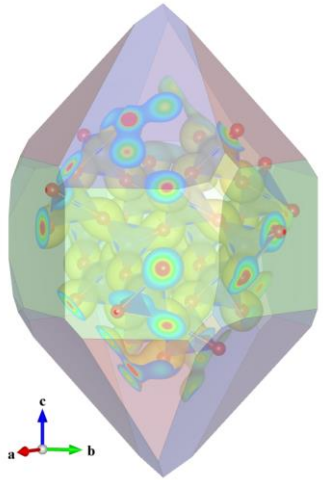
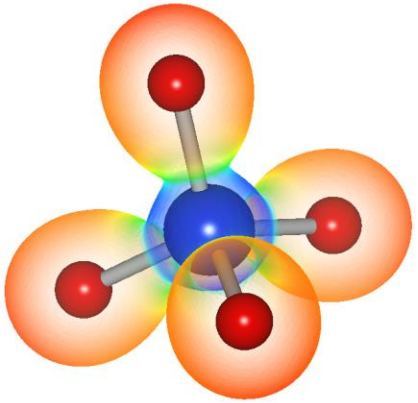
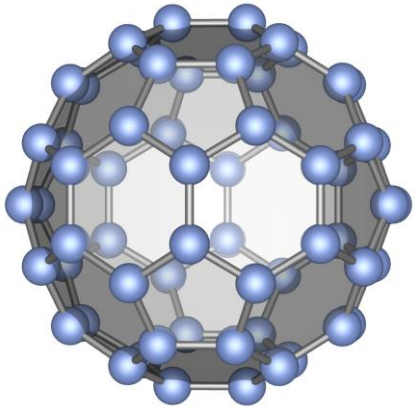
Symmetry, topology, and visualization of crystal structures







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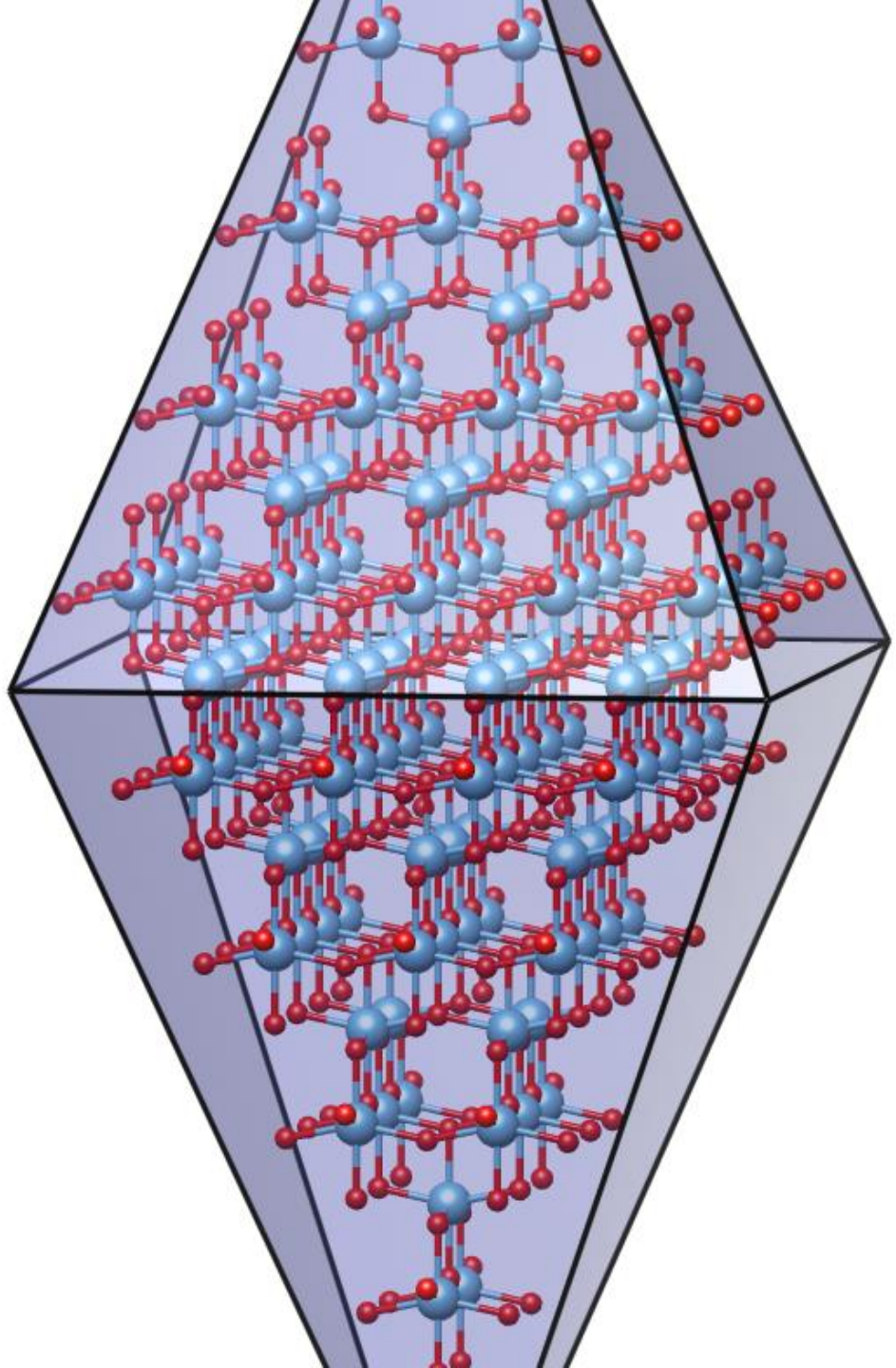
第1回 ハイパーマテリアルWeb若手研究会　2020.05.20



Contents

- Basic linear algebra in crystallography
- Conversions and comparison of structures using VESTA
- Command line interface of VESTA
- Practices

Unit cell

Representation of a unit cell $\boldsymbol{A} = (\boldsymbol{a} \quad \boldsymbol{b} \quad \boldsymbol{c})$

$$= \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix}$$

Affine transformation by $\boldsymbol{A}$

Fractional coordinates

$$\boldsymbol{r} = \begin{pmatrix} u \\ v \\ w \end{pmatrix}$$

Cartesian coordinates

$$\boldsymbol{X} = \begin{pmatrix} x \\ y \\ x \end{pmatrix} = \boldsymbol{A}\boldsymbol{r}$$

$$= (\boldsymbol{a} \quad \boldsymbol{b} \quad \boldsymbol{c}) \begin{pmatrix} u \\ v \\ w \end{pmatrix}$$

$$= \begin{pmatrix} ua_x & vb_x & wc_x \\ ua_y & vb_y & wc_y \\ ua_z & vb_z & wc_z \end{pmatrix}$$

Metric matrix

Choice of ***A*** is arbitrary

VESTA adopts the following convention

$$\boldsymbol{A} = \begin{pmatrix} a_x & b_x & c_x \\ 0 & b_y & c_y \\ 0 & 0 & c_z \end{pmatrix}$$

Alternatively, you can choose

$$\boldsymbol{A} = \begin{pmatrix} a_x & 0 & 0 \\ a_y & b_y & 0 \\ a_z & b_z & c_z \end{pmatrix}$$

or any other orientation

$$\boldsymbol{G} = \boldsymbol{A}^T \cdot \boldsymbol{A} = \begin{pmatrix} \boldsymbol{a}^2 & \boldsymbol{a}.\boldsymbol{b} & \boldsymbol{a}.\boldsymbol{c} \\ \boldsymbol{a}.\boldsymbol{b} & \boldsymbol{b}^2 & \boldsymbol{b}.\boldsymbol{c} \\ \boldsymbol{a}.\boldsymbol{c} & \boldsymbol{b}.\boldsymbol{c} & \boldsymbol{c}^2 \end{pmatrix}$$

G does not depend on choice of ***A***. It is unique for a given set of unit cell parameters.

Unit cell volume: $\boldsymbol{V^2} = \det(\boldsymbol{G})$

Reciprocal lattice and metric matrix of reciprocal lattice

Reciprocal lattice

$$\boldsymbol{A}^* = \boldsymbol{A}^{-1} = \begin{pmatrix} \boldsymbol{a}^* \\ \boldsymbol{b}^* \\ \boldsymbol{c}^* \end{pmatrix} = \begin{pmatrix} a_x^* & a_y^* & a_z^* \\ b_x^* & b_y^* & b_z^* \\ c_x^* & c_y^* & c_z^* \end{pmatrix}$$

Metric matrix

$$\boldsymbol{G}^* = \boldsymbol{G}^{-1} = \left(\boldsymbol{A}^T \cdot \boldsymbol{A}\right)^{-1} = \left(\boldsymbol{A}^* \cdot \boldsymbol{A}^{*T}\right) = \begin{pmatrix} \boldsymbol{a}^{*2} & \boldsymbol{a}^*.\boldsymbol{b}^* & \boldsymbol{a}^*.\boldsymbol{c}^* \\ \boldsymbol{a}^*.\boldsymbol{b}^* & \boldsymbol{b}^{*2} & \boldsymbol{b}^*.\boldsymbol{c}^* \\ \boldsymbol{a}^*.\boldsymbol{c}^* & \boldsymbol{b}^*.\boldsymbol{c}^* & \boldsymbol{c}^{*2} \end{pmatrix}$$

$$\boldsymbol{A}^*\boldsymbol{A} = \begin{pmatrix} \boldsymbol{a}^* \\ \boldsymbol{b}^* \\ \boldsymbol{c}^* \end{pmatrix} (\boldsymbol{a} \quad \boldsymbol{b} \quad \boldsymbol{c}) = \begin{pmatrix} \boldsymbol{a}^*.\boldsymbol{a} & \boldsymbol{a}^*.\boldsymbol{b} & \boldsymbol{a}^*.\boldsymbol{c} \\ \boldsymbol{b}^*.\boldsymbol{a} & \boldsymbol{b}^*.\boldsymbol{b} & \boldsymbol{b}^*.\boldsymbol{c} \\ \boldsymbol{c}^*.\boldsymbol{a} & \boldsymbol{b}^*.\boldsymbol{c} & \boldsymbol{c}^*.\boldsymbol{c} \end{pmatrix} = \boldsymbol{I}$$

$$\boldsymbol{G}^*\boldsymbol{G} = \boldsymbol{G}\boldsymbol{G}^* = \boldsymbol{I}$$

Reciprocal lattice vectors

Reciprocal lattice vector

$$\boldsymbol{h} = (h \quad k \quad l)$$

Cartesian coordinates

$$\boldsymbol{X}^* = (x \quad y \quad z) = \boldsymbol{h}\boldsymbol{A}^*$$

$$= (h \quad k \quad l)\begin{pmatrix} \boldsymbol{a}^* \\ \boldsymbol{b}^* \\ \boldsymbol{c}^* \end{pmatrix}$$

- Normal vector of lattice plane (*h k l*)
- Length of the reciprocal lattice vector corresponds to 1/*d*, where *d* is inter-planar spacing of (*h k l*)

Scalar products: $\boldsymbol{X}^*\boldsymbol{X} = \boldsymbol{h}\boldsymbol{A}^*\boldsymbol{A}\boldsymbol{r} = (h \quad k \quad l)\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \boldsymbol{h}\boldsymbol{r}$

$$\frac{\mathbf{1}}{\boldsymbol{d}^2} = \boldsymbol{d}^{*2} = \boldsymbol{X}^*(\boldsymbol{X}^*)^T = \boldsymbol{h}\boldsymbol{A}^*(\boldsymbol{h}\boldsymbol{A}^*)^T = \boldsymbol{h}\boldsymbol{A}^*\boldsymbol{A}^{*T}\boldsymbol{h}^T = (h \quad k \quad l)\,\boldsymbol{G}^*\begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Symmetry operations

Coordinates

$$\boldsymbol{X} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Symmetry operations

Mirror, inversion, rotation, rotoinversion

translation

$$\boldsymbol{W} = \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix}, \qquad \boldsymbol{w} = \begin{pmatrix} w_x \\ w_y \\ w_z \end{pmatrix}$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} w_x \\ w_y \\ w_z \end{pmatrix}$$

$$\boldsymbol{X}' = \boldsymbol{W}\boldsymbol{X} + \boldsymbol{w}$$

Symmetry operations

Coordinates

$$\mathbb{X} = \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}$$

Symmetry operations

$$\mathbb{W} = \begin{pmatrix} \boldsymbol{W} & \boldsymbol{w} \\ \boldsymbol{o} & 1 \end{pmatrix} = \begin{pmatrix} W_{11} & W_{12} & W_{13} & w_x \\ W_{21} & W_{22} & W_{23} & w_y \\ W_{31} & W_{32} & W_{33} & w_z \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} x' \\ y' \\ z' \\ 1 \end{pmatrix} = \begin{pmatrix} W_{11} & W_{12} & W_{13} & w_x \\ W_{21} & W_{22} & W_{23} & w_y \\ W_{31} & W_{32} & W_{33} & w_z \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}$$

$$\mathbb{X}' = \mathbb{W}\mathbb{X}$$

By using additional row to make the matrix square, inverse operation can be easily computed by $\mathbb{W}^{-1}$.

Transformation of coordinate systems

$$\mathbb{P} = \begin{pmatrix} \boldsymbol{P} & \boldsymbol{p} \\ \boldsymbol{o} & 1 \end{pmatrix}$$

$$\mathbb{Q} = \mathbb{P}^{-1} = \begin{pmatrix} \boldsymbol{P} & \boldsymbol{p} \\ \boldsymbol{o} & 1 \end{pmatrix}^{-1} = \begin{pmatrix} \boldsymbol{P^{-1}} & \boldsymbol{-P^{-1}p} \\ \boldsymbol{o} & 1 \end{pmatrix}$$

$$\mathbb{Q} = \begin{pmatrix} \boldsymbol{Q} & \boldsymbol{q} \\ \boldsymbol{o} & 1 \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} & q_1 \\ Q_{21} & Q_{22} & Q_{23} & q_2 \\ Q_{31} & Q_{32} & Q_{33} & q_3 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

3 × 3 rotation part

3 × 1 translation part

Basis vectors: $\boldsymbol{A' = AP}$

Metric matrix: $\boldsymbol{G' = P^T G P}$

Metric matrix: $\boldsymbol{G^{*\prime} = Q G^* Q^T}$

Coordinates: $\mathbb{X}' = \mathbb{Q}\mathbb{X}$

Miller indices: $\boldsymbol{h' = hP}$

Symmetry operations: $\mathbb{W}' = \mathbb{Q}\mathbb{W}\mathbb{P}$

The same relation is also true when dimension > 3

Definition of a group

- Identity element

  There exists an element e in G such that,

  $e \bullet a = a \bullet e = a$ for any element a in G.

- Inverse element

  For each a in G, there exists an inverse element a^{-1} in G, such that

  $a \bullet a^{-1} = a^{-1} \bullet a = e$

- Associative

  For all a, b and c in G, $(a \bullet b) \bullet c = a \bullet (b \bullet c)$.

- Closed

  For all a, b in G, $a \bullet b$, is also in G.

Generators of symmetry operations

Generators of the icosahedral space group $Fm\overline{35}$ $(m\overline{35}^2)$

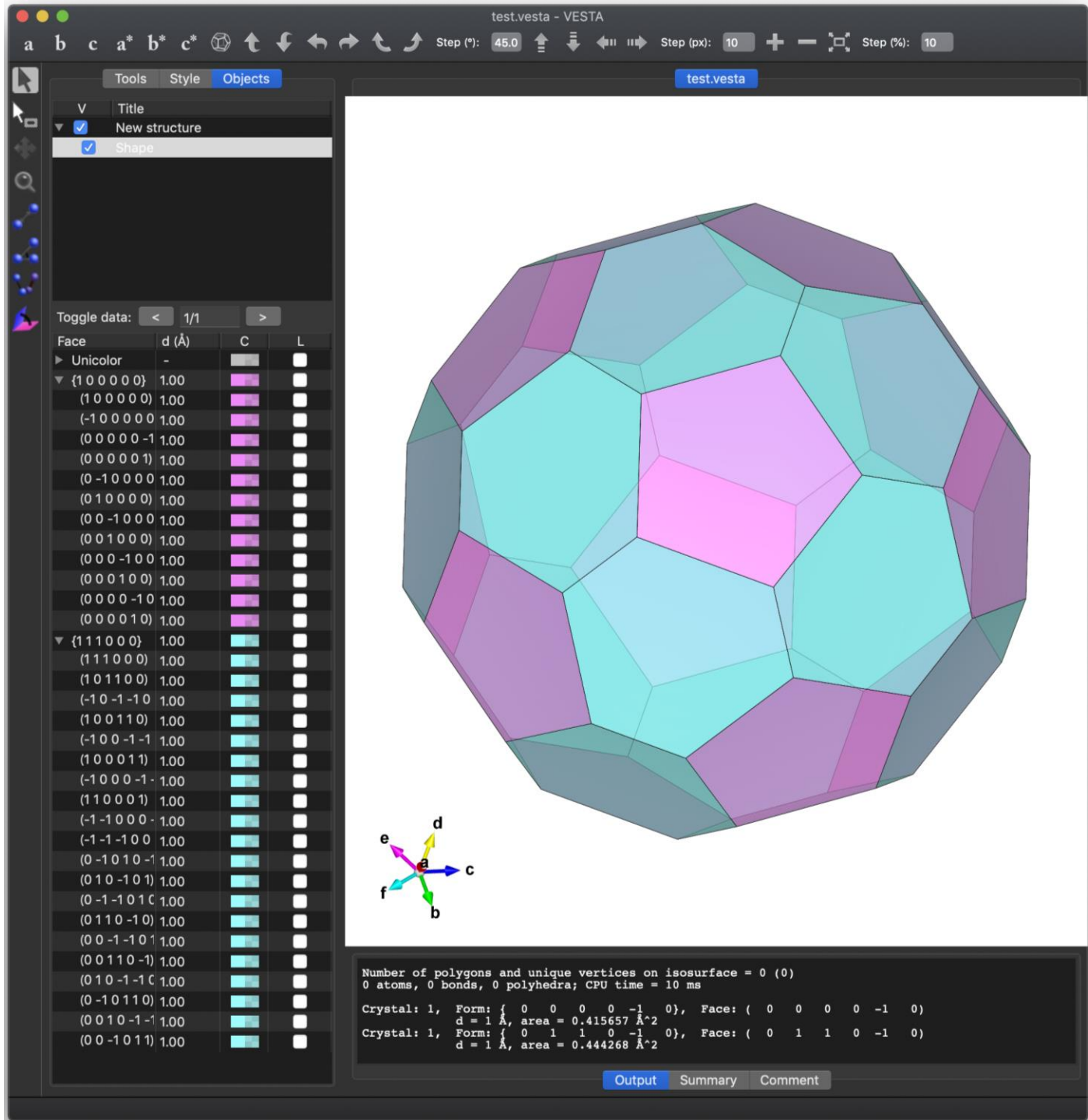
$R_{51} \equiv x,w,y,z,u,v$

$R_{31} \equiv y,z,x,w,-u,-v$

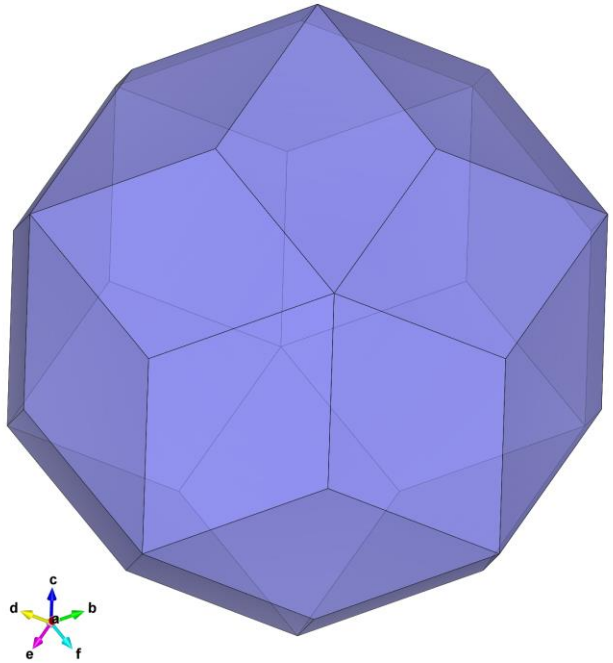
$R_{21} \equiv -x,-y,-w,-v,-u,-z$

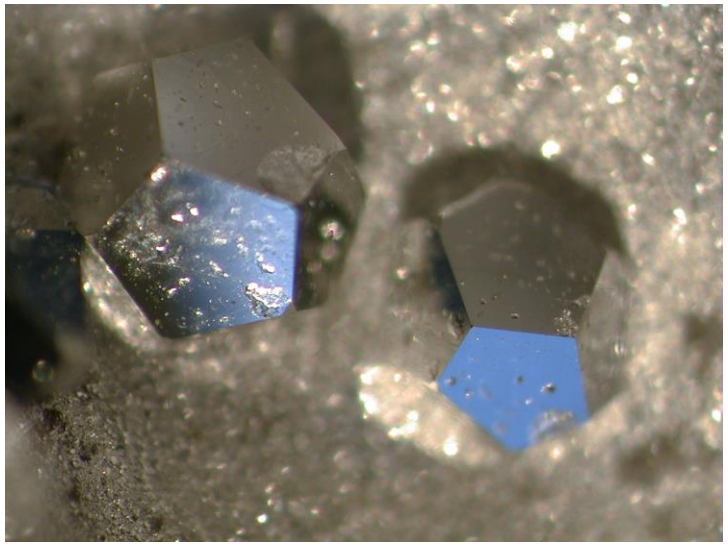
$I \equiv -x,-y,-z,-u,-v,-w$

$(t \equiv 1/2,1/2,0,0,0,0)$

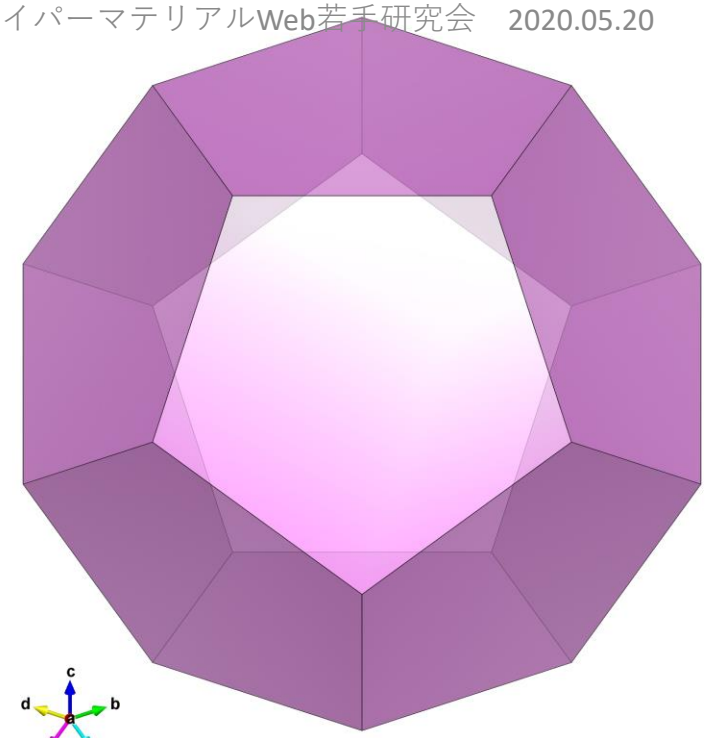


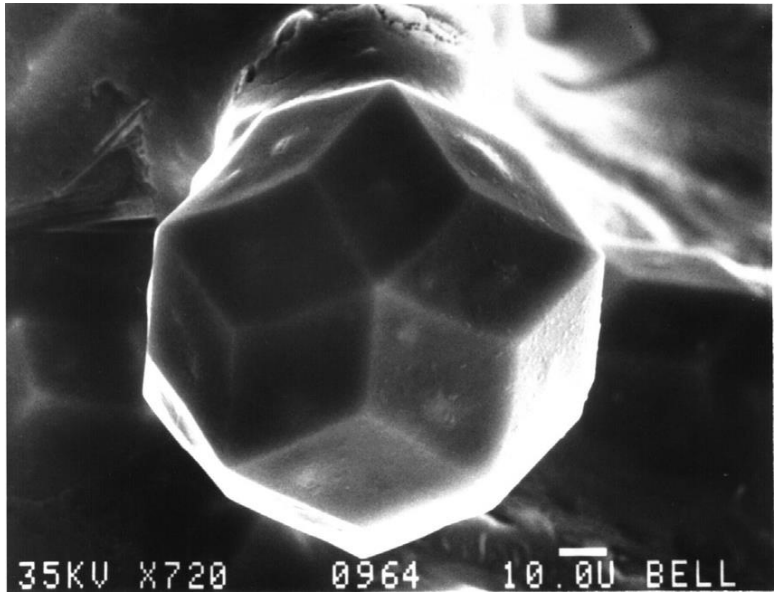
Visualization of quasicrystal morphology



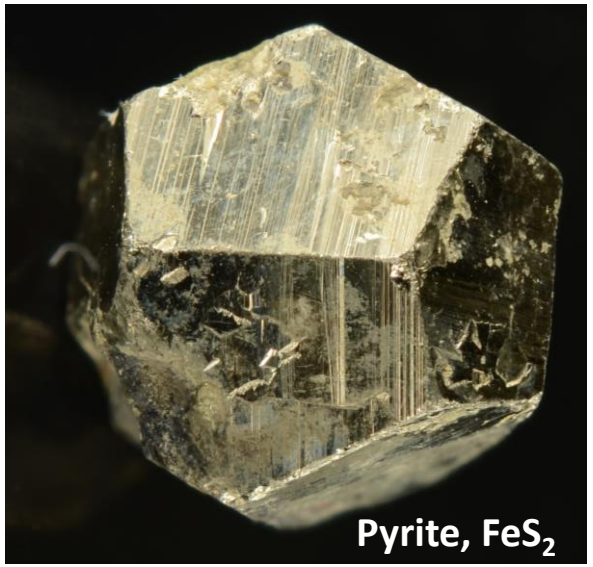


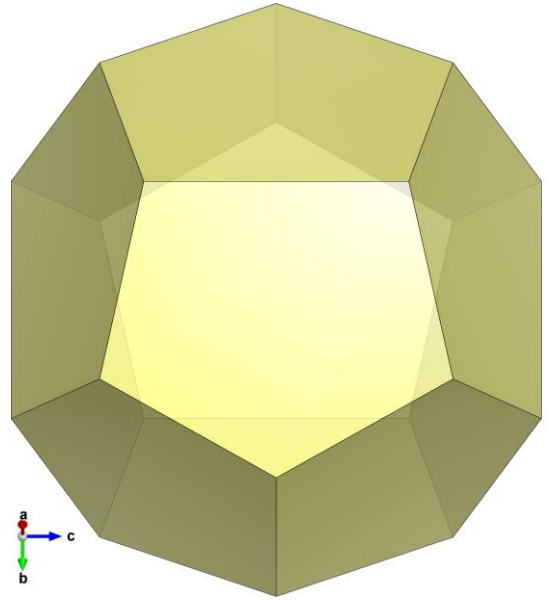
Zn-Mg-Dy decagonal phase
(撮影: 蔡安邦教授)





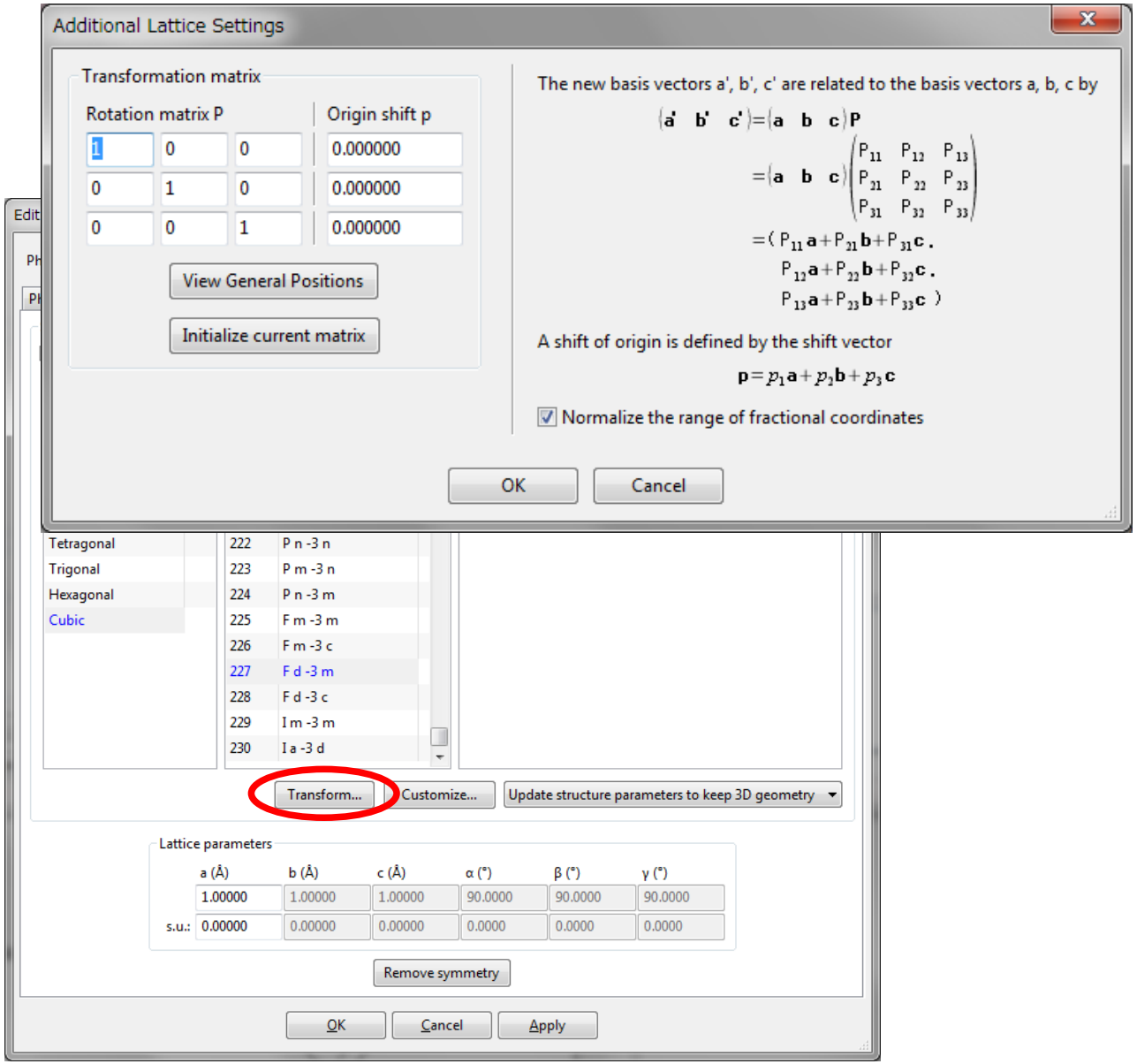
Rhombic triacontahedral
morphology
in Al-Li-Cu alloy
(Kortan et al., 1989)

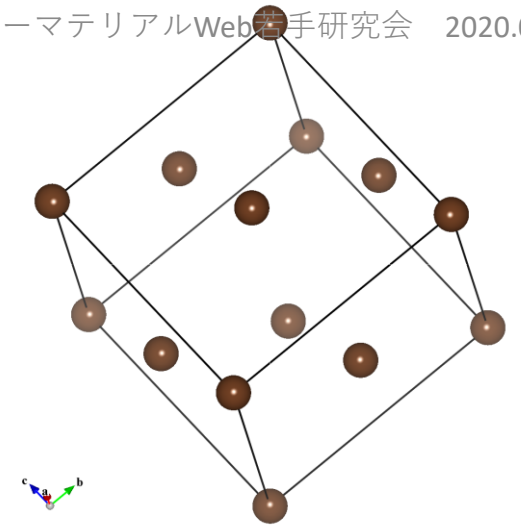




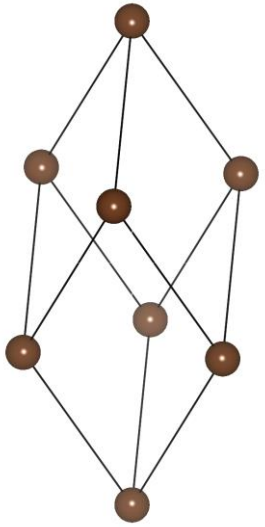
Transformation of coordinate systems

- Edit → Edit Data → Unit cell → Transform



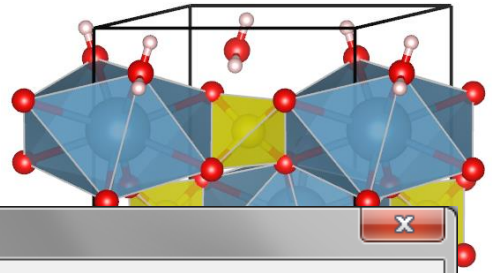


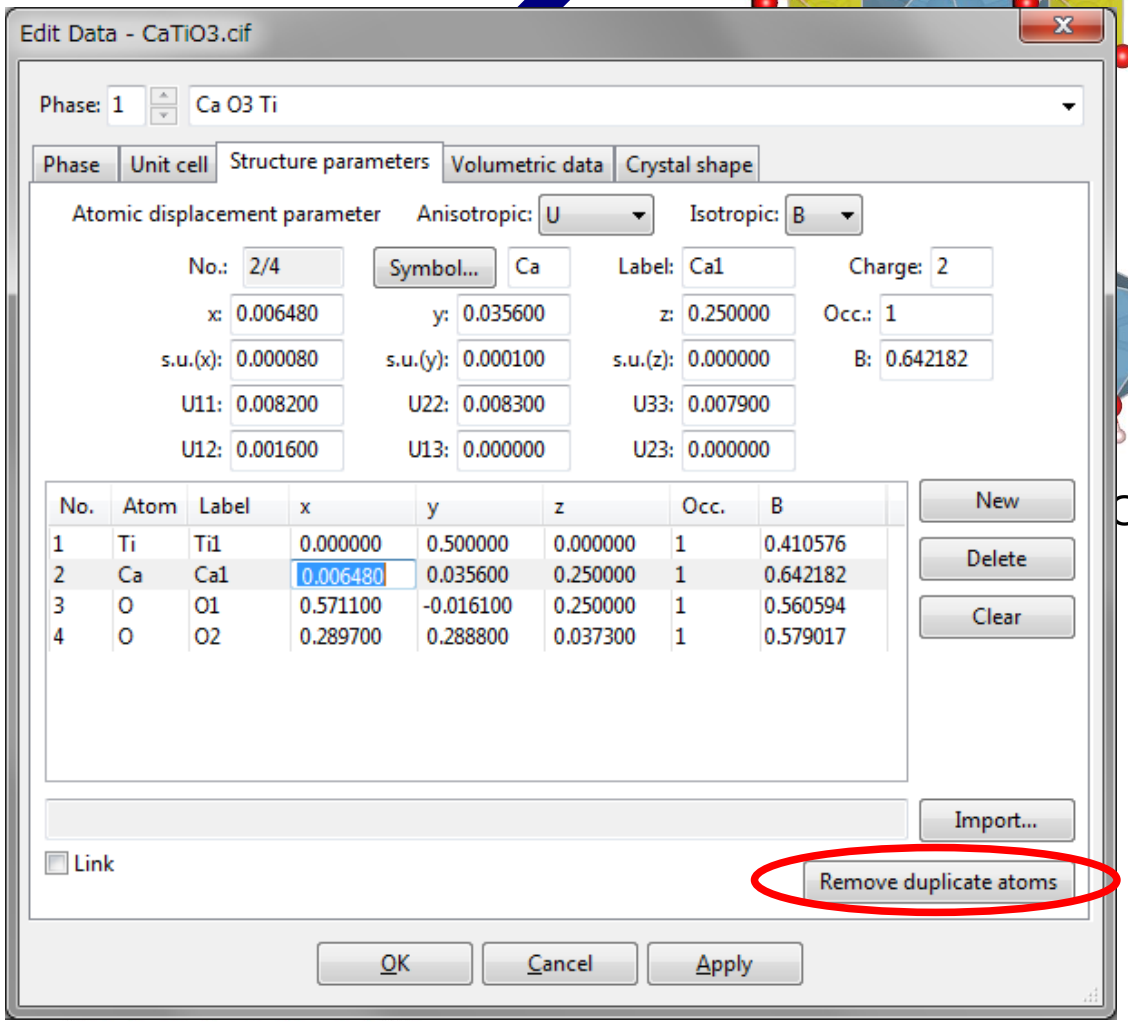
$$F \rightarrow P \quad \begin{pmatrix} 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 1/2 & 0 \end{pmatrix}$$

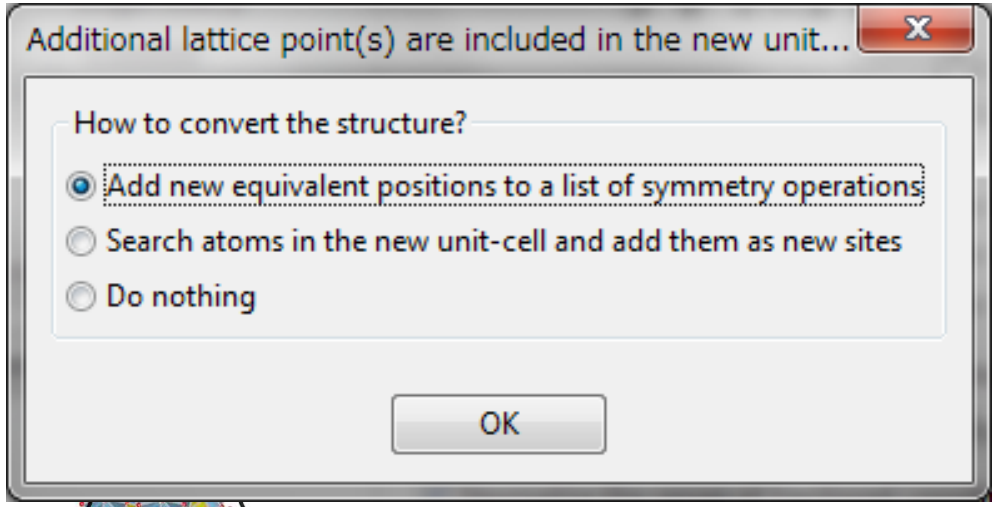


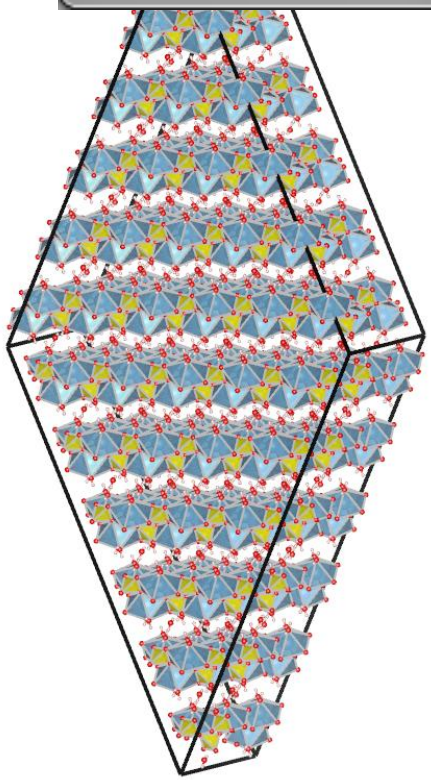
$$P \rightarrow F \quad \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}$$

Transformation of coordinate systems

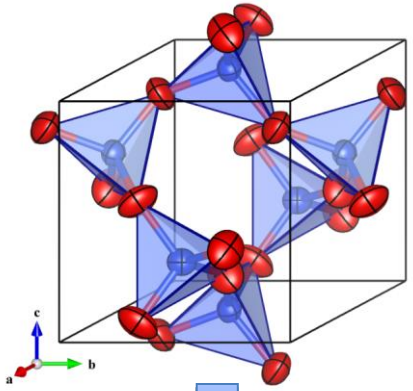


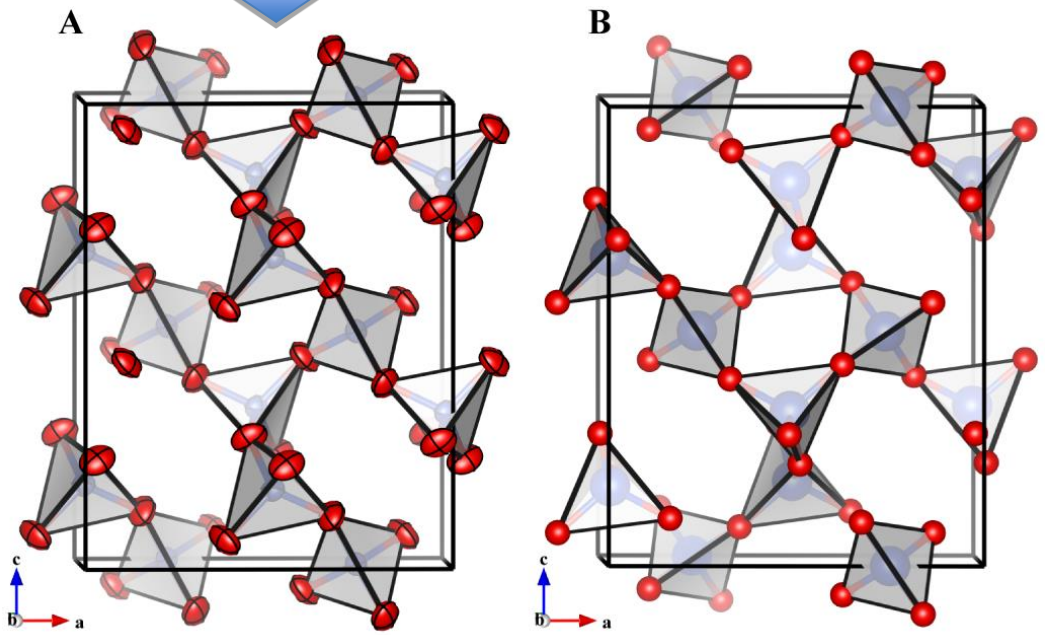






Conversion of a structure to its subgroup / supergroup





$P3_121 \rightarrow C2$ $\quad$ $C2 \rightarrow C2$ with $c'=2c$ $\quad$ Transformation matrix

$$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1/3 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1/3 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Translation of the origin

New basis vectors ***a′***, ***b′***, ***c′***, specified by lattice vectors [*u v w*] (column vector) using basis vectors of the current setting.

A: A monoclinic setting of quartz unit cell with $a'=2a+b$, $b'=b$, and $c'=2c$. B: Unit cell of a silica polymorph moganite.

Practice 1 – 3

Conversion of a structure to its subgroup / supergroup

- Press “Remove Symmetry” button in the Unit cell tab in Edit Data dialog box (When symmetry lowers)
- Set a transformation matrix.
- Automatically search and add additional lattice points or additional sites if necessary. (The structure should look correct at this step)
- Press the “Remove Symmetry” button again. (This operation will reset the transformation matrix to the identity matrix.)
- Set a new space group.
- Use the “Remove duplicate atoms” button. (Merge closely adjacent atoms into single site)

Conversion of a structure to its subgroup / supergroup

- Press “Remove Symmetry” button in the Unit cell t
  (When symmetry lowers)
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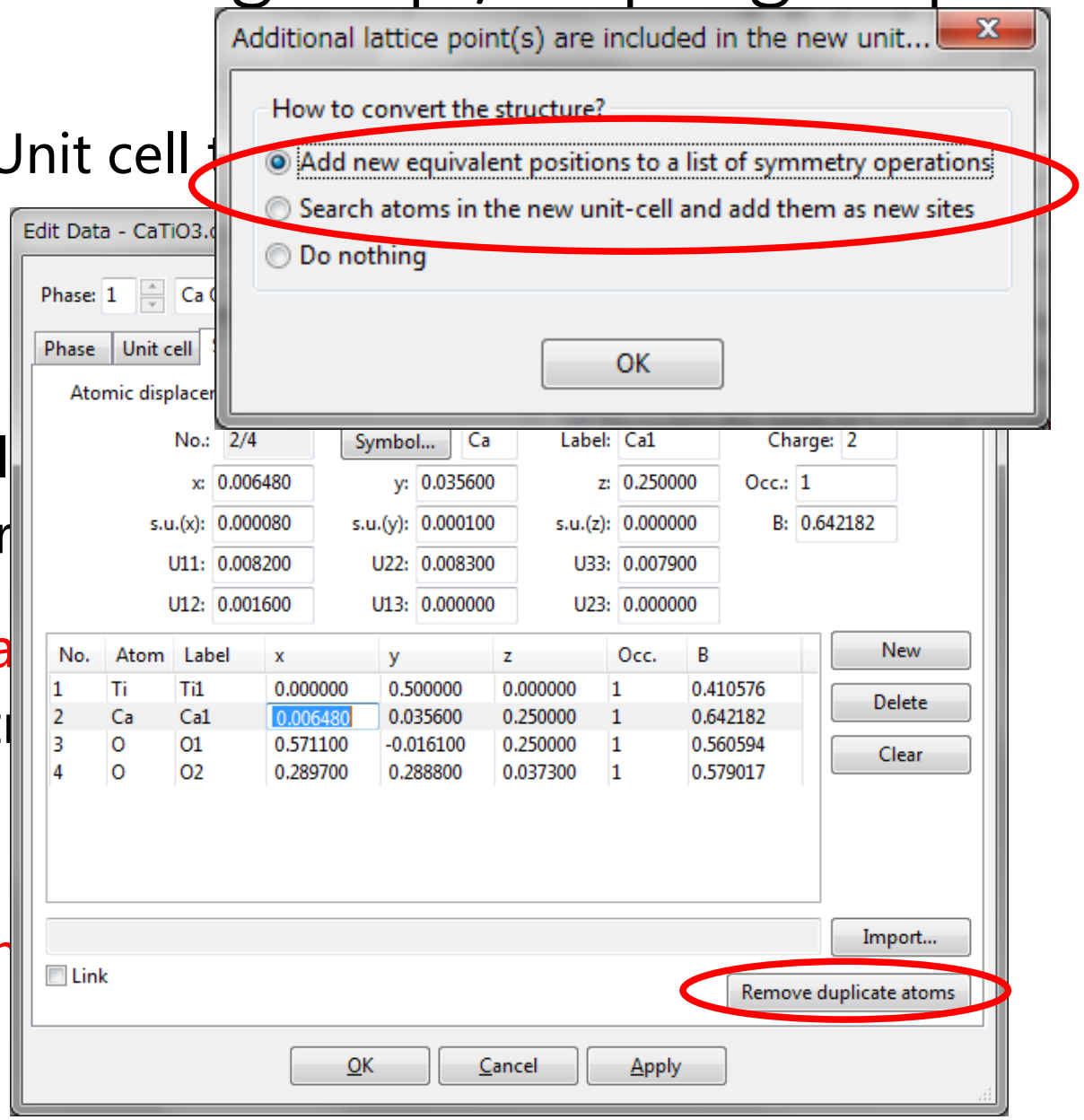
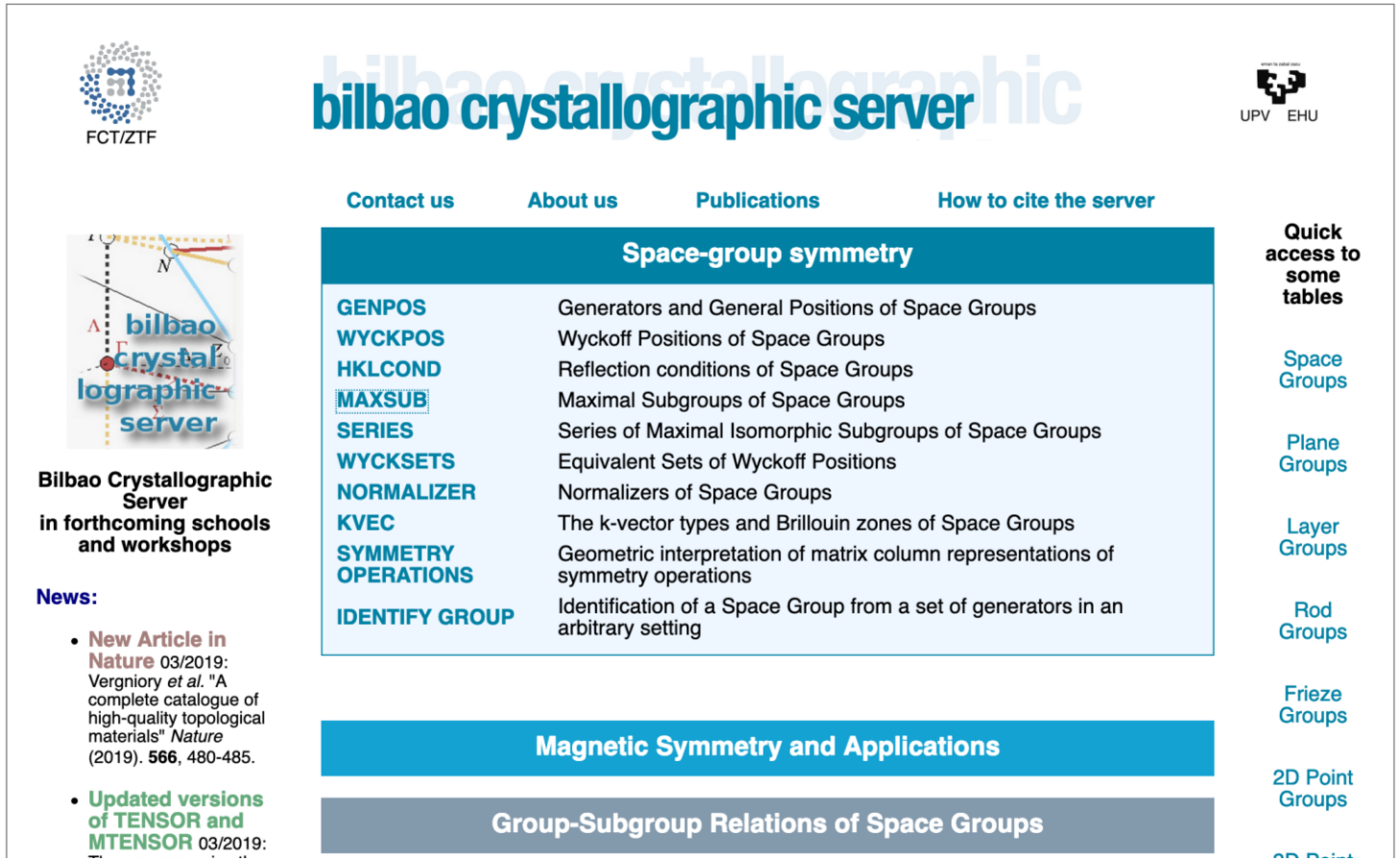
- Press the “Remove Symmetry” button aga
  transformation matrix to the identity matr
- Set a new space group.
- Use the “Remove duplicate atoms” buttor
  single site)



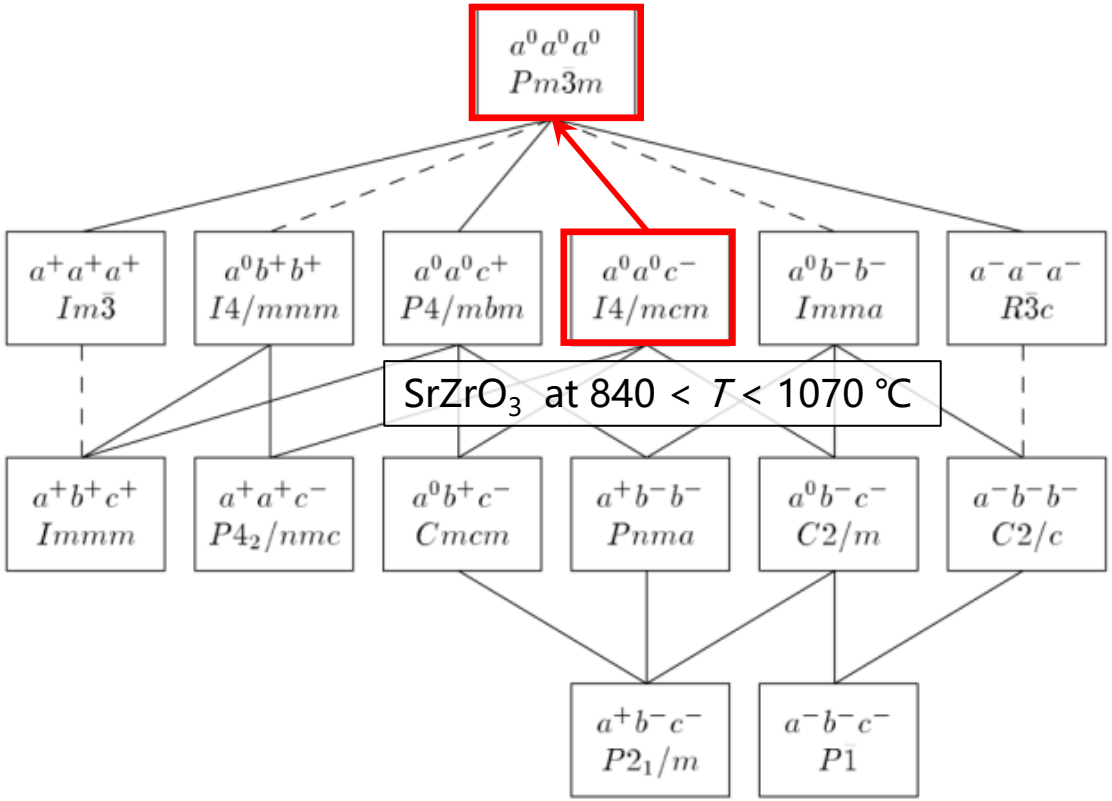
Conversion of a structure to its subgroup / supergroup



Bilbao crystallographic server (http://www.cryst.ehu.es/)

- Space-group symmetry -> MAXSUB
- Group-Subgroup Relations of Space Groups -> MINSUP

Conversion of a structure to its subgroup / supergroup



A schematic diagram indicating the group–subgroup relationships among the 15 space groups associated with octahedral tilting in perovskites (Howard et al., 2000).

Even with MINSUP, transformation matrix from supergroup → subgroup is shown.
For inverse conversion, inversion matrix needs to be calculated

*I*4/*mcm* ← *P*4/*mmm*

$$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ -1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

*P*4/*mmm* ← *Pm*3*m*

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

Inversion matrix (*I*4/*mcm* → *Pm*3*m*)

$$\begin{pmatrix} 1/2 & -1/2 & 0 & 0 \\ 1/2 & 1/2 & 0 & -1/2 \\ 0 & 0 & 1/2 & -1/4 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Practice 4

Conversion of a structure to its supergroup without calculating inverse matrix

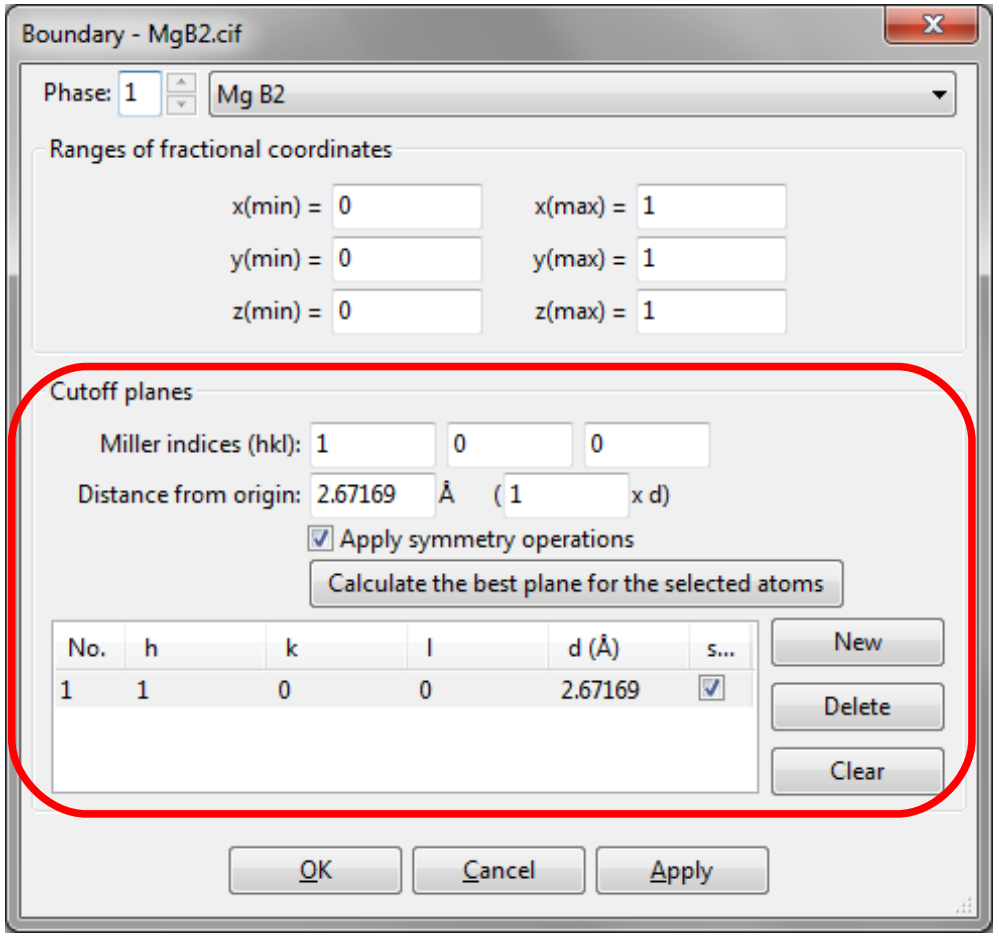
- In the “Edit Data” dialog box, change an option to the “Keep structure parameters unchanged” mode. Then input a transformation matrix from the desired supergroup to the current space group.

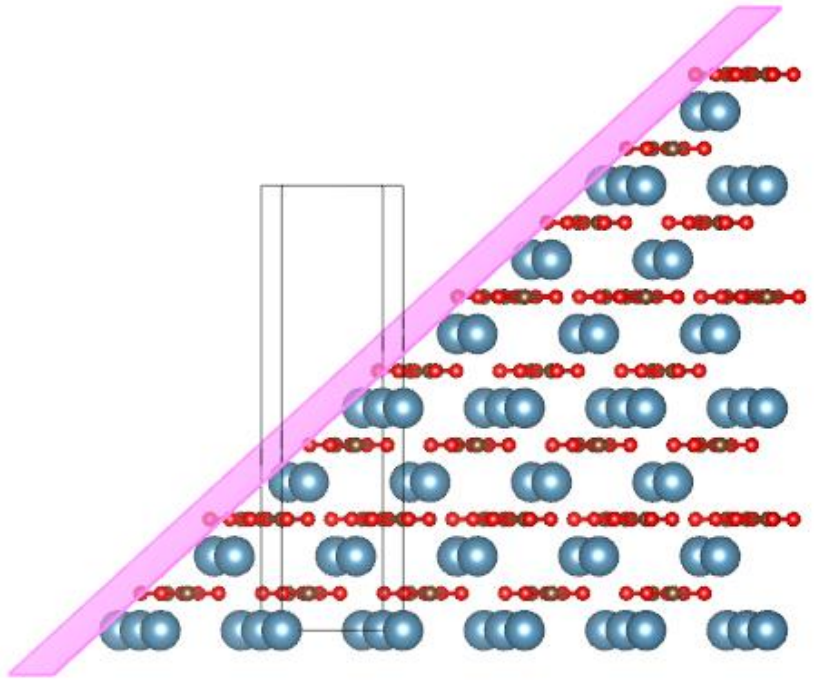
$$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ -1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

The result will be the same as “transformation from the supergroup *Pm*3*m* to *I*4/*mcm*” by this matrix

- Revert to the “Update structure parameters to keep 3D geometry” mode.
- Open the Transform dialog again and revert the matrix to the identity matrix. (DO NOT use the Initialize button. Input manually.)
- Change the space group to the supergroup.
- Use the “Remove duplicate atoms” if necessary.

Cut a structure by lattice planes





Practice 5

Command line interface of VESTA

Commands that work without GUI

-i *file*　Read a file without visualization

-save *file*　Save data to *file*.
parameters: format=rietan; option=cartesian,pcell,reduced,as_displayed

-list bond　Output information of unique bonds in the text area

-list angle　Output information of unique bond angles in the text area

-list poly　Output information of unique polyhedra in the text area

-merge_split_site dmin=*x*　Perform “Remove duplicate atoms”

-calcf out=*file*　Calculate structure factors and output to *file*

parameters: source=*n* lambda=*x* resolution=*x* anomalous=*n*
source:　0: X-ray (default); 1: Neutron
lambda:　wave length of the source in angstrom
resolution:　minimum d-spacing of hkl in angstrom

(Blue letters are optional parameters)

Command line interface of VESTA

Commands that work without (continued)

-rotate_x *angle*	Rotate 3D graphics around the *x*-axis
-rotate_y *angle*	Rotate 3D graphics around the *y*-axis
-rotate_z *angle*	Rotate 3D graphics around the *z*-axis

Commands that can be used when GUI is executed

-open *file*	Read a *file* and visualize
-reopen *file*	Reload data from a *file* and update 3D graphics
-close *file*	Close a tab showing the *file*. Close currently selected tab if no file specified.
-export_img scale=*n* *file*	Export an image to *file*.
-flush	Update screen after some operation, e.g. rotating data

Command line interface of VESTA:　Usage 1

Without GUI (combine with -nogui option)

- Windows & Linux

  VESTA -nogui -i test.cif -o format=rietan test.ins

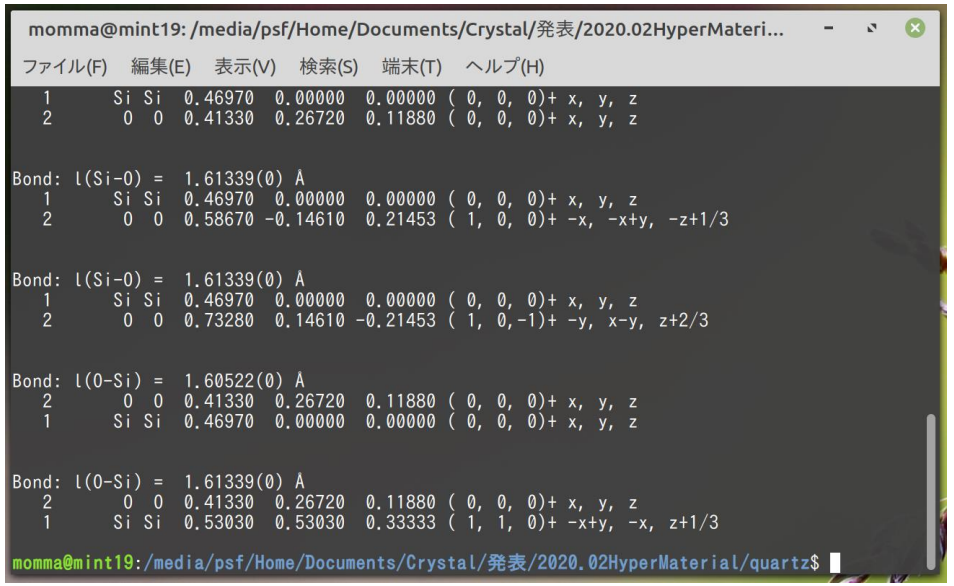
  VESTA -nogui -i test.cif -o option=cartesian test.vasp

  VESTA -nogui -i test.cif -list bond angle poly

(On windows, no texts will be output to the command prompt, so nothing happens on the last example)

- macOS

  This mode does not currently work on macOS



Command line interface of VESTA:　Usage 2

With GUI (texts will be output to the text area of VESTA main window)

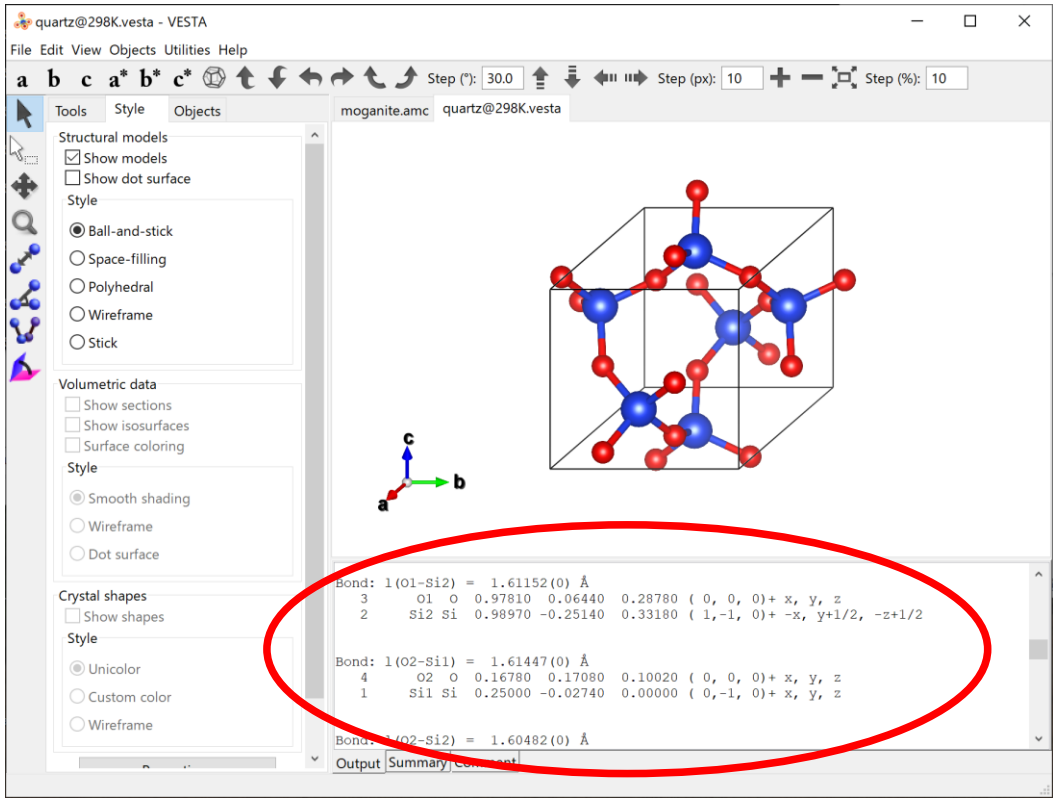
- Windows & Linux

  VESTA -open test.cif

  VESTA -list bond

  VESTA -export_img test.png

  VESTA close



- macOS

  open -n -a VESTA.app --args -list angle

  open -n -a VESTA.app --args -save format=rietan test.ins

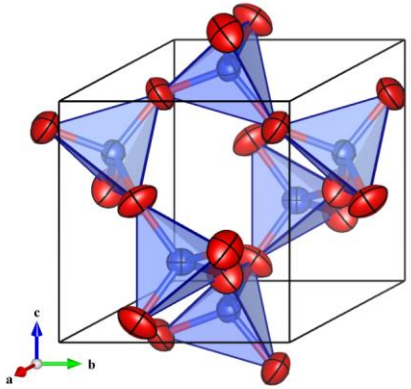
Practices

1. Comparison of two structures
2. Conversion of quartz structure
3. Align positions and orientations of data with different unit-cell settings
4. Conversion of $SrZrO_3$ from *I*4/*mcm* to *Pm*3*m*
5. Align the (111) slice of Ir metal parallel to graphene
6. Find possible stacking sequences of polytypes

If you haven't installed VESTA on your PC yet,
please download the latest version from

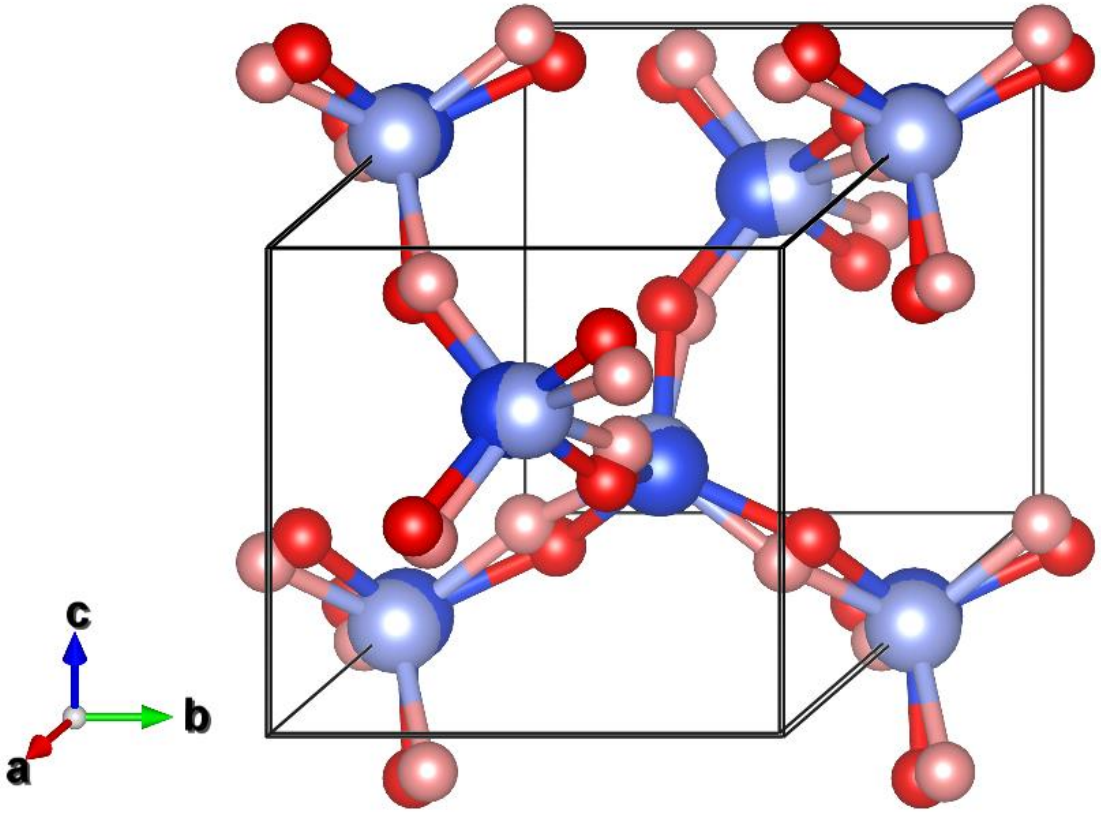
http://jp-minerals.org/vesta/en/download.html

Practice 1. Comparison of two structures

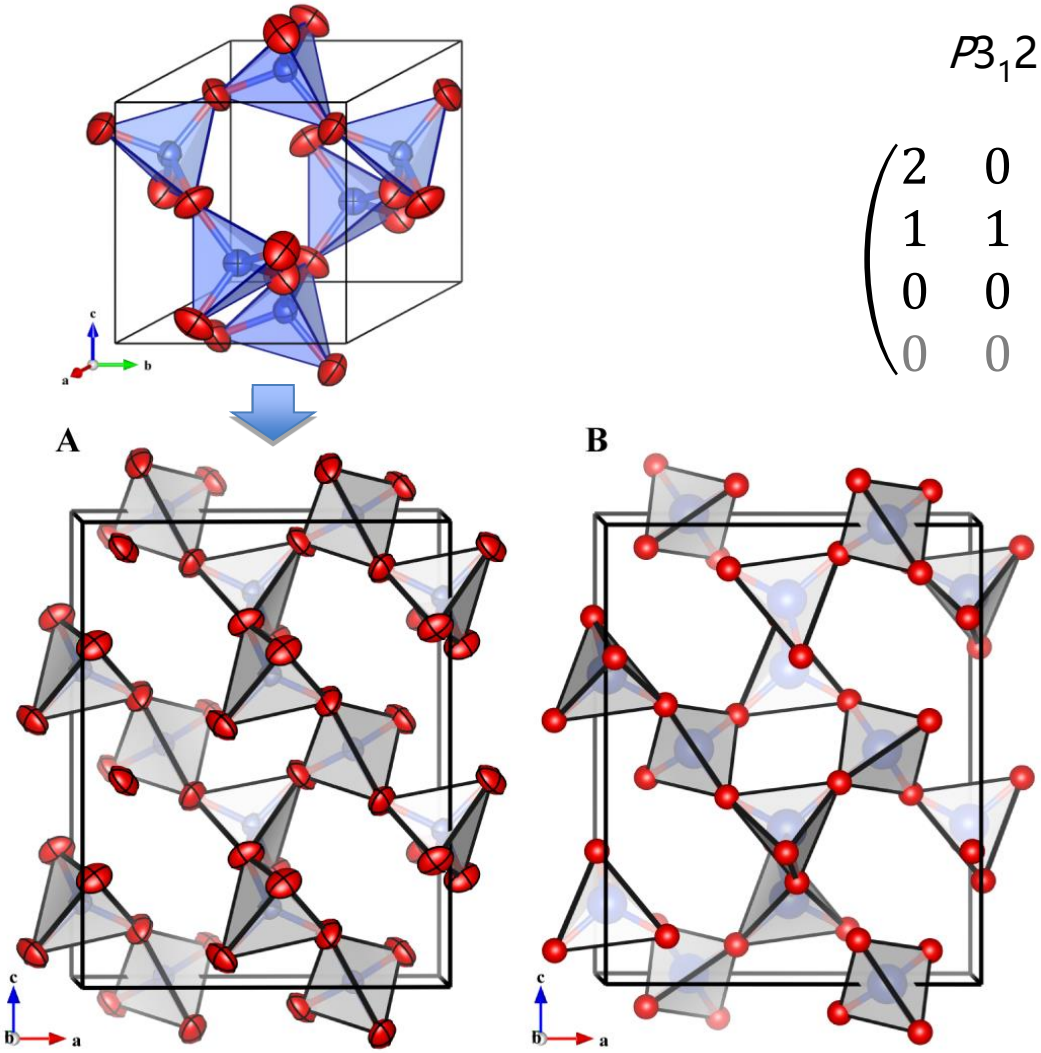


What to do: Align low-T and high-T data of quartz in the same window

1. Open quartz/quartz@298K.vesta
2. Import quartz/quartz@920K.amc
3. Set the origin of the low-T data to match with high-T data
   (set 0,0,2/3 as the origin shift *p* of low-T data)



Practice 2. Conversion of quartz structure



$P3_121 \rightarrow C2$　　$C2 \rightarrow C2$ with $c'=2c$　　Transformation matrix

$$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1/3 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1/3 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

A: A monoclinic setting of quartz unit cell with $a'=2a+b$, $b'=b$, and $c'=2c$. B: Unit cell of a silica polymorph moganite.

1. Open quartz/quartz@298K.vesta
2. Remove symmetry
3. Set the above transformation matrix
4. Remove symmetry again (to reset the transformation matrix)
5. Set space group *C*2
6. Remove duplicate atoms
7. Compare with quartz/moganite.amc

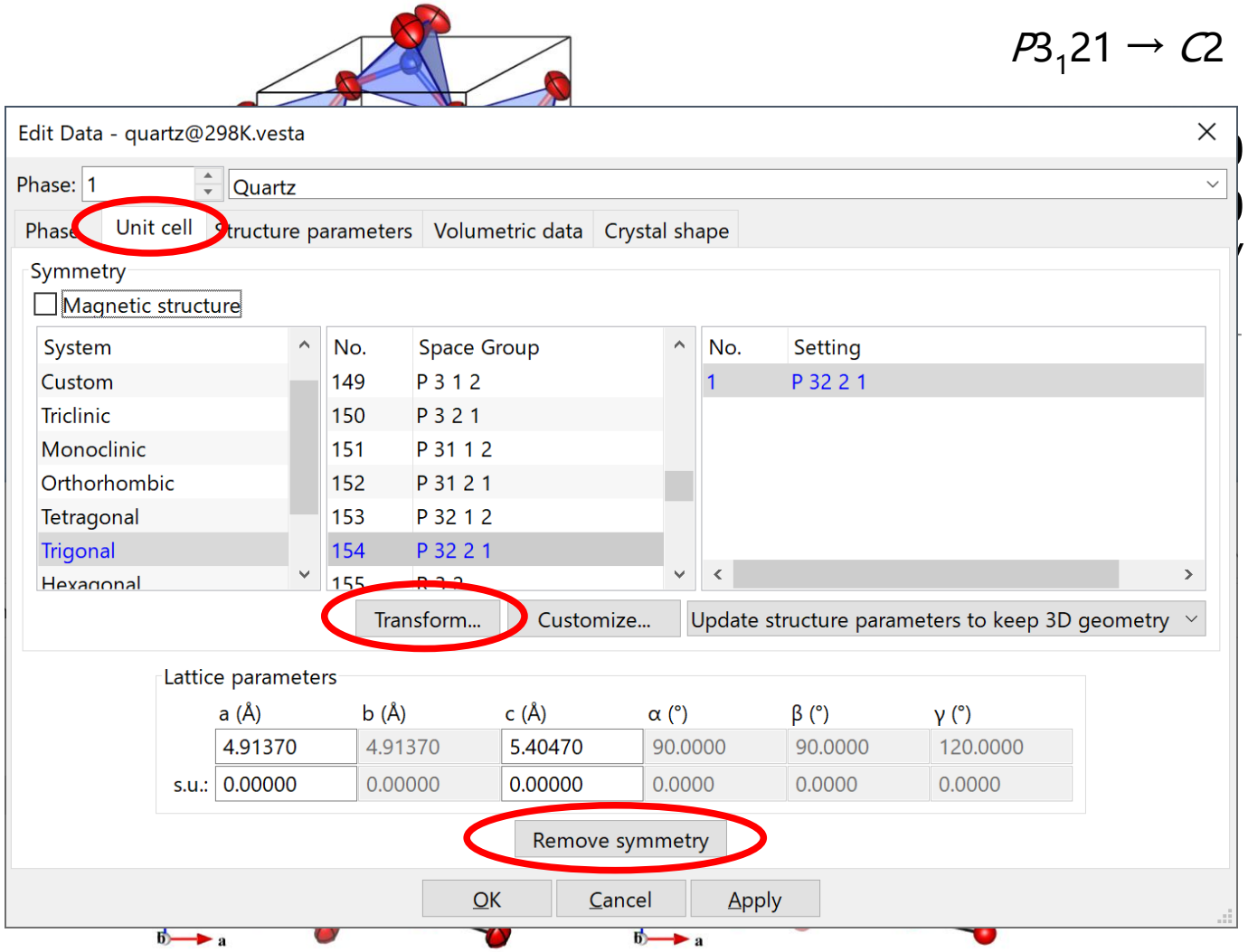
Practice 2. Conversion of quartz structure

$P3_121 \rightarrow C2$

$C2 \rightarrow C2$ with $c'=2c$

Transformation matrix

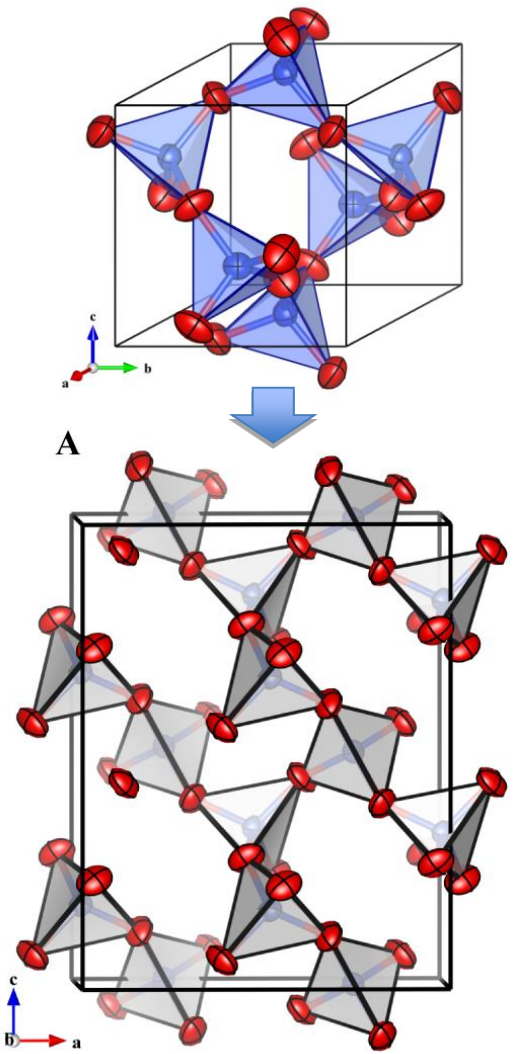
$$\begin{pmatrix} & & \\ & & \\ & & /3 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1/3 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$



A: A monoclinic setting of quartz unit cell with $a'=2a+b$, $b'=b$, and $c'=2c$. B: Unit cell of a silica polymorph moganite.

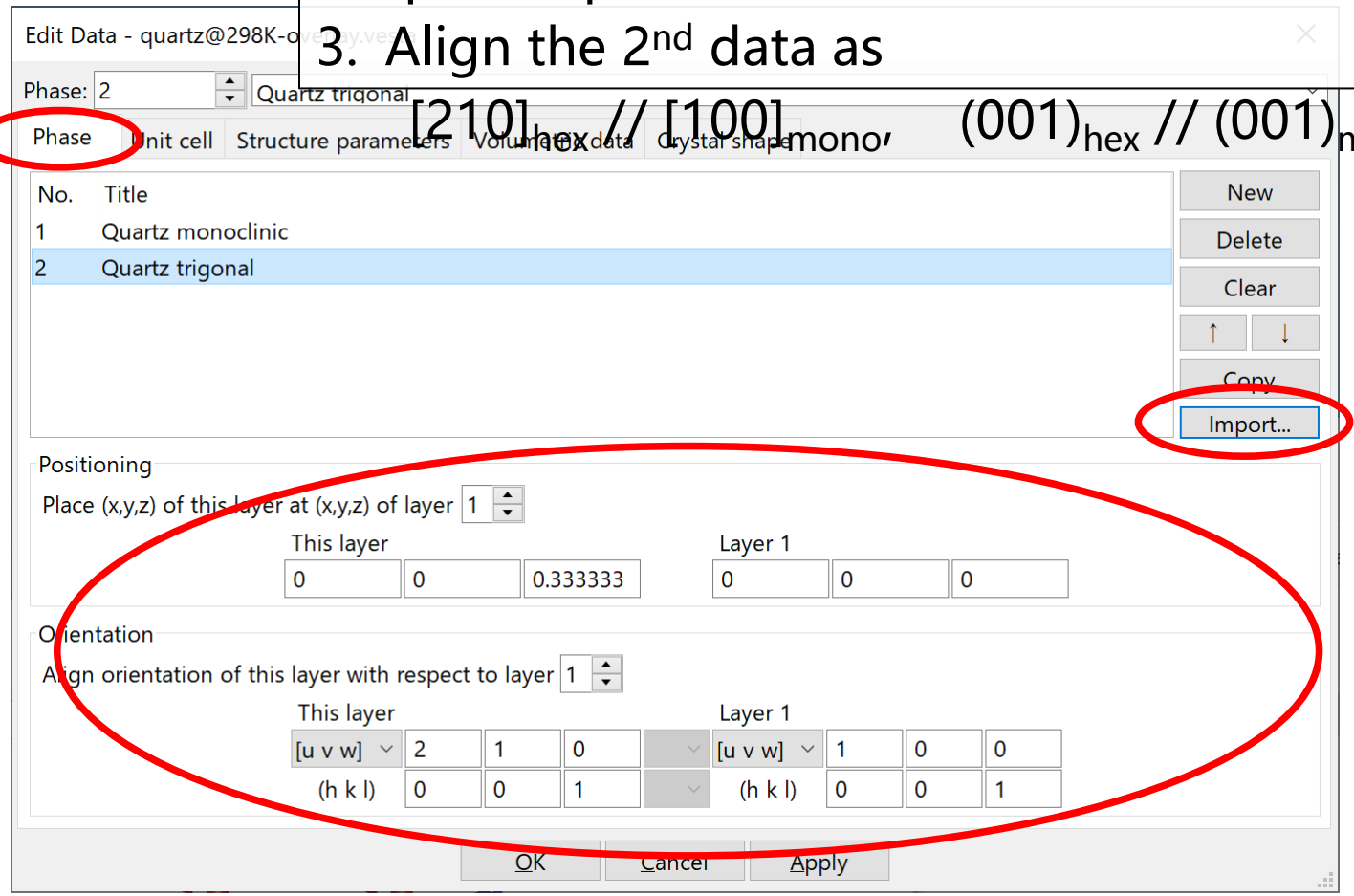
1. Open quartz/quartz@298K.vesta
2. Remove symmetry
3. Set the above transformation matrix
4. Remove symmetry again (to reset the transformation matrix)
5. Set space group $C2$
6. Remove duplicate atoms
7. Compare with quartz/moganite.amc

Practice 3. Align positions and orientations of data with different unit-cell settings

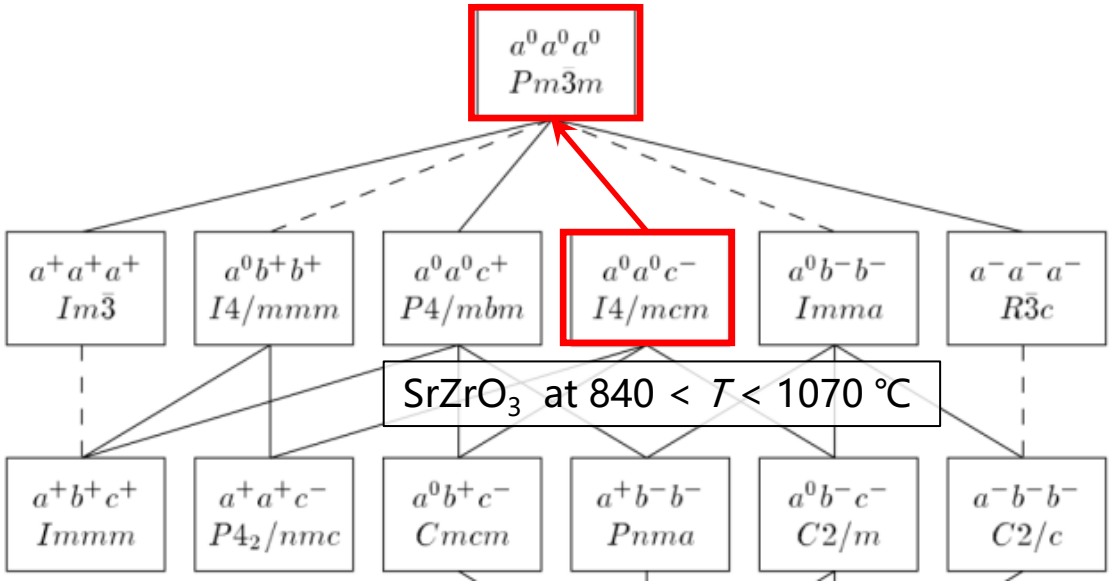


1. Open the quartz data transformed to C2 cell in the practice 2.
2. Import the original quartz/quartz@298K.vesta
3. Align the 2nd data as

$[210]_{hex}$ // $[100]_{mono}$, $(001)_{hex}$ // $(001)_{mono}$



Practice 4. Conversion of $SrZrO_3$ from *I*4/*mcm* to *Pm*3*m*



*I*4/*mcm* ← *P*4/*mmm*

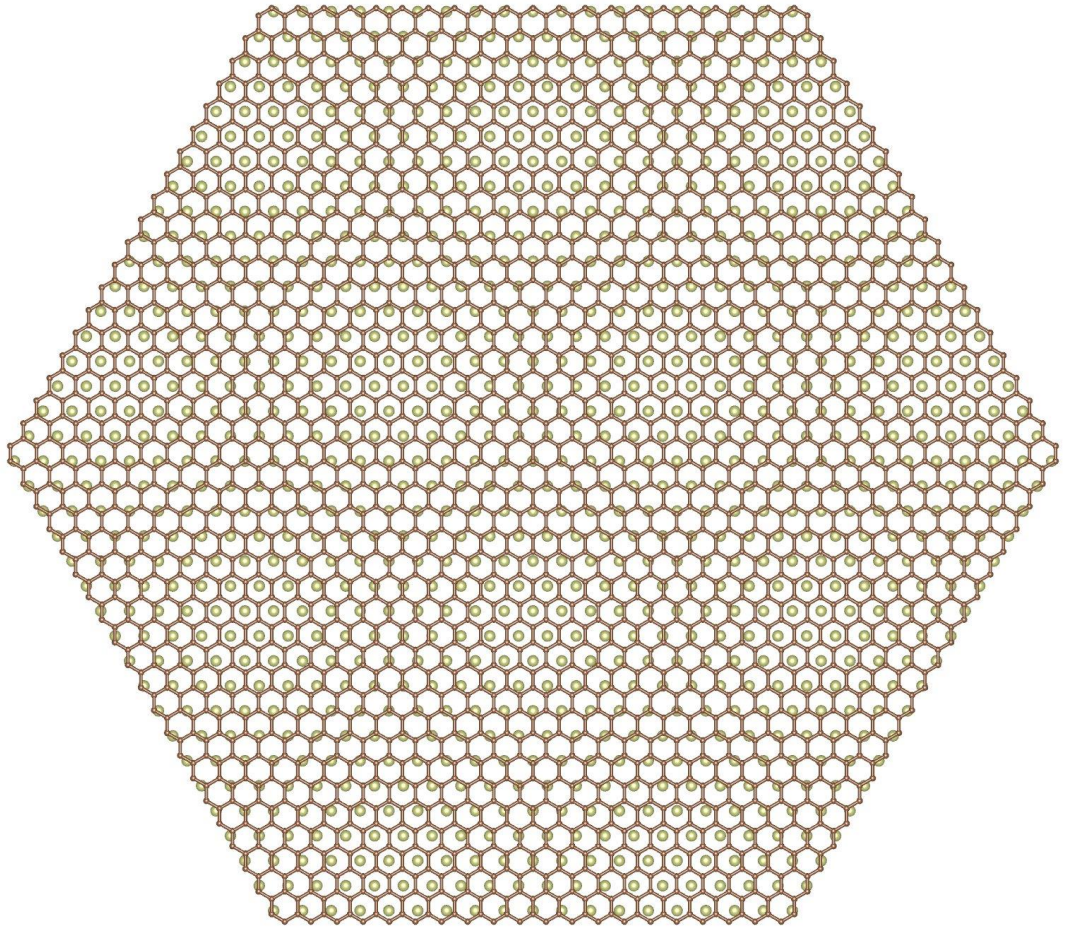
$$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ -1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

*P*4/*mmm* ← *Pm*3*m*

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

1. Open SrZrO3/ SrZrO3Perovskite_I4mcm.cif
2. Open **Edit Data** dialog, and change to "Keep structure parameters unchanged" mode.
3. Set the above transformation matrix
4. Revert to "Update structure parameters to keep 3D geometry" mode
5. Revert the transformation matrix to identity matrix
6. Set Space group to *Pm*3*m*, and perform **Remove duplicate atoms**

Practice 5. Align the (111) slice of Ir parallel to graphene

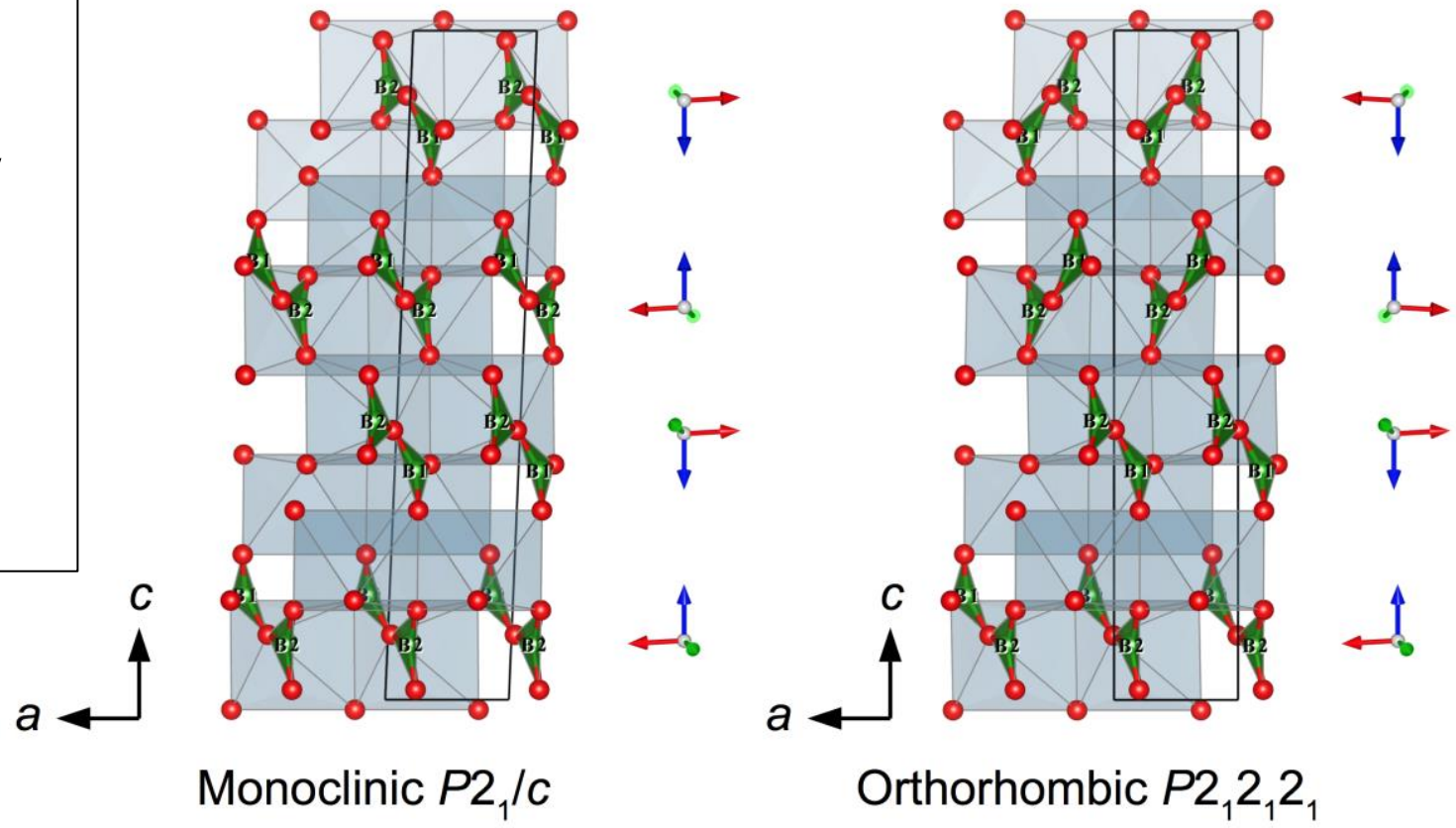


1. Open Ir-graphene/Ir-unitcell.vesta
2. Set **Boundary** as -9 <= *x, y, z* <= 9
3. Set Cut off plane and create a slice of (111)
4. Import Ir-graphene/graphite.vesta as 2nd phase
5. Align orientation as
   $[001]_{graphite}$ // [111]Ir,　$(010)_{graphite}$ // $(\bar{1}\bar{1}2)_{Ir}$
6. Set **Boundary** of 2nd phase as
   -24 <= *x, y* <= 24, 0 <= *z* <= 0.5

Practice 6. Find possible stacking sequences of polytypes

Background:

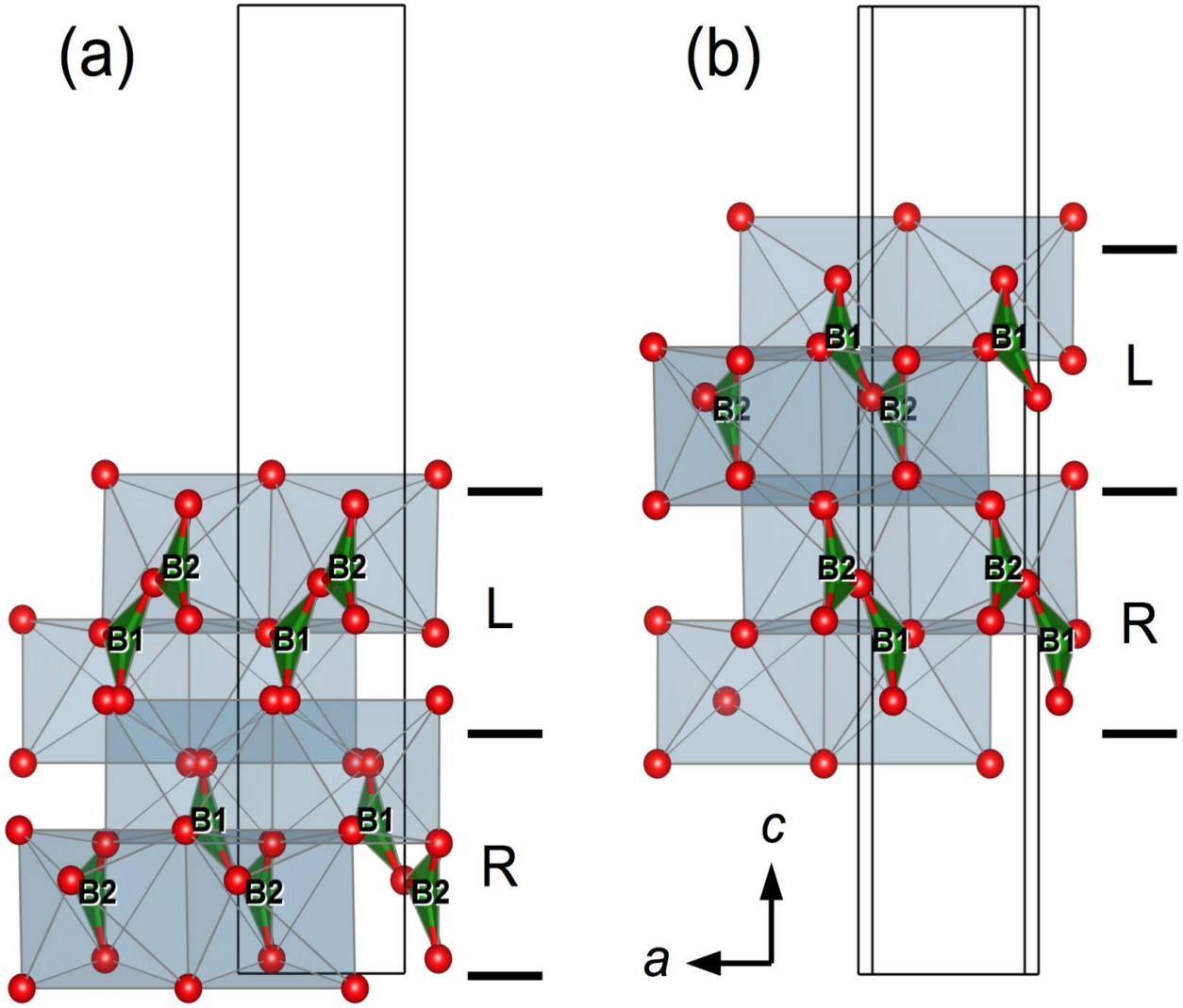
- New mineral shimazakiite, (CaB_2O_5), was found.
- Structure of the orthorhombic polytype ($P2_12_12_1$) was first solved.
- Existence of a monoclinic polytype was suggested from TEM observation.



Shimazakiite-4*M*　　Shimazakiite-4*O*

2 polytypes of shimazakiite (CaB_2O_5)

How layers can be stacked in shimazakiite-4M?

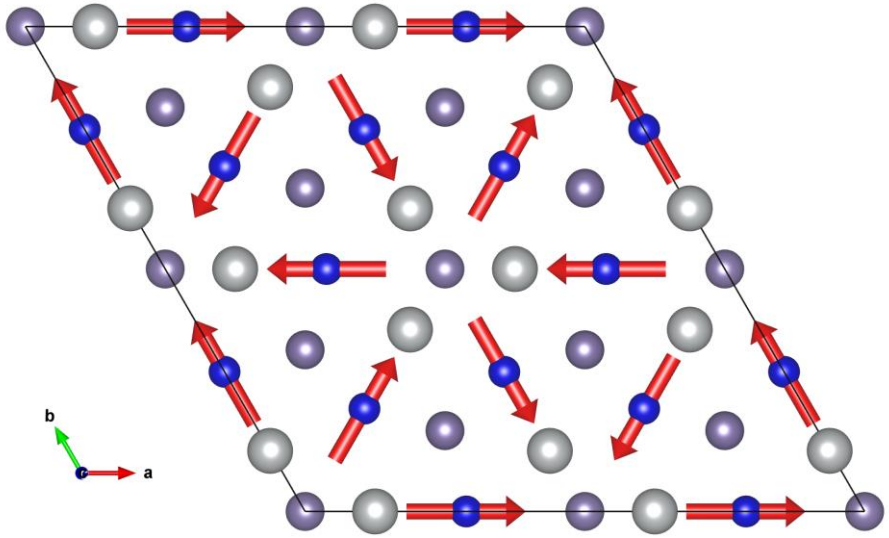


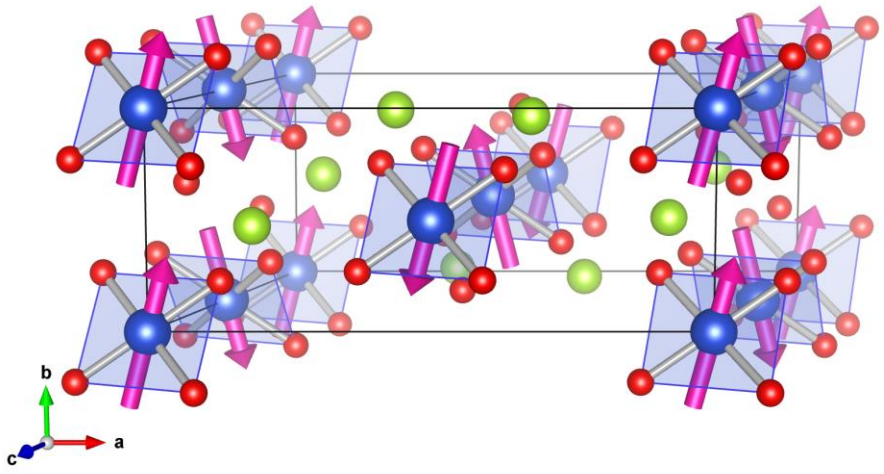
What to do: Starting from 4O structure, create enantiomorphic layer structure, rotate and shift each layer, and find possible stacking positions.

1. Open shimazakiite/shiimazakiite-4O.vesta
2. Copy the phase data in **Edit Data** dialog
3. Transform the copied structure to enantiomorphic
4. Set **Boundary** of 1st phase as ¼ <= z <= ½
5. Set **Boundary** of 2nd phase as ½ <= z <= ¾
6. Find the best matching position
7. Try other types of staking

Appendix I

Magnetic structures





Magnetic structures

Commensurate structure

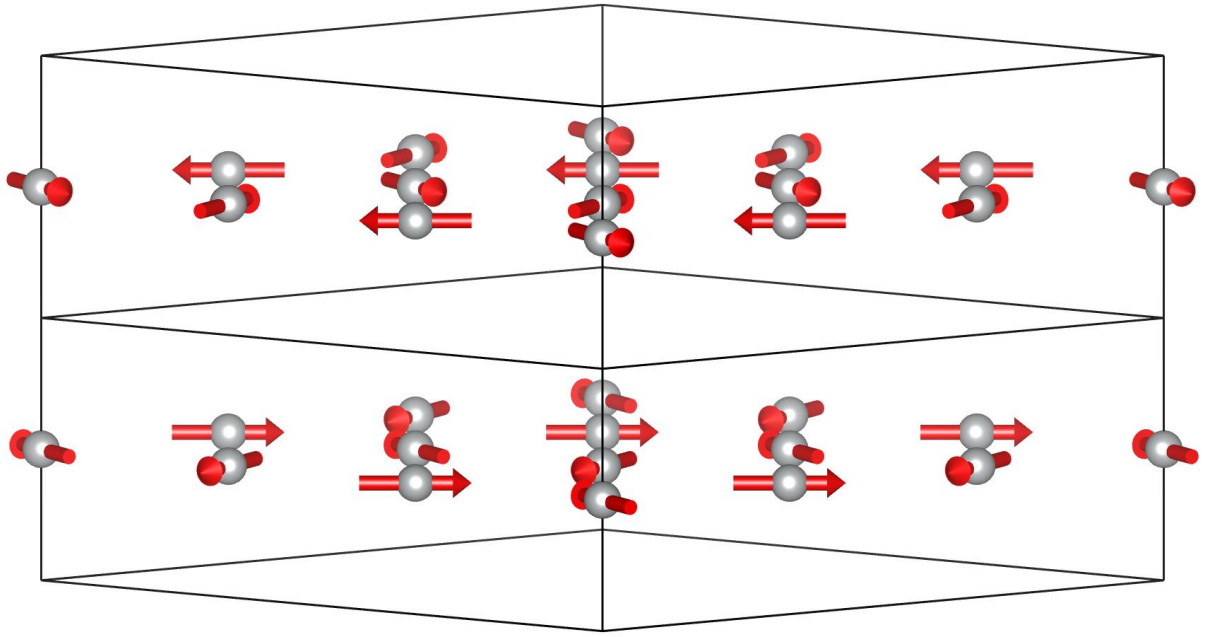
1651 magnetic space groups

Incommensurate structure

Magnetic unit cell ≥ Crystallographic unit cell

BNS setting
(Belov-Neronova-Smirnova notation)
Based on magnetic unit cell
(translation < 1)

OG setting
(Opechowski-Guccione notation)
Based on crystallographic space groups
(translation can be larger than 1)



Magnetic structure of $Ba_3Nb_2NiO_9$

Classification of magnetic space groups

Magnetic space groups derived from $I4_1/amd$

F: Symmetry elements of space group $I4_1/amd$
G: Symmetry elements of magnetic groups

BNS setting		OG setting	
#141.551	$I4_1/amd$	#141.1.1213	$I4_1/amd$
#141.552	$I4_1/amd1'$	#141.2.1214	$I4_1/amd1'$
#141.553	$I4_1/a'md$	#141.3.1215	$I4_1/a'md$
#141.554	$I4_1'/am'd$	#141.4.1216	$I4_1'/am'd$
#141.555	$I4_1'/amd'$	#141.5.1217	$I4_1'/amd'$
#141.556	$I4_1'/a'm'd$	#141.6.1218	$I4_1'/a'm'd$
#141.557	$I4_1/am'd'$	#141.7.1219	$I4_1/am'd'$
#141.558	$I4_1'/a'md'$	#141.8.1220	$I4_1'/a'md'$
#141.559	$I4_1/a'm'd'$	#141.9.1221	$I4_1/a'm'd'$
#141.560	I_c4_1/amd	#134.10.1141	P_I4_2/nnm

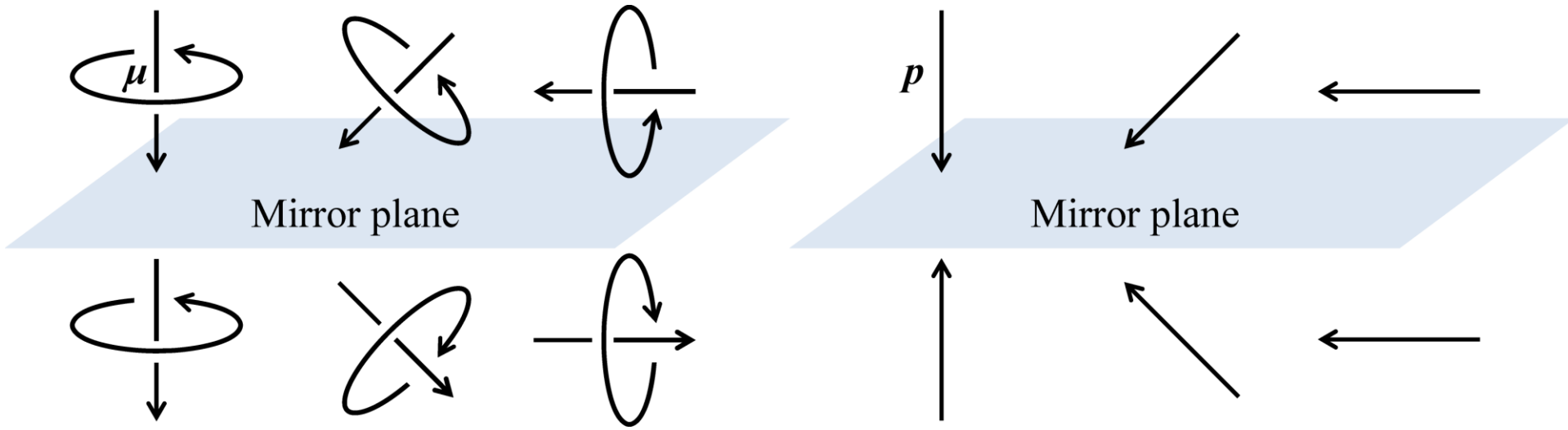
Type 1: ***G*** = ***F*** (Federov group)

Type 2: ***G*** = ***F*** + ***F***1’ (Grey group)

Type 3: ***G*** = ***D*** + (***F*** - ***D***)1’
(D: Translationgleiche / t-subgroup)
Translational elements are retained but point group is reduced

Type 4: ***G*** = ***D*** + (***F*** - ***D***)1’
(D: Klassengleiche / k-subgroup)
Point group is retained but with a loss of translations

Axial and polar vectors



Axial vector
(magnetic moment)

Polar vector
(electric dipole moment)

Magnetic symmetry operations

$$\mathbb{Q} = \begin{pmatrix} \boldsymbol{Q} & \boldsymbol{q} \\ \boldsymbol{o} & 1 \end{pmatrix}$$

$$= \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} & q_1 \\ Q_{21} & Q_{22} & Q_{23} & q_2 \\ Q_{31} & Q_{32} & Q_{33} & q_3 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

3 × 3 rotation part

3 × 1 translation part

Time reversal

The last row does not contain any information, so we can reuse it to keep time reversal information. When multiplying matrices, however, a special trick is required for not inverting translational component by time reversal operation.

$$\begin{pmatrix} x' \\ y' \\ z' \\ 1 \end{pmatrix} = \mathbb{Q} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}$$

Atomic coordinates

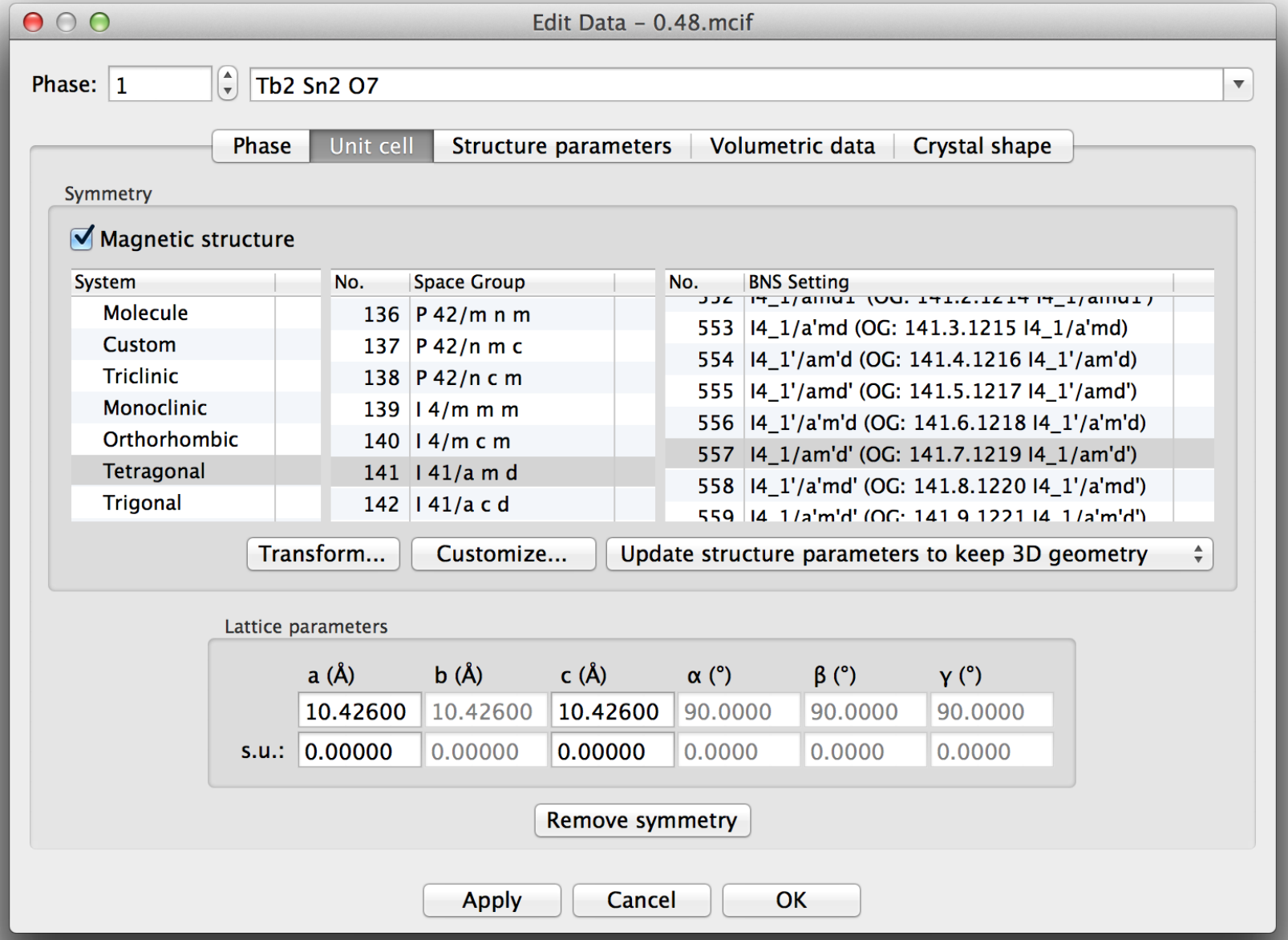
$$\mu' = \left| \mathbb{Q} \right| Q\mu$$

Axial vector (μ)
(magnetic moment)

$$p \not\Leftarrow Qp$$

Polar vector (p)
(electric dipole moment)

Magnetic space groups



Magnetic symmetry operations

Equivalent Positions – magndata_3.1_TmAgGe_59709.mcif

Phase: 1 5yOhtAoR

Rotation matrix (W)

1	0	0
0	1	0
0	0	1

Translation vector (w)

0.000000
0.000000
0.000000

Time reversal (t)

1

General equivalent positions

No.	x'	y'	z'	t	mx'	my'	mz'
1	x	y	z	+1	mx	my	mz
2	-y	x-y+1/2	z	+1	-my	mx-my	mz
3	-x+y+1/2	-x	z	+1	-mx+my	-mx	mz
4	x-y+1/2	-y	-z	+1	mx-my	-my	-mz
5	y	x	-z	+1	my	mx	-mz
6	-x	-x+y+1/2	-z	+1	-mx	-mx+my	-mz
7	-x+y+1/2	-x	-z	-1	-mx+my	-mx	-mz
8	x	y	-z	-1	mx	my	-mz
9	-y	x-y+1/2	-z	-1	-my	mx-my	-mz
10	-x	-x+y+1/2	z	-1	-mx	-mx+my	mz
11	x-y+1/2	-y	z	-1	mx-my	-my	mz
12	y	x	z	-1	my	mx	mz

Close

Symmetry operation $\mathbb{W}$ transforms x, y, z to x', y', z'.

$$\mathbb{W}=\begin{pmatrix} \mathbf{W} & \mathbf{w} \\ 0 & 1 \end{pmatrix}=\begin{pmatrix} W_{11} & W_{12} & W_{13} & w_1 \\ W_{21} & W_{22} & W_{23} & w_2 \\ W_{31} & W_{32} & W_{33} & w_3 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

The (3x3) matrix W is the rotational part.

The (3x1) column matrix w is the translational part.

Transformed coordinates (x', y', z') are related to (x, y, z) by

$$\begin{pmatrix} x' \\ y' \\ z' \\ 1 \end{pmatrix}=\begin{pmatrix} W_{11} & W_{12} & W_{13} & w_1 \\ W_{21} & W_{22} & W_{23} & w_2 \\ W_{31} & W_{32} & W_{33} & w_3 \\ 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}$$

$$=\begin{pmatrix} W_{11}x+W_{12}y+W_{13}z+w_1 \\ W_{21}x+W_{22}y+W_{23}z+w_2 \\ W_{31}x+W_{32}y+W_{33}z+w_3 \\ 1 \end{pmatrix}$$

1.0.14_CsFeCl3.mcif - VESTA

File Edit View Objects Utilities Help

a b c a* b* c* Step (°): 30.0 Step (px): 10 Step (%): 10

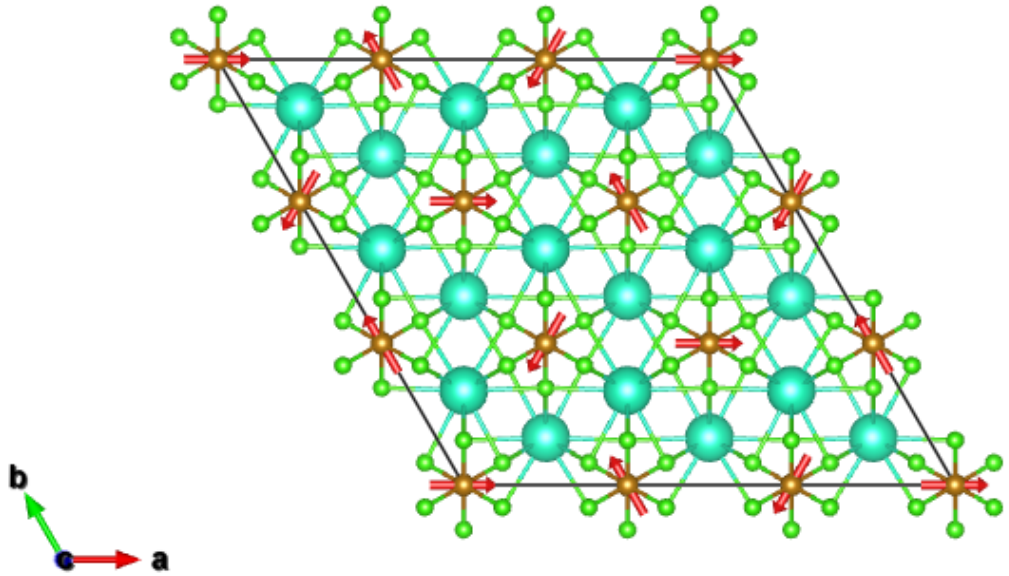
Tools Style Objects

V	Title
☑	5yOhtAoR
☑	Atoms
☑	Bonds
☑	Polyhedra

Toggle data: < 1/1 >

Site	r (Å)	C	L	S	V
Cl	0.99		☐	☐	☑
Cl1_	0.99		☐	☐	☑
Cl1_	0.99		☐	☐	☑
Cl1_	0.99		☐	☐	☑
Cl1_	0.99		☐	☐	☑
Fe	1.26		☐	☐	☑
Fe1	1.26		☐	☐	☑
Cs	2.72		☐	☐	☑
Cs1_	2.72		☐	☐	☑
Cs1_	2.72		☐	☐	☑
Cs1_	2.72		☐	☐	☑

Diamond.vesta quartz-kihara.amc xTiO2.vesta 1.0.14_CsFeCl3.mcif




```
Parent space group name              P 6_3/m m c
Parent space group number            194
Transformation from parent           3a,3b,c; 0,0,0
Transformation to parent             1/3a,1/3b,c; 0,0,0
Magnetic space group name (BNS)      P-6'2'm
Magnetic space group number (BNS)    189.223
Transformation from standard setting a-b,a+2b,c; 1/3,1/3,3/4
Transformation to standard setting   2/3a+1/3b,-1/3a+1/3b,c; 8/9,7/9,1/4

Lattice parameters
```

Output Summary Comment

Creation of vectors

- Edit → Vectors