1, -2, 0)$, etc. This is another parallel and antiparallel arrangement of moments, as suggested for 17–24 K, though the different direction of the moments should be noted. The constraints on the directions of moments are further reduced if we set the order parameter to (a, b), direction C1.

Next we list the magnetic structures produced by the action of these different A-point irreps:

```
*SET MAGNETIC
*SHOW PARENT
*SHOW SUBGROUP
*SHOW BASIS
*SHOW ORIGIN
*SHOW DIRECTION VECTOR
*DISPLAY ISOTROPY
Parent          Irrep Subgroup       Dir      Basis Vectors             Origin
152.34 P3_1211' A1    154.44 P_c3_221 P1 (a)   (1,0,0),(0,1,0),(0,0,2)   (0,0,0)
152.34 P3_1211' A2    154.44 P_c3_221 P1 (a)   (1,0,0),(0,1,0),(0,0,2)   (0,0,1/2)
152.34 P3_1211' A3    5.16 C_c2       P1 (a,0) (-1,-2,0),(1,0,0),(0,0,2) (0,0,1/3)
152.34 P3_1211' A3    5.16 C_c2       P2 (0,a) (-1,-2,0),(1,0,0),(0,0,2) (0,0,5/6)
152.34 P3_1211' A3    1.3 P_S1        C1 (a,b) (0,1,0),(-1,0,0),(0,0,2)  (0,0,0)
*
```

Based on the above analysis of magnetic moments, we would conclude that the magnetic structure in the range 17 K to 24 K has the symmetry of C_c2 arising from irrep A3, direction P1 or P2, and that below 17 K has the symmetry of P_c3_221 arising from irrep A2. The three-fold symmetry axis is evidently maintained under the action of irrep A2, but it is not surprising that it cannot be maintained when moments are aligned perpendicular to this axis as occurs under the action of irrep A3. Note that the two C_c2 structures differ in choice of origin.

The original purpose of this work was to obtain magnetic symmetries and to carry out magnetic structure refinement using the program GSAS [A. C. Larson and R. B. von Dreele, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratory Report LAUR 86-748 (2004)]. The first step is to express the $FePO_4$ structure in the settings of those symmetries prior to refinement. The new settings can be obtained using the basis vectors and origin listed above. Currently ISOTROPY in magnetic mode does not do this, but if the same cell and origin can be found in its nonmagnetic mode then ISOTROPY can be used for this purpose. Recalling that Fe is at Wyckoff $3a$, and noting that P is at Wyckoff $3b$ and O at Wyckoff $6c$, the structures in the new settings can be obtained as indicated below. Consider the structure for irrep A2. We first check that the nonmagnetic isotropy subgroup has the same basis vectors and origin as the magnetic subgroup shown above.

```
*SET NOMAGNETIC
*VALUE IRREP A2
*CANCEL SHOW IRREP
*CANCEL SHOW DIRECTION VECTOR
*VALUE WYCKOFF A B C
*DISPLAY ISOTROPY
Parent     Subgroup   Dir Basis Vectors           Origin
152 P3_121 154 P3_221 P1  (1,0,0),(0,1,0),(0,0,2) (0,0,1/2)
*
```

It does, so we can proceed to obtain the atomic positions in the setting of the subgroup.

```
*CANCEL SHOW BASIS
*CANCEL SHOW ORIGIN
*SHOW WYCKOFF SUBGROUP
*DISPLAY ISOTROPY
Parent     Subgroup   Dir Wyckoff New Wyckoff
152 P3_121 154 P3_221 P1  a       c, x'=x, y'=0, z'=-1/12
                          b       b, x'=x
                                  a, x'=x
                          c       c, x'=x, y'=y, z'=-1/4+1/2z
                                  c, x'=-y, y'=x-y, z'=-1/12+1/2z
*
```

We do the same for irrep A3, first for direction P1.

```
*CANCEL SHOW WYCKOFF SUBGROUP
*VALUE IRREP A3
*VALUE DIRECTION P1
*SHOW BASIS
*SHOW ORIGIN
*DISPLAY ISOTROPY
Parent     Subgroup Dir Basis Vectors            Origin
152 P3_121 5 C2     P1  (1,2,0),(1,0,0),(0,0,-2) (0,0,1/3)
*
```

We note that these basis vectors are not exactly the same as those we obtained for the magnetic subgroup, but we can force ISOTROPY to use the basis vectors we want.

```
*VALUE BASIS -1,-2,0 1,0,0 0,0,2
*VALUE ORIGIN 0,0,1/3
*SHOW SUBGROUP ALTERNATE
*DISPLAY ISOTROPY
Parent     Subgroup Alt Dir Basis Vectors             Origin
152 P3_121 5 C2     yes P1  (-1,-2,0),(1,0,0),(0,0,2) (0,0,1/3)
*
```

The `yes` in the `Alt` column indicates that we were successful. Now we can obtain the atomic positions in the setting of the subgroup.

```
*CANCEL SHOW BASIS
*CANCEL SHOW ORIGIN
*SHOW WYCKOFF SUBGROUP
*DISPLAY ISOTROPY
Parent     Subgroup Alt Dir Wyckoff New Wyckoff
152 P3_121 5 C2     yes P1  a       a, y'=x
                                    c, x'=-1/2x, y'=-1/2x, z'=1/6
                         ‘          c, x'=1/2x, y'=-1/2x, z'=1/3
                                    b, y'=x
                             b      c, x'=0, y'=x, z'=1/4
                                    c, x'=-1/2x, y'=-1/2x, z'=5/12
                                    c, x'=-1/2x, y'=-1/2x, z'=11/12
                             c      c, x'=-1/2y, y'=x-1/2y, z'=5/6+1/2z
                                    c, x'=-1/2x+1/2y, y'=-1/2x-1/2y, z'=1/2z
                                    c, x'=1/2x, y'=-1/2x+y, z'=1/6+1/2z
                                    c, x'=-1/2y, y'=x-1/2y, z'=1/3+1/2z
                                    c, x'=-1/2x+1/2y, y'=-1/2x-1/2y, z'=1/2+1/2z
                                    c, x'=1/2x, y'=-1/2x+y, z'=2/3+1/2z
*
```

We repeat this also for direction P2.

```
*CANCEL SHOW WYCKOFF SUBGROUP
*VALUE DIRECTION P2
*VALUE ORIGIN 0,0,5/6
*SHOW BASIS
*SHOW ORIGIN
*DISPLAY ISOTROPY
Parent     Subgroup Alt Dir Basis Vectors             Origin
152 P3_121 5 C2     yes P2  (-1,-2,0),(1,0,0),(0,0,2) (0,0,5/6)
*CANCEL SHOW BASIS
*CANCEL SHOW ORIGIN
*SHOW WYCKOFF SUBGROUP
*DISPLAY ISOTROPY
Parent     Subgroup Alt Dir Wyckoff New Wyckoff
152 P3_121 5 C2     yes P2  a       c, x'=0, y'=x, z'=3/4
                                    c, x'=-1/2x, y'=-1/2x, z'=11/12
                                    c, x'=-1/2x, y'=-1/2x, z'=5/12
                             b      a, y'=x
                                    c, x'=-1/2x, y'=-1/2x, z'=1/6
                                    c, x'=1/2x, y'=-1/2x, z'=1/3
                                    b, y'=x
                             c      c, x'=-1/2y, y'=x-1/2y, z'=7/12+1/2z
                                    c, x'=-1/2x+1/2y, y'=-1/2x-1/2y, z'=3/4+1/2z
                                    c, x'=1/2x, y'=-1/2x+y, z'=11/12+1/2z
                                    c, x'=1/2y, y'=x-1/2y, z'=11/12-1/2z
```

```
                                    c, x'=-1/2x, y'=-1/2x+y, z'=7/12-1/2z
                                    c, x'=1/2x-1/2y, y'=-1/2x-1/2y, z'=3/4-1/2z
*
```

The output shows the Wyckoff positions and the variable coordinates in the final structures in terms of those in the parent structure. In the parent, the Fe and P are both on special positions, Wyckoff a and b, respectively. As regards the two structures in C_c2, it is interesting to note that the structure at origin (0,0,1/3) has some Fe atoms at special positions Wyckoff a and b while the P are at what appear to be general positions, whereas in the structure at origin (0,0,5/6) there are some P atoms at special positions and the Fe atoms are at general positions. [Note that in the magnetic subgroup C_c2, $(0, x, 1/4)$ is at the Wyckoff position $4b$ $(0, y, 1/4; m_x, 0, m_z)$ (see ISO-MAG Table at iso.byu.edu) so that not all atoms at general points in $C2$ are at general points in C_c2.] We can use ISOTROPY to look at the site symmetries in both the parent and subgroup structures.

```
*CANCEL SHOW ALL
*CANCEL VALUE ALL
*SHOW PARENT
*SHOW WYCKOFF POINTGROUP
*VALUE PARENT 152
*VALUE WYCKOFF A B C
*DISPLAY PARENT
Parent     Wyckoff Points, Point Groups
152 P3_121 a C2, b C2, c C1
*VALUE PARENT 5
*DISPLAY PARENT
Parent Wyckoff Points, Point Groups
5 C2   a C2, b C2, c C1
*
```

This confirms our earlier statement that for irrep A3, direction P1, giving the C_c2 structure with origin (0,0,1/3), some Fe atoms, those at Wyckoff a and b continue to lie on two-fold axes in the lower symmetry magnetic structure.

We remark that care must be exercised in the application of GSAS to this kind of problem. For example, the analysis in C_c2 is achieved by working in $C2$, the atoms at the edge center being introduced by changing the setting of the parent structure into the that of the larger magnetic cell as described, then constraining the positions and magnetic moments on these edge centering atoms to obtain the desired results.

Now we move to a consideration of hematite, α-Fe_2O_3. There have been many studies on hematite and its magnetic structures [C. G. Shull, W. A. Strauser & E. O. Wollan, *Phys. Rev.* **83**, 333–345, (1951); A. H. Morrish, *Canted Antiferromagnetism: Hematite*, World Scientific, (1994); R. J. Harrison, *Rev. Mineral. Geochem.* **63**, 113–143 (2006)]. There are similarities with $FePO_4$ in that both compounds show a spin reorientation transition (in hematite, the Morin transition), but also differences in that Fe_2O_3 in its higher-temperature magnetic phase displays weak ferromagnetism. The ISOTROPY analysis offers the opportunity to demonstrate additional features of the program.

The space group for the parent high-temperature structure is No. 167, $R\bar{3}c$, with the magnetic Fe^{3+} ion at Wyckoff position $12c$ and the O^{2-} ion at Wyckoff $18e$. In this case the magnetic unit cell is the same size as the conventional chemical unit cell, so the magnetic ordering is associated with irreps at the Γ-point, $k = 0, 0, 0$. Ferromagnetism, whether weak or otherwise, can arise from zone center (Γ-point) irreps but not from zone boundary irreps as were active in the case of $FePO_4$. This point can be made for hematite using ISOTROPY, on the basis that magnetic moment is a pseudo vector, *i.e.*, a pseudo tensor of rank 1.

```
*CANCEL SHOW ALL
*CANCEL VALUE ALL
*VALUE PARENT 167
*VALUE KDEGREE 0
*VALUE RANK 1
*SHOW MACRO PSEUDO
*SHOW IRREP
*DISPLAY DISTORTION
Irrep (ML) Basis Functions
GM2+       z
GM3+       x,y
*
```

Evidently the only irreps that can give rise to a net ferromagnetic moment are Γ-point irreps: GM2+ giving a magnetic moment along the three-fold axis, and GM3+ giving a moment in the basal plane. Note that the x and y shown here refer to axes along and perpendicular to the crystallographic a axis in the hexagonal setting of $R\bar{3}c$.

In this example we will first list the magnetic space group symmetries of the different structures produced by the action of GM irreps. (We omit showing the origin due to lack of horizontal space.)

```
*SET MAGNETIC
*VALUE KPOINT GM
*SHOW SUBGROUP
*SHOW BASIS
*SHOW IRREP
*SHOW DIRECTION VECTOR
*DISPLAY ISOTROPY
Irrep Subgroup       Dir            Basis Vectors
GM1+  167.103 R-3c   P1 (a)         (1,0,0),(0,1,0),(0,0,1)
GM2+  167.107 R-3c'  P1 (a)         (1,0,0),(0,1,0),(0,0,1)
GM3+  15.85 C2/c     P1 (a,-1.732a) (-2/3,-1/3,2/3),(0,-1,0),(2/3,1/3,1/3)
GM3+  15.89 C2'/c'   P2 (a,0.577a)  (-2/3,-1/3,2/3),(0,-1,0),(2/3,1/3,1/3)
GM3+  2.4 P-1        C1 (a,b)       (-1/3,-2/3,1/3),(-1/3,1/3,1/3),(-2/3,-1/3,-1/3)
GM1-  167.106 R-3'c' P1 (a)         (1,0,0),(0,1,0),(0,0,1)
GM2-  167.105 R-3'c  P1 (a)         (1,0,0),(0,1,0),(0,0,1)
GM3-  15.87 C2'/c    P1 (a,-1.732a) (-2/3,-1/3,2/3),(0,-1,0),(2/3,1/3,1/3)
```

```
GM3-  15.88 C2/c'    P2 (a,0.577a)  (-2/3,-1/3,2/3),(0,-1,0),(2/3,1/3,1/3)
GM3-  2.6 P-1'       C1 (a,b)       (-1/3,-2/3,1/3),(-1/3,1/3,1/3),(-2/3,-1/3,-1/3)
*
```

and then proceed to examine the moment arrangements in detail:

```
*VALUE WYCKOFF C
*SHOW MICROSCOPIC VECTOR PSEUDO
*DISPLAY DISTORTION
Irrep (ML) Point        Projected Pseudo Vectors
GM1+       (0,0,z)      (0,0,1)
           (0,0,-z+1/2) (0,0,-1)
           (0,0,-z)     (0,0,1)
           (0,0,z+1/2)  (0,0,-1)
GM2+       (0,0,z)      (0,0,1)
           (0,0,-z+1/2) (0,0,1)
           (0,0,-z)     (0,0,1)
           (0,0,z+1/2)  (0,0,1)
GM3+       (0,0,z)      (1,1,0), (-0.577,0.577,0)
           (0,0,-z+1/2) (0,-1,0), (1.155,0.577,0)
           (0,0,-z)     (1,1,0), (-0.577,0.577,0)
           (0,0,z+1/2)  (0,-1,0), (1.155,0.577,0)
GM3+       (0,0,z)      (0.577,-0.577,0), (1,1,0)
           (0,0,-z+1/2) (1.155,0.577,0), (0,1,0)
           (0,0,-z)     (0.577,-0.577,0), (1,1,0)
           (0,0,z+1/2)  (1.155,0.577,0), (0,1,0)
GM1-       (0,0,z)      (0,0,1)
           (0,0,-z+1/2) (0,0,-1)
           (0,0,-z)     (0,0,-1)
           (0,0,z+1/2)  (0,0,1)
GM2-       (0,0,z)      (0,0,1)
           (0,0,-z+1/2) (0,0,1)
           (0,0,-z)     (0,0,-1)
           (0,0,z+1/2)  (0,0,-1)
GM3-       (0,0,z)      (1,1,0), (-0.577,0.577,0)
           (0,0,-z+1/2) (0,1,0), (-1.155,-0.577,0)
           (0,0,-z)     (-1,-1,0), (0.577,-0.577,0)
           (0,0,z+1/2)  (0,-1,0), (1.155,0.577,0)
GM3-       (0,0,z)      (0.577,-0.577,0), (1,1,0)
           (0,0,-z+1/2) (-1.155,-0.577,0), (0,-1,0)
           (0,0,-z)     (-0.577,0.577,0), (-1,-1,0)
           (0,0,z+1/2)  (1.155,0.577,0), (0,1,0)
*
```

Again, it will be useful to examine the moments in order of increasing z coordinate. It is necessary, however, to take into account the fact that for each z listed above, the

rhombohedral lattice places equivalent atoms at heights $z + 1/3$ and $z + 2/3$. Noting that $z \approx 0.355$, we find the sequence shown below:

	z at equivalent position	value with $z = 0.355$
$(0, 0, -z)$	$-z + 2/3$	0.312
$(0, 0, z)$	z	0.355
$(0, 0, -z + 1/2)$	$-z + 1/2 + 1/3$	0.478
$(0, 0, z + 1/2)$	$z + 1/2 + 2/3 - 1$	0.522

The Fe^{3+} evidently lie in pairs of rather closely spaced layers, such that each pair of layers can be and henceforth will be described as a single buckled layer. These pairs of layers are separated from each other by a somewhat larger spacing.

Irrep GM1+ gives moments, when sorted as indicated, in the sequence (0,0,1), (0,0,1), $(0, 0, -1)$, $(0, 0, -1)$, *i.e.*, the moments lie along the z direction, all the moments in one buckled layer pointing in one direction, and all the moments on the next pointing in the opposite direction. This is reported to be the structure of hematite (magnetic symmetry $R\bar{3}c$) found below the Morin transition.

Irrep GM2+ shows all the moments as (0,0,1). It is a ferromagnetic structure, with moments pointing in the z direction. This structure is not observed.

Irrep GM3+ is a two-dimensional irrep and induces two independent modes. First, we set the order parameter to be $(a, -a\sqrt{3})$, direction P1, so that the magnetic space group is $C2/c$. The resulting moments are given by the first vector in each mode added to $-\sqrt{3}$ times the second vector in each mode. The sequences for the two modes are as follows:

		Mode 1	Mode 2
$(0, 0, -z)$	0.312	$(2, 0, 0)$	$(-2/\sqrt{3}, -4/\sqrt{3}, 0)$
$(0, 0, z)$	0.355	$(2, 0, 0)$	$(-2/\sqrt{3}, -4/\sqrt{3}, 0)$
$(0, 0, -z + 1/2)$	0.478	$(-2, -2, 0)$	$(2/\sqrt{3}, -2/\sqrt{3}, 0)$
$(0, 0, z + 1/2)$	0.522	$(-2, -2, 0)$	$(2/\sqrt{3}, -2/\sqrt{3}, 0)$

First we note that the moments in one buckled layer are all in the same direction, and that they change direction from one buckled layer to the next. Secondly we see that the moments lie in the basal plane. A pure antiferromagnetic structure, with moments $(-2, -1, 0)$ and $(2, 1, 0)$ can be obtained by combining these modes in the ratio $-\sqrt{3} : 1$. There is no symmetry requirement for the modes to be combined in this ratio, and in general they are not, a situation known as spin canting. This gives rise to "weak" ferromagnetism. If we suppose that the modes are combined in the ratio $\alpha : \beta$, we can show that the moments in successive (buckled) layers are $A(2, 1, 0) + B(0, -1, 0)$ and $A(-2, -1, 0) + B(0, -1, 0)$ where $A = (\alpha - \beta/\sqrt{3})/2$ and $B = (\alpha + 3\beta/\sqrt{3})/2$. If we set $\alpha : \beta$ at $-\sqrt{3} : 1$, we recover the pure antiferromagnetic structure just described, otherwise we find a ferromagnetic component along (0,-1,0). This moment is at right angles to the (2,1,0) directions of the antiferromagnetic moments and is also in accord

with the results (ferromagnetic moment directions) given for GM3+ at the start of the hematite analysis. The structure just described, including the weak ferromagnetism, is considered to be the magnetic structure of hematite above the Morin transition.

A similar analysis can be carried out if we choose the order parameter to be $(a, a/\sqrt{3})$, direction P2. Combining the modes again in the ratio $-\sqrt{3}:1$ gives a pure antiferromagnetic structure with moments (0,1,0) and $(0,-1,0)$, and a canted magnetic structure gives a ferromagnetic resultant along (2,1,0). The magnetic space group symmetry is $C2'/c'$.

The structures arising from the irreps GM1−, GM2− and GM3− all have oppositely directed moments within each buckled layer. Such structures are not observed and will not be considered further here.

Finally, we develop the Landau potential and Gibbs free energy from the polynomial Invariants for the structure above the Morin transition, where the primary irrep is GM3+. We choose the order parameter for GM3+ to be in the P1 direction.

```
*CANCEL SHOW ALL
*CANCEL VALUE ALL
*VALUE PARENT 167
*VALUE IRREP GM1+ GM2+ GM3+
*VALUE DIRECTION P1 P1 P1
*DISPLAY INVARIANT
Deg Invariants
1   n1
2   n1^2
2   n2^2
2   n3^2
3   n1^3
3   n1n2^2
3   n1n3^2
3   n3^3
4   n1^4
4   n1^2n2^2
4   n2^4
4   n1^2n3^2
4   n2^2n3^2
4   n3^4
4   n1n3^3
*
```

Let Q_1, Q_2, Q_3 be the magnetic order parameters `n1`,`n2`,`n3` associated with irreps GM1+,GM2+,GM3+.

The invariants above were obtained in the nonmagnetic mode, since ISOTROPY does not produce invariants in the magnetic mode. However, it is simple to extract the desired magnetic invariants from the above list. The time reversal operator changes the sign of

the order parameter, and since the terms in the polynomial expansion must be invariant under all the operations of the parent space group, including time reversal, only the invariants in even powers of the magnetic order parameters are retained. This means the Landau potential, *i.e.*, the expansion in powers of Q_3, the primary order parameter, can be written as

$$G = \tfrac{1}{2}a(T - T_N)Q_3^2 + \tfrac{1}{4}bQ_3^4 + \cdots,$$

where a and b are Landau coefficients, T is temperature, and T_N the temperature (Neél temperature) of the transition to the magnetically ordered phase.

We now examine how the magnetic distortions described by Q_1 and Q_2 couple to the primary distortion Q_3. We find from the ISOTROPY output above the even-degree polynomials which couple these parameters and include them in our expansion, which becomes:

$$G = \tfrac{1}{2}a(T - T_N)Q_3^2 + \tfrac{1}{4}bQ_3^4 + \lambda_5 Q_1^2 Q_3^2 + \lambda_6 Q_1 Q_3^3 + \lambda_7 Q_2^2 Q_3^2 + \cdots,$$

where the λ_i are different coupling coefficients. Values for Q_1 and Q_2 are determined from the equilibrium conditions, $\partial G/\partial Q_1 = \partial G/\partial Q_2 = 0$:

$$\frac{\partial G}{\partial Q_1} = 2\lambda_5 Q_1 Q_3^2 + \lambda_6 Q_3^3 = 0 \quad \text{gives} \quad Q_1 = -\frac{\lambda_6}{2\lambda_5} Q_3,$$

whereas

$$\frac{\partial G}{\partial Q_2} = 2\lambda_7 Q_2 Q_3^2 = 0 \quad \text{gives} \quad Q_2 = 0.$$

Thus, Q_1 a secondary magnetic distortion and is proportional to Q_3. Q_2 is not a secondary distortion in this case. If we choose the direction of the order parameter for irrep GM3+ to be $(0, a)$, then we find that Q_2 appears as a secondary magnetic distortion, but not Q_1. It can be shown by similar means that there are no secondary distortions associated with any of the irreps GM1−, GM2−, or GM3−.

The strains in this system transform according to irreps GM1+ and GM3+, so invariants can be taken from the list above. The relevant terms are those linear in strain and quadratic in the magnetic order parameter. The expansion including strain and order parameter coupling has been developed [L. Oravova1, Z. Zhang, N. Church, R. J. Harrison, C. J. Howard and M. A. Carpenter, *J. Phys.: Condens. Matter* **25**, 259501, (2013)].

This is the end of Case Study 4. You may exit the program:

```
*QUIT
```