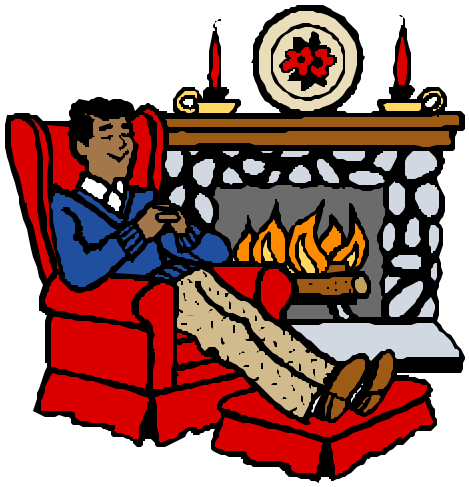
Rigid Body Constraints in GSAS



The Fireside Guide

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Overview /Summary

- What are restraints/constraints?
- What is a rigid body?
- When should I use it?
- How do I implement it in GSAS?
- What are TLS tensors?

Vocabulary

- Constraint: A rigorously applied limit

  e.g. rigid bodies, space group.

  Non-negotiable! Must be obeyed

- Restraint: A loosely applied limit

  e.g. soft/slack bond distance “constraints”.

  Treated as another set of observations. Adjust relative weight of restraint vs. “real” data, and therefore how much “notice” the refinement takes of restraint

- Rigid Body: a geometrical constraint applied to a molecule or known fragment

When to use constraints/restraints

- When a piece of chemical/structural information is known “for certain”; e.g. NH_4 is tetrahedral, Si-O is 1.61A.

- e.g. as a “guiding hand” during refinement for complex systems. The constraint could be used in the early stages, and perhaps released at the end.

- Where the degree of over-determination is low. It is best to have a high ratio of observations:variables. If there is a lot of peak overlap or many variables, a constraint can reduce the number of terms in the LSQ matrix. [Note: a restraint keeps the same number of variables in the matrix]

Constraints

Space Group:

P1: a,b,c, α, β, γ: 6 variables

Fm3m: a=b=c, $\alpha=\beta=\gamma=90°$: 1 variable

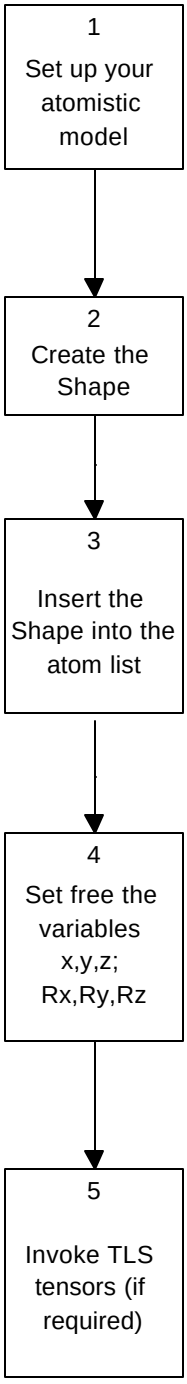
Rigid Body:

Ignoring other symmetry constraints:

- Atomistic: N, 4H 5 x 3(xyz) =15 variables
- RB: NH4, 3 rotations($R_xR_yR_z$) + 3 translations (xyz) =6 variables
- Reduce number of variables by 9 per NH_4 molecule

Overview of Process of Refining an RB in GSAS

Overview of Process Required To Set up an RB Refinement in GSAS



i.e. start a normal GSAS EXP file with atomic positions

Define your tetrehaedron, octahedron, any irregular polyhedron

Match the positons defined in your Rigid Body to the atom list. Atoms in the RB must be sequential in the atom list!

Once inserted, the positional variables of the RB constraint override your atomistic variables. Both sets must agree in logic to refine the positional variable of the RB

Only used if you want to model the thermal motion of the RB as a truly rigid shape.

Numbers in boxes reflected in headings of later example slides in [] to link example back to this chart

RB frame and crystal frame

- The RB we will define is in Cartesian coordinates (in A)
- The atom list is in fractional coordinates of the axes defined by the space group
- Therefore there is a transformation relationship between the two:
  - X//a, Z//a⊗b, Y//(a⊗b) ⊗a
  - X//a, Y//b, Z//c for cubic, tetragonal, orthorhombic)

TLS tensors

- Describe rigid body thermal motion and replace atomistic displacements
  - T=translation: $6T_{ij}$
  - L=libration: $6L_{ij}$
  - S=Screw: 8(9) S_{ij} (helical motion)
- Number of components determined by point symmetry of molecule;

e.g. cubic:

$T_{11}=T_{22}=T_{33}$

$T_{12}=T_{23}=T_{13}=0$

- Ref: Schomaker and Trueblood, Acta Cryst B24, p63 (1968)

How many components do I need?

Acta Cryst. (1968). B **24**, 63

On the Rigid-Body Motion of Molecules in Crystals*

BY VERNER SCHOMAKER
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AND K. N. TRUEBLOOD
Department of Chemistry,† University of California, Los Angeles, California 90024, *U.S.A.*

(*Received* 15 *May* 1967)

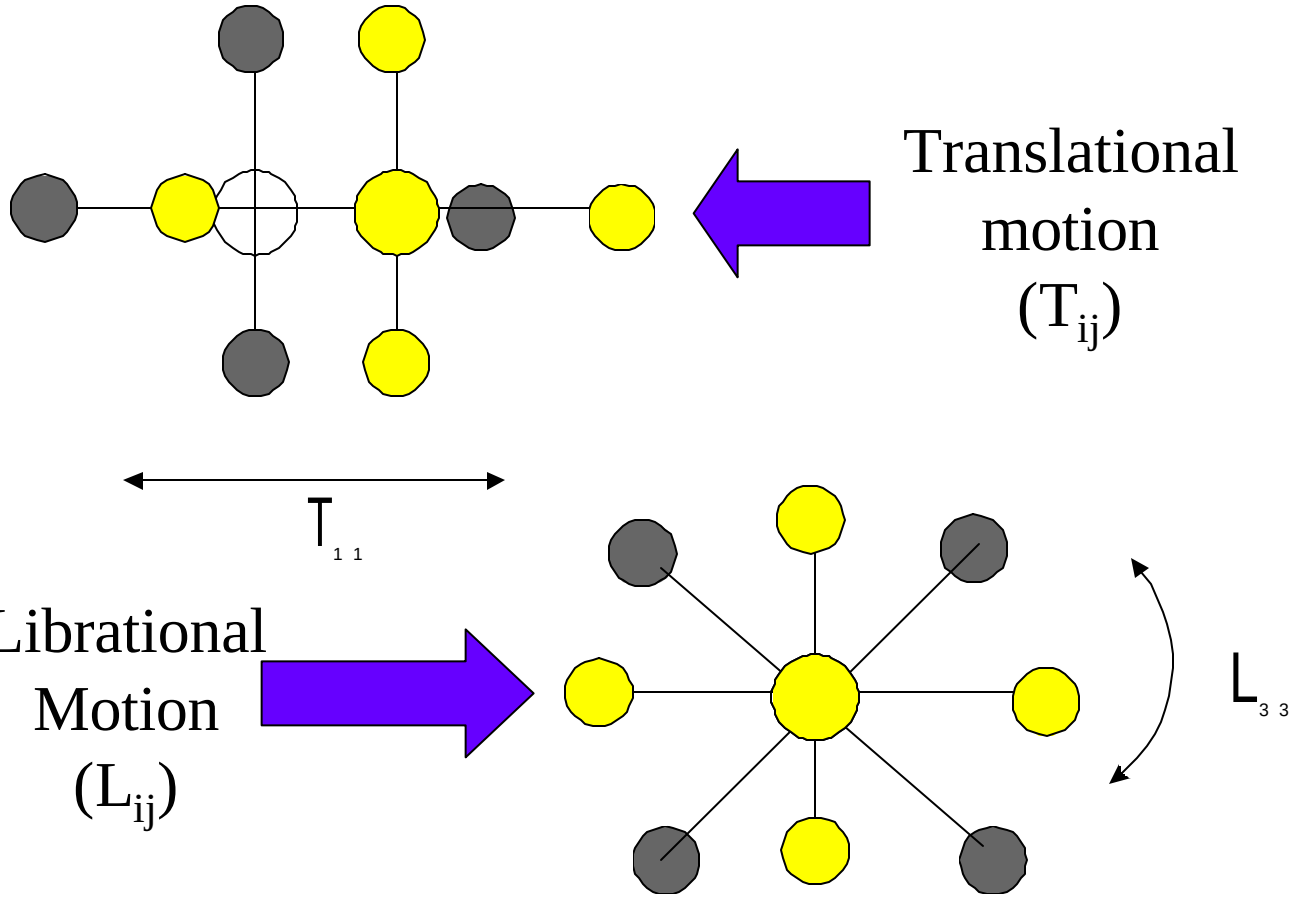


Table 4. *Site-symmetry requirements imposed by the crystallographic point groups*[a]

Point group	$\bar{\mathbf{u}}, \bar{\mathbf{t}}, \bar{\mathbf{S}}_a$	U, L, T	$\bar{\lambda}$	S	Comments[b]
C_1-1	$\begin{pmatrix}1\\2\\3\end{pmatrix}$	$\begin{pmatrix}11 & 12 & 13\\12 & 22 & 23\\13 & 23 & 33\end{pmatrix}$	$\begin{pmatrix}1\\2\\3\end{pmatrix}$	$\begin{pmatrix}11 & 12 & 13\\21 & 22 & 23\\31 & 32 & 33\end{pmatrix}$	The general case considered at length in the foregoing discussion.
$C_i-\bar{1}$	0	$\begin{pmatrix}11 & 12 & 13\\12 & 22 & 23\\13 & 23 & 33\end{pmatrix}$	$\begin{pmatrix}1\\2\\3\end{pmatrix}$	0	Corresponds to Cruickshank's treatment.
C_2-2	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	$\begin{pmatrix}11 & 12 & 0\\12 & 22 & 0\\0 & 0 & 33\end{pmatrix}$	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	$\begin{pmatrix}11 & 12 & 0\\21 & 22 & 0\\0 & 0 & 33\end{pmatrix}$	Each axis can have a helical component. S_{12} and $S_{21}\rightarrow 0$ by tranformation to axes at different heights, still intersecting **2**. Third axis along **2**.
C_s-m	$\begin{pmatrix}1\\2\\0\end{pmatrix}$	$\begin{pmatrix}11 & 12 & 0\\12 & 22 & 0\\0 & 0 & 33\end{pmatrix}$	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	$\begin{pmatrix}0 & 0 & 13\\0 & 0 & 23\\31 & 32 & 0\end{pmatrix}$	No helical components. S_{13} *etc.*$\rightarrow 0$ by displacing two axes in the plane and the intersection of the third with the plane.
$C_{2h}-2/m$	0	$\begin{pmatrix}11 & 12 & 0\\12 & 22 & 0\\0 & 0 & 33\end{pmatrix}$	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	0	
D_2-222	0	$\begin{pmatrix}11 & 0 & 0\\0 & 22 & 0\\0 & 0 & 33\end{pmatrix}$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 22 & 0\\0 & 0 & 33\end{pmatrix}$	Unequal helicals intersecting at origin of D_2.
$C_{2v}-mm2$	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	$\begin{pmatrix}11 & 0 & 0\\0 & 22 & 0\\0 & 0 & 33\end{pmatrix}$	0	$\begin{pmatrix}0 & 12 & 0\\21 & 0 & 0\\0 & 0 & 0\end{pmatrix}$	Two axes normal to the twofold axis, not at same level.
$D_{2h}-mmm$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 22 & 0\\0 & 0 & 33\end{pmatrix}$	0	0	
C_4-4, C_3-3, C_6-6	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 33\end{pmatrix}$	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	$\begin{pmatrix}11 & 12 & 0\\-12 & 11 & 0\\0 & 0 & 33\end{pmatrix}$ [c]	Two axes normal to symmetry axis at same level, with equal helicals.
$S_4-\bar{4}$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 33\end{pmatrix}$	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	$\begin{pmatrix}11 & 12 & 0\\12 & -11 & 0\\0 & 0 & 0\end{pmatrix}$ [d]	Two equal and opposite helicals, equally and oppositely displaced along $\bar{4}$.
$C_{4h}-4/m$, $C_{3i}-\bar{3}$, $C_{3h}-\bar{6}$, $C_{6h}-6/m$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 33\end{pmatrix}$	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	0	
D_4-422, D_3-32, D_6-622	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 33\end{pmatrix}$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 33\end{pmatrix}$ [c]	Two equal helicals through origin.
$C_{4v}-4mm$, $C_{3v}-3m$, $C_{6v}-6mm$	$\begin{pmatrix}0\\0\\3\end{pmatrix}$	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 33\end{pmatrix}$	0	$\begin{pmatrix}0 & 12 & 0\\-12 & 0 & 0\\0 & 0 & 0\end{pmatrix}$ [c]	No helicals; axes normal to axis 3 at same level.
$D_{2d}-\bar{4}2m$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 33\end{pmatrix}$	0	$\begin{pmatrix}11 & 0 & 0\\0 & -11 & 0\\0 & 0 & 0\end{pmatrix}$ [d],[e]	Equal and opposite helicals normal to $\bar{4}$ through origin.
$D_{4h}-(4/m)mm$, $D_{3d}-\bar{3}m$, $D_{3h}-\bar{6}m2$, $D_{6h}-(6/m)mm$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 33\end{pmatrix}$	0	0	
$T-23$, $O-432$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 11\end{pmatrix}$	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 11\end{pmatrix}$ [c]	
T_h-m3, $T_d-\bar{4}3m$, O_h-m3m	0	$\begin{pmatrix}11 & 0 & 0\\0 & 11 & 0\\0 & 0 & 11\end{pmatrix}$	0	0	

ND_4ReO_4 - an example

- Unique effect in NQR: temperature and pressure coefficient both positive.
- Highly anisotropic thermal expansion
- Want to understand physical origin of effect
- Diffraction data back to 1970s
- Finally solved with RBs and spin model

Reference: IP Swainson and RJC Brown *Acta Cryst* **B53** 76-81 (1997)

ND_4ReO_4 - an example

- Space group: $I4_1/a$
  - a=(5.88-6.00Å), c=(12.99-12.40Å) over (298-20K)
- ND_4 sits on point symmetry –4: T_{11}, T_{33}, L_{11}, L_{33}, S_{11}, S_{12}
- Previously modelled as a single ND_4 ion with large atomic U_{ij}.
- Re-modelled with Ising spin model [two orientations, occupation a f(T)].

ND_4ReO_4 - Single orientation refinement

Letters in **green** are entries into EXPEDT
Letters in **red** are to notice output/changes

ND_4ReO_4-atomistic model [1]

[Menu LA]

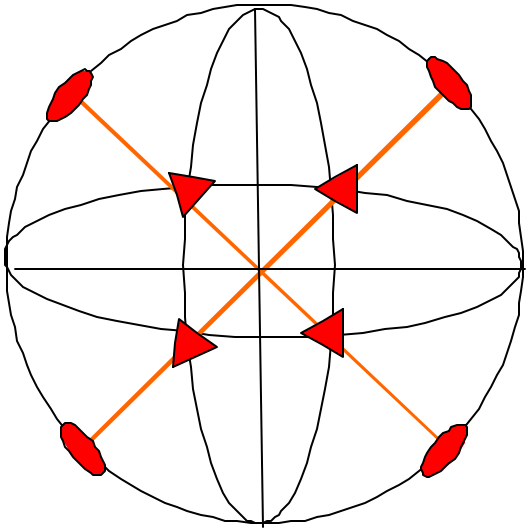
Select editing option for Least Squares calculation (<?>,A,B,F,,L,O,R,S,T,X) >a
Phase No.1 There are 5 atoms for this phase
Title: ND4ReO4 atomistic model
Give atom editing command (<?>,C,D,E,F,I,K,L,M,S,T,U,V,X,,+,-,*,/) > l

SER	TYPE	X	Y	Z	FRAC	NAME	UISO	CODE	STSYM	MULT	FXU
1	N	0.50000	0.75000	0.12500	1.00000	N(1)		A XU	-4(001)	4	000
U11,U22,U33,U12,U13,U23 =		0.02313	0.02313	0.01812	0.00000	0.00000	0.00000				
2	D	0.54684	0.89347	0.16773	**0.50000**	D(2)		A XU	1	16	000
U11,U22,U33,U12,U13,U23 =		0.10732	0.06210	0.07106	-0.02478	-0.03187	-0.00014				
3	D	0.45999	0.62841	0.17560	**0.50000**	D(3)		A XU	1	16	000
U11,U22,U33,U12,U13,U23 =		0.02655	0.01653	0.01970	0.00163	-0.00711	0.01170				
4	RE	0.00000	0.25000	0.12500	1.00000	RE(4)		A XU	-4(001)	4	000
U11,U22,U33,U12,U13,U23 =		0.01642	0.01642	0.00938	0.00000	0.00000	0.00000				
5	O	0.20241	0.37126	0.04576	1.00000	O(5)		A XU	1	16	000
U11,U22,U33,U12,U13,U23 =		0.02833	0.03014	0.01922	-0.00421	0.00598	-0.00019				

Above is the listing of the atomic structure. Note two copies of symmetrically identical D atom, with a fractional occupancy of 0.5 ! This is for the RB definition (see following slides).

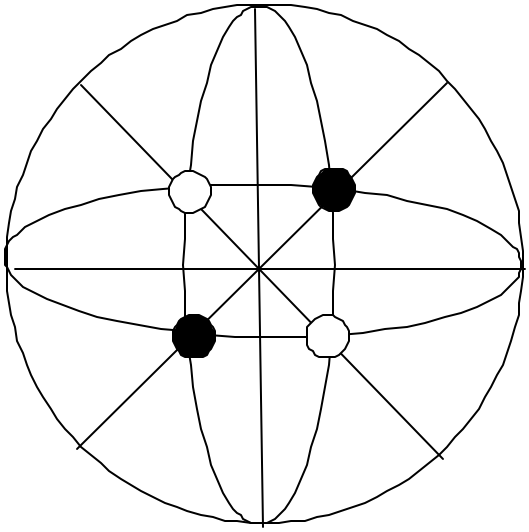
Defining the shape [2]

- We can use existing (symmetry) constraints to reduce the number of atoms we need to define.

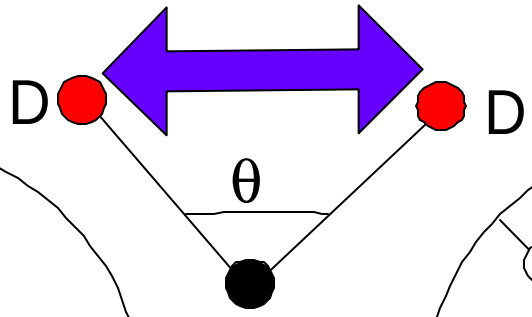


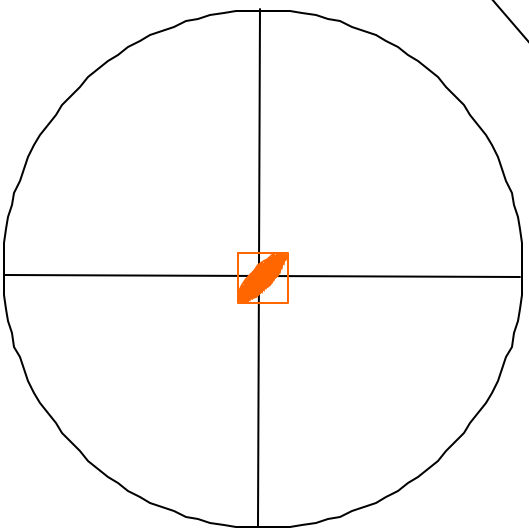
m3

ND_4 full molecular symmetry



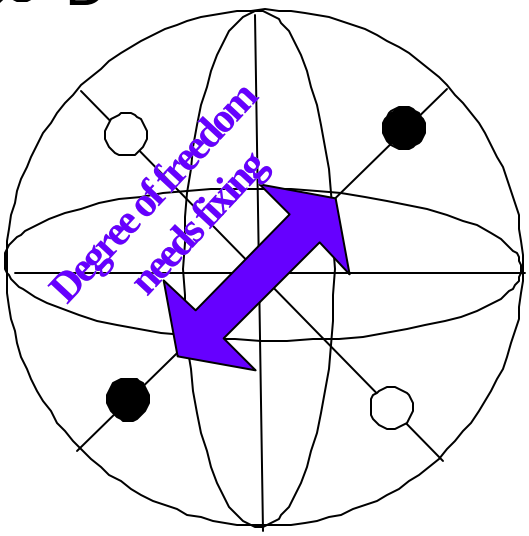
Can define tetrahedron as origin (N) + 4 <111> vectors (D)





$\bar{4}$

ND_4 site symmetry in xtal



ND_4 site symmetry -4 requires only 2 atoms to define tetrahedron: fix θ at 109° 28'.

Creating the shape [2]

[Menu LB]

Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >**X**
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >**B**
No rigid bodies have been defined
Enter rigid body editing option desired (<?>,A,B,L,P,X) >**B**
Enter number of atoms in rigid body (0 to quit) >**3** **N(1),D(2),D(3)**
Enter number of translations (1-9) to build rigid body >**1** **The N-D bond**
Translation no. 1
Enter translation distance >**1** **Scales the vectors below:**
Rigid body atom no. 1
Enter vector X, Y and Z >**0.0 0.0 0.0** **N(1)**
Rigid body atom no. 2
Enter vector X, Y and Z >**0.5917841 0.5917841 0.5917841** **D(2) [111]**
Rigid body atom no. 3
Enter vector X, Y and Z >**-0.5917841 -0.5917841 0.5917841** **D(3) [-1-1 1]**

Here we used N-D=1.0506Å (refined at 4K)
There is a arbitrary choice here:
1) Use unity translation distance (as above) and define <111> vectors as sqrt(1.0506/3)
2) Use bond length as translation distance, define <111> vectors as unit vectors sqrt(1/3)

ND_4ReO_4- List the RB

Enter rigid body editing option desired
(<?>,A,B,C,D,E,I,L,P,R,X) >**L**

There are 1 types of rigid bodies

Rigid body type 1 has 3 atoms defined by 1 translation operators.

Translation 1 Magnitude 1.00000 pn = 0 Damp = 0

atom vectors

1 0.0000000 0.0000000 0.0000000
2 0.5917841 0.5917841 0.5917841
3 -0.5917841-0.5917841 0.5917841

As we defined!

Rigid body no. 1 is not used in phase 1

If uncertain, there is no harm in over-defining (e.g. including all 4 atoms and adjusted fractional occupancies to 0.25, to keep stoichiometry)

Inserting the RB into the Crystal Frame [3]

Enter rigid body editing option desired (<?>,A,B,C,D,E,I,L,P,R,X)
>**I 1 1 Insert RB type 1 at atom # 1 [map N to N]**

Rigid body no. 1 will be created in this phase

Enter rigid body origin X, Y & Z locations >**.5 .75 .125**

Enter no. 1 rotation axis (X,Y or Z) and angle >/

Enter no. 2 rotation axis (X,Y or Z) and angle >/

Enter no. 3 rotation axis (X,Y or Z) and angle >/

Enter no. 4 rotation axis (X,Y or Z) and angle >/

Enter no. 5 rotation axis (X,Y or Z) and angle >/

Enter no. 6 rotation axis (X,Y or Z) and angle >/

Enter rigid body editing option desired (<?>,A,B,C,D,E,I,L,P,R,X) >

Note:

1) **From this point onwards [insertion], your atom list is purely a subservient template/place holder for your RB**
2) **\ had we typed, e.g., 0, 0.3 0.25 at the "RB origin" line it would have changed xyz in the atom menu to 0,0.3,0.25.**
3) **At the moment we have taken the default orientation of the RB in the crystal frame by "slashing" all the rotation angles**

Inserting the RB: List to see effect [3]

Enter rigid body editing option desired (<?>,A,B,C,D,E,I,L,P,R,X) >**L**
There are 1 types of rigid bodies
Rigid body type 1 has 3 atoms defined by 1 translation operators.

Translation 1 Magnitude 1.00000 pn = 0 Damp = 0
atom vectors
1 0.0000000 0.0000000 0.0000000
2 0.5917841 0.5917841 0.5917841
3 -0.5917841-0.5917841 0.5917841
Phase 1 Rigid body type 1 Body 1
First atom is 1
Location is 0.5000000 0 0 0.7500000 0 0 0.1250000 0 0
Rotation deg. pn d
R1( ) 0.000 0 0 R2( ) 0.000 0 0 R3( ) 0.000 0 0
R4( ) 0.000 0 0 R5( ) 0.000 0 0 R6( ) 0.000 0 0

Random!

Atom coordinates for atom seq. 2 name D(2)
Old values = 0.546566 0.893232 0.167623
New values = 0.598817 0.848817 0.172472
Atom coordinates for atom seq. 3 name D(3)
Old values = 0.459768 0.628235 0.175674
New values = 0.401184 0.651183 0.172472

Our RB has now changed the atomic xyz of the D atoms, as we have put the RB in at a random orientation

Inserting RB [3]: Summary so far

- Until inserted, the defined RB shape is NOT part of the refinement
- You can insert as many copies of one type of RB as you like, with independent positions and orientations
- We selected atom 1 (N) of atom list to correspond to position 1 of our RB (with I 1 1)
  - The rigid body origin choice we made (0.5,0.75,0.125) OVERRIDES the atom list:
    - if we had chosen (0.5,0.75,0.0) it would have CHANGED the atom list to N 0.5 0.75 0.0

Setting RB parameters free [4]

- There are two classes of variables:
  1. Those affecting the definition of the RB
     - magnitude (bond lengths)
     - basis (shape)
     - changing these changes ***every*** insertion (copy) in the crystal
  2. Those affecting the specific insertion (copy) of the RB
     - Rotational and translational parameters (Rx, Ry, Rz, X, Y, Z, TLS)
     - Altering these changes only one ***specific*** insertion (copy)

More on RB variables

- You must ensure that the flags (X,U) in the atom list agree with the parameters you set free in the RB menu:
  - Setting atom flags free but fixing RB parameters leaves atoms unvaried.
  - Setting RB flags free but leaving atom flags fixed causes errors.
  - Turning on RB flags that are constrained by crystal symmetry causes errors. e.g. rotations not allowed by point symmetry
- Therefore parameters (X, Y, Z), (R_x R_y R_z), "translation distance" in RB menu *requires* ALL the atoms associated with RB to have X flag. Similar truths apply to TLS and U flag.

Special note: Rotations about the centre-of-mass (N) will not change the position of N, but its X-flag in the atom menu must be on, even if atomic xyz of N will not change!

ND_4ReO_4- Freeing RB variables [4]

Enter rigid body editing option desired (<?>,A,B,C,D,E,I,L,P,R,X) >l
There are 1 types of rigid bodies
Rigid body type 1 has 3 atoms defined by 1 translation operators.
Translation 1 Magnitude 1.00000 pn = 0 Damp = 0
atom vectors
1 0.0000000 0.0000000 0.0000000
2 0.5917842 0.5917842 0.5917842
3 -0.5917842-0.5917842 0.5917842
Phase 1 Rigid body type 1 Body 1
First atom is 1
Location is 0.5000000 0 0 0.7500000 0 0 0.1250000 0 0
Rotation deg. pn d
R1( ) 0.000 0 0 R2( ) 0.000 0 0 R3( ) 0.000 0 0
R4( ) 0.000 0 0 R5( ) 0.000 0 0 R6( ) 0.000 0 0
Enter rigid body editing option desired (<?>,A,B,C,D,E,I,L,P,R,X) >e 1
Rigid body no. 1 no. of atoms = 3 no. trans. oprs. = 1
Translation oper no. 1 Magnitude = 1.00000 pn = 0 Damp = 0
Atom sx sy sz
1 0.0000000 0.0000000 0.0000000
2 0.5917842 0.5917842 0.5917842
3-0.5917842-0.5917842 0.5917842

e 1 edits the RB type: anything changed here would affect all copies (insertions)

ND_4ReO_4- Changing parameters defining RB

Enter rigid body type editing command (<?>,A,C,D,L,N,T,V,X) >v
Enter translation magnitude parameter number >0
Translation oper no. 1 Magnitude = 1.00000 pn = 0 Damp = 0
Atom sx sy sz
1 0.0000000 0.0000000 0.0000000
2 0.5917842 0.5917842 0.5917842
3-0.5917842-0.5917842 0.5917842
Enter rigid body type editing command (<?>,A,C,D,L,N,T,V,X) >

V is the toggle for vary (ON/OFF) as in most other menus. The RB menu is where GSAS is more like DBWS/Fullprof. You assign parameter numbers (pn's).

pn=0 means OFF pn 0 means ON

Here we have decided to leave it OFF

Simple Constraints in RBs

Constraints are achieved by giving two variables the same pn:

1. **Uncorrelated: e.g. T_{11} ^{1} T_{22}. Give T_{11} pn=1, T_{22}, pn=2.**
2. **100% Correlation: e.g. T_{11}=T_{22}. Give T_{11} pn=1, T_{22}, pn=1**
3. **100% Anticorrelation: e.g., T_{11} pn=1, T_{22} pn=-1.**

ND_4ReO_4 - Changing RB insertion parameters

Enter rigid body editing option desired (<?>,A,B,C,D,E,I,L,P,R,X) >c 1 1
For rigid body no. 1 of type 1 in phase 1
The first atom in the group will be atom no. 1
R1() pn R2( ) pn R3( ) pn R4( ) pn R5( ) pn R6( ) pn
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
TX pn TY pn TZ pn
0.50000 0 0.75000 0 0.12500 0 damp = 000000000
No TLS matrices defined for this rigid body
Enter rigid body editing command (<?>,C,D,L,T,V,X) >C
Do you want to change the rigid body origin (Y/<N>)? >N
Do you want to change the rigid body rotations (Y/<N>)? >Y
Enter no. 1 rotation axis (X,Y or Z) and angle >Z
Enter no. 1 rotation angle >10
Enter no. 2 rotation axis (X,Y or Z) and angle >/ / / / /
For rigid body no. 1 of type 1 in phase 1
The first atom in the group will be atom no. 1
R1(Z) pn R2() pn R3() pn R4() pn R5() pn R6() pn
10.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
TX pn TY pn TZ pn
0.50000 0 0.75000 0 0.12500 0 damp = 000000000
No TLS matrices defined for this rigid body
Enter rigid body editing command (<?>,C,D,L,T,V,X) >

Change 1st insertion (copy) of 1st RB type

Change

We know N xyz

We don't know D xyz well

Give starting rotation of Z=10° (we could have done this during insertion)

ND_4ReO_4 - Varying the RB rotation angles [4]

Enter rigid body editing command (<?>,C,D,L,T,V,X) >**v**
Enter rigid body rotation no. 1 parameter number >**1**
Enter rigid body rotation no. 2 parameter number >**/**
For rigid body no. 1 of type 1 in phase 1
The first atom in the group will be atom no. 1

Now make this rotation variable (pn=1)

R1(Z)	pn	R2( )	pn	R3( )	pn	R4( )	pn	R5( )	pn	R6( )	pn
10.000	1	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0

TX	pn	TY	pn	TZ	pn	
0.50000	0	0.75000	0	0.12500	0	damp = 000000000

No TLS matrices defined for this rigid body
Enter rigid body editing command (<?>,C,D,L,T,V,X) >**d**
Enter new Rotation no. 1 damping factor (0 to 9) >**9**
Enter new Rotation no. 2 damping factor (0 to 9) >**/**

Damp pn=1 90%

For rigid body no. 1 of type 1 in phase 1
The first atom in the group will be atom no. 1

R1(Z)	pn	R2( )	pn	R3( )	pn	R4( )	pn	R5( )	pn	R6( )	pn
10.000	1	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0

TX	pn	TY	pn	TZ	pn	
0.50000	0	0.75000	0	0.12500	0	damp = 900000000

No TLS matrices defined for this rigid body
Enter rigid body editing command (<?>,C,D,L,T,V,X) >

ND_4ReO_4- Incorporating TLS tensors [5]

Enter rigid body editing command (<?>,C,D,L,T,V,X) >**c**
Do you want to change the rigid body origin (Y/<N>)? >**n**
Do you want to change the rigid body rotations (Y/<N>)? >**n**
Do you want to change the T tensor elements (Y/<N>)? >**y**
Enter new value for T11 >**.01 .01 .01 /**
Do you want to change the L tensor elements (Y/<N>)? >**y**
Enter new value for L11 >**30 30 30 /**
Do you want to change the S tensor elements (Y/<N>)? >**/**

Giving isotropic starting parameters

For rigid body no. 1 of type 1 in phase 1
The first atom in the group will be atom no. 1

R1(Z)	pn	R2( )	pn	R3( )	pn	R4( )	pn	R5( )	pn	R6( )	pn
-27.005	1	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0

TX	pn	TY	pn	TZ	pn	
0.50000	0	0.75000	0	0.12500	0	damp = 900000000

The TLS data are: damping T 0 L 0 S 0

elem.	value	pn	elem.	value	pn	elem.	value	pn
T11	1.00	0	T22	1.00	0	T33	1.00	0
T12	0.00	0	T13	0.00	0	T23	0.00	0
L11	30.00	0	L22	30.00	0	L33	30.00	0
L12	0.00	0	L13	0.00	0	L23	0.00	0
S12	0.0000	0	S13	0.0000	0	S21	0.0000	0
S23	0.0000	0	S31	0.0000	0	S32	0.0000	0
SAA	0.0000	0	SBB	0.0000	0			

Note factor of 100 in Tij!

Enter rigid body editing command (<?>,C,D,L,T,V,X) >

Tij in Å² (*100), L_{ij} in deg²

ND_4ReO_4- Varying the TLS parameters [5]

Enter rigid body editing command (<?>,C,D,L,T,V,X) >**v**
Enter rigid body rotation no. 1 parameter number >/
Enter T11 parameter no. >**2 2 3**
Enter T12 parameter no. >/
Enter L11 parameter no. >**4 4 5 /**
Enter S12 parameter no. >/
For rigid body no. 1 of type 1 in phase 1
The first atom in the group will be atom no. 1

T11=T22 T33

L11=L22 L33
(Sij » 0, so are ignored here)

R1(Z)	pn	R2( )	pn	R3( )	pn	R4( )	pn	R5( )	pn	R6( )	pn
-27.005	1	0.000	0	0.000	0	0.000	0	0.000	0	0.000	0

TX	pn	TY	pn	TZ	pn	
0.50000	0	0.75000	0	0.12500	0	damp = 900000000

The TLS data are: damping T 0 L 0 S 0

elem.	value	pn	elem.	value	pn	elem.	value	pn
T11	1.00	2	T22	1.00	2	T33	1.00	3
T12	0.00	0	T13	0.00	0	T23	0.00	0
L11	30.00	4	L22	30.00	4	L33	30.00	5
L12	0.00	0	L13	0.00	0	L23	0.00	0
S12	0.0000	0	S13	0.0000	0	S21	0.0000	0
S23	0.0000	0	S31	0.0000	0	S32	0.0000	0
SAA	0.0000	0	SBB	0.0000	0			

Enter rigid body editing command (<?>,C,D,L,T,V,X) >

Implemented constraints, subject to –4 site symmetry as listed by Schomaker and Trueblood

ND_4ReO_4 - Results: atom list

[Menu LA]

Phase No. 1 There are 5 atoms for this phase

Title: ND4ReO4 Rigid Body

Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >L

SER	TYPE	X	Y	Z	FRAC	NAME	UISO	CODE	STSYM	MULT	FXU
1	N	0.50000	0.75000	0.12500	1.00000	N(1)		A XU	-4(001)	4	000
U11,U22,U33,U12,U13,U23 =		0.02230	0.02230	0.02414	0.00000	0.00000	0.00000				
2	D	0.54317	0.88291	0.17247	0.50000	D(2)		A XU	1	16	000
U11,U22,U33,U12,U13,U23 =		0.06327	0.03519	0.04330	-0.01020	-0.00418	-0.01288				
3	D	0.45683	0.61709	0.17247	0.50000	D(3)		A XU	1	16	000
U11,U22,U33,U12,U13,U23 =		0.06327	0.03519	0.04330	-0.01020	0.00418	0.01288				
4	RE	0.00000	0.25000	0.12500	1.00000	RE(4)		A XU	-4(001)	4	000
U11,U22,U33,U12,U13,U23 =		0.01743	0.01743	0.00921	0.00000	0.00000	0.00000				
5	O	0.20243	0.37148	0.04594	1.00000	O(5)		A XU	1	16	000
U11,U22,U33,U12,U13,U23 =		0.02769	0.02895	0.01970	-0.00537	0.00881	0.00108				

Note that the atomic flags for N(1), D(2) and D(3) are X (to allow for the RB rotation) and U (to allow TLS refinement). The ReO_4 group is a regular atomistic refinement

ND_4ReO_4 - Results: Rigid Body list

[Menu LB]

There are 1 types of rigid bodies

Rigid body type 1 has 3 atoms defined by 1 translation operators.

Translation 1 Magnitude 1.00000 pn = 0 Damp = 0

atom vectors

1 0.0000000 0.0000000 0.0000000

2 0.5917841 0.5917841 0.5917841

3 -0.5917841-0.5917841 0.5917841

Phase 1 Rigid body type 1 Body 1

First atom is 1

Location is 0.5000000 0 0 0.7500000 0 0 0.1250000 0 0

Rotation deg. pn d

R1(Z) -27.005 1 9 R2( ) 0.000 0 0 R3( ) 0.000 0 0

R4( ) 0.000 0 0 R5( ) 0.000 0 0 R6( ) 0.000 0 0

T-matrix 0.0223 0.0223 0.0241 0.0000 0.0000 0.0000

PN 2 2 3 0 0 0

L-matrix 89.79 89.79 162.66 0.00 0.00 0.00

PN 4 4 5 0 0 0

S-matrix 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000

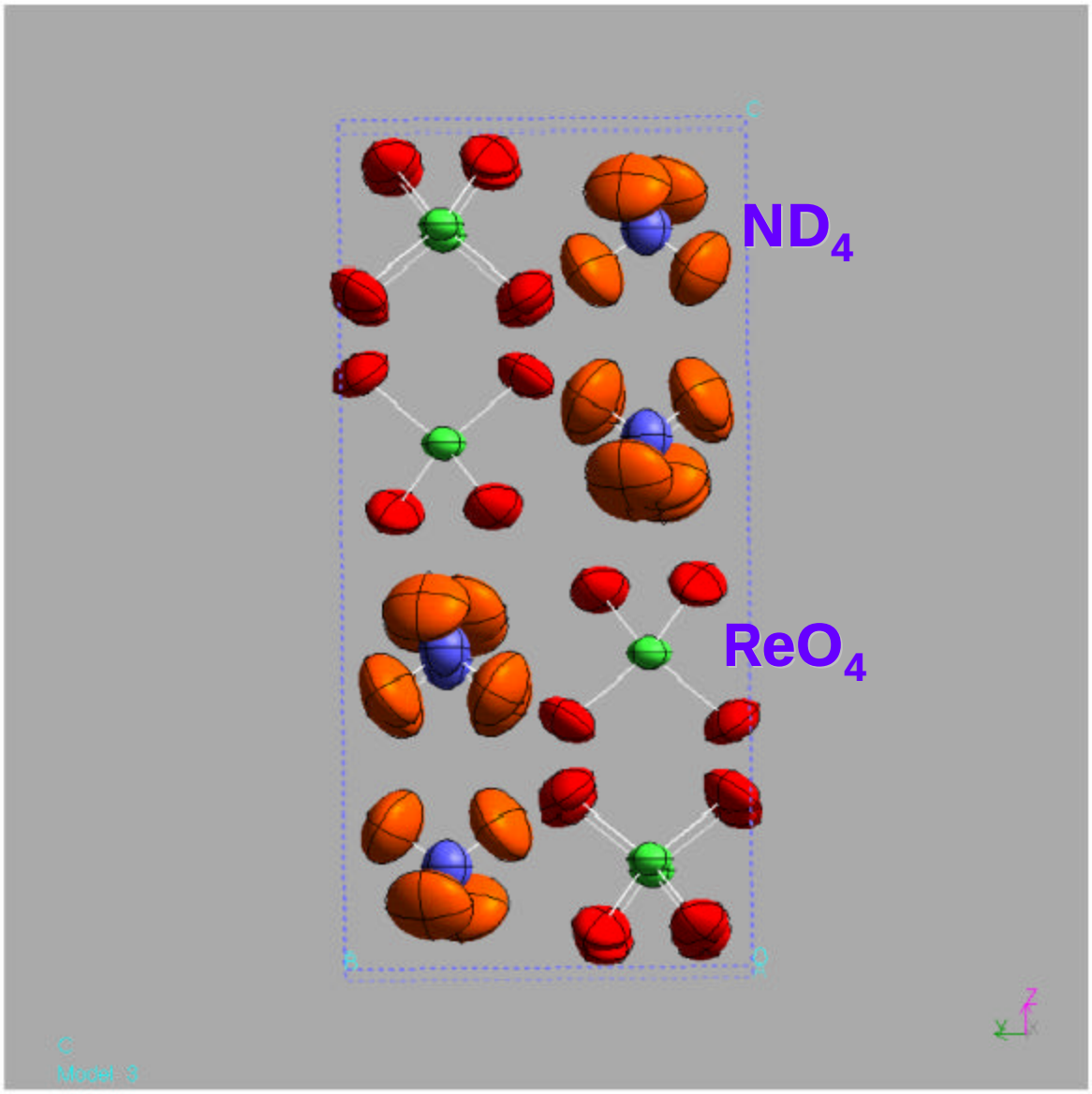
PN 0 0 0 0 0 0 0 0

Find a relatively isotropic Tij: T11=T22»T33

Find highly anisotropic Lij: Large librations about Z

Reflected in following picture

Single ND_4 orientation



ND_4ReO_4 pseudo-spin refinement (2 orientations)

- Has the same RB as before inserted twice to represent two different pseudo-spins
- Vary the fractional occupancy of each ND_4 orientation
- Also constrained the two pseudo-spins to have the same temperature factors (TLS)

ND_4ReO_4 Pseudo-spin model [1]

[Menu LA]

Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >l

SER TYPE X Y Z FRAC NAME UISO CODE STSYM MULT FXU

1 N 0.50000 0.75000 0.12500 0.50000 N(1) A XU -4(001) 4 000

U11,U22,U33,U12,U13,U23 = 0.02923 0.02923 0.01971 0.00000 0.00000 0.00000

2 D 0.54637 0.88257 0.17200 0.42579 D(2) AFXU 1 16 000

U11,U22,U33,U12,U13,U23 = 0.06011 0.04585 0.04896 -0.00568 -0.00683 -0.01953

3 D 0.45363 0.61743 0.17200 0.42579 D(3) AFXU 1 16 000

U11,U22,U33,U12,U13,U23 = 0.06011 0.04585 0.04896 -0.00568 0.00683 0.01953

4 RE 0.00000 0.25000 0.12500 1.00000 RE(4) A XU -4(001) 4 000

U11,U22,U33,U12,U13,U23 = 0.01914 0.01914 0.01595 0.00000 0.00000 0.00000

5 O 0.20563 0.36949 0.04645 1.00000 O(5) A XU 1 16 000

U11,U22,U33,U12,U13,U23 = 0.02873 0.03435 0.02357 -0.00580 0.01223 0.00190

6 N 0.50000 0.75000 0.12500 0.50000 N(6) A XU -4(001) 4 000

U11,U22,U33,U12,U13,U23 = 0.02923 0.02923 0.01971 0.00000 0.00000 0.00000

7 D 0.42187 0.86671 0.17200 0.07421 D(7) AFXU 1 16 000

U11,U22,U33,U12,U13,U23 = 0.05645 0.04950 0.04896 0.00843 0.01151 -0.01719

8 D 0.57813 0.63329 0.17200 0.07421 D(8) AFXU 1 16 000

U11,U22,U33,U12,U13,U23 = 0.05645 0.04950 0.04896 0.00843 -0.01151 0.01719

We join refinement at the end. The set-up is similar to single orientation refinement.

NOTE:

1. **Added extra three atoms to hold 2nd RB copy in 2nd orientation.**
2. **We have set atomic constraints (in atom menu so that (FRAC 2 = FRAC 3) = 0.5- (FRAC 6 = FRAC 7)**
3. **Majority species is close to that of single RB refinement**

ND_4ReO_4 Pseudo-spin model RB list

[Menu LB]

There are 1 types of rigid bodies
Rigid body type 1 has 3 atoms defined by 1 translation operators.
Translation 1 Magnitude 1.00000 pn = 0 Damp = 0
atom vectors
1 0.0000000 0.0000000 0.0000000
2 0.5917841 0.5917841 0.5917841
3 -0.5917841-0.5917841 0.5917841

Use one single RB Type (definition)

Single spin solution –25.005°

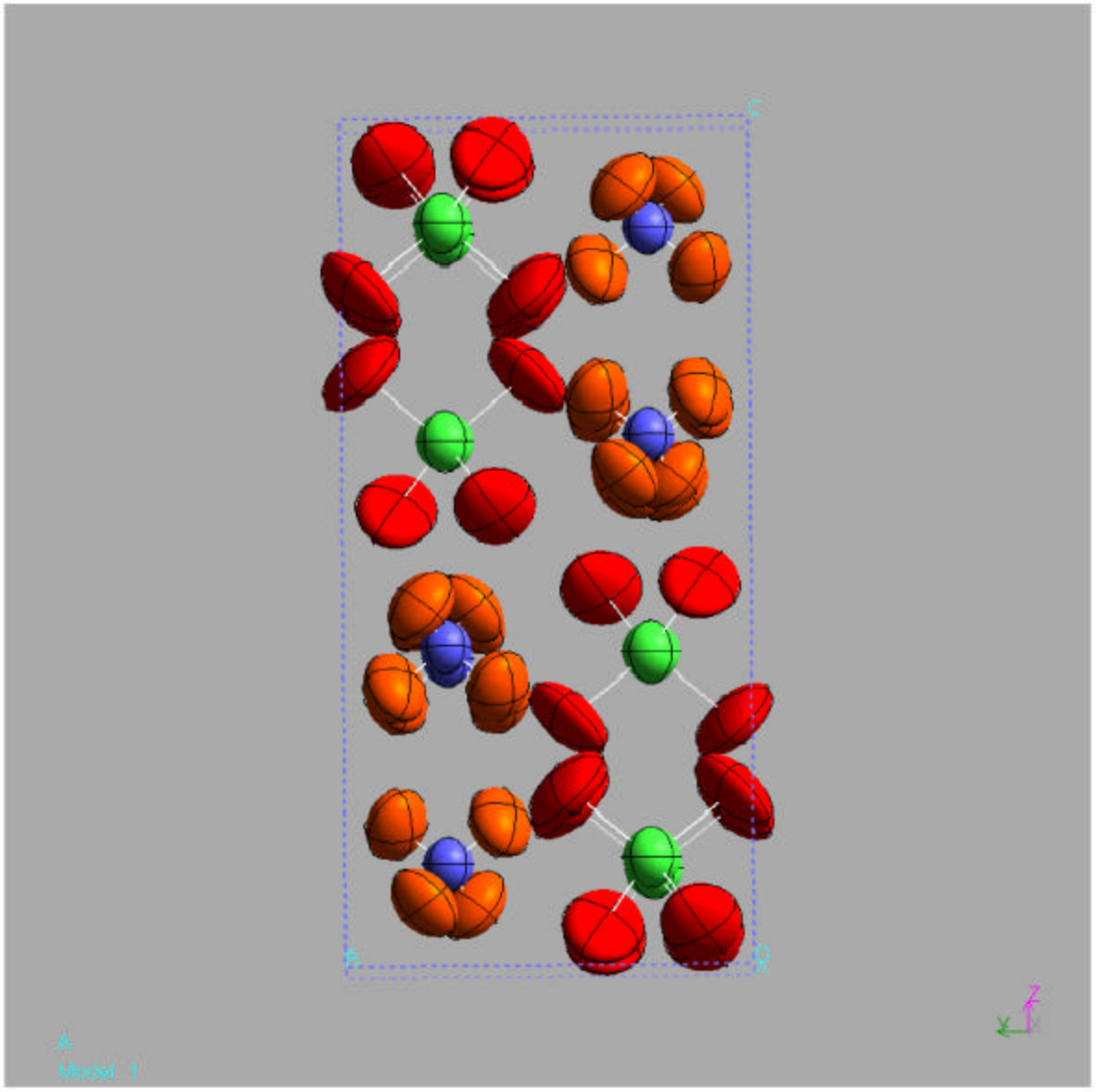
Phase 1 Rigid body type 1 Body 1
First atom is 1
Location is 0.5000000 0 0 0.7500000 0 0 0.1250000 0 0
Rotation deg. pn d
R1(Z) **-25.722 6** 0 R2( ) 0.000 0 0 R3( ) 0.000 0 0
R4( ) 0.000 0 0 R5( ) 0.000 0 0 R6( ) 0.000 0 0
T-matrix **0.0292 0.0292 0.0197** 0.0000 0.0000 0.0000
PN **2 2 3** 0 0 0
L-matrix **137.13 137.13** 85.49 0.00 0.00 0.00
PN **4 4 5** 0 0 0
S-matrix 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
PN 0 0 0 0 0 0 0 0

Inserted with I 1 1 (Majority spin)

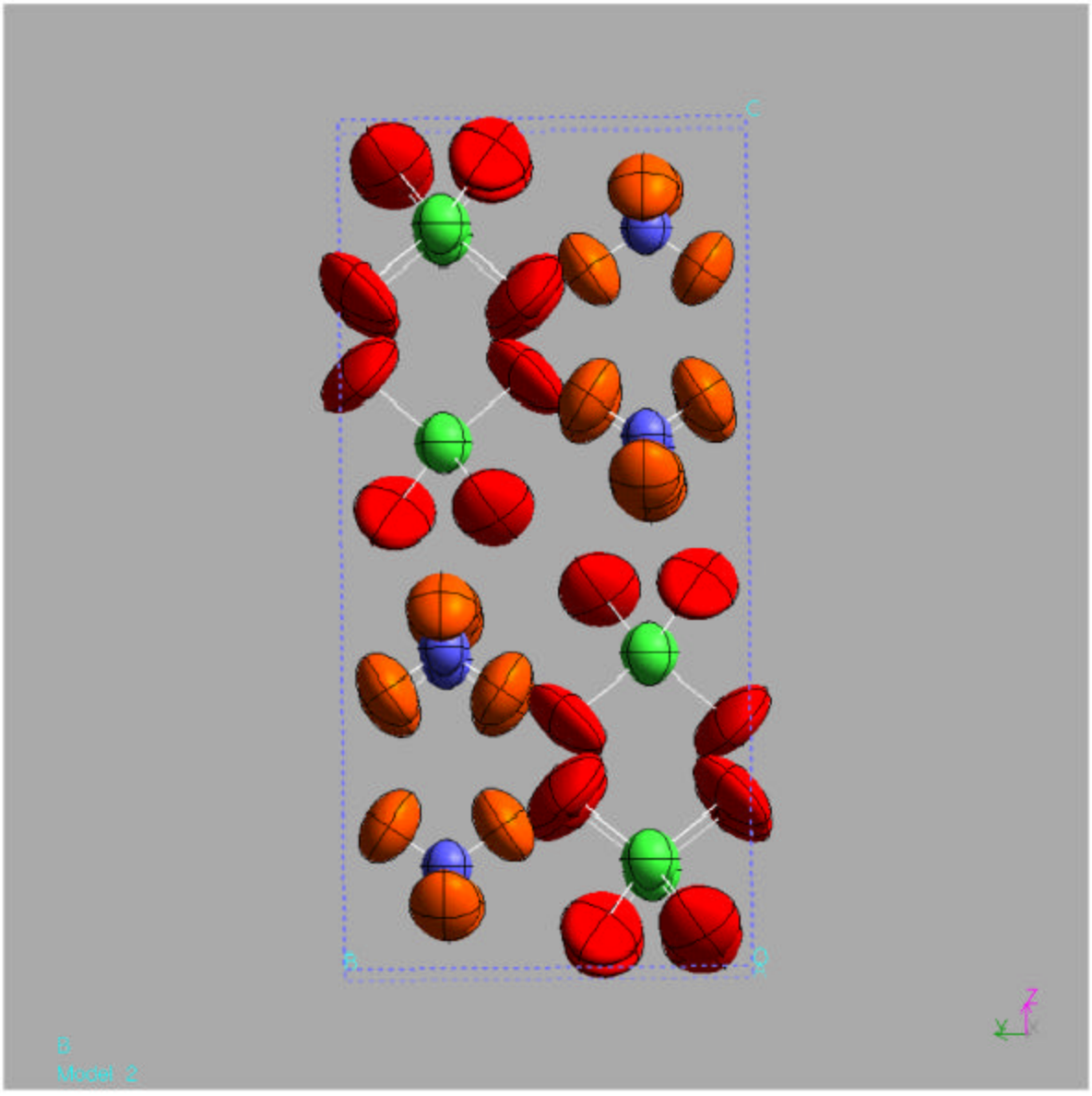
Phase 1 Rigid body type 1 Body 2
First atom is 6
Location is 0.5000000 0 0 0.7500000 0 0 0.1250000 0 0
Rotation deg. pn d
R1(Z) **-78.800 7** 0 R2( ) 0.000 0 0 R3( ) 0.000 0 0
R4( ) 0.000 0 0 R5( ) 0.000 0 0 R6( ) 0.000 0 0
T-matrix **0.0292 0.0292 0.0197** 0.0000 0.0000 0.0000
PN **2 2 3** 0 0 0
L-matrix **137.13 137.13 85.49** 0.00 0.00 0.00
PN **4 4 5** 0 0 0
S-matrix 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
PN 0 0 0 0 0 0 0 0

Inserted with I 1 6 (Minority spin)

ND_4 pseudo-spin orientation #1

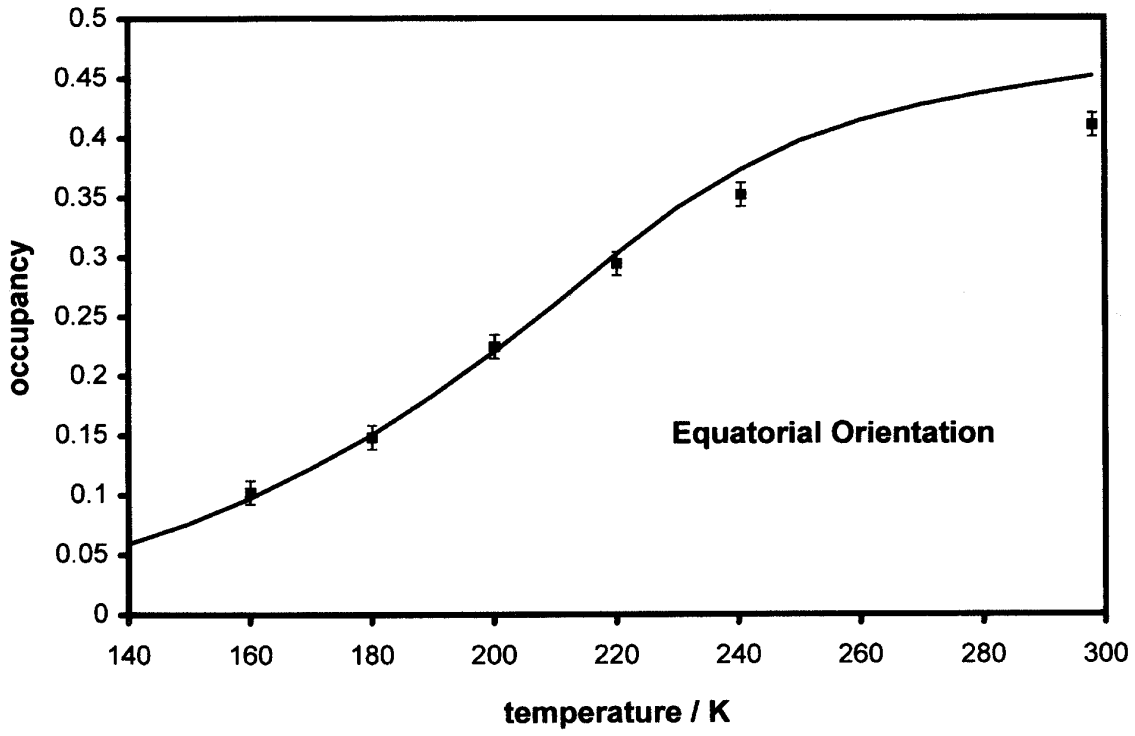


ND_4 pseudo-spin orientation #2



Which model is correct?

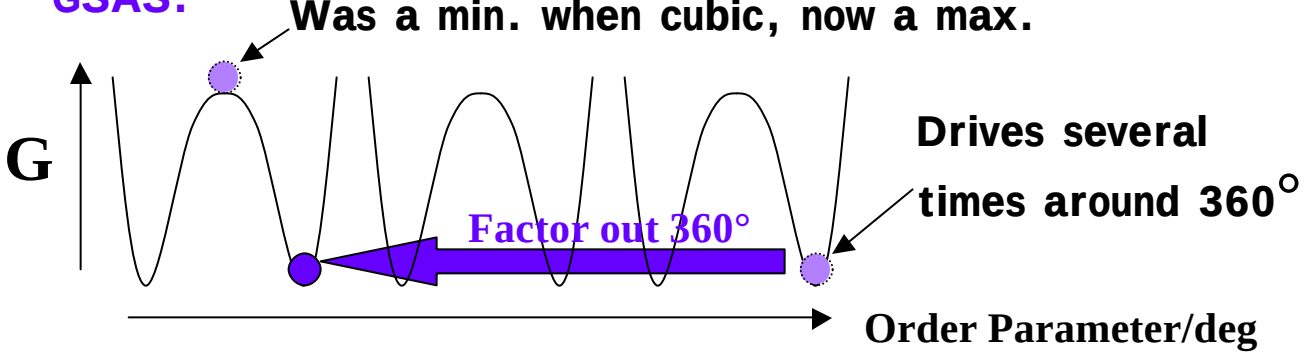
- Similar R, χ^2 –could use Hamilton's test
- Test pseudo-spin model against existing theory: points are related to RB refinement with pseudo-spin model



Examples of other uses - $(ND_4)_2PdCl_6$

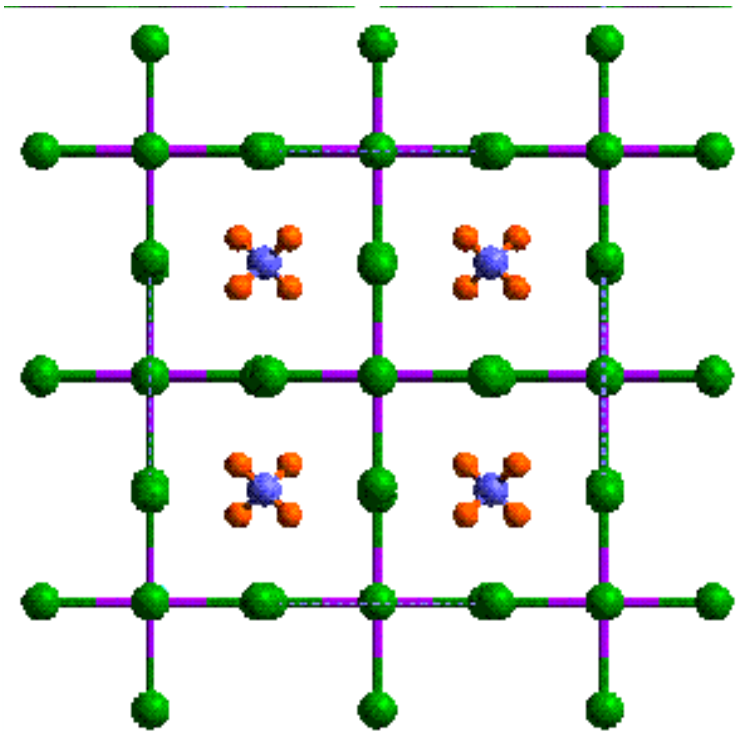
- Deuteration-induced phase transition ⇒ unknown space group and unknown D ordering
- Highest ΔS of all the ND_4-antifluorites
- Low T phase was indexed and RB mapped from cubic phase. Free the rotations and translations (highly damped)
- Hint: GSAS may "crash" with, e.g., R_x values of 4313° recorded in the LST file and *** in the EXP file

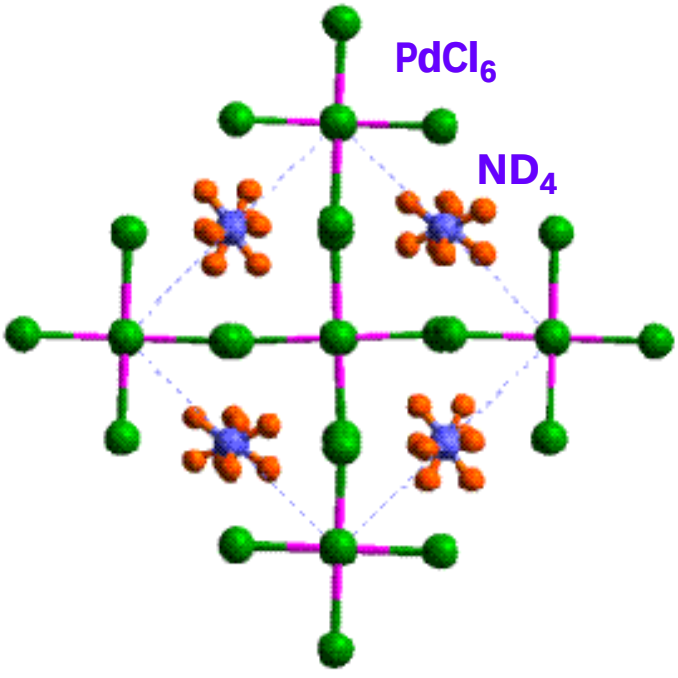
Factor out multiples of 360°. Go back one level of EXPEDT and enter as starting value – frequently good value. This may be "fixed" in future versions of GSAS.



$(ND_4)_2PdCl_6$

Can go from RT Þ 4K with no intervening data. Using RBs, GSAS will still find orientation. This is true where there are intermediate phases and also translational degrees of freedom of the RB!

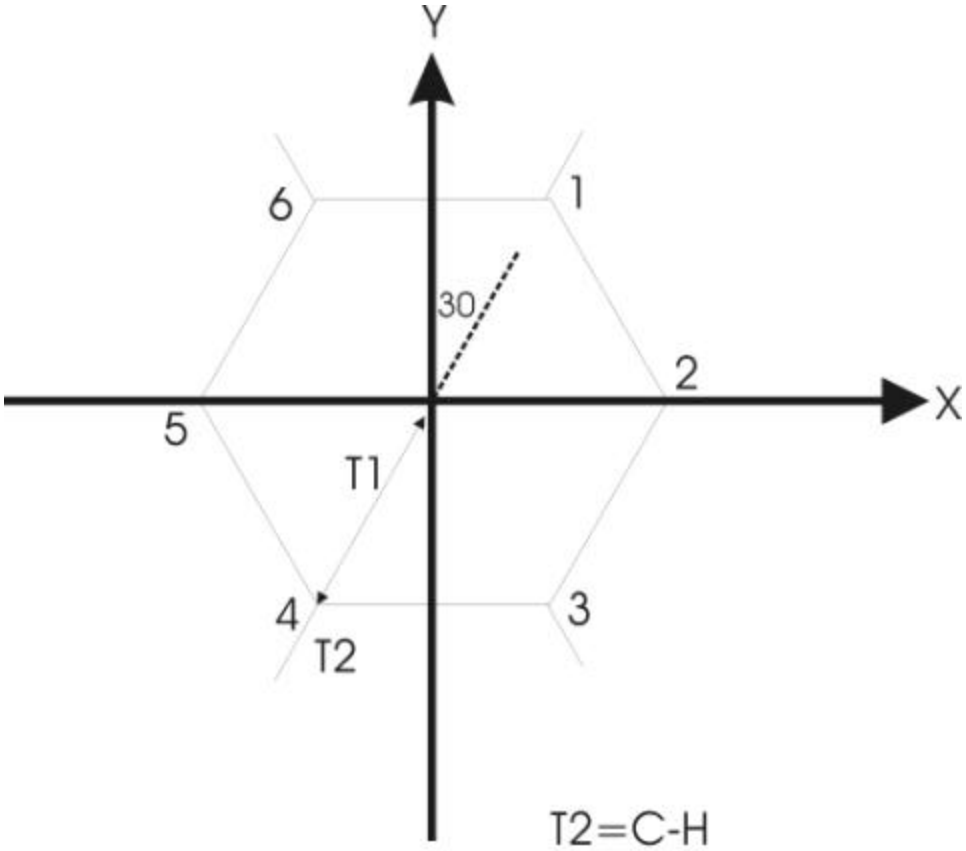


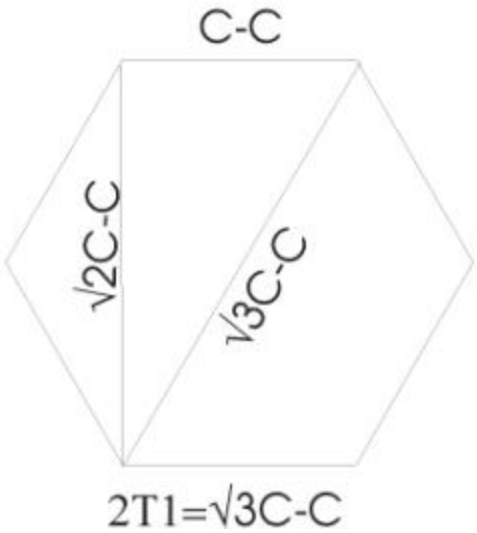


Cubic

Monoclinic

More Complicated RB's >1 Translation





e.g.; P174 "modern" GSAS manual

Atoms and translations

Assuming all 6C,H need defining:

$$\begin{bmatrix} C1 \\ C2 \\ C3 \\ C4 \\ C5 \\ C6 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 1 & 0 \\ \frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 \\ -\frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 \\ 0 & -1 & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \end{bmatrix} T1 + \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} T2$$

$$\begin{bmatrix} H1 \\ H2 \\ H3 \\ H4 \\ H5 \\ H6 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 1 & 0 \\ \frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 \\ -\frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 \\ 0 & -1 & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \end{bmatrix} T1 + \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 1 & 0 \\ \frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 \\ -\frac{1}{2} & \frac{-\sqrt{3}}{2} & 0 \\ 0 & -1 & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \end{bmatrix} T2$$

- Need 12 atoms in atom list
- Define RB with 2 translations:

  T1=√3/2 C-C

  T2=C-H

  unit vectors as above
- Insert into 12 atom “place holder”

Summary

- Definition of constraint
- Definition of simple RB
- Reduce atoms necessary for RB definition using symmetry
- Definition vs. insertion
- Constraints amongst RBs
- Use of TLS tensors

Where to get more information

- References:

- The Rietveld Method, IUCr Monographs on Crystallography 5. RA Young (ed) OUP 1993 (esp. Ch 10, Ch3)

- GSAS Manual LAUR86-748. RB Von Dreele and A Larson 1985

- V Schomaker and KN Trueblood. Acta Cryst **B24**, 63, 1968

Please email me with any errors or suggestions for future revisions