

# Refinement of modulated structures with Jana examples

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# Outline

- Structure factor formula for simple harmonic modulation
- Diffraction pattern induced by modulation function
- What can be modulated? Which parameters are refined?
- Program Jana2006
- Two ways how to solve modulated structure
- Example: sodium carbonate by classical method
- Verification of results from Fourier maps
- Distances and t-plots
- Plotting of modulated structures
- Example: Chromium diphosphate solved by charge flipping
- Discontinuous functions
- Commensurate refinement
- Composite structures [skipped]
- Magnetic structures
- Where to get more information?

# Structure factor and diffraction pattern

$$\mathbf{r}_\nu = \mathbf{r}_{\nu,0} + \mathbf{u}_\nu(\tau),$$

where  $\tau$  is  $x_4$  of undisplaced position.

The displaced position has  $x_4 = \tau + \mathbf{q}\mathbf{u}_\nu$

Contribution of an interval  $d\tau$  to the Fourier coefficient  $h_1, h_2, h_3, m$ :

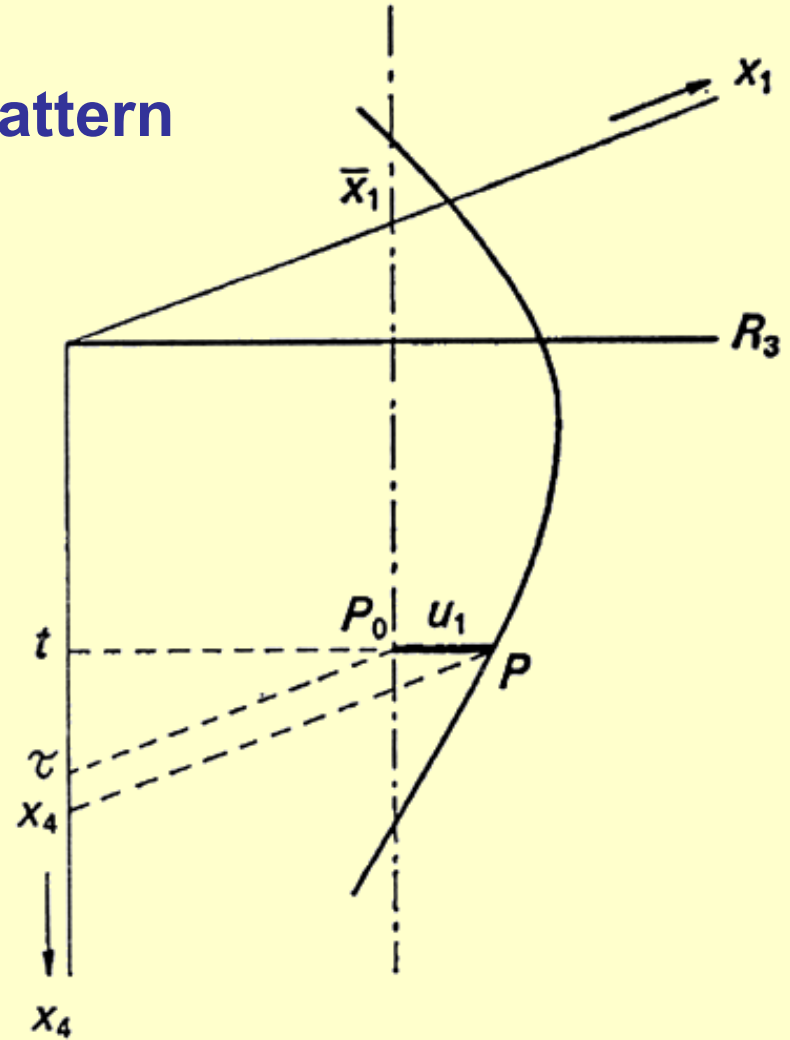
$$f_\nu d\tau \exp\left[2\pi i(h_1x_1 + h_2x_2 + h_3x_3 + mx_4)\right] =$$

$$f_\nu d\tau \exp\left[2\pi i(\mathbf{H}\mathbf{r}_\nu + mx_4)\right] =$$

$$f_\nu d\tau \exp\left[2\pi i(\mathbf{H}\mathbf{r}_{\nu,0} + \mathbf{H}\mathbf{u}_\nu + m\mathbf{q}\mathbf{u}_\nu + m\tau)\right]$$

$$F(h_1, h_2, h_3, m) = \sum_\nu f_\nu \exp(2\pi i\mathbf{H}\mathbf{r}_{\nu,0})$$

$$\times \int_0^1 d\tau \exp\left[2\pi i(\mathbf{H} + m\mathbf{q})\mathbf{u}_\nu + m\tau\right]$$



(de Wolff, Acta Cryst. A30,777)

The integral can be calculated by Gaussian method.

An older way uses analytical method with Bessel functions. The analytical calculation shows clearly relationship between modulation waves and diffraction pattern.

## Positional modulation with a simple harmonic wave

$$\mathbf{r}_v(\mathbf{n}) = \mathbf{r}_{v,0} + \mathbf{U}_{vs1} \sin\left[2\pi\mathbf{q}(\mathbf{r}_{v,0} + \mathbf{n})\right]$$

Contribution from atom at  $\mathbf{r}_v + \mathbf{n}$ : (form factors corrected for temperature movement)

$$F_{v,\mathbf{n}}(\mathbf{Q}) = f_v^T(\mathbf{Q}) \exp\left[2\pi i \mathbf{Q} \cdot (\mathbf{r}_v + \mathbf{n})\right] = f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_v) \exp(2\pi i \mathbf{Q} \cdot \mathbf{n})$$

$$F_{v,\mathbf{n}}(\mathbf{Q}) = f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_{v,0}) \exp\left\{2\pi i \mathbf{Q} \cdot \mathbf{U}_{vs1} \sin\left[2\pi\mathbf{q}(\mathbf{r}_{v,0} + \mathbf{n})\right]\right\} \exp(2\pi i \mathbf{Q} \cdot \mathbf{n})$$

Jacobi - Anger expansion:

$$\exp(iz \sin \alpha) = \sum_{l=-\infty}^{\infty} J_l(z) \exp(il\alpha)$$

In our case  $z = 2\pi\mathbf{Q} \cdot \mathbf{U}_{vs1}$

$$F_{v,\mathbf{n}}(\mathbf{Q}) = f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_{v,0}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{n}) \sum_{l=-\infty}^{\infty} J_l(2\pi\mathbf{Q} \cdot \mathbf{U}_{vs1}) \exp\left[2\pi il\mathbf{q}(\mathbf{r}_{v,0} + \mathbf{n})\right] =$$

$$f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_{v,0}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{n}) \sum_{l=-\infty}^{\infty} J_l(2\pi\mathbf{Q} \cdot \mathbf{U}_{vs1}) \exp(2\pi il\mathbf{q}\mathbf{r}_{v,0}) \exp(2\pi il\mathbf{q}\mathbf{n}) =$$

$$f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_{v,0}) \sum_{l=-\infty}^{\infty} J_l(2\pi\mathbf{Q} \cdot \mathbf{U}_{vs1}) \exp(2\pi il\mathbf{q}\mathbf{r}_{v,0}) \exp\left[2\pi i(\mathbf{Q} + l\mathbf{q})\mathbf{n}\right]$$

Summation for all  $\mathbf{n}$ :

$$F_v(\mathbf{Q}) = f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_{v,0}) \sum_{l=-\infty}^{\infty} J_l(2\pi\mathbf{Q} \cdot \mathbf{U}_{vs1}) \exp(2\pi il\mathbf{q}\mathbf{r}_{v,0}) \sum_{\mathbf{n}} \exp\left[2\pi i(\mathbf{Q} + l\mathbf{q})\mathbf{n}\right]$$

Contribution of atom  $\nu$  to the structure factor for 3d crystal :

$$F_\nu(\mathbf{Q}) = f_\nu(|\mathbf{Q}|) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_\nu) \sum_{\mathbf{n}} \exp\{2\pi i \mathbf{Q} \cdot \mathbf{n}\} =$$

$$f_\nu(|\mathbf{Q}|) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_\nu) \frac{\sin \pi N_1 \mathbf{Q} \cdot \mathbf{a}_1}{\sin \pi \mathbf{Q} \cdot \mathbf{a}_1} \frac{\sin \pi N_2 \mathbf{Q} \cdot \mathbf{a}_2}{\sin \pi \mathbf{Q} \cdot \mathbf{a}_2} \frac{\sin \pi N_3 \mathbf{Q} \cdot \mathbf{a}_3}{\sin \pi \mathbf{Q} \cdot \mathbf{a}_3} \\ \exp\left\{\pi i \mathbf{Q} \cdot \left((N_1 - 1)\mathbf{a}_1 + (N_2 - 1)\mathbf{a}_2 + (N_3 - 1)\mathbf{a}_3\right)\right\}$$

This function has maxima if  $\mathbf{Q} \cdot \mathbf{a}_1$ ,  $\mathbf{Q} \cdot \mathbf{a}_2$  and  $\mathbf{Q} \cdot \mathbf{a}_3$  are integers. This occurs if

$$\mathbf{Q} = \mathbf{H} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^*, \quad h_i \text{ integers, } \mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$$

Contribution of atom  $\nu$  to the structure factor in case of simple harmonic modulation :

$$F_\nu(\mathbf{Q}) = f_\nu^T(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_{\nu,0}) \sum_{l=-\infty}^{\infty} J_l(2\pi \mathbf{Q} \cdot \mathbf{U}_{\nu s l}) \exp(2\pi i l \mathbf{q} \cdot \mathbf{r}_{\nu,0}) \sum_{\mathbf{n}} \exp[2\pi i (\mathbf{Q} + l\mathbf{q}) \cdot \mathbf{n}]$$

This function has maxima if  $(\mathbf{Q} + l\mathbf{q}_1) \cdot \mathbf{a}_1$ ,  $(\mathbf{Q} + l\mathbf{q}_2) \cdot \mathbf{a}_2$  and  $(\mathbf{Q} + l\mathbf{q}_3) \cdot \mathbf{a}_3$  are integers.

This occurs if

$$\mathbf{Q} + l\mathbf{q} = \mathbf{H} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^*, \quad h_i \text{ integers, } \mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$$

$$\mathbf{Q} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^* + m\mathbf{q} = \mathbf{H} + m\mathbf{q} \quad l = -m$$

$$F_v(\mathbf{Q}) = f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_{v,0}) \sum_{l=-\infty}^{\infty} J_l(2\pi \mathbf{Q} \cdot \mathbf{U}_{vs1}) \exp(2\pi i l \mathbf{q} \cdot \mathbf{r}_{v,0}) \sum_{\mathbf{n}} \exp[2\pi i (\mathbf{Q} + l\mathbf{q}) \cdot \mathbf{n}]$$

This function has maxima at

$$\mathbf{Q} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^* + m\mathbf{q} = \mathbf{H} + m\mathbf{q} \quad l = -m$$

Contribution of atom  $v$  to the reflection  $(h, k, l, m)$ :

$$F_v(\mathbf{Q}) =$$

$$f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_{v,0}) \exp(-2\pi i l \mathbf{q} \cdot \mathbf{r}_{v,0}) J_{-m}(2\pi \mathbf{Q} \cdot \mathbf{U}_{vs1}) \exp(2\pi i l \mathbf{q} \cdot \mathbf{r}_{v,0}) S =$$

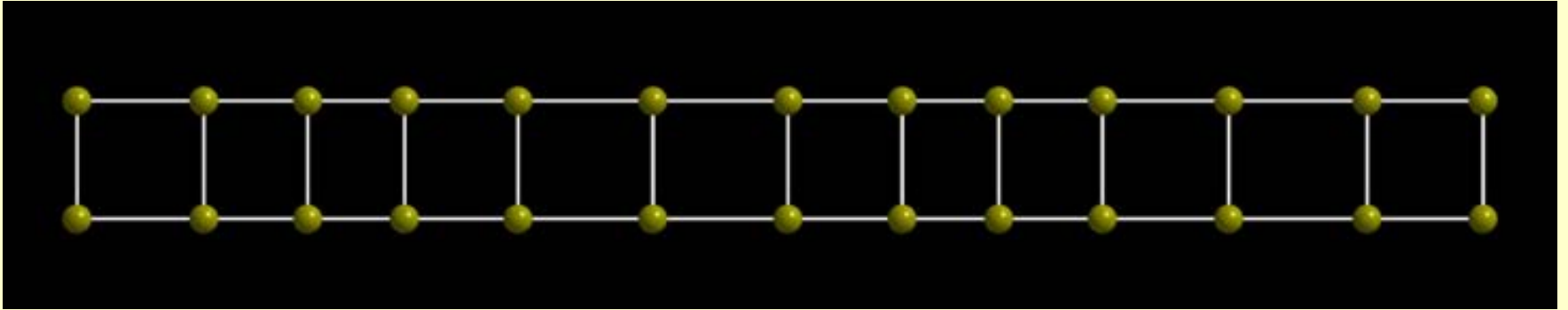
$$f_v^T(\mathbf{Q}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_{v,0}) J_{-m}(2\pi \mathbf{Q} \cdot \mathbf{U}_{vs1}) S$$

where  $S$  is result of summation over  $\mathbf{n}$ .

Conclusions :

1. One harmonic wave generates satellites up to the "infinite" order.
2. Intensity of the satellite  $(h, k, l, m)$  is proportional to the square of the Bessel function of the order  $m$
3. Intensity of satellites grows with  $\mathbf{Q} \cdot \mathbf{U}_v$

## Simulation of a simple longitudinal modulation



$$\mathbf{q} = (\alpha, \beta, 0)$$

$$\mathbf{u} = U \cos(2\pi \mathbf{q} \cdot \mathbf{r})$$

$$F = f \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) J_{-m}(2\pi \mathbf{U} \cdot \mathbf{Q})$$

$$\mathbf{U} = (U_x, 0, 0)$$

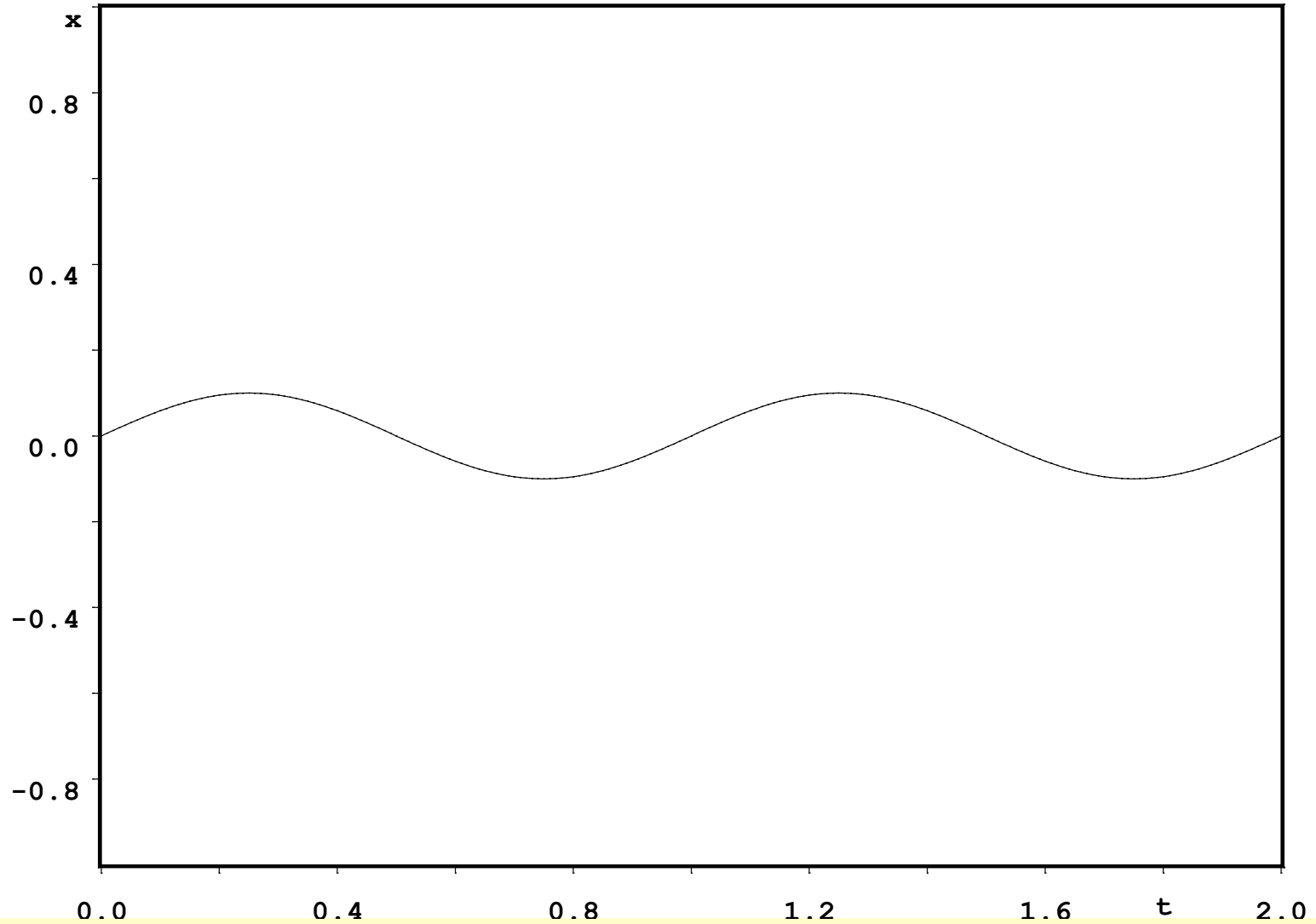
We shall show how the simulated diffraction pattern depends on the modulation amplitude, i.e.  $U_x$ , and that with a large amplitude we can see higher order satellites generated with the first modulation wave.

The cos term can be replaced by sin term used in the previous calculations.

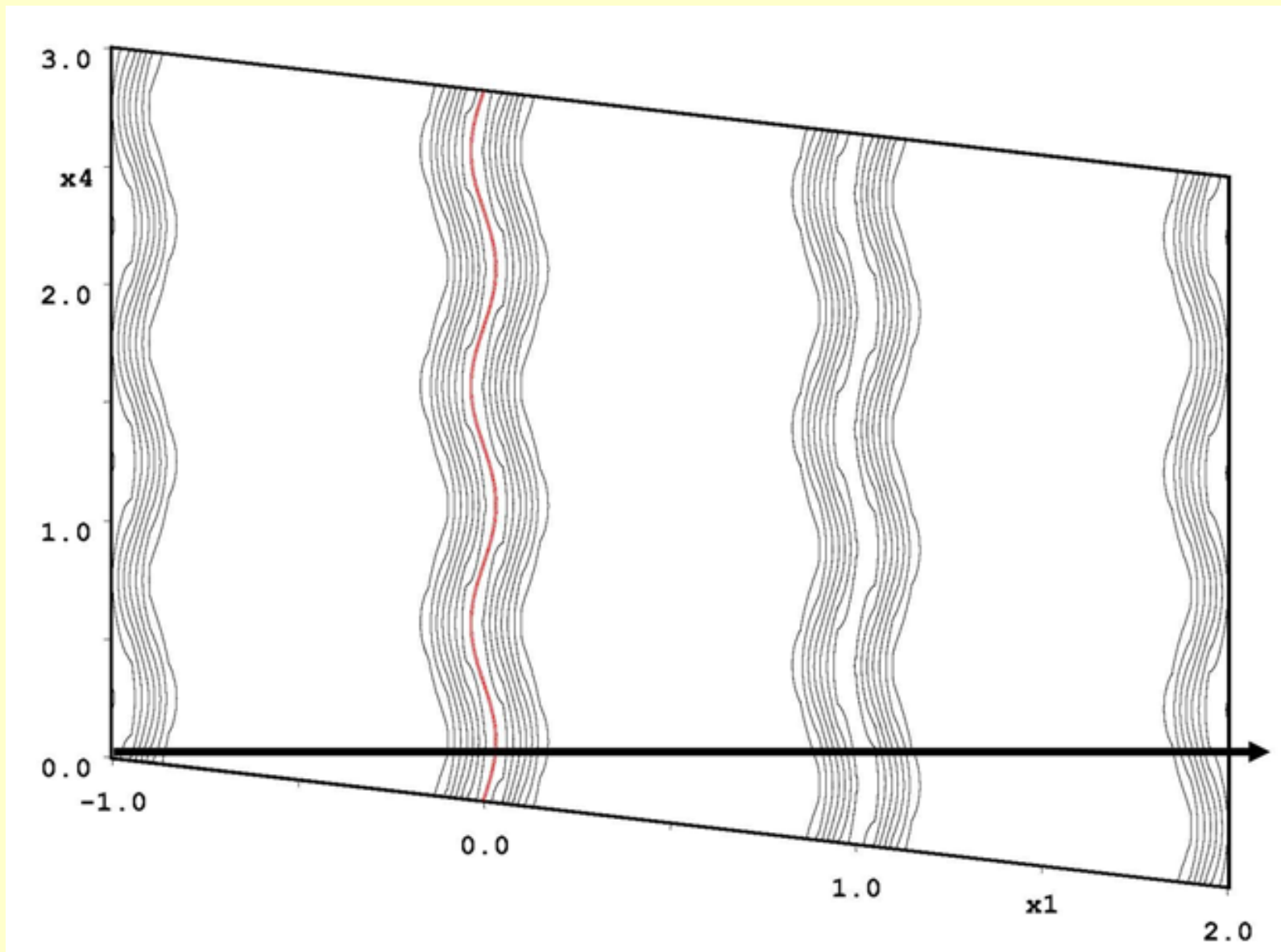
This would only shift the figures.



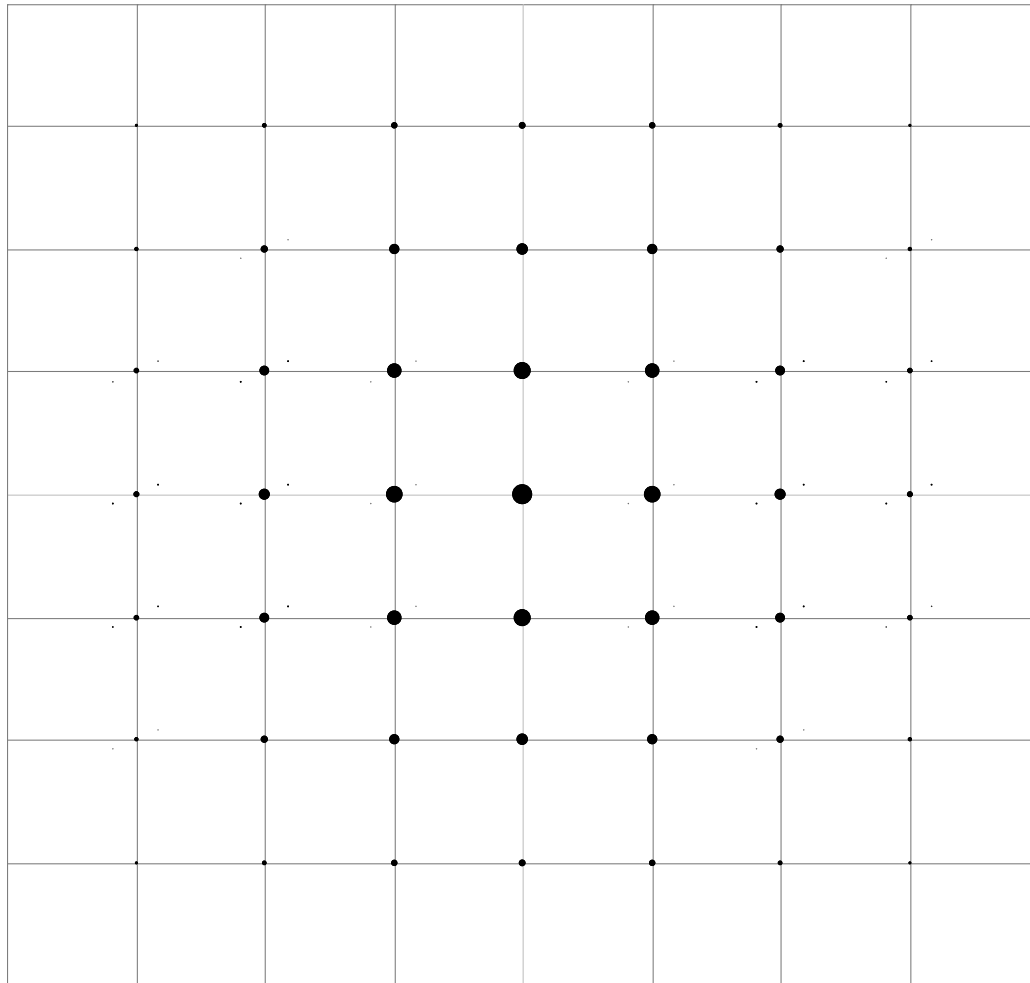
Positional modulation longitudinal  
1st harmonic 0.1Å  
Modulation function



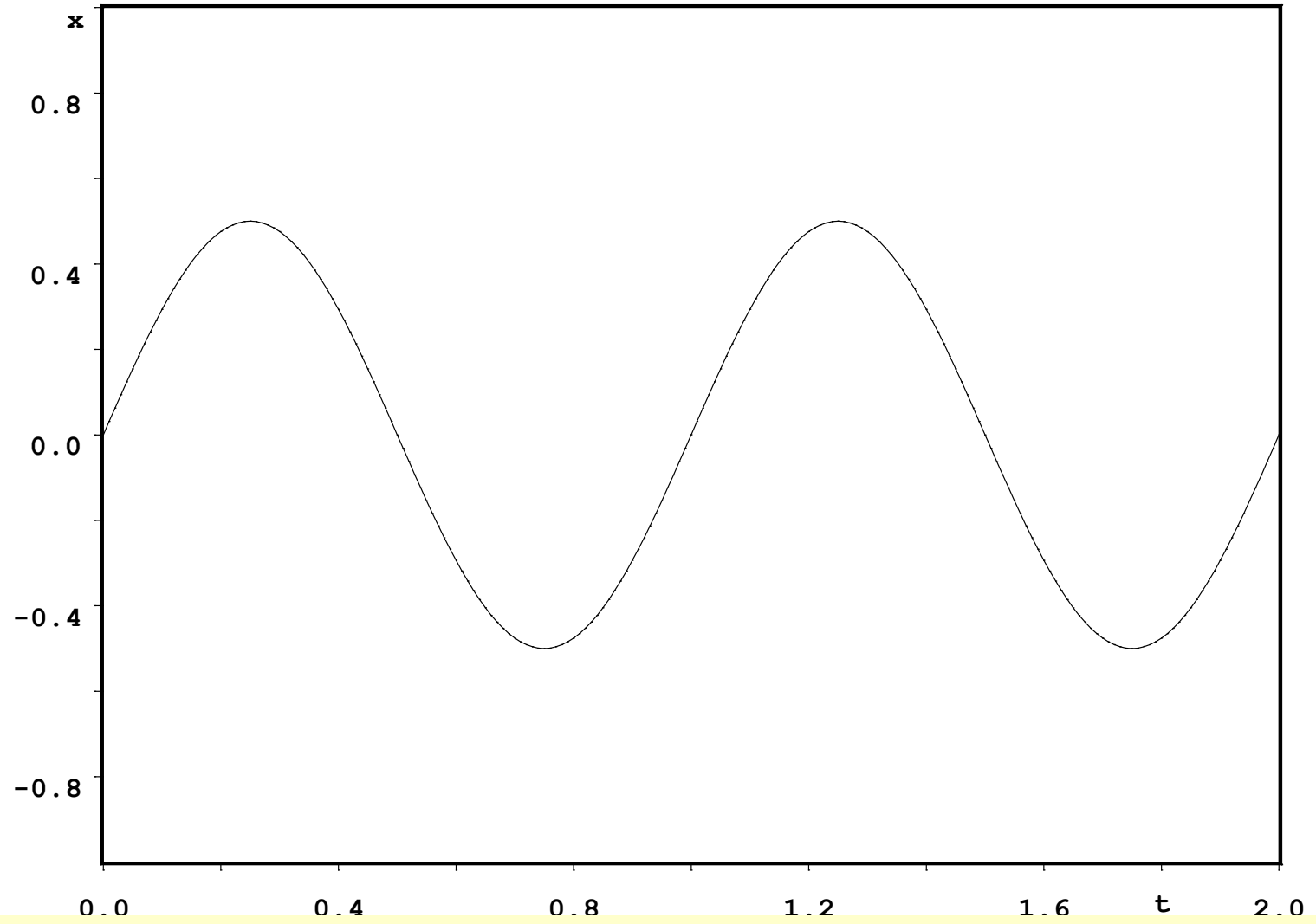
Positional modulation longitudinal  
1st harmonic 0.1Å  
Fourier map



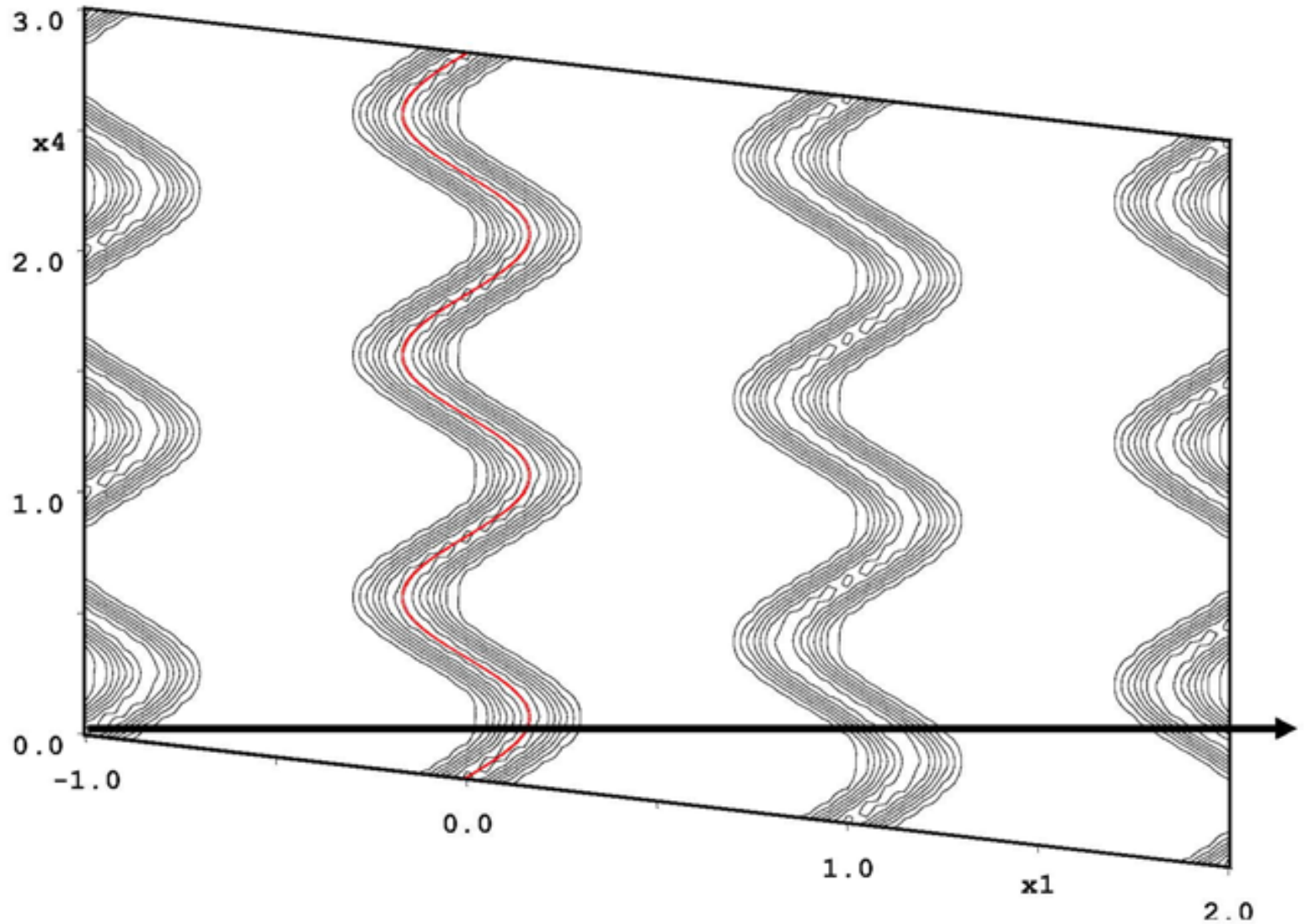
Positional modulation longitudinal  
1st harmonic  $0.1\text{\AA}$   
Diffraction pattern



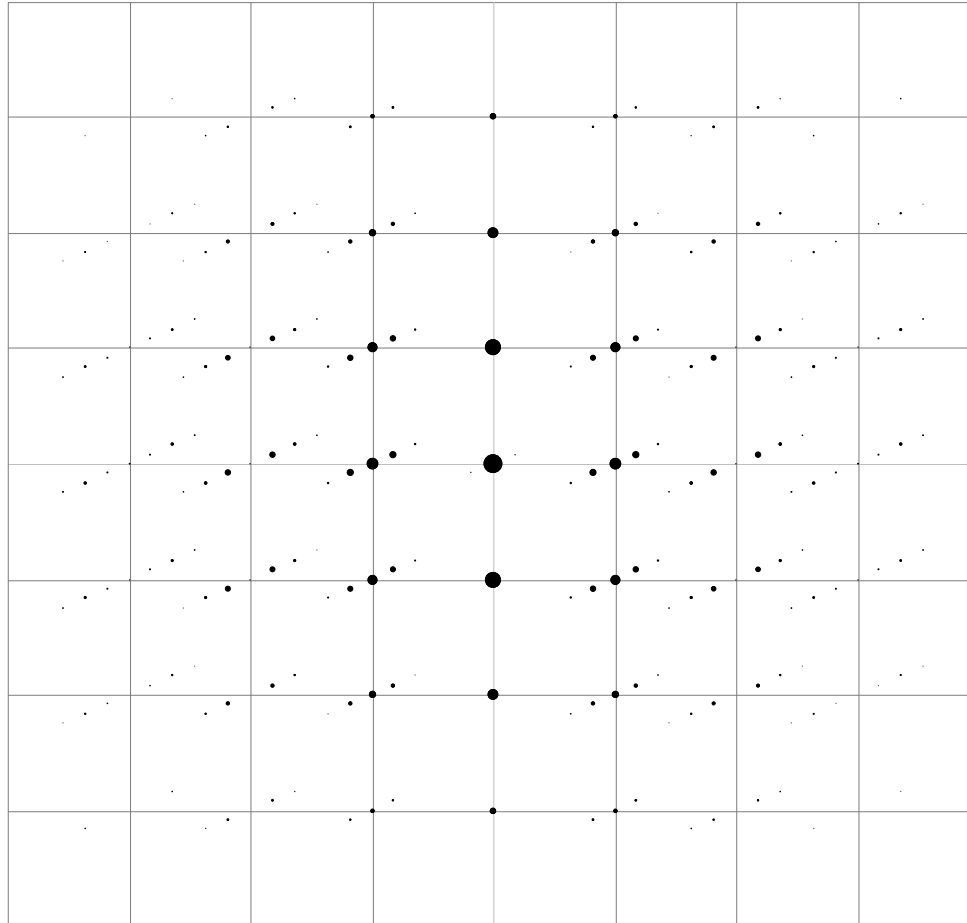
Positional modulation longitudinal  
1st harmonic 0.5Å  
Modulation function



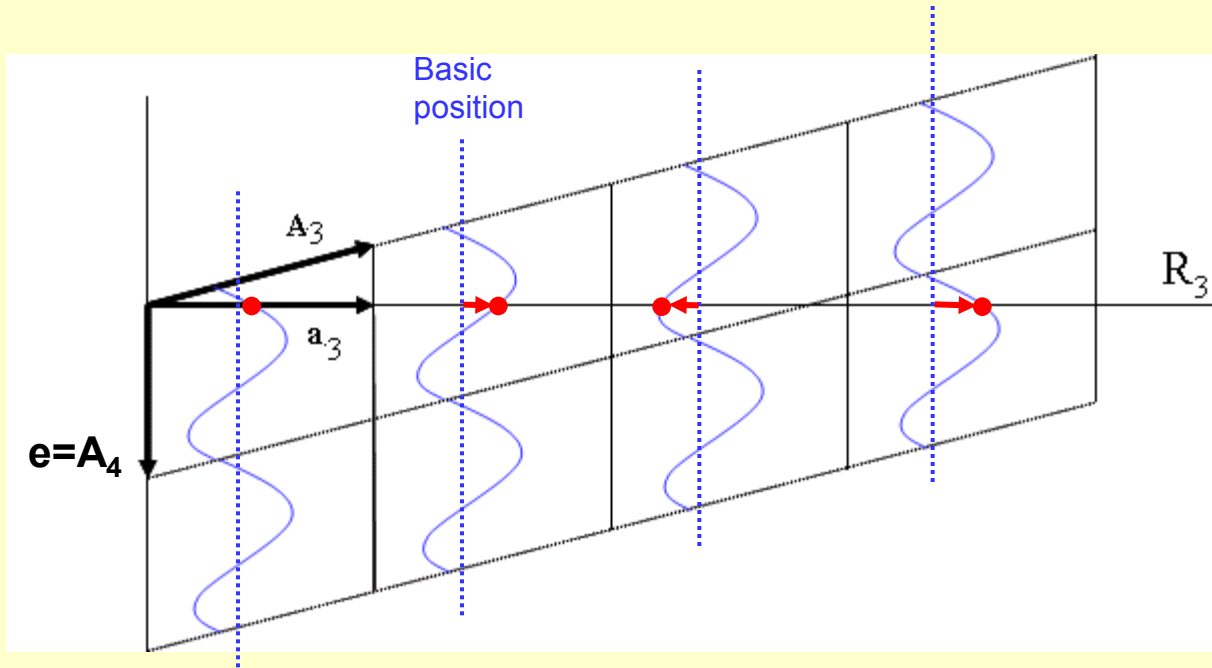
Positional modulation longitudinal  
1st harmonic  $0.5\text{\AA}$   
Fourier map



Positional modulation longitudinal  
1st harmonic  $0.5\text{\AA}$   
Diffraction pattern



# Parameters for position modulation



Basic position  
x  
average position

The same fractional coordinates in  $A_3$  and  $a_3$ .

The atom is displaced from its basic position by a periodic modulation function that can be expressed as a Fourier expansion. In the first approximation intensities of satellites reflections up to order  $m$  are determined by modulation waves of the same order.

$$\mathbf{r} = \bar{\mathbf{r}} + \mathbf{u}$$

$$\mathbf{u}(\bar{x}_4) = \sum_{n=1}^m \mathbf{U}_{s,n} \sin(2\pi n \bar{x}_4) + \sum_{n=1}^m \mathbf{U}_{c,n} \cos(2\pi n \bar{x}_4)$$

## **What can be modulated** *(in Jana2006)*

positions of individual atoms

positions of rigid bodies

ADP of individual atoms (harmonic or anharmonic)

Displacement parameters of rigid bodies -TLS tensors (harmonic or anharmonic)

occupation of individual atoms

occupation of rigid bodies

magnetic moments



# Jana2006

Program for structure analysis of crystals periodic in three or more dimensions from diffraction data

Václav Petříček, Michal Dušek & Lukáš Palatinus  
Institute of Physics, Prague, Czech Republic

**1980 SDS:** *Program for solution and refinement of 3d structures*

**1984 Jana :** *Refinement program for modulated structures*

**1996 Jana96:** *Modulated and 3d structures in one program. Graphical interface for DOS and UNIX X11.*

**1998 Jana98 :** *Improved Jana96. First widely used version. Graphical interface for DOS, DOS emulation and UNIX X11*

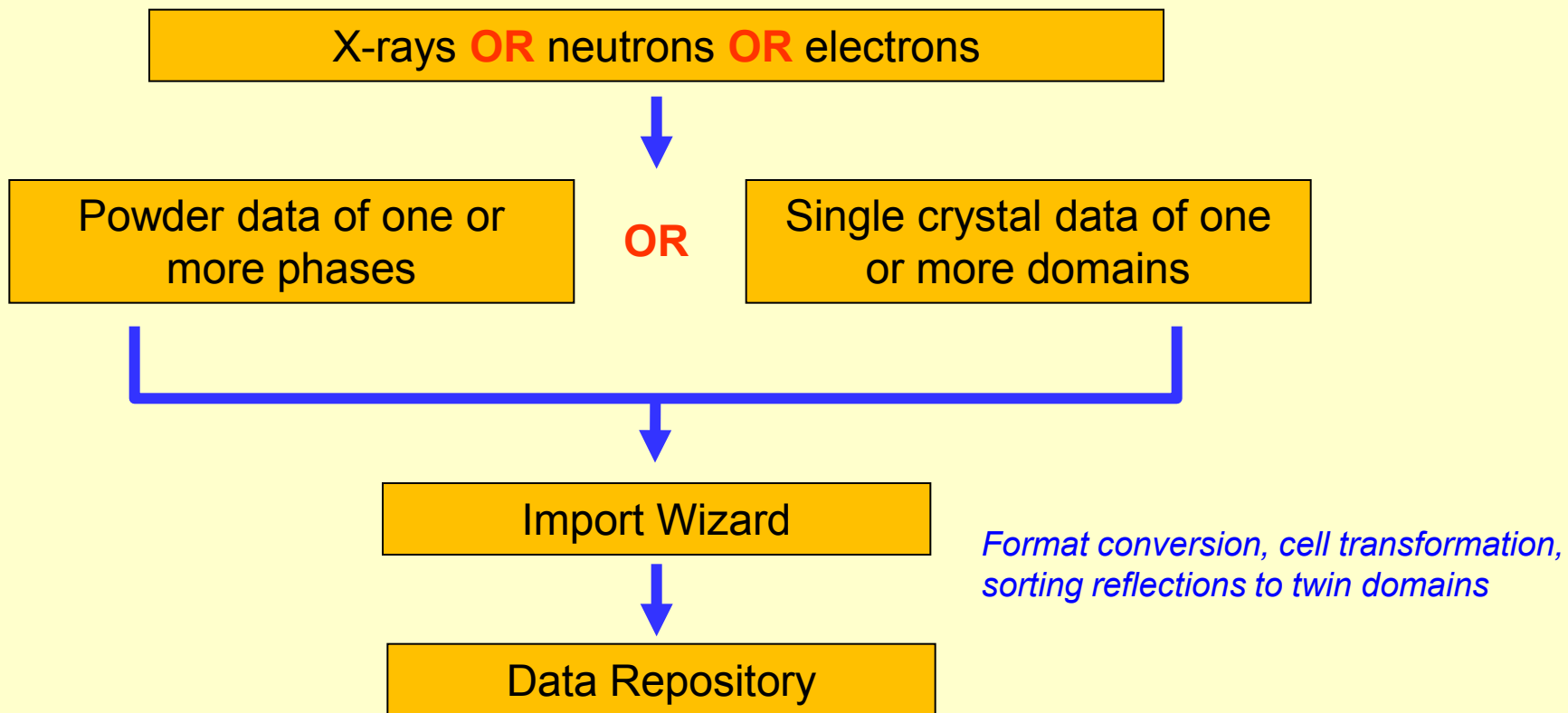
**2000 Jana2000:** *Support for powder data and multiphase refinement. Graphical interface for Win32 and UNIX X11.*

**2006 Jana2006:** *Combination of data sources, magnetic structures, TOF data. Dynamical allocation of memory. Only for Windows.*

# Institute of Physics, Prague 6, Cukrovarnická street



# Data input



The screenshot shows a window titled "Data repository" with a table of data files. The table has three columns: "File", "Type", and "Radiation". The first row is highlighted in blue. Below the table are several buttons: "Info", "Reimport", "Modify", "Delete", "Undelete", "Import new", "Esc", and "Ok".

File	Type	Radiation
ba6co6_neutrons.m92	Powder CW	Neutrons 1.594
ba6co6do16.xy	Powder CW	X-rays 1.54051
D:\PASCAL\sadcentreject.hkl	I(hkl) imported	X-rays Mo K(alpha)

# Program Scheme

↓ *Reading of one or more data sets*

M95 + M50

↓ *Determining symmetry, merging symmetry equivalent reflections, absorption correction  
Refinement of powder profile parameters*

M90, M41

↓ *Solution (by calling external programs)*

M40



*Refinement  
Transformation  
Introduction of twinning  
Change of symmetry*



Plotting, geometry parameters, Fourier maps ....

M95	data repository
M90	refinement reflection file
M50	basic crystal information, form factors, program options
M40	structure model

# Topics covered by Jana2006

Service crystallography

Advanced tools

Incommensurate structures

Commensurate structures

Composite structures

Magnetic structures

Jana2006 is still old fashioned: written in Fortran; not using external libraries (except basic graphics); not written by a team of programmers → flexibility

## NOT included in Jana2006:

**Phase problem solution:** calls SIR97,2000,2004; EXPO, EXPO2004, Superflip

**Plotting:** calls Diamond, Vesta, MC (marching cube) and other plotting software

**Validations and geometry analysis:** relies on Platon

# Where to start?

**Specify type of the file to be imported**

Single crystal:  known diffractometer formats  reflection file corrected for LP and absorption

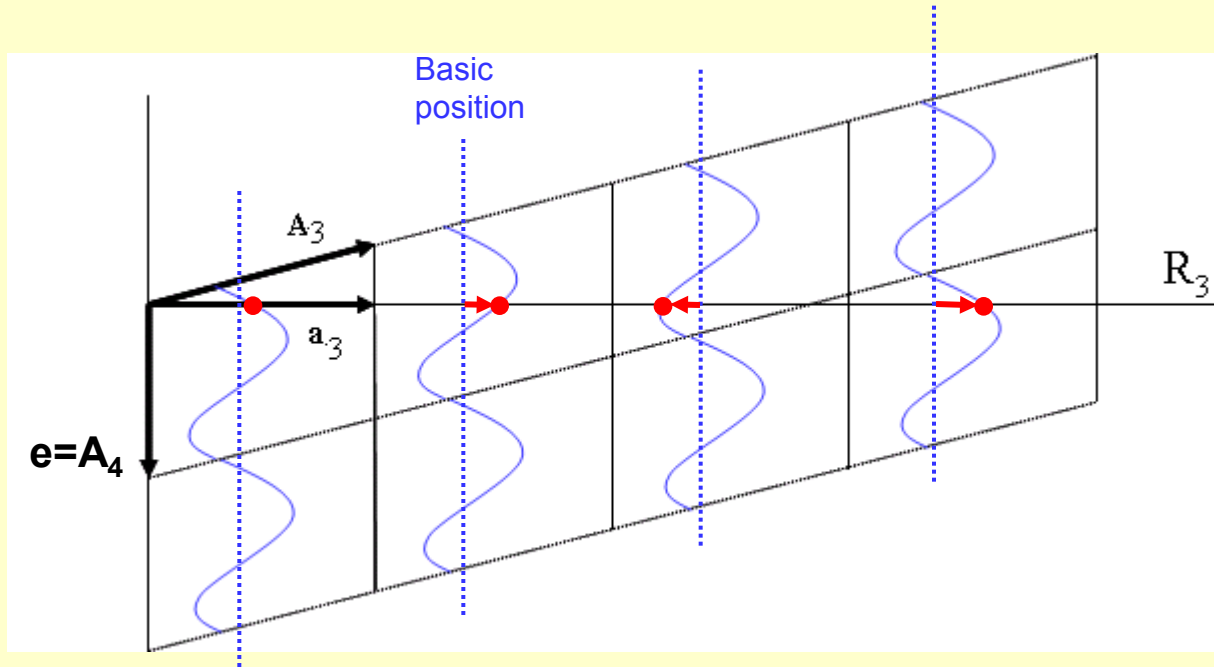
**Data reduction file from:**

File name:

<input type="radio"/> <u>CAD4</u>	<input type="radio"/> <u>IPDS Stoe</u>
<input type="radio"/> <u>Nonius-CCD</u>	<input type="radio"/> <u>D9-ILL</u>
<input type="radio"/> <u>Siemens P4</u>	<input type="radio"/> <u>ILL-Vivaldi</u>
<input type="radio"/> <u>Bruker-CCD</u>	<input type="radio"/> <u>ISIS SXD</u>
<input checked="" type="radio"/> <u>Oxford Diffraction-CCD</u>	<input type="radio"/> <u>Hasylab F1</u>
<input type="radio"/> <u>Oxford Diffraction-PD</u>	<input type="radio"/> <u>Hasylab HUBER</u>
<input type="radio"/> <u>Rigaku-CCD</u>	<input type="radio"/> <u>Hasylab XDS</u>
<input type="radio"/> <u>Saclay format</u>	<input checked="" type="radio"/> <u>Free format of <math>h, 1, [Sig(1)]</math></u>
<input type="radio"/> <u>PSI format</u>	

<input type="radio"/> <u>Debye-Scherrer method</u>
<input type="radio"/> <u>Bragg-Brentanno method - Fixed Divergence Slit</u>
<input type="radio"/> <u>Bragg-Brentanno method - Variable Divergence Slit</u>
<input checked="" type="radio"/> <u>Another/unknown method</u>

# Two ways how to solve modulated structure



1. Through average structure solved from main reflections. The modulation is then refined from small arbitrary displacements
2. Directly using charge flipping. It yields 3+d electron density map which can be interpreted in terms of basic positions and their modulations

# Simple example: $\delta$ -Na<sub>2</sub>CO<sub>3</sub> solved by classical way

Alpha  
9.02, 5.21, 6.50  
90, 90, 90  
P6<sub>3</sub>/mmm

757K

Beta  
8.98, 5.25, 6.21  
90, 90.33, 90  
C2/m

628K

Gamma  
8.92, 5.25, 6.05  
90, 101.35, 90  
C2/m( $\alpha 0 \gamma$ )  
q=(0.182,0,0.322)

170K

Delta  
8.90, 5.24, 6.00  
90, 101.87, 90  
C2/m( $\alpha 0 \gamma$ )  
q=(1/6,0,1/3)

*Change of rotation symmetry*

*Change of translation symmetry*

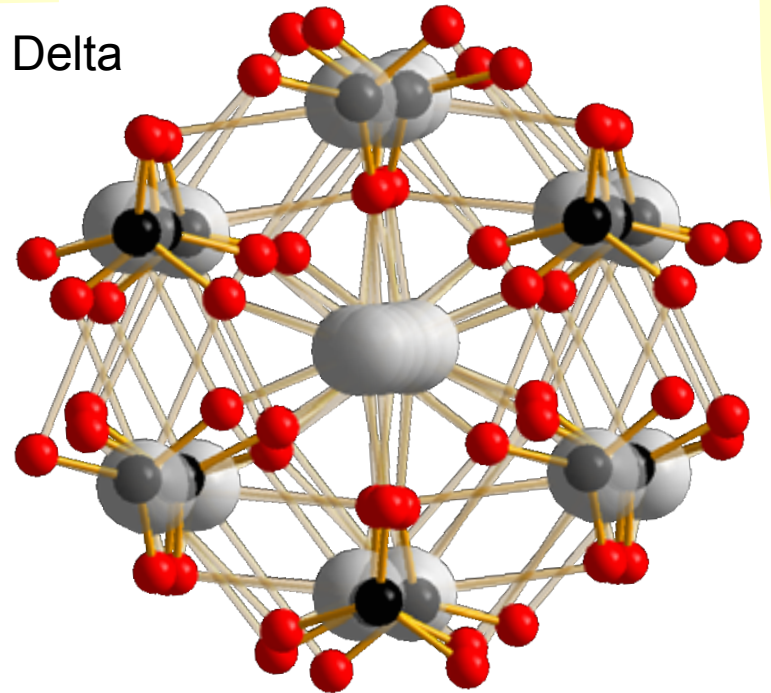
Average structure from main reflections

Arbitrary displacement for the first position modulation wave for all atoms

More position modulation waves for all atoms

ADP modulation

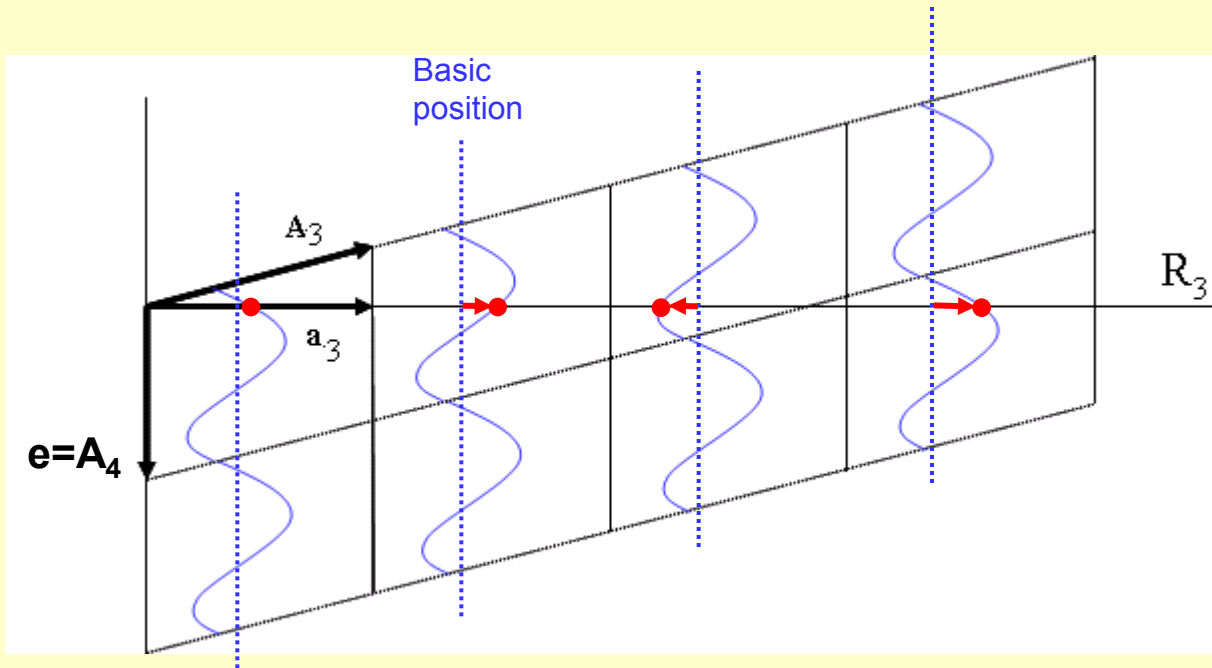
Delta



← *this launches Jana2006*



# Verification of results from Fourier maps



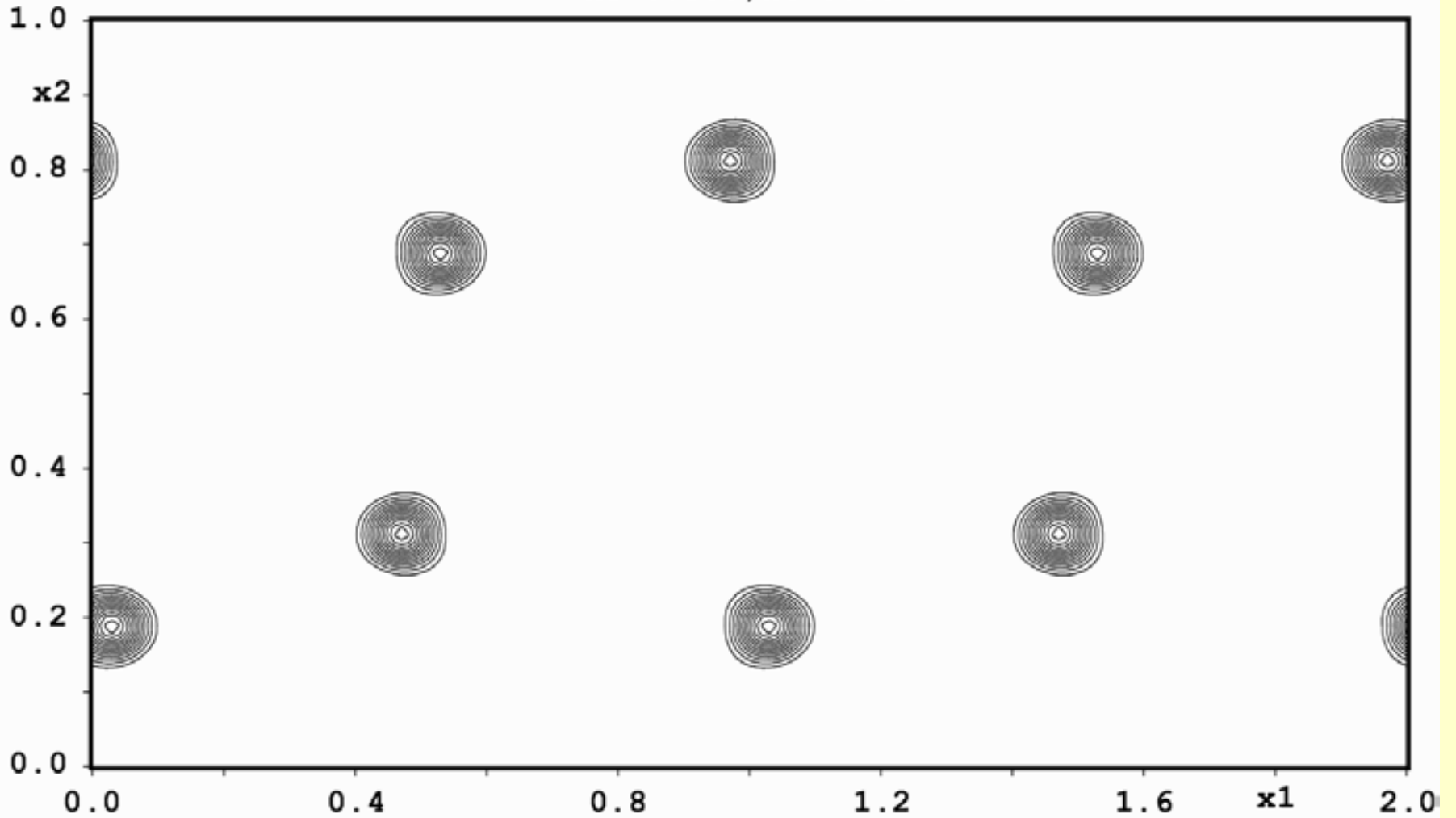
The  $A_3 - A_4$  sections show modulation functions.

The  $A_3 - A_3$  sections show periodicity and symmetry.

The  $R_3 - R_3$  sections show real space electron density.

$\mathbf{A}_3 - \mathbf{A}_3$  sections

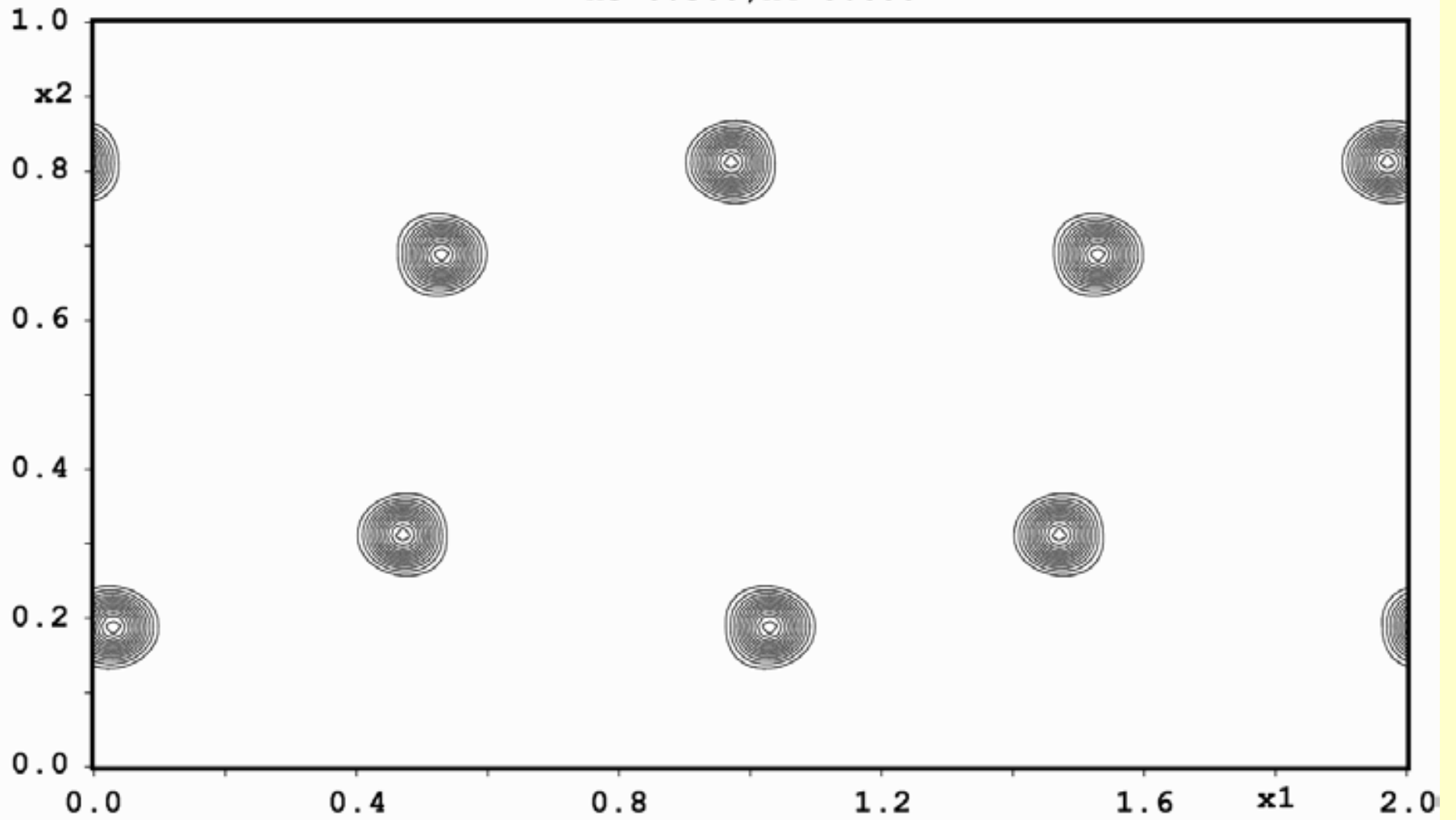
$x_3=0.500, x_4=0.000$



Jana notation:  $\mathbf{A}_1=x_1, \mathbf{A}_2=x_2, \mathbf{A}_3=x_3, \mathbf{A}_4=x_4$

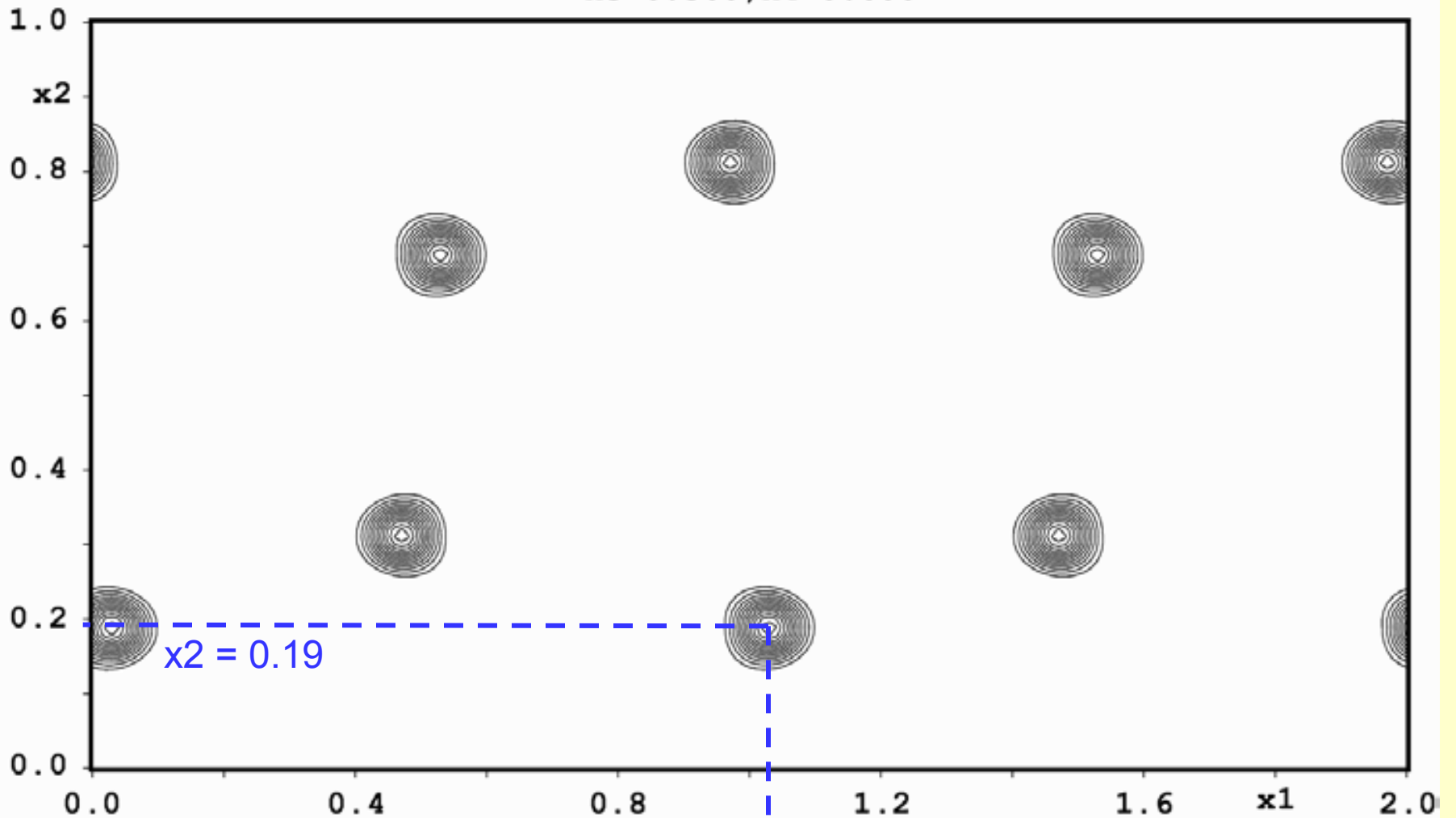
$\mathbf{A}_3 - \mathbf{A}_3$  sections

$x_3=0.500, x_4=0.000$



$A_3 - A_3$  sections

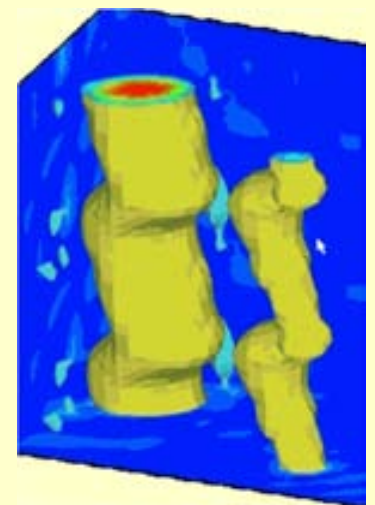
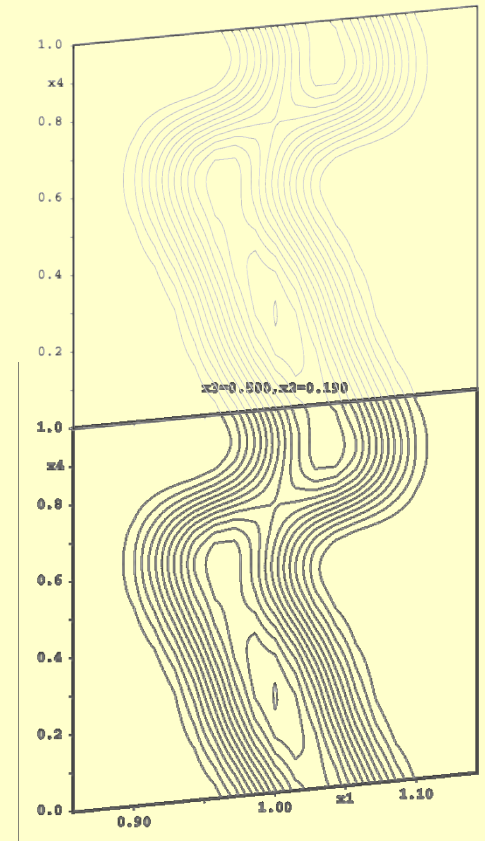
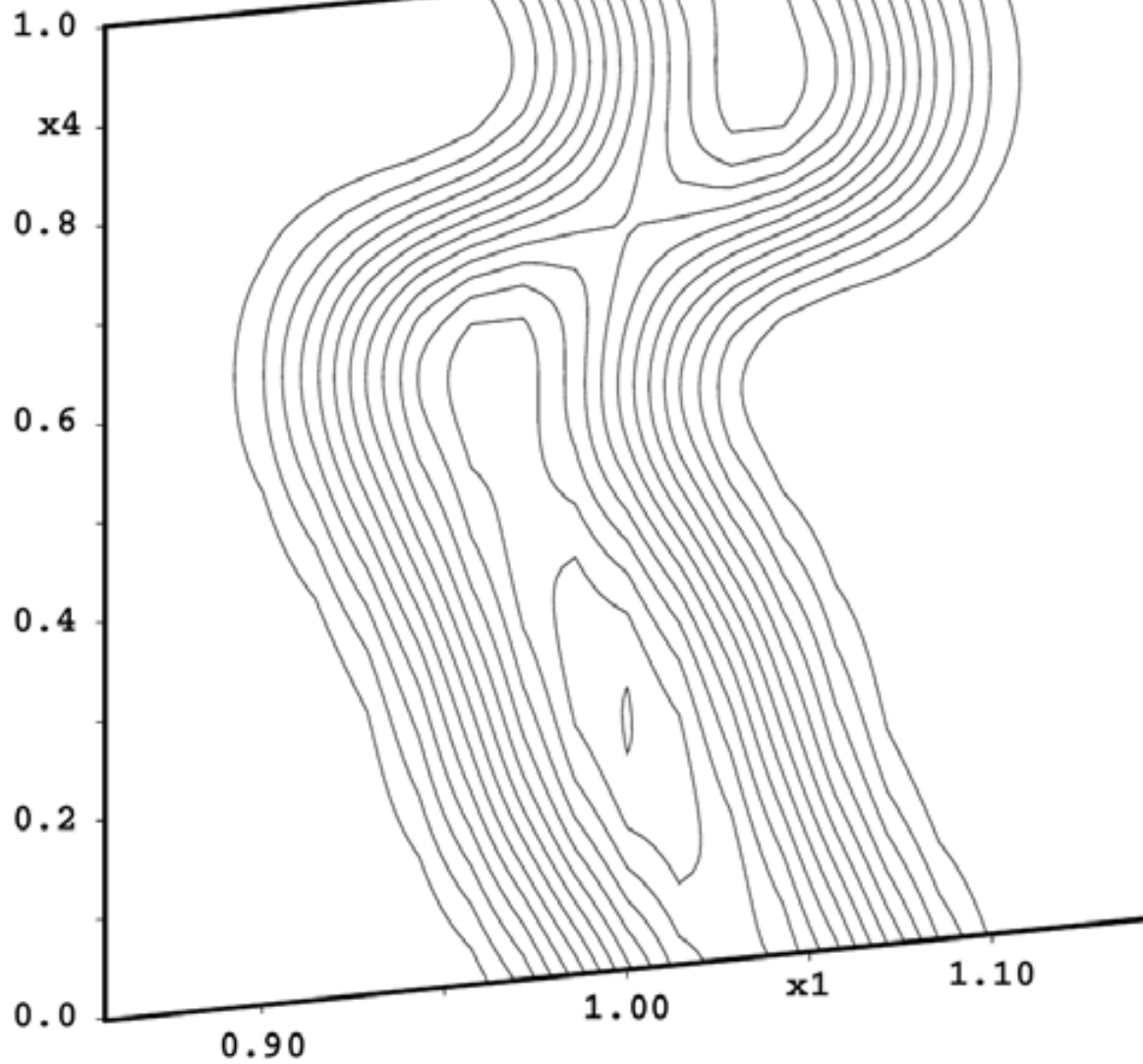
$x_3=0.500, x_4=0.000$



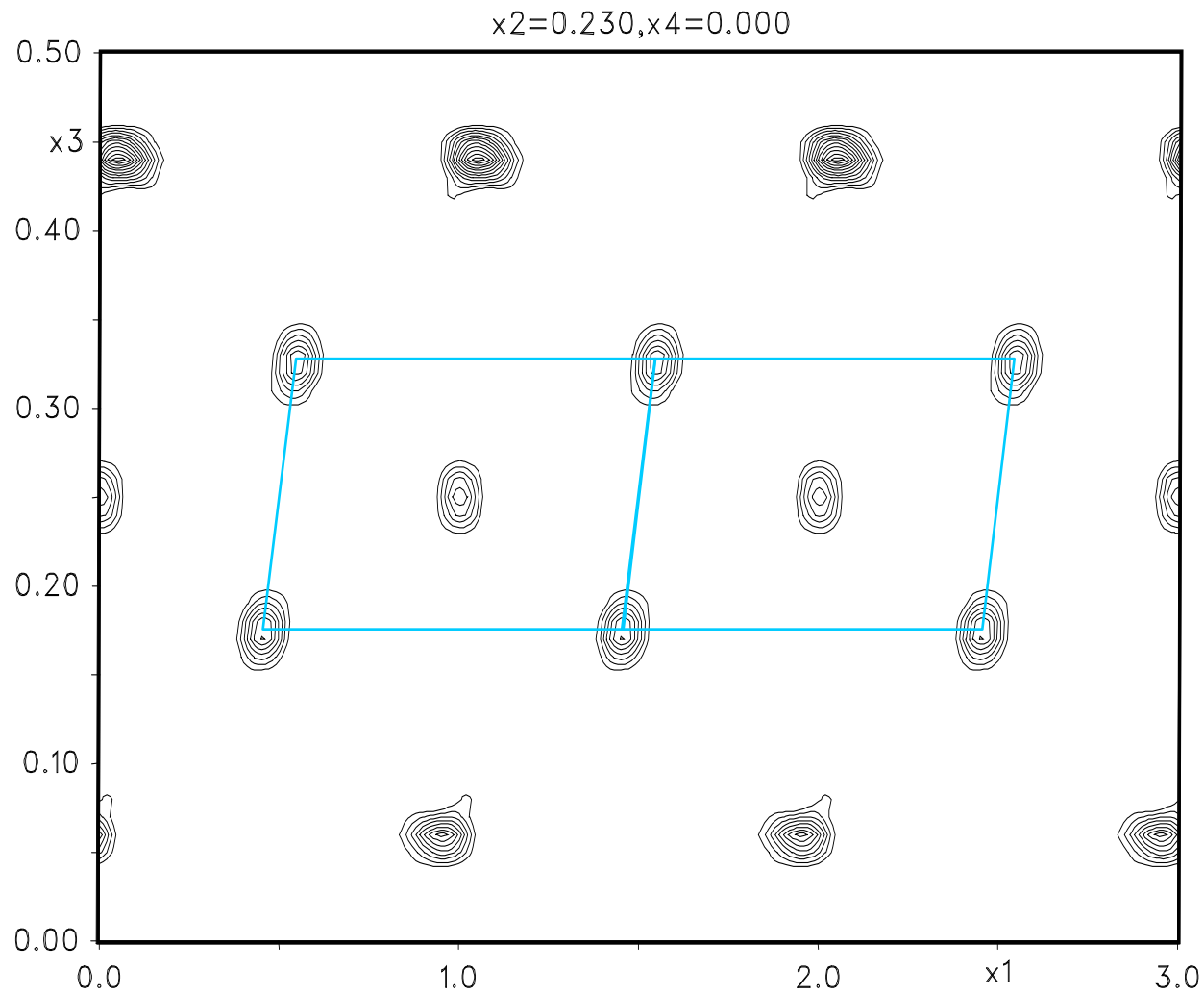
$x_1$  between 0.97  
and 1.03

# $A_3 - A_4$ sections

$x_3=0.500, x_2=0.190$

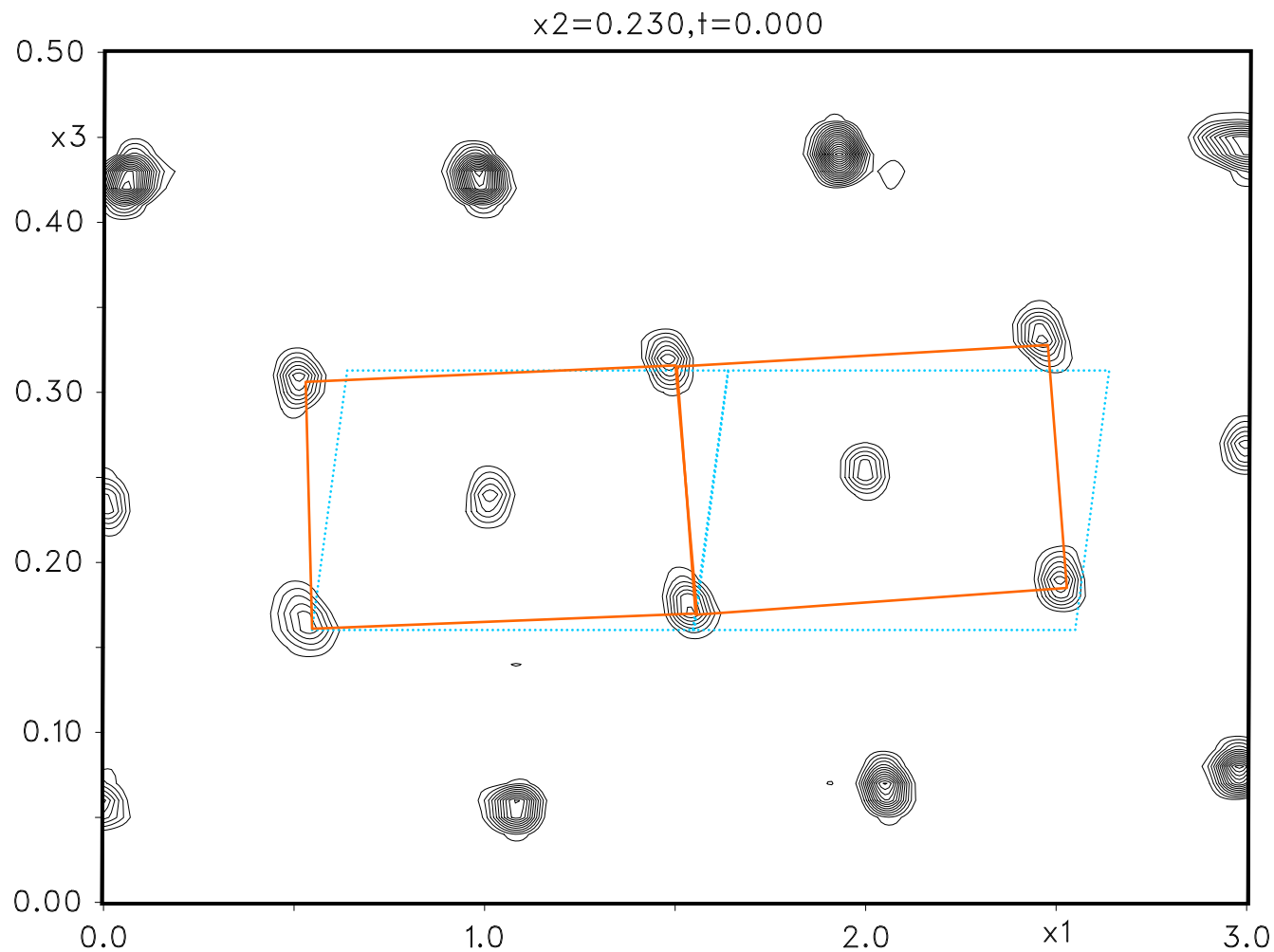


# The difference between $\mathbf{A}_3 - \mathbf{A}_3$ and $\mathbf{R}_3 - \mathbf{R}_3$



$\mathbf{A}_3 - \mathbf{A}_3$  sections show periodicity. Geometry is distorted.

# The difference between $\mathbf{A}_3 - \mathbf{A}_3$ and $\mathbf{R}_3 - \mathbf{R}_3$



$\mathbf{R}_3 - \mathbf{R}_3$  sections show proper geometry. Periodicity is broken.

# How Fourier works for $\delta$ - $\text{Na}_2\text{CO}_3$ ; what does it say about number of modulation waves and about modulation of ADP?

Fourier commands

Basic Scope Peaks

automatically explicitely by a central point

Use default map orientation

Map axes: 1st=horizontal, 2nd=vertical, 3rd=section, ...

	1st	2nd	3rd	4th	minimum	maximum	step
x1	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>			
x2	<input checked="" type="radio"/>						
x3	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>				
x4	<input type="radio"/>	<input checked="" type="radio"/>			0	2	0.01

Center Na3 Scope [A] 1 2 1 Step [A] 0.02

Refresh scope

Reset to default

This will calculate a parallelepiped  $1 \times 2 \times 1$  Å centered at the basic position of Na3.

The two dimensional sections x2-x4 will be stacked along x1 and x3.

The number of sections will be  $1/0.02$  along x1 and  $1/0.02$  along x3.

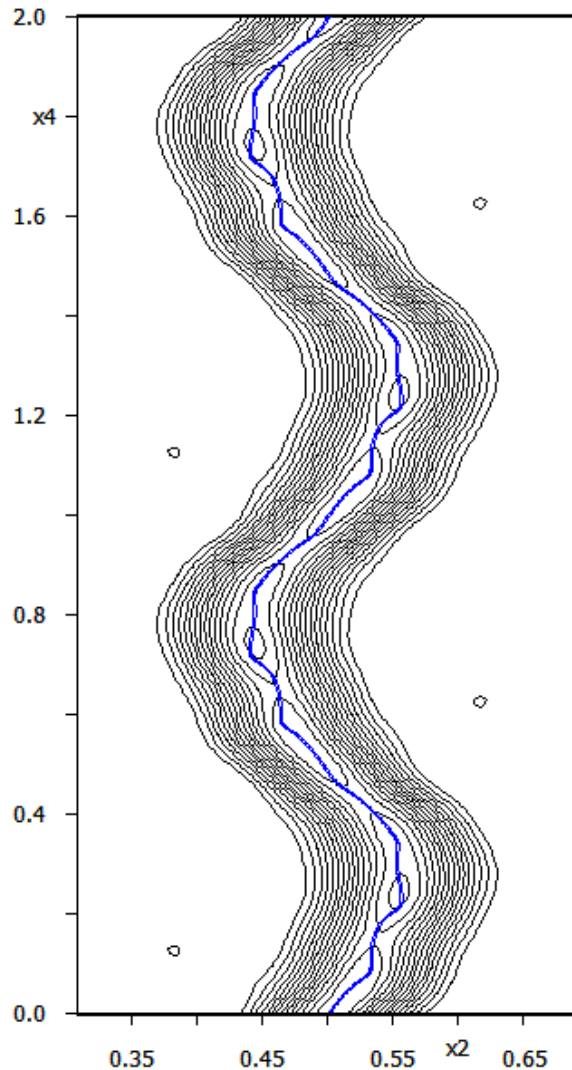
The physical dimension of the plot along x4 will be 2 Å



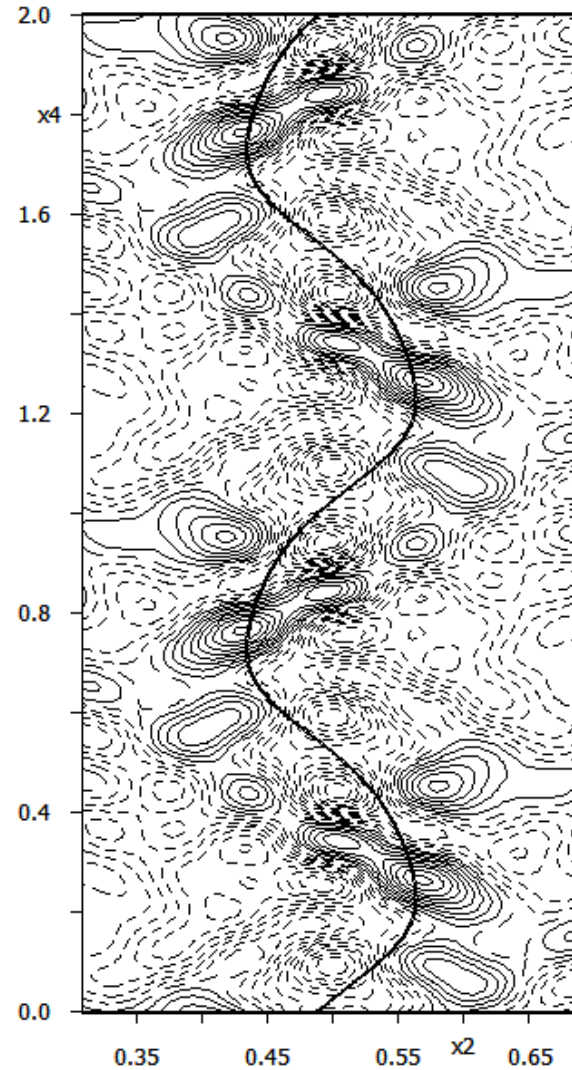
← this launches Jana2006



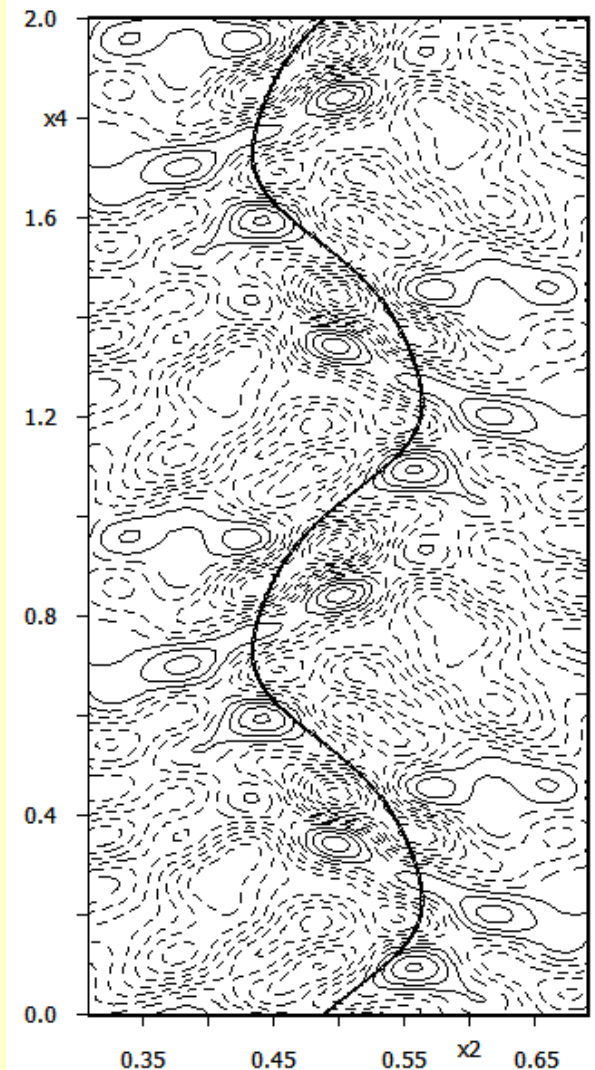
$x_3=0.249, x_1=0.164$



$x_3=0.748, x_1=0.171$



$x_3=0.748, x_1=0.171$

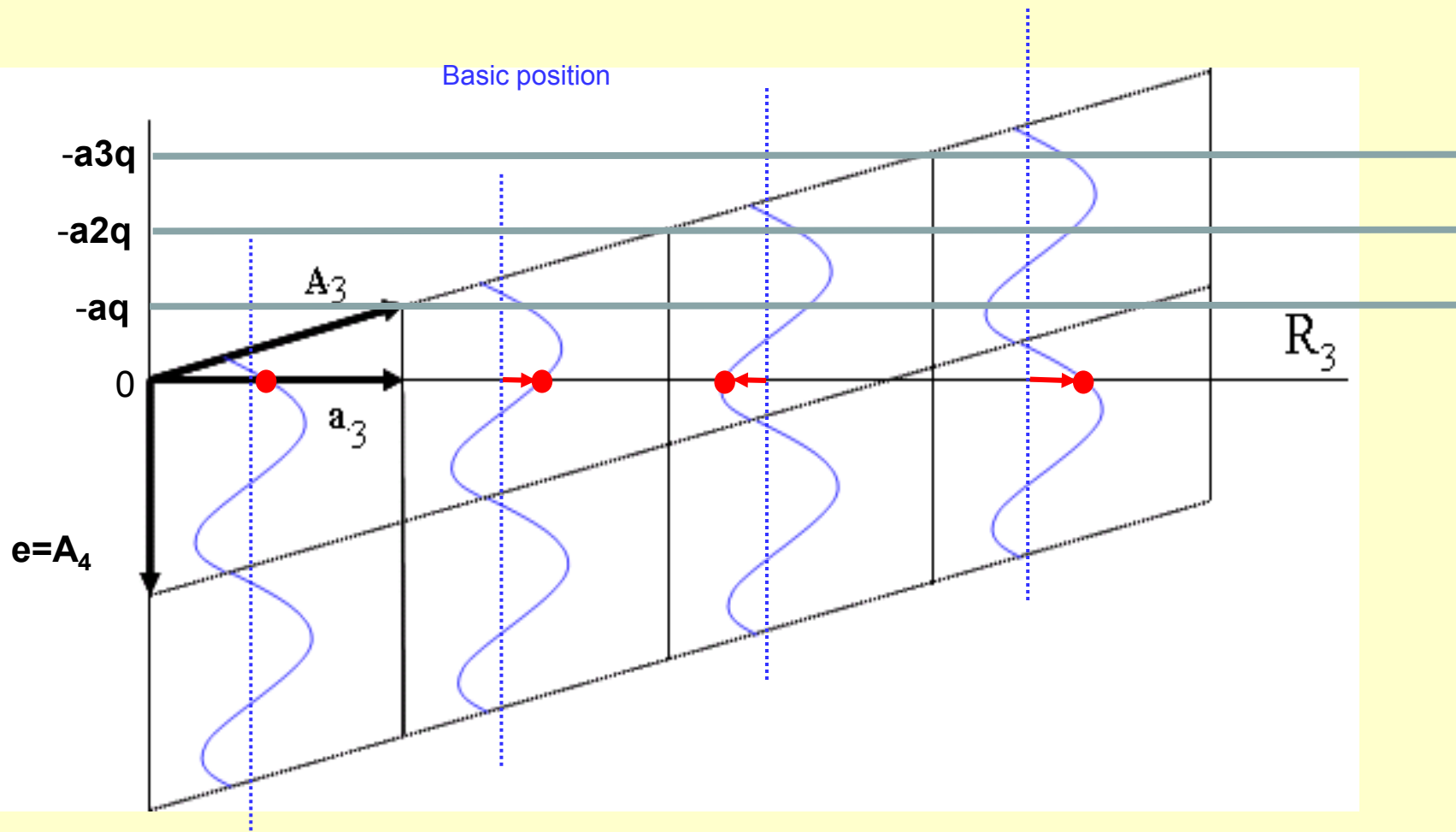


Carbon with eight position modulation waves. This causes also problem with ADP modulation.

Sodium ( $\text{Na}_3$ ) without (left) and with modulation of ADP. Contour step 0.1

# Distances and t-plots

Changing  $t$  by  $naq$  shifts origin by  $n$  unit cells. This can be used to visualize modulated structure from cell to cell.



Changing  $t$  from 0 to 1 can be used to visualize all possible (but not neighboring) configurations of modulated structure.

Applications:

“Animated” Fourier sections

“Animated” plots of the structure

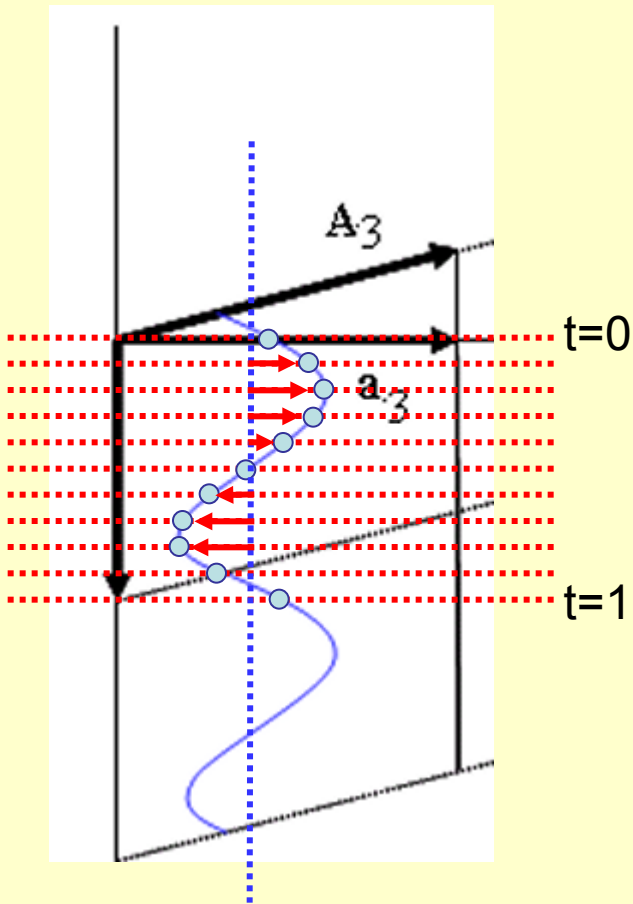
Graphical representation of modulated parameters (so-called  $t$ -plots)

Calculation of distances

Examples with sodium carbonate:

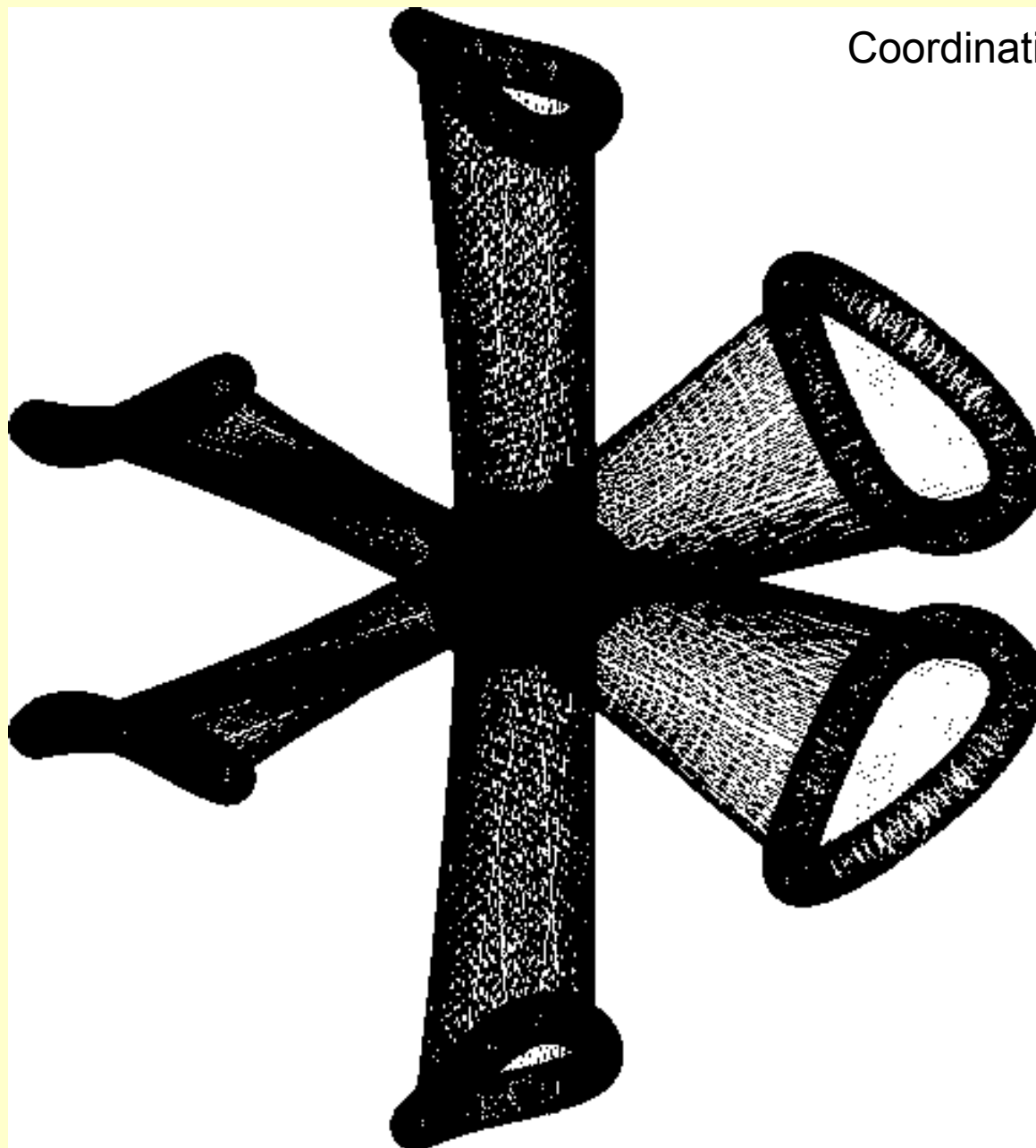


← *this launches Jana2006*



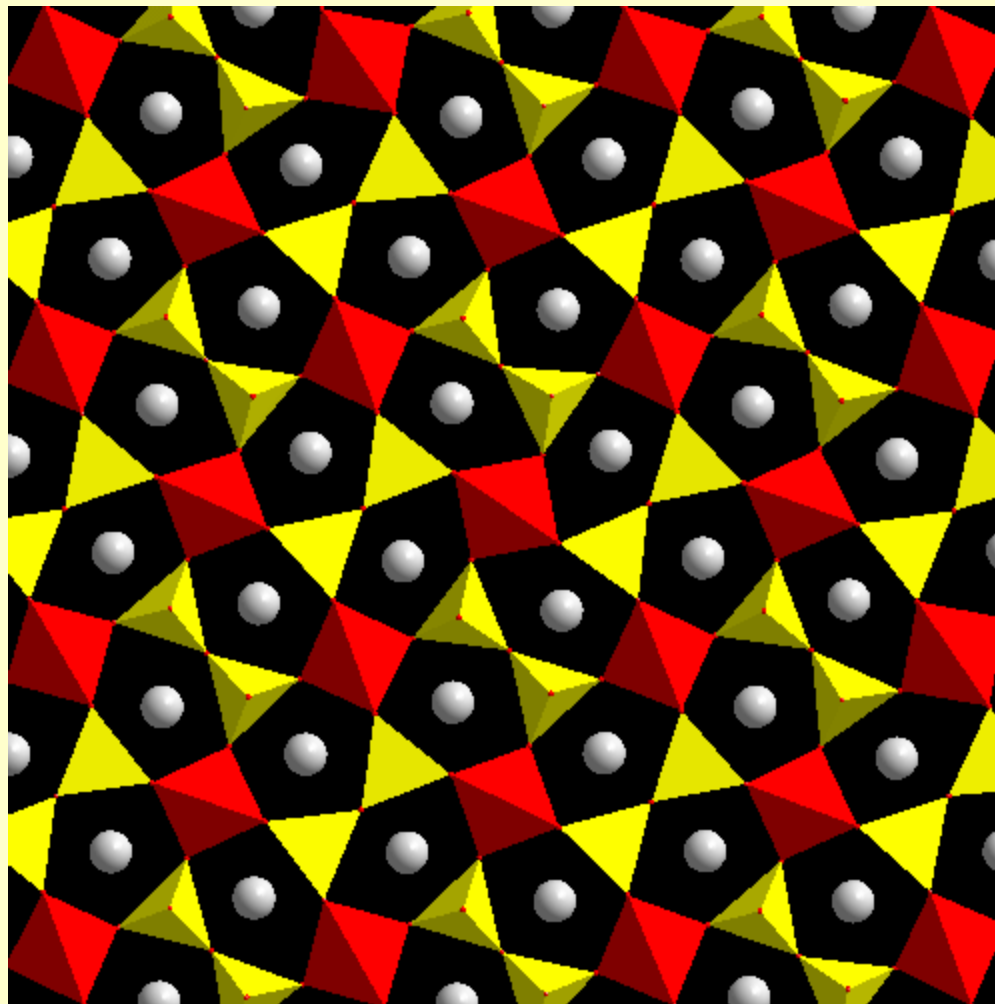
Coordination of As in  $\text{KAsF}_4(\text{OH})_2$

(logo Jana2006)



Natural melilite from San Venanzo, Umbria, Italy

Formula:  $(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.98}\text{Al}_{0.02})\text{O}_7$



# Chromium diphosphate

Beta

6.97, 8.45, 4.60  
90, 107.90, 90  
C2/m

364K

Alpha3

7.05, 8.41, 4.64  
90, 108.71, 90  
C2/m( $\alpha 0 \gamma$ )0s  
q=(-1,0,0.5)

345K

Alpha2

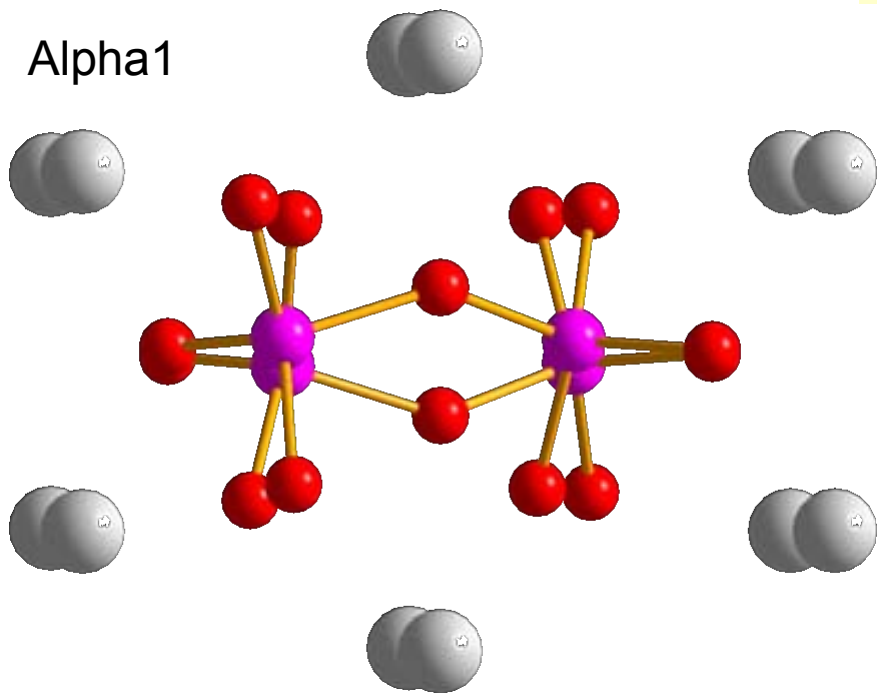
7.02, 8.40, 4.62  
90, 108.59, 90  
C2/m( $\alpha 0 \gamma$ )0s  
q=(0.361,0,-0.471)

285K

Alpha1

7.05, 8.41, 4.64  
90, 108.71, 90  
C2/m( $\alpha 0 \gamma$ )  
q=(-1/3,0,1/2)

Alpha1



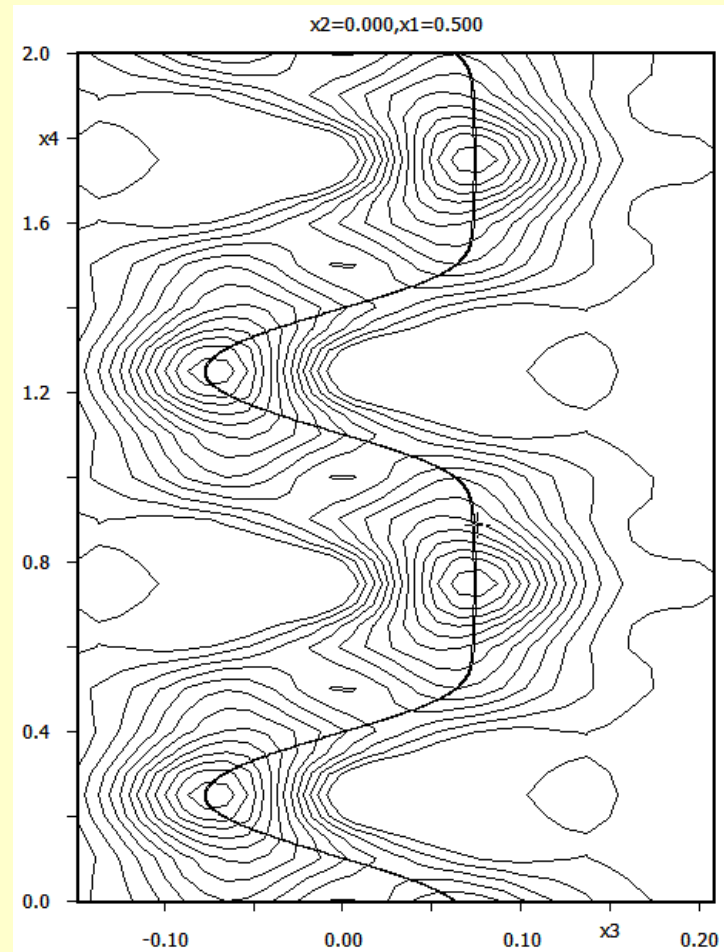
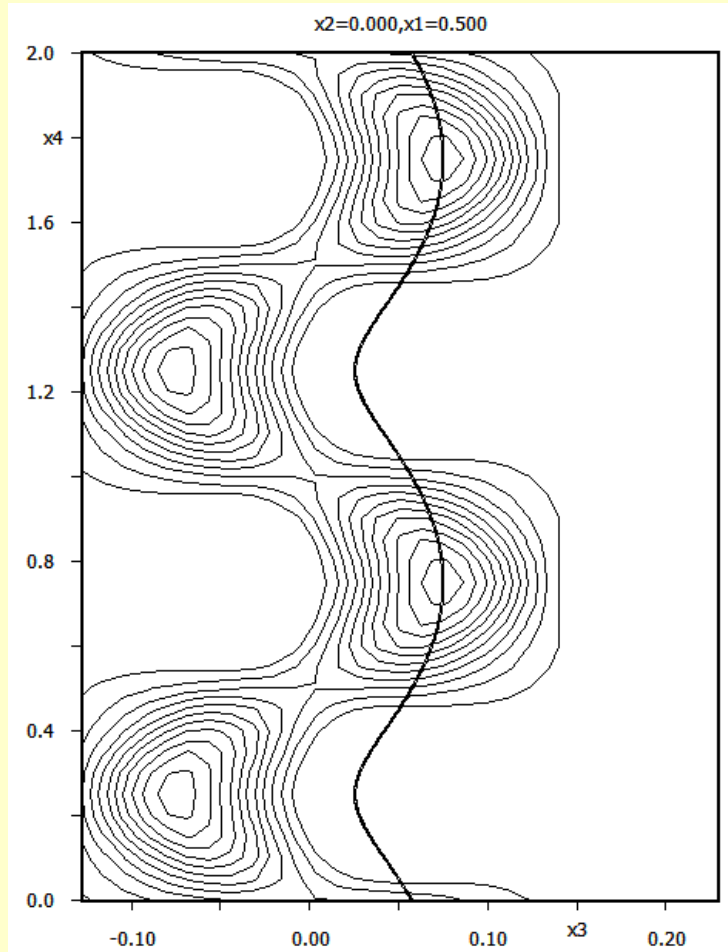
In case of  $\text{Cr}_2\text{P}_2\text{O}_7$  no change of rotation symmetry occurs. The phases alpha1, alpha2 and alpha3 represent various ways how to resolve the disorder observed in the phase beta.

*Lukas Palatinus et al., Acta Cryst. (2006). B62, 556–566*

# Solution of chromium diphosphate by Charge flipping



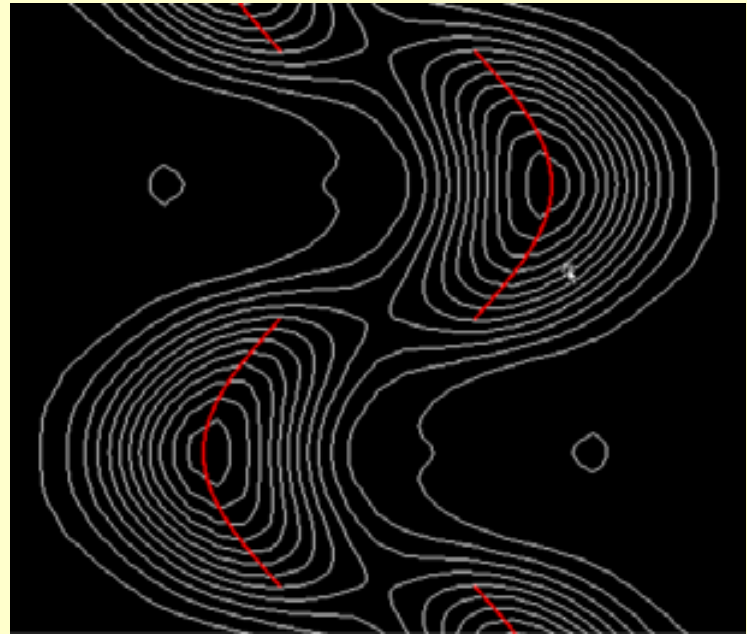
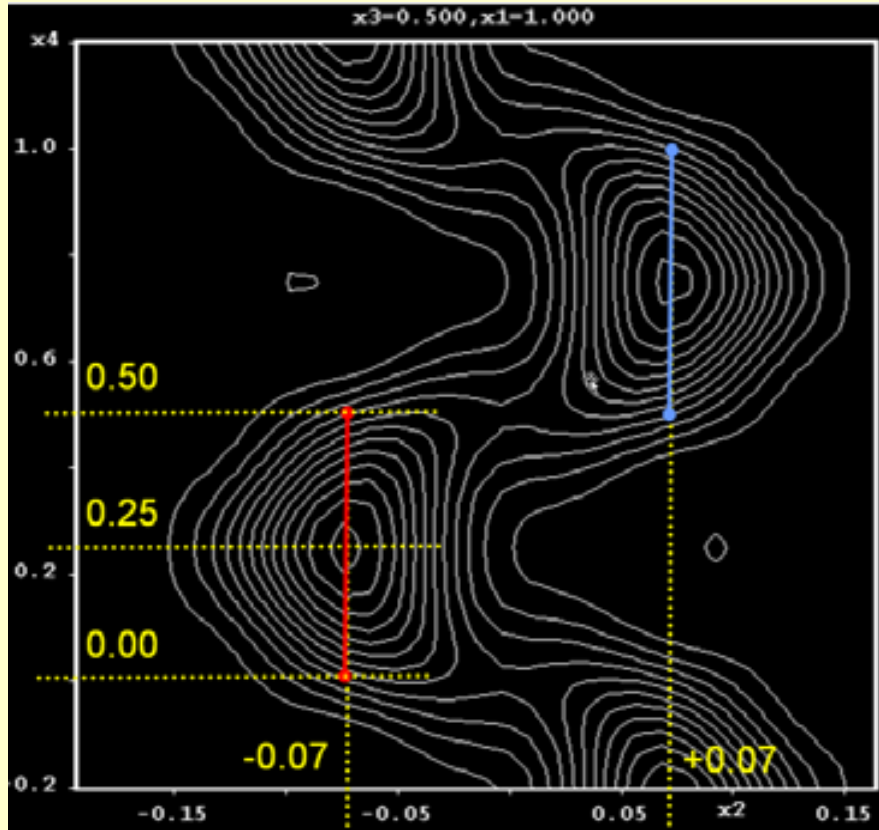
← *this launches Jana2006*



Bridging oxygen from charge flipping

refined with three position modulation waves

# Crenel function



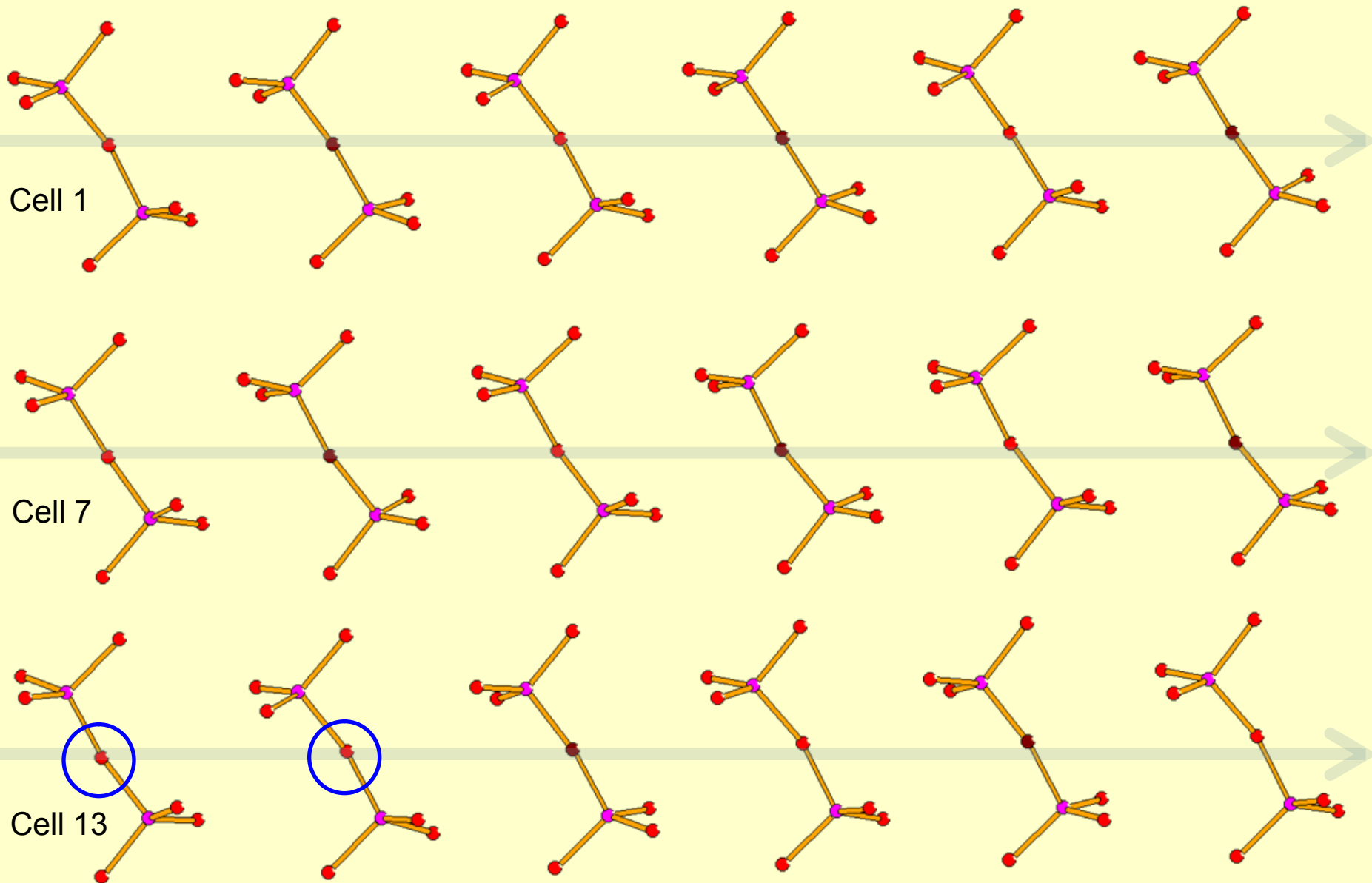
Crenel function combined with modulation of position

Definition of crenel function from Fourier map

Crenel function describes definition interval for an atom. Crenel reduces occupancy but two crenel functions may together describe full occupancy.

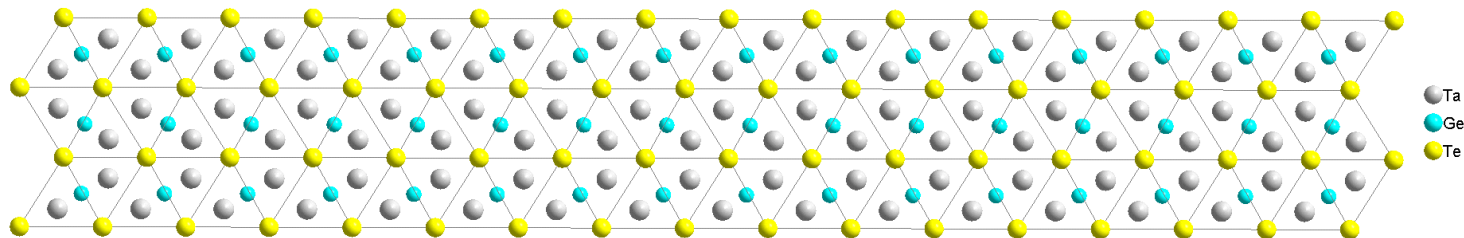
For combining crenel function with position modulations Jana2006 uses Legendre polynomials



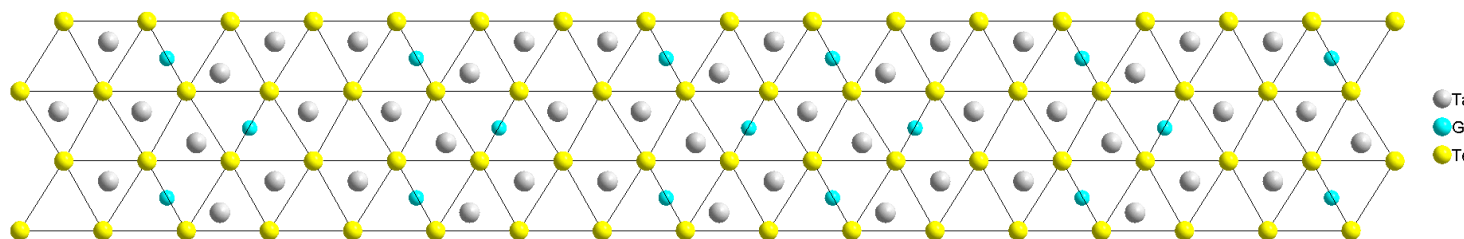


Modulated structure of  $\text{Cr}_2\text{P}_2\text{O}_7$  expanded in the  $c$  direction

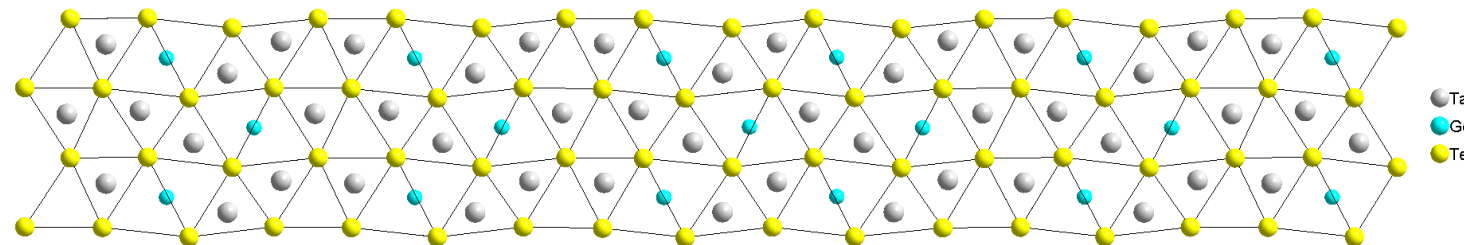
TaGe<sub>0.354</sub>Te – Acta Cryst., B52, 100, (1996).



Average structure



Crenel occupation modulation

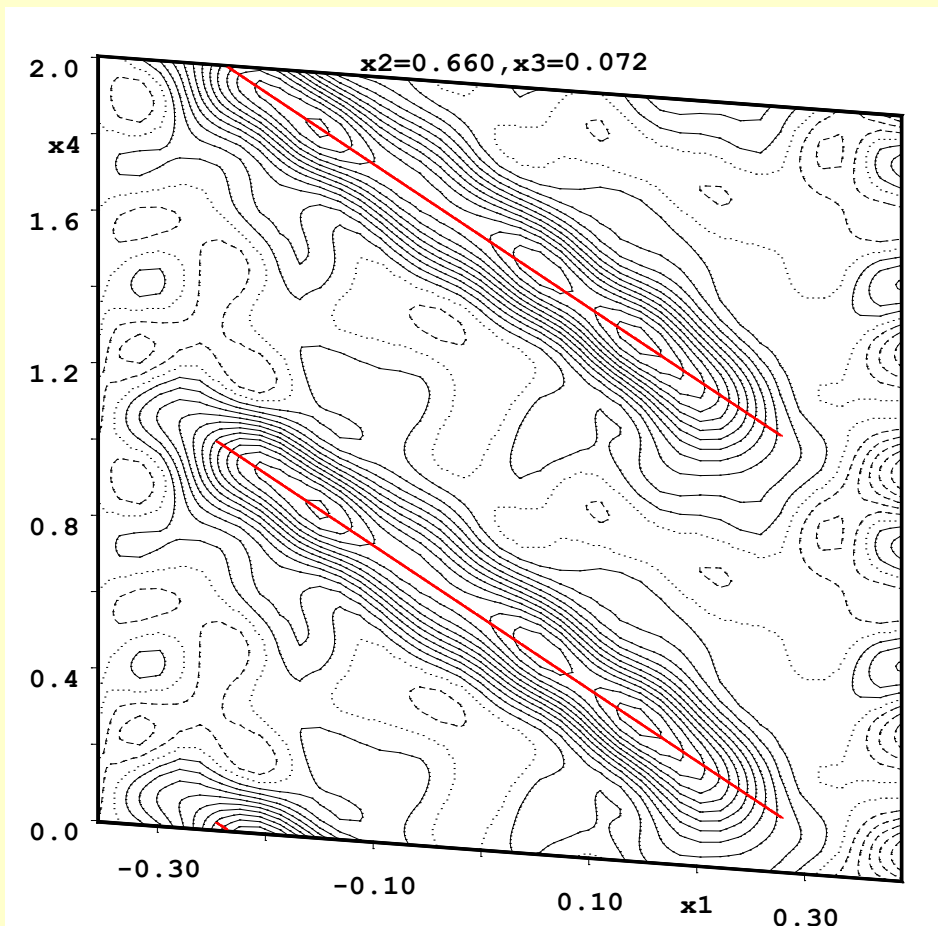


Crenel occupation modulation and harmonic positional modulation

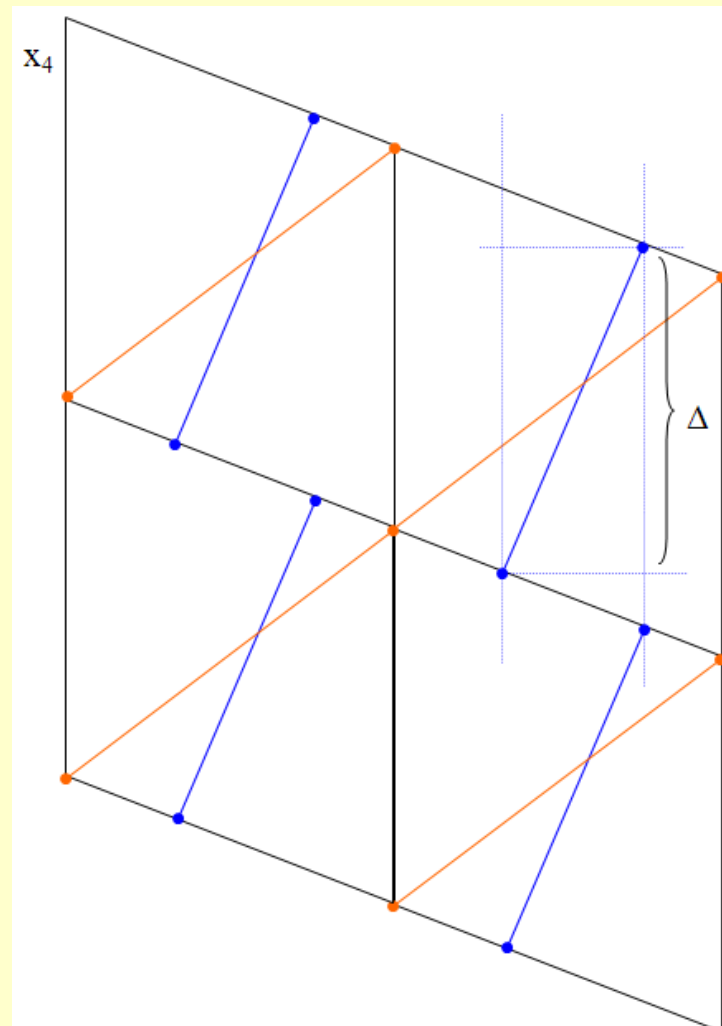
# Sawtooth function



V.Petříček, Y.Gao, P.Lee & P.Coppens,  
*Phys.Rev.B*, **42**, 387-392, (1990)

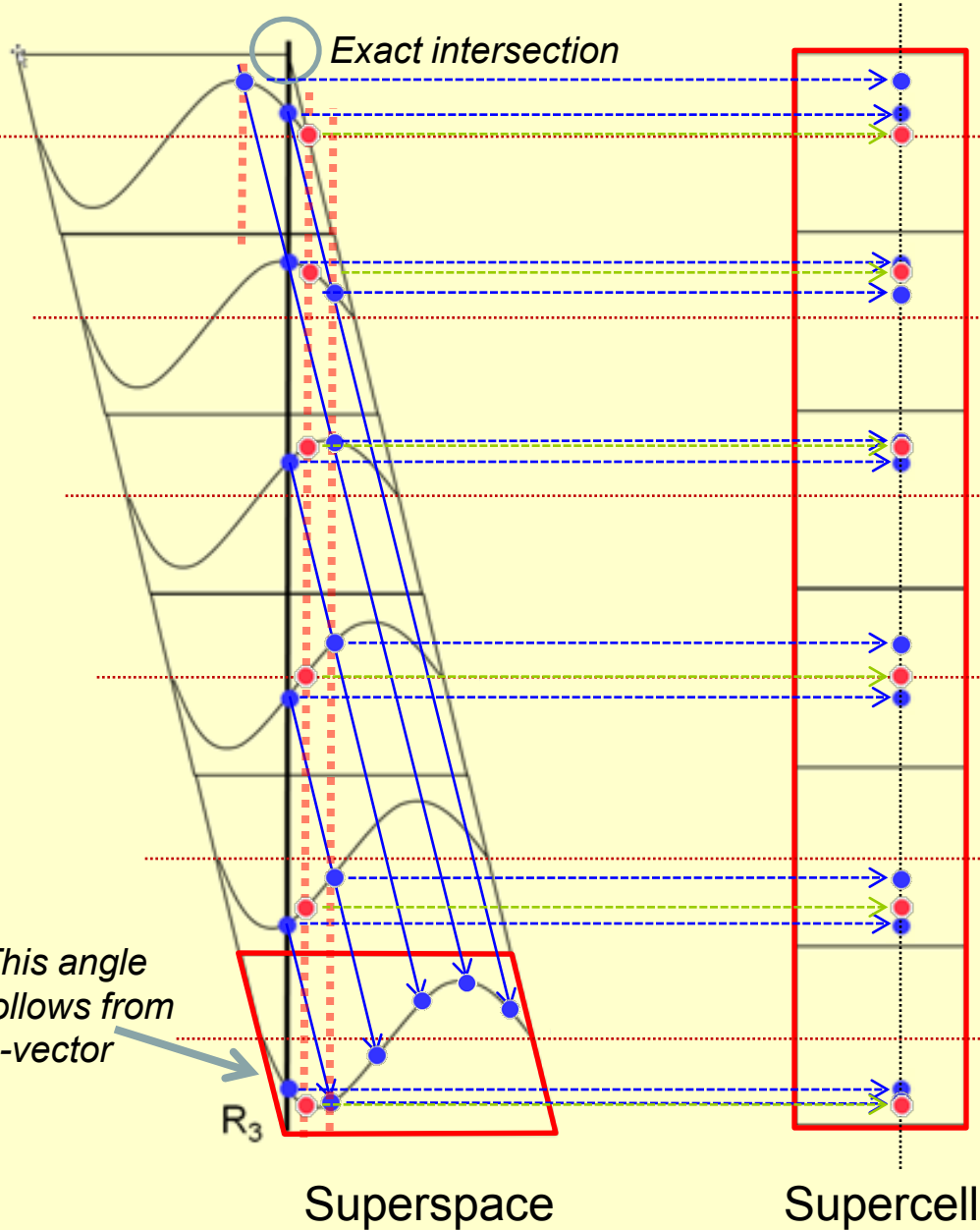


Oxygen atom at Bi layer



Relationship to composite structures

# Commensurate structures



Example of a six-fold commensurate structure

Gamma- $\text{Na}_2\text{CO}_3$   
 8.92, 5.25, 6.05  
 90, 101.35, 90  
 $C2/m(\alpha 0 \gamma)$   
 $q=(0.182, 0, 0.322)$

170K

Delta- $\text{Na}_2\text{CO}_3$   
 8.90, 5.24, 6.00  
 90, 101.87, 90  
 $C2/m(\alpha 0 \gamma)$   
 $q=(1/6, 0, 1/3)$

**Superspace description:** 4d cell, atomic position + modulation function, superspace symmetry

**Supercell description:** 3d six-fold supercell, atomic positions in six cells, 3d symmetry

Both descriptions are equivalent.

Origin of  $R_3$  section may influence symmetry in the supercell.

To

Del  
8.90  
90,  
C2/  
q=(

The

- To
- D
- H

Sho

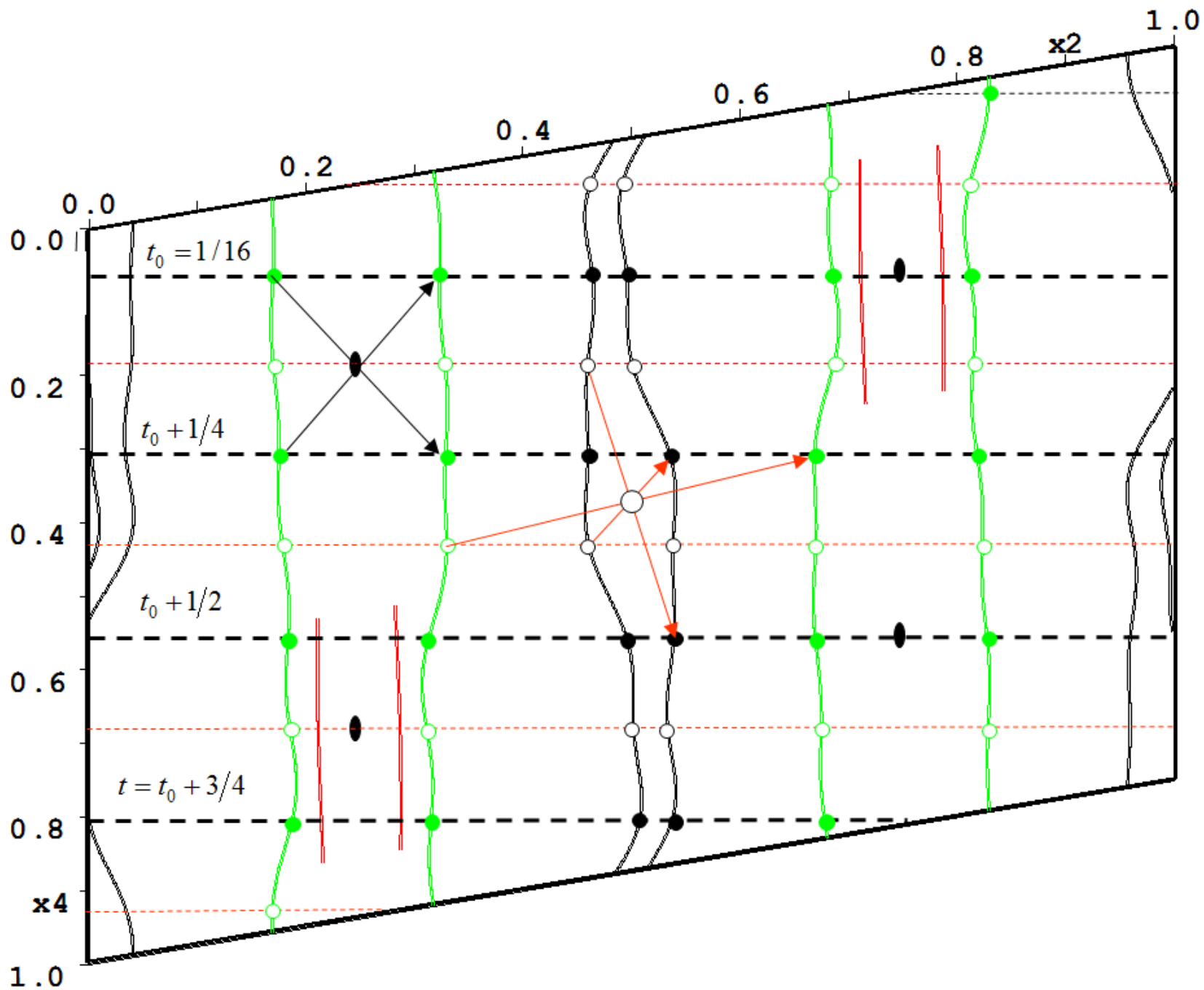
Disp  
at 0

Se

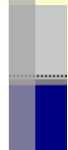
Dis  
pos

P2

t-z



y  
from  
d in



# Commensurate families

Commensurate family can be derived from the parent incommensurate structure by changing q-vector and t-zero. By this way we can relate three-dimensional structures which are at the first glance very different.

Example:  $M_2P_2O_7$  diphosphates are derived from the parent phase  $\alpha_2$ .

Alpha2- $Cr_2P_2O_7$ 7.02, 8.40, 4.62 90, 108.59, 90 C2/m( $\alpha_0\gamma$ )0s q=(0.361,0,-0.471)	285K	Alpha1- $Cr_2P_2O_7$ 7.05, 8.41, 4.64 90, 108.71, 90 C2/m( $\alpha_0\gamma$ ) q=(-1/3,0,1/2)
--	------	--

Metal (II)	q-vector	t-zero	space group in the supercell
Cr, Zn	$(-\frac{1}{3}, 0, \frac{1}{2})$	0	I2/c
Co, Mg, Ni	$(\frac{1}{2}, 0, \frac{1}{2})$	$\frac{1}{8}$	B2 <sub>1</sub> /c
Cu	$(0, 0, \frac{1}{2})$	0	C2/c

# Magnetic structures

Magnetic structure factor:

$$\vec{F}_M(\mathbf{h}) = p \sum_i f_i(h) T_i(\mathbf{h}) \vec{S}_i \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_i)$$

$f_i$  magnetic form factor

$T_i$  temperature factor

$\vec{S}_i$  magnetic moment

$\mathbf{r}_i$  atomic position

Intensity of magnetic diffraction:

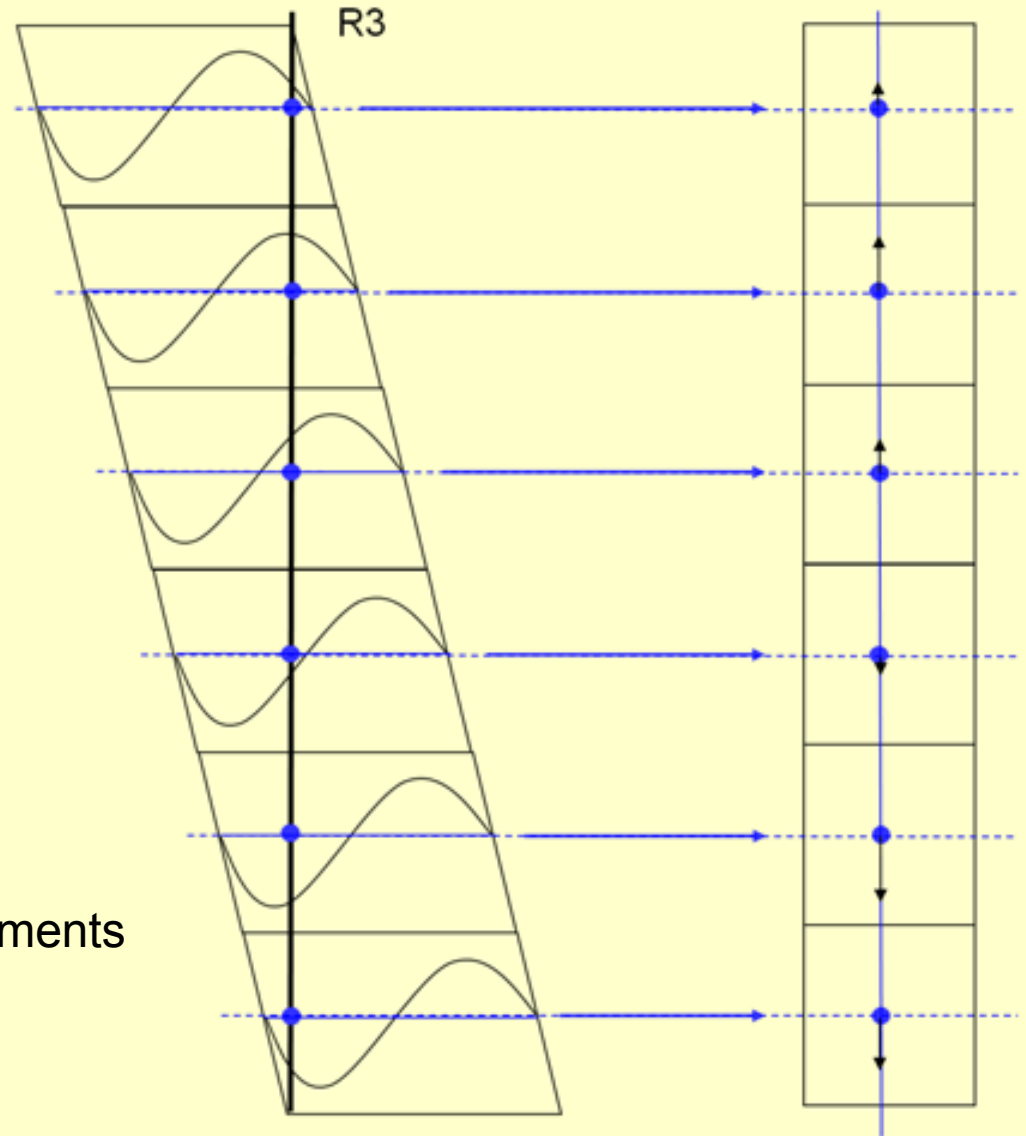
$$I_M(\mathbf{h}) = \vec{F}_M^2(\mathbf{h}) - [\mathbf{h}/h \cdot \vec{F}_M(\mathbf{h})]^2$$

Total intensity:

$$I(\mathbf{h}) = I_N(\mathbf{h}) + I_M(\mathbf{h})$$

The distribution of the magnetic moments over the nuclear structure can be described by a modulation wave:

$$\mathbf{S}_i(x_4) = \mathbf{S}_{i0} + \sum_{n=1}^N [\mathbf{S}_{ins} \sin(2\pi n x_4) + \mathbf{S}_{ikc} \cos(2\pi n x_4)]$$



# More information

jana.fzu.cz



**Jana2006** is a crystallographic program focused to solution, refinement and interpretation of difficult, especially modulated structures. It calculates structures having up to three modulation vectors from powder as well as single crystal data measured with X-ray or neutron diffraction. The input diffraction data can be unlimitedly combined, the combination of powder neutron data with single crystal X-ray data being a typical example. The structure solution can be done using the built-in charge flipping algorithm or by calling an external direct methods program. Jana can handle multiphase structures (for both powder and single crystal data), merohedric twins as well as twins with partial overlap of diffraction spots, commensurate and composite structures. It contains powerful transformation tools for symmetry (group-subgroup relations), cell parameters and commensurate-supercell relations. Wide scale of constrains and restrains is available including a powerful rigid body approach and possibility to define a local symmetry affecting only part of the structure. The latest development of Jana concerns magnetic structures.

**More about Jana2006** (PowerPoint presentation, 10MB)

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Czech Republic

Academy of Sciences | Institute of Physics  
Dept of Structure Analysis | Laboratory of Crystallography  
ECA-SIG#3 | Contact Us

CRYSTALLOGRAPHIC COMPUTING SYSTEM FOR STANDARD AND MODULATED STRUCTURES

*Vaclav Petricek, Michal Dusek & Lukas Palatinus*

## News

**April 1, 2010** Maintenance release of **Jana2006 for Windows** can be obtained in **Download area**. It cumulates various improvements and bug fixes. [More ...](#)

**January 26, 2010** **The Third Ad Hoc Workshop on Jana2006**, 8-9 March 2010. [More ...](#)

**January 06, 2010** **The Second Ad Hoc Workshop on Jana2006**, 18-19 Jan 2010. [More ...](#)

**January 05, 2010** **International school on aperiodic crystals**. [More ...](#)

**October 21, 2009** Maintenance release of **Jana2006 for Windows** can be obtained in **Download area**. It cumulates various improvements and bug fixes. [More ...](#)

**September 16, 2009** **Ad hoc workshops on Jana**. We offer informal two days workshops on topics selected by participants. [More ...](#)

**October 23, 2008** Maintenance release of **Jana2006 for Windows** can be obtained in **Download area**. It cumulates various improvements and bug fixes. [More ...](#)

**October 14, 2008** Eset NOD32 antivirus slows down Jana2006. [More ...](#)

**July 25, 2008** **The first stable version of Jana2006 for Windows**. This program is the successor of Jana2000. Currently only Windows version is available, Unix version as well as manual are under development. The Stable version will be changed occasionally, the everyday work will be immediately available in the Latest version. Registered users will be informed about new Stable versions. Jana2006 can be obtained in **Download area**.

**July 22, 2008** **New web page for Jana** contains all information about Jana2006 and the previous version Jana2000. We have partially changed also download locations, please do not use old links.

**December 28, 2007** **Final version of Jana2000** - see the **Download area**. No further development is expected in Jana2000.

**Ad hoc workshops on Jana: [details here](#)**

**March 2011: [7th Workshop in Bayreuth](#)**



## Ad hoc workshops on Jana

Ad hoc workshops are small two days workshops organized in Praha by authors of Jana software. As soon as five people register for one or more topics listed below and some overlap in topics is found we shall create program of the workshop and discuss it with the participants. Then we shall fix the date of the workshop and arrange accomodation. Registration to a workshop with fixed program and/or date is possible for another five participants. Participants pay themselves all their expenses and they are expected to bring their own laptops with **Windows**. The registration fee is zero (in Czech Crowns). Workshop certificates are issued by our skilled artists on demand.

### Topics

- (INT1) Introduction to Jana software, solution of simple 3d structures
- (INT2) Introduction to modulated structures, solution of simple 4d structures
- (PWD) Refinement of powder data
- (TW) Twins and multiphases of 3d and modulated structures
- (CHF) Application of charge flipping to 3d and modulated structures
- (DIS) Disorder, mixed sites, application of rigid body refinement for disordered structures
- (RIG) Rigid body refinement and application of local symmetry
- (CRENEL) Discontinuous modulation functions (crenel and sawtooth)
- (COMM) Commensurate structures
- (COMP) Composite structures
- (FIVE) Five dimensional structures
- (MAG) Magnetic structures
- (ELD) Electron diffraction
- any other topic (please specify)

**6th Jana2006 ad hoc workshop** Two days in December 2010, registration is open.

**Special jana2006 workshop on electron diffraction** Two days in 2011, registration is open.

**Special jana2006 workshop on magnetic structures** Two days in 2011, registration is open.

**FUTURE jana2006 ad hoc workshops** This link serves for collecting requirements for future Jana2006 Ad Hoc workshops. As soon as an overlap in topics is found a new Ad Hoc Workshop is organized.

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Still freeware ....  
(the driving force are citations)

Jana2006 is continuously supported by Academy of Sciences of the Czech Republic and (occasionally) by (unpredictable) Grant agency of the CR

**YPO - Y(PO<sub>3</sub>)<sub>3</sub>**

Example for solution of simple modulated structure

janainst.msi (Jana2006 from 14<sup>th</sup> September or later)

Diamond installation

Diamond licence valid before 17 October

Printed cookbook