tutorial session VI
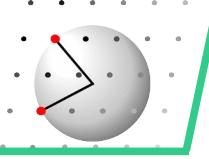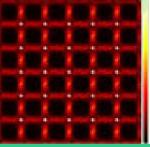
domains

domain

(3D) extended modification of the crystal structure

locally changed structure   domains in a strict sense
some nm to some µm

local dissolutions   cluster

**aspects needed to describe a domain**

orientation relationship host <==> guest   (ir)regular intergrowth
$lattice_{host}$ <==> $lattice_{guest}$

interface host <==> guest   smooth interface
rough, irregular interface

distribution of domains   (irr)regular distribution

origin

very often in connection with phase transitions
indirectly in relation to host/guest structures and intercalated structures
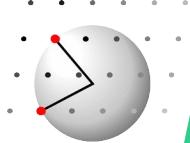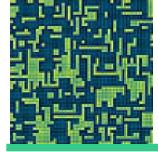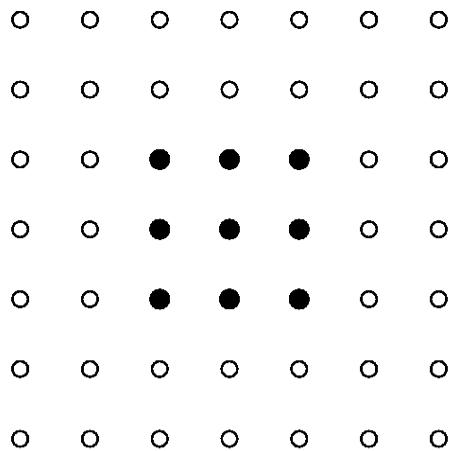
simple domain
   identical lattice
    smooth interface

simple domain
    different structure
    smooth interface

simple domain
    different structure
    uneven interface
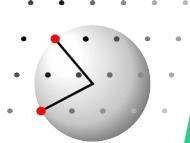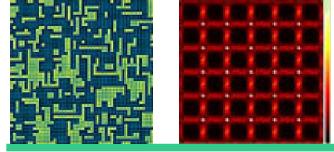
if randomly distributed:
diffuse maxima at
common Bragg reflections

if randomly distributed:
diffuse maxima at
individual Bragg reflections

diffuse maxima at
individual Bragg reflections

Run discus_suite
Switch to directory:
    Lectures/10_Domain/CUBE

Use Macro dom.cube.mac

suite > @dom.cube.mac

Use

 jmol   with file cube.cif

As well
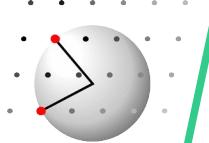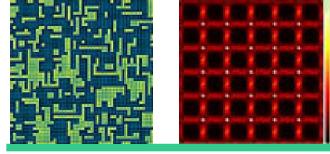
```
read                                        # switch to read menu
cell dom.host.cube.cell,7,7,1               # read an asymmetric unit expand
#
domain                                      # switch to domain level
  rese                                      # reset everything
  mode    pseudo                            # Interpret pseudo atoms
  input   dom.cube.pseudo                   # List of domain origins
  assign char,si,cube                       # interpret "SI" as a cube shaped
  assign fuzzy,si,1.5                       # define distance to host atoms
  assign cont, si,dom.guest.cube.stru       # domain structure is in this file
  assign shape ,si,1,  1. , 0. , 0. ,  0.   # Define a cube shaped domain
  assign shape ,si,2,  0. , 1. , 0. ,  0.   # that is +- 1 unit cells large
  assign shape ,si,3,  0. , 0. , 1. ,  0.   #
  assign orient,si,1,  1. , 0. , 0. ,  0.   # Domain content shall be rotated
  assign orient,si,2,  0. , 1. , 0. ,  0.   # by this matrix (here unit matrix)
  assign orient,si,3,  0. , 0. , 1. ,  0.   #
  set     distance, all, 2.55               # Define distance to internal
  set     distance, new, 2.71               # boundary for old and new atoms
  show
  run
exit
```
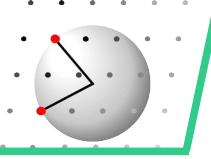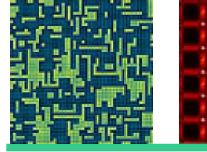
```
title Domain list for simple domains
spcgr  P4
cell    2.50, 2.50, 2.50, 90.00, 90.00, 90.00
atom
SI    0.00000  0.00000  0.00000    0.05
```

The domain list is a simple DISCUS structure file

Here one pseudo atom at 0,0,0
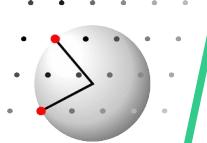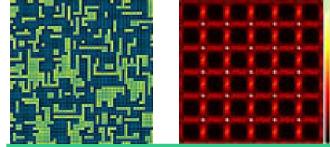
Run discus_suite

Switch to directory:
   Lectures/10_Domain/CUBE

Use Macro dom.cube.mac

suite > @dom.cube.mac

Edit file dom.cube.pseudo
**Change the position of the SI atom,**
Add new SI atoms...

**Use**

jmol   with file cube.cif
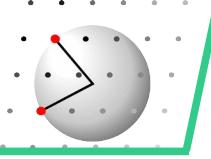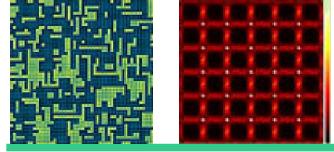
as well

Run discus_suite

Switch to directory:
     Lectures/10_Domain/CUBE

Use Macro dom.tilt.mac

suite > @dom.tilt.mac

Edit file dom.tilt.mac
**Lines 46 to 48 contain a rotation matrix**
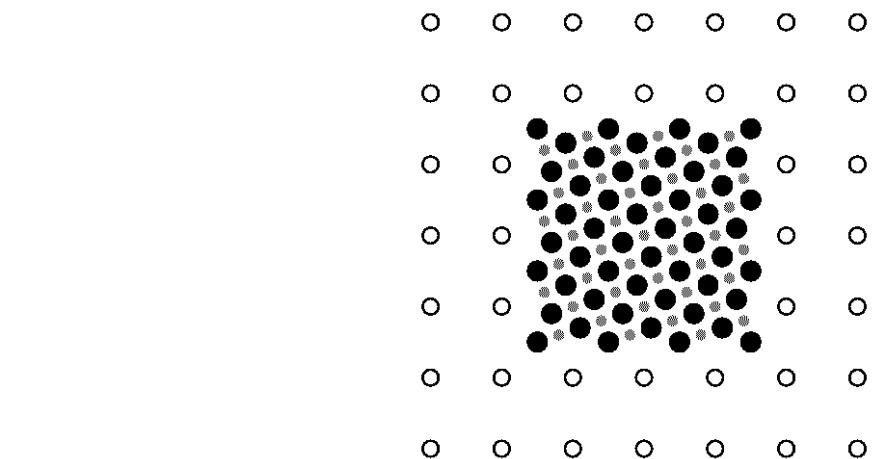
Use

jmol   with file tilt.cif

as well
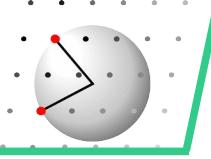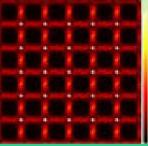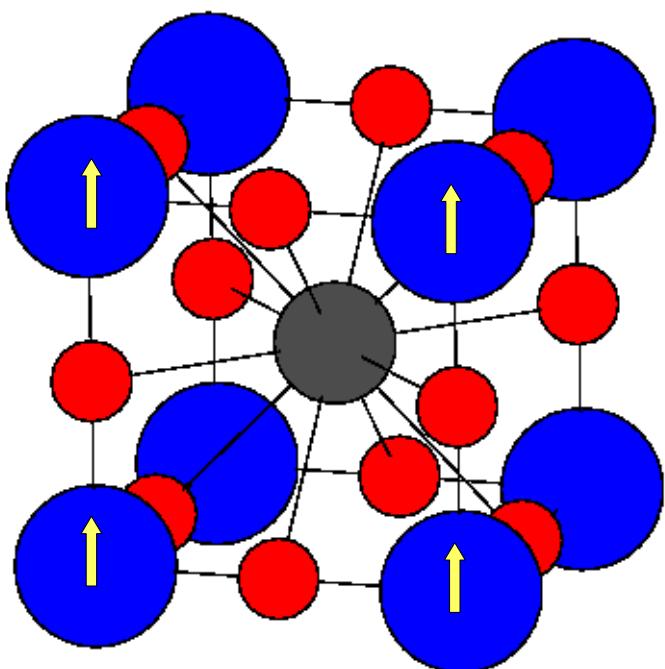
high temperature phase

cubic Pm3m

Ti   0,0,0   octahedron site

Sr   ½, ½, ½

O   ½,0,0

low temperature phase (simplified)

tetragonal P4mm

c/a $\neq$ 1

shift of Ti along [001]

in Pm3m equivalent:	[100]	[010]	[001]

independent nucleation   three different possible orientations

relaxation within one unit cell   equal relaxation in neighboring cells
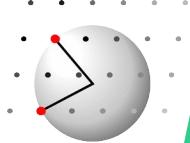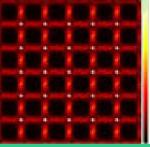
simulation of the disordered low temperature structure

A)   random selection of individual unit cells ==> introduce a local distortion

relax neighboring cells (in random sequence)
until whole crystal has been distorted

extended book keeping and search for unit cells that are distorted already!

B)   'detour' via dummy-atoms (dummy-domains)

1.   cubic primitive crystal with three different atoms A,B,C at equal amounts

2.   sort atoms A,B,C with positive correlation

3.   relax distances A-A, B-B, C-C

4.   replace atoms A by unit cell distorted along [100]
       replace atoms B by unit cell distorted along [010]
       replace atoms C by unit cell distorted along [001]
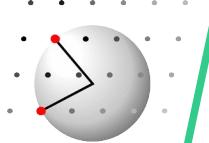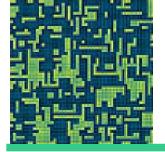
B) 'detour' via dummy-atoms (dummy-domains)

1. cubic primitive crystal with three atoms A,B,C in equal amounts
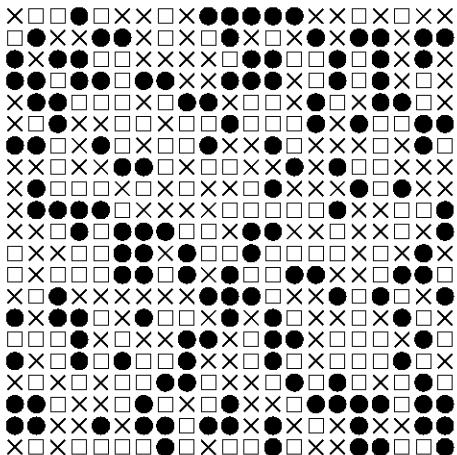
atom A represents a unit cell
that is distorted along [100]
correpondingly for B and C

Distance between atoms: lattice constant a
atom position: 0,0,0

2. sort atoms A,B,C with positive correlations

Neighbors along: <100>

pairs: A-B, A-C, B-C
each with correlation > 0

Crystal, build up of three different 'atoms',
all at ideal positions, no distortions
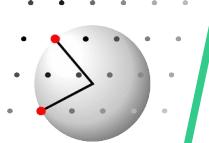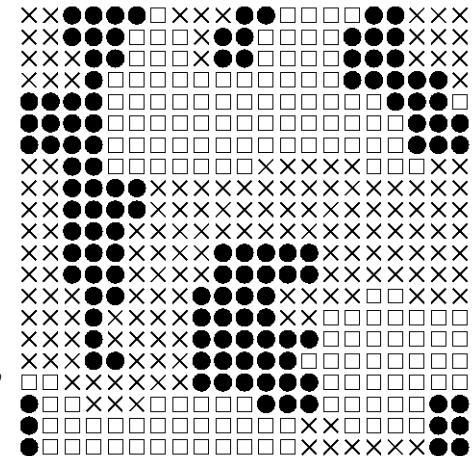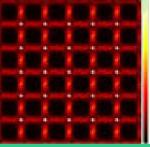
B)   'detour' via dummy atoms (dummy domains)

3.   local distortions

A:[100]

B: [010]

C: [001]

?
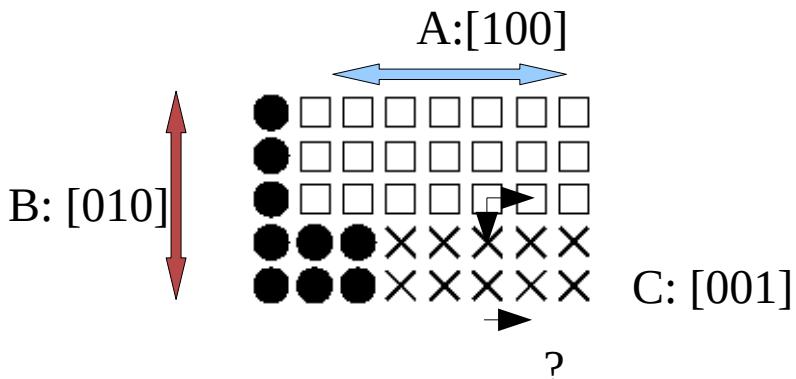
pair A-A: distanc along   [100] is a_0*k with k ~ 1.0025
[010] is a_0/k
[001] is a_0/k

pair A-X: distance along   [100] is a_0 distortion of A along [100] induces
[010] is a_0 shift of /C along [100]
[001] is a_0

If interface is long,
dislocations will occur

angle A-A-A   90°
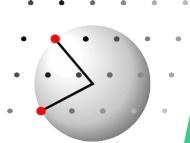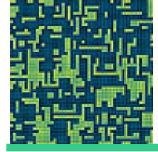
diffraction pattern of the relaxed structure

all 'atoms' are identical!

A:[100]

B: [010]

C: [001]
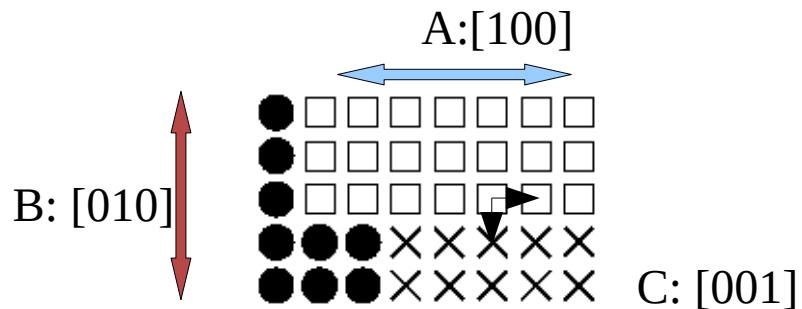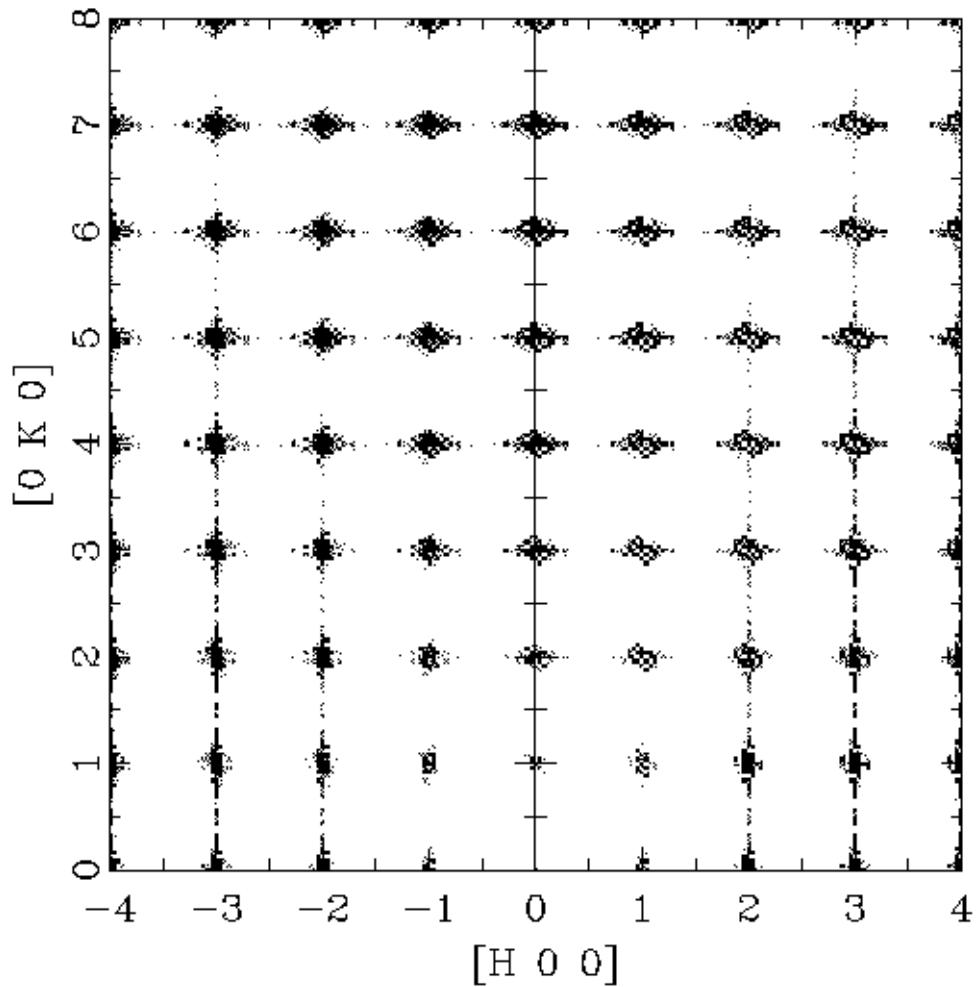
diffuse maxima at Bragg positions

extended domains of locally equal atoms

weak diffuse streaks

shift of the domains
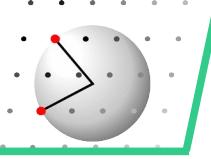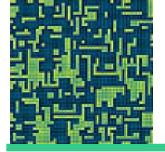
B)   'detour' via dummy atoms (dummy domains)

4.   replace atoms A by a unit cell that is distorted along [100]
        correspondingly replace B by a unit cell that is distorted along [010]
        correpondingly for C

A:[100]

B: [010]

C: [001]

?
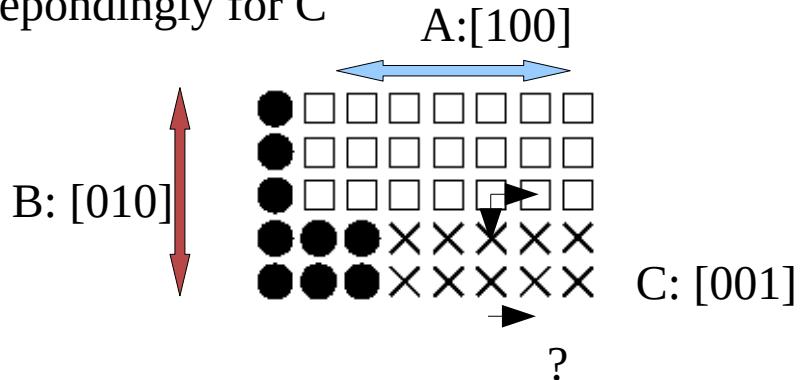
metric remains cubic

transform atoms within a [100] domain by:

$$\begin{pmatrix} k & 0 & 0 \\ 0 & 1/k & 0 \\ 0 & 0 & 1/k \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

in addition, relative shift of atoms along ±[100]
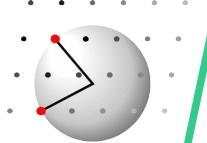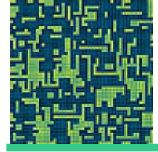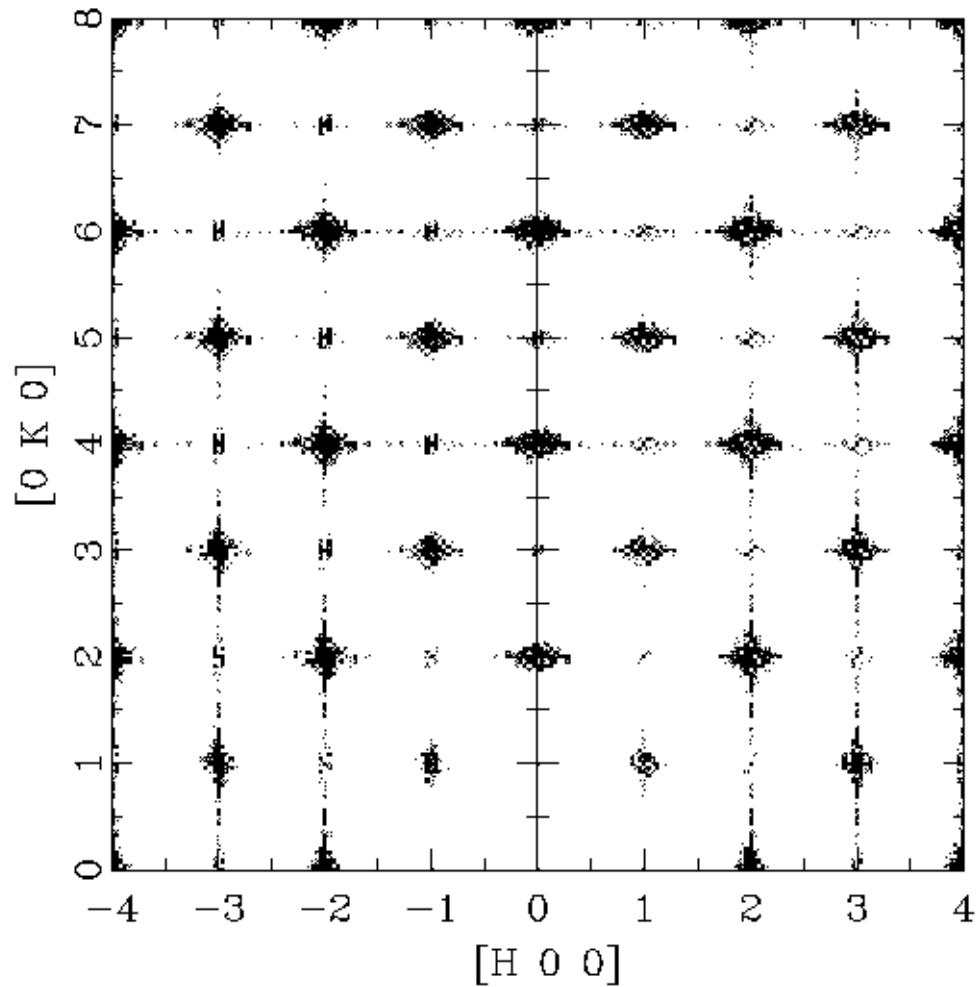
diffraction pattern of the relaxed and replaced structure

A:[100]

B: [010]

C: [001]
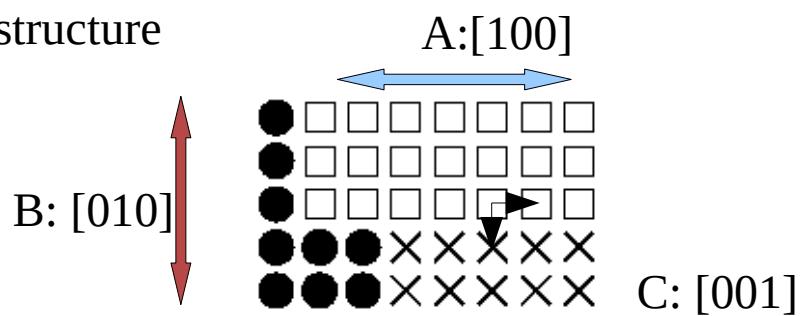
diffuse maxima at Bragg positions

extended domains that consist of unit cells, locally distorted along the same direction

$I_{h+k+l = 2n} > I_{h+k+l = 2n+1}$

weak diffuse streaks

shift of domains

Lehrstuhl für Kristallographie und Strukturphysik
Universität Erlangen-Nürnberg
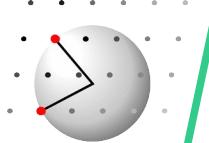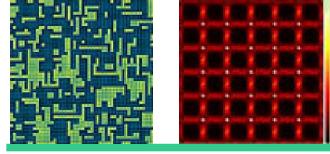
Run discus_suite

Switch to directory:
      Lectures/10_Domain/Perovskite

Use Macro dom.perov.mac

suite > @dom.perov.mac

The macro takes you through the steps
Plots follow at the end