

# RMCPow Tutorial

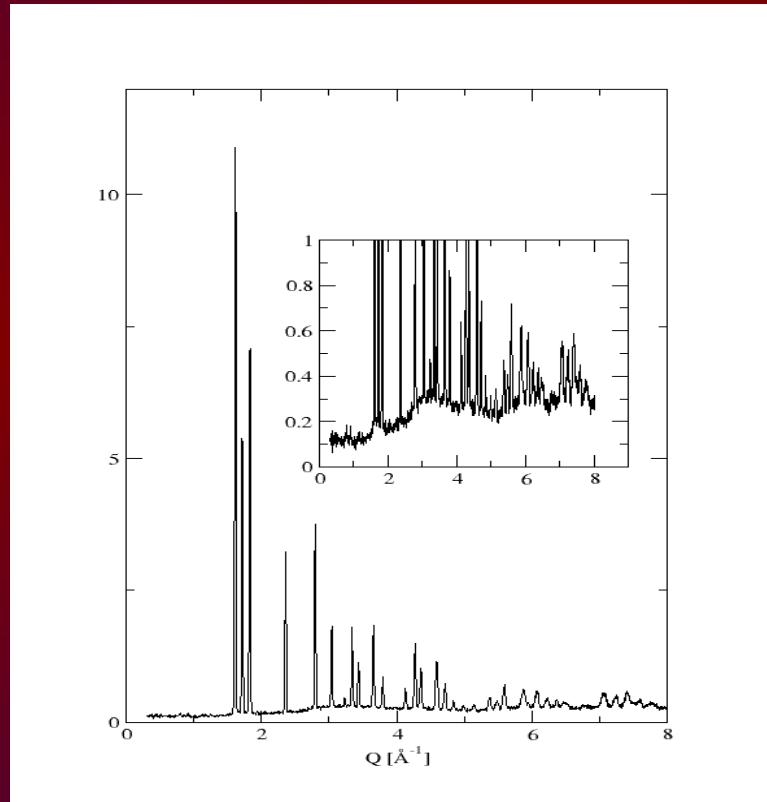
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# Outline

- Why does it need?
- How does it work? Strong and weak points
- Examples: carbon tetrabromide ordered and plastic crystalline phases

# Disorder and diffuse scattering

Diffuse scattering: all coherent scattering, which is not Bragg-scattering

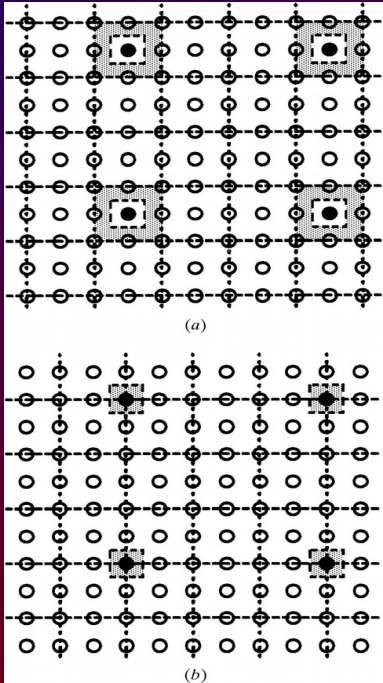


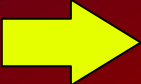
# What is RMCPOW?

- Its name is come from **R**everse **M**onte **C**arlo for **P**OWder diffraction, because this is the first RMC application to deal with disorder on crystalline systems (*Møllergård, Acta Cryst. A55 (1999) 783*)
- All part of the fit to the dataset(s) is performing only in the Q-space

# How does it work?

(Mellergård, A, McGreevy, R L, *Acta Cryst* **A55** (1999) 783.)



- Finite lattice instead of infinite  superlattice approximation
- Categorizing the :
  - Reciprocal lattice points of the unitcell: Bragg-
  - Others: diffuse-scattering contributions
- For Bragg: collection and applying resolution function
- For diffuse: creating mean value

## The main advantages:

- Does not need high Q region to fit
- Modelling the magnetic structure is possible
- Possible to fit to: neutron- (monochromatic and tof) and x-ray (laboratory and synchrotron) diffraction datasets

## Inconveniences:

- Computationally costly
- Exact knowledge of the Bravais cell and the lattice parameters are necessary (refinement of these are not possible)

# Examples – before we start

We need the following information to start a simulation:

- Lattice parameters
- Experimental datasets
- Resolution function of the instrument(s)
- Starting model

Each simulation consists of **.cfg**, **.dat** and **experimental dataset** files.

- **.cfg**: we are going to create with the help of **Crystal**
- **.dat**: it is needed to edit it by hand
- **Experimental datasets**: same as in RMC\_POT (additional feature: possibility to include uncertainty of the data as 3<sup>rd</sup> column)

# About $\text{CBr}_4$ – neutron powder diffraction pattern (SLAD, Studsvik)

L. Temleitner and L. Pusztai, PRB 81, 134101 (2010)

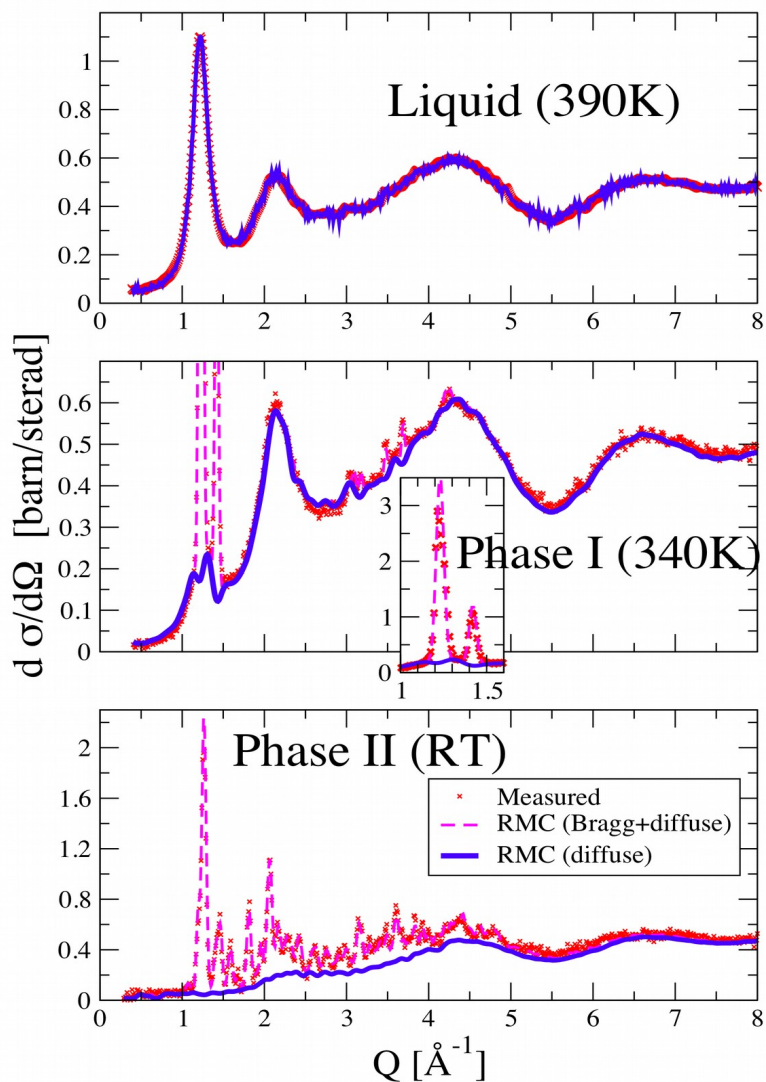
Its phases at ambient pressure:

gaseous:  $465\text{K} < T$

liquid:  $365\text{K} < T < 465\text{K}$

I (plastic):  $319\text{K} < T < 365\text{K}$ , spacegroup:  $\text{Fm}\bar{3}\text{m}$ ;  $a=8.81..8.85\text{ \AA}$   
(Dolling et al., 1979)

II (ordered):  $T < 319\text{K}$  spacegroup:  $\text{C}2/\text{c}$ ;  $a=21.43\text{ \AA}$ ,  $b=12.12\text{ \AA}$ ,  
 $c=21.02\text{ \AA}$ ,  $\beta=110.88^\circ$  (More et al., 1977)





# CBr4 phase II – Crystal input file from equilibrium positions (Acta Cryst. B33 (1977) 368. More et al.)

Spacegroup: C2/c (No. 15)

Lattice parameters:  $a=21.43\text{\AA}$ ,  $b=12.12\text{\AA}$ ,  $c=21.02\text{\AA}$ ,  
 $\beta=110.88^\circ$

We are creating  $1 \times 2 \times 1$  monoclinic supercell

Equilibrium positions

To create starting configuration:

> Crystal.exe cbr4\_II\_RT.atom

Reading parameters from

.....

Total no of generated atoms is        320

Output file [.cfg] > cbr4\_II

```
[.false.]>>      ! apply to existing .cfg?
15 1>      >      ! spg no, setting 1
21.43 12.12 21.02 90.0 110.88 90.0>      ! a1,a2,a3,g1,g2,g3
4 1 2 1>      >      ! isym,n1,n2,n3
n>      >      ! no displacements
2>      >      ! No. of atom types
4>      >      ! No. of C Wyckoff sites
8f 0.3450 0.7090 0.8710>      ! Wyckoff site,x,y,z C1
8f 0.6260 0.1840 0.6230>      ! Wyckoff site,x,y,z C2
8f 0.3790 0.9410 0.6200>      ! Wyckoff site,x,y,z C3
8f 0.5960 0.4680 0.8780>      ! Wyckoff site,x,y,z C4
16>      >      ! No. of C Wyckoff sites
8f 0.3545 0.7726 0.7904>      ! Wyckoff site,x,y,z Br11
8f 0.2697 0.7690 0.8935>      ! Wyckoff site,x,y,z Br12
8f 0.4248 0.7368 0.9488>      ! Wyckoff site,x,y,z Br13
8f 0.3322 0.5591 0.8527>      ! Wyckoff site,x,y,z Br14
8f 0.7064 0.1023 0.6432>      ! Wyckoff site,x,y,z Br21
8f 0.6296 0.2636 0.7038>      ! Wyckoff site,x,y,z Br22
8f 0.5516 0.0892 0.6002>      ! Wyckoff site,x,y,z Br23
8f 0.6167 0.2821 0.5458>      ! Wyckoff site,x,y,z Br24
8f 0.4578 0.8503 0.6389>      ! Wyckoff site,x,y,z Br31
8f 0.3906 0.0411 0.6930>      ! Wyckoff site,x,y,z Br32
8f 0.3029 0.8419 0.6035>      ! Wyckoff site,x,y,z Br33
8f 0.3656 0.0272 0.5451>      ! Wyckoff site,x,y,z Br34
8f 0.6025 0.5475 0.8037>      ! Wyckoff site,x,y,z Br41
8f 0.6762 0.4902 0.9542>      ! Wyckoff site,x,y,z Br42
8f 0.5214 0.5257 0.8942>      ! Wyckoff site,x,y,z Br43
8f 0.5844 0.3107 0.8608>      ! Wyckoff site,x,y,z Br44
.true.> >      ! RMC coordinates used in output
```



# CBr4 phase II – initial configuration checking

ConfPlot:

```
> screen /w9  
> o
```

Open .cfg file (1<sup>st</sup> line  
only for Linux users)

```
> plot
```

```
--  
> unitcell 1 2 1  
> plot
```

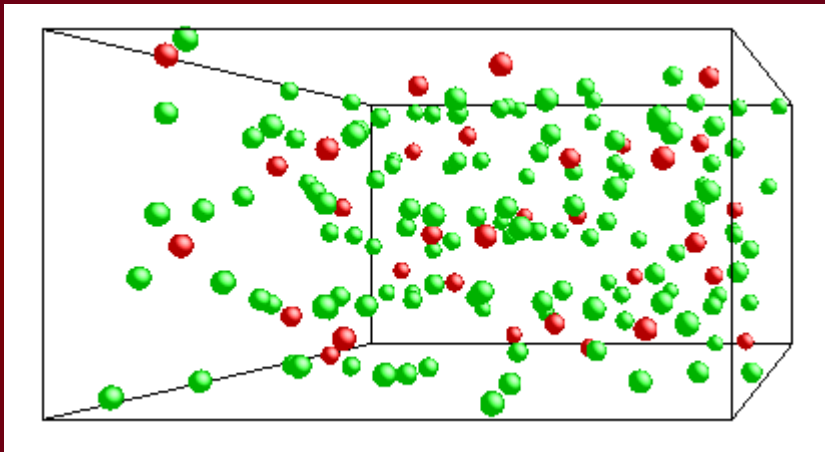
To create condensed  
view

```
> cplot
```

Contour plot

```
> dplot
```

Density plot



# CBr4 phase II – .dat file

## supercell and general run parameters

Head and printing  
informations

```
CBr4 II phase, room temperature
0 0» » » ! ncoll,ncycles
500 0 120 5 ! iprint,iplot,timelim,timesav
21.43 12.12 21.02 90.0 110.88 90.0» » ! a1,a2,a3,g1,g2,g3
0 0 0 0 0 0» » ! lattice parameters flags
4 1 2 1 » » ! isym,n1,n2,n3
```

Spacegroup: C2/c (No. 15)

Lattice parameters:  $a=21.43\text{\AA}$ ,  
 $b=12.12\text{\AA}$ ,  $c=21.02\text{\AA}$ ,  
 $\beta=110.88^\circ$

We have been creating 1x2x1  
monoclinic supercell

# CBr<sub>4</sub> phase II – .dat file constraints in real space

We have 2 nuclear types:

Carbon and bromine – their positions allowed to alter maximum 0.05 Å.

Minimal distance approach constraint is applied between CC, Cbr and BrBr atoms

Molecule kept together with coordination constraints (shape is tetrahedral, bond distance is about 1.93 Å):

e.g. C-Br 1.88..1.98 Å should be between 4 and 4. It should be fulfilled for 100% of pairs with the given sigma.

```
2 0 » » » ! ntypes,ntypesm
0.05 0.05 » » » ! delta
0 0.0 » » » ! nswap,swapfrac
0 0.0 » » » ! nref,reffrac
4.5 1.88 3.05 » » » ! rcut
3 » » » » ! ncoord
1 2 1.88 1.98 4 4 1.00 0.0000001 ! C-Br intermolecular
2 2 3.05 3.25 3 4 1.00 0.0000001 ! Br-Br intermolecular
2 1 1.88 1.98 1 1 1.00 0.0000001 ! Br-C intermolecular
0 » » » » ! navc
0 » » » » ! nval
```

# CBr4 phase II – .dat fájl

## total scattering diffraction dataset 1.

We have 1 neutron dataset

We are using internal smoothing.

We are going to apply „cbr4a.fqd” dataset from 0.29 to 8.0 Å<sup>-1</sup>, reading and writing data in Q-space.

We suppose, error bars related to sqrt of the data, sigma parameter is 0.005

We are renormalise data and constant background

```
1 0 0> > > ! nexpn,nexpn,nsingle
0.005 0.2> > > ! dqp,swdt
0 0 0> > > ! ijob,iexist, ipart
cbr4_ordered_RT.txt
0 0> > > ! xin,xout
0.29 8.00 0> > > ! xmin,xmax,nx
0> > > ! nexcl
0.0> > > ! mur
2 0.005> > > ! isign,sigman
1 0> > > ! nbpol,nbfix
0.0 0> > > ! alpha0,flag
1.0 0> > > ! beta,flag
20.0 1.2 1> > > ! rwdt,qwmax,profile
1.111898 0.0 0.0 > > > ! wave,zero
0 0 0> > > ! wave flags
1.706727 -0.921428 0.352766 0.0 ! U,V,W,IG,eta
0 0 0 0> > > ! resolution flags
0> > > ! wextn
1> > > ! nuclear scattering
1> > > ! C noccn
C 1.0> > > ! symbol,coccn
1> > > ! Br noccn
Br 1.0> > > ! symbol,coccn
0> > > ! nlc
```

# CBr4 phase II – .dat fájl

## total scattering diffraction dataset 2.

We are taking into account Bragg-peaks for 20x FWHM and calculating Bragg-contributions 1.2 times higher Q-range. Also, we are applying Gaussian profile.

The wavelength is 1.111898 Å

Cagliotti parameters are:

U=1.706727, V=-0.921428, W=0.352766, which will be fixed during the run

Each site is occupied by fully carbons and bromines

```
1 0 0> > > ! nexpn,nexpn,nsingle
0.005 0.2> > > ! dqp,swdt
0 0 0> > > ! ijob,iexist, ipart
cbr4_ordered_RT.txt
0 0> > > ! xin,xout
0.29 8.00 0> > > ! xmin,xmax,nx
0> > > ! nexcl
0.0> > > ! mur
2 0.005> > > ! isign,sigman
1 0> > > ! nbpol,nbfix
0.0 0> > > ! alpha0,flag
1.0 0> > > ! beta,flag
20.0 1.2 1> > > ! rwdt,qwmax,profile
1.111898 0.0 0.0> > > ! wave,zero
0 0 0> > > ! wave flags
1.706727 -0.921428 0.352766 0.0 ! U,V,W,IG,eta
0 0 0 0> > > ! resolution flags
0> > > ! wextn
1> > > ! nuclear scattering
1> > > ! C noccn
C 1.0> > > ! symbol,coccn
1> > > ! Br noccn
Br 1.0> > > ! symbol,coccn
0> > > ! nlc
```

# CBr4 phase II time to start simulations...

You can accelerate simulation, if you choose smaller Q-range

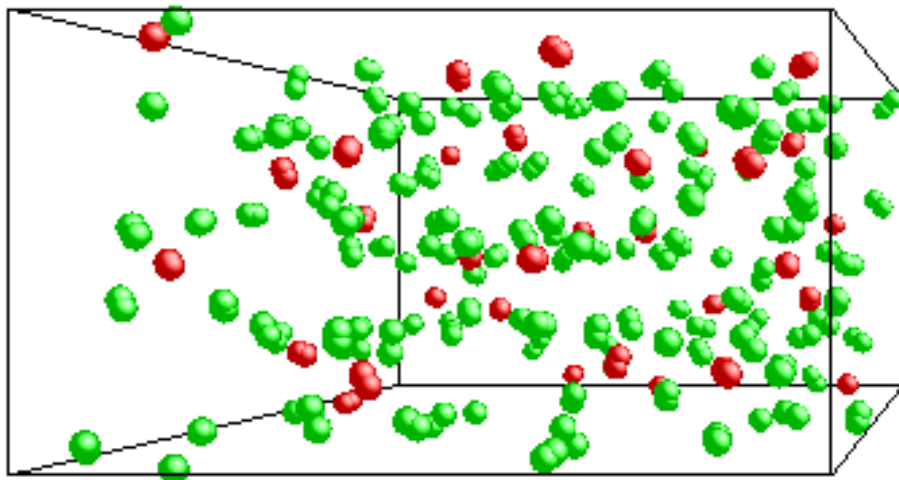
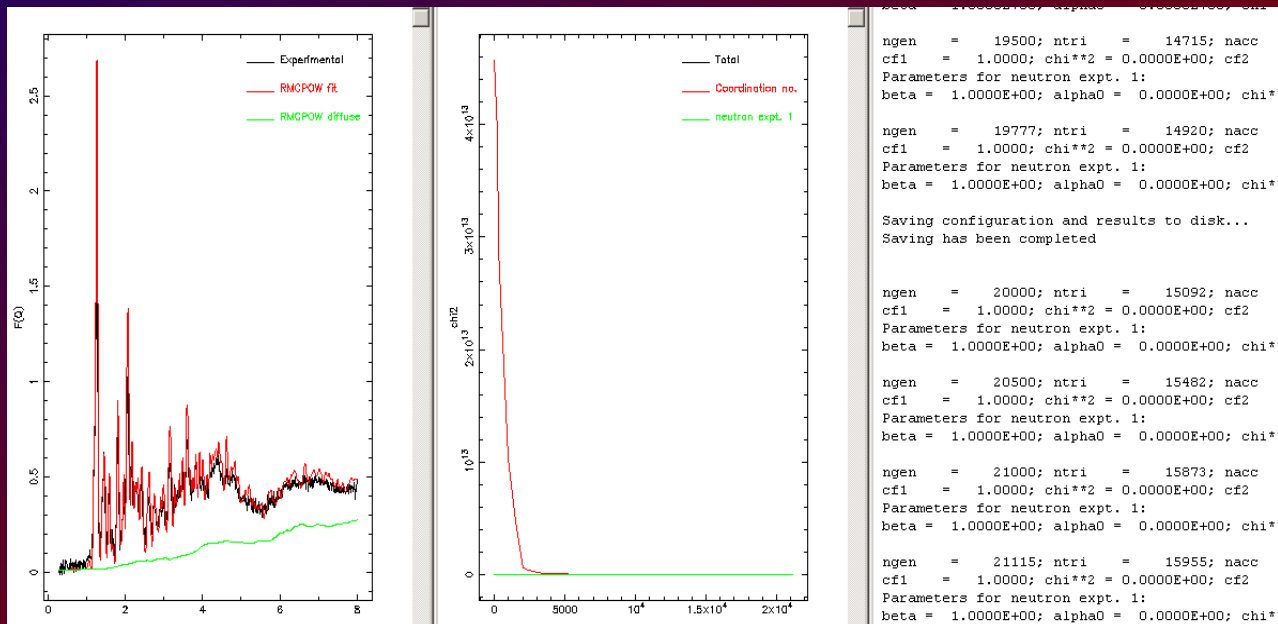
If you reached better agreement, try to improve it by refining renormalization, constants and profile parameters

```
CBr4 II phase, room temperature
0 0> > > > ! ncoll,ncycles
500 0 120 5 > > > ! iprint,iplot,timelim,timesav
21.43 12.12 21.02 90.0 110.88 90.0> > > ! a1,a2,a3,g1,g2,g3
0 0 0 0 0 0> > > ! lattice parameters flags
4 1 2 1> > > ! isym,n1,n2,n3
2 0> > > ! ntypes,ntypesm
0.05 0.05> > > ! delta
0 0.0> > > ! nswap,swapfrac
0 0.0> > > ! nref,reffrac
4.5 1.88 3.05> > > ! rcut
3> > > ! ncoord
1 2 1.88 1.98 4 4 1.00 0.0000001 ! C-Br intermolecular
2 2 3.05 3.25 3 4 1.00 0.0000001 ! Br-Br intermolecular
2 1 1.88 1.98 1 1 1.00 0.0000001 ! Br-C intermolecular
0> > > ! navc
0> > > ! nval
1 0 0> > > ! nexpn,nexpn,nsingle
0.005 0.2> > > ! dqp,swdt
0 0 0> > > ! ijob,iexist, ipart
cbr4_ordered_RT.txt
0 0> > > ! xin,xout
0.29 8.00 0> > > ! xmin,xmax,nx
0> > > ! nexcl
0.0> > > ! mur
2 0.005> > > ! isign,sigman
1 0> > > ! nbpol,nbfix
0.0 0> > > ! alpha0,flag
1.0 0> > > ! beta,flag
20.0 1.2 1> > > ! rwdt,qwmax,profile
1.111898 0.0 0.0> > > ! wave,zero
0 0 0> > > ! wave flags
1.706727 -0.921428 0.352766 0.0 ! U,V,W,IG,eta
0 0 0 0> > > ! resolution flags
0> > > ! wextn
1> > > ! nuclear scattering
1> > > ! C noccn
C 1.0> > > ! symbol,coccn
1> > > ! Br noccn
Br 1.0> > > ! symbol,coccn
0> > > ! nlc
```



# CBr<sub>4</sub> phase II

## if you were enough time...



..you can observe, that diffuse scattering is the result of the structure of molecule remains stable against thermal displacements – the molecule performs libration around equilibrium positions

# CBr<sub>4</sub> phase I – problem description and solution guide

The carbon atoms obtain equilibrium positions (4a site), but the bromine atoms are not.

There are many ways to simulate the structure

## Cautious strategy:

Creating bromine atoms, which fulfill cutoffs and coordination constraints, then move them by series of individual displacements

Disadvantage: slow

## Faster strategy:

Creating atoms on the 32f site, whose half is occupied by bromines. With swap moves and weak coordination constraint(s) (cc), randomize distribution of bromine atoms (without experimental data). Then fit the experimental data by allowing atomic displacements.

there is a chance, that cc won't be 100%

# CBr4 I – 1<sup>st</sup> strategy creating configuration

To create starting configuration:

> Crystal.exe cbr4\_l\_c.atom

Reading parameters from

.....

Total no of generated atoms is        32

Output file [.cfg] > cbr4\_lcarbon

Then adding atoms relative to the carbon positions by **AddAtomRel cbr4\_l.add:**

```
cbr4_lcarbon
1 > > > !Type to add
4> > > !Number of atoms to add
f> > > !Randomize orientation
1.5758 0.0 1.1143> !Vector to add
-1.5758 0.0 1.1143> !vector to add
0.0 1.5758 -1.1143> !vector to add
0.0 -1.5758 -1.1143> !vector to add
cbr4_l> > > !Output cfg
```

```
!false.>> ! apply to existing .cfg?
225 1> > > ! spg no, setting 1
8.85 8.85 8.85 90.0 90.0 90.0> ! a1,a2,a3,g1,g2,g3
6 2 2 2> > > ! isym,n1,n2,n3
n> > > ! no displacements
1> > > ! No. of atom types
1> > > ! No. of C Wyckoff sites
4a 0.0000 0.0000 0.0000> ! Wyckoff site,x,y,z Cl
.true.> > > ! RMC coordinates used in output
```