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Incommensurately modulated crystals

Gervais Chapuis, LCr

EPFL

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Incommensurately modulated crystals and applications

Examples of modulated structures

- Na_2CO_3
- A member of the scheelite family, $KSm(MoO_4)_2$
- Extension of the structure type concept exemplified with the scheelite structures
  - Applications: structure property relations
- The complex structure of metallic elements
  - Barium, Rubidium
  - Gallium II (2.8 GPa)

Acta Cryst. (1964). **17**, 614

An anomaly in the crystal structure of Na_2CO_3.

By Elly Brouns and J. W. Visser, *Technische Physische Dienst T.N.O.-T.H.*, and P. M. de Wolff, *Technische Hogeschool, Delft, The Netherlands*

In the course of routine investigations we tried to index the powder pattern of anhydrous sodium carbonate. This proved to be uncommonly difficult. A clue to the solution was eventually obtained through application of a computer method (de Wolff 1963). This led to a *C*-centered monoclinic unit cell (Table 1) which, however, did not explain all powder lines. A considerable number (roughly 20% of the total) of lines, mostly of weak intensity, withstood every attempt either to incorporate them on the basis of a multiple cell, or to eliminate them by different ways of chemical preparation.

Table 1. *Crystallographic data of* Na_2CO_3 *at various temperatures*

Phase	Temp. (°C)	*a*	*b*	*c*	*β*	**p**	1/*p*	*Z*
γ	23	8·90 Å	5·24 Å	6·04 Å	101·2°	0·182**a*** + 0·318**c***	16·3 Å	4
γ	330	8·96	5·24	6·20	99·7	0·154**a*** + 0·286**c***	19·0	4
β	440	9·00	5·24	6·31	96·9	—	—	4
α	500	(9·01)*	5·20	6·50	90	—	—	2
α	790	(9·05)*	5·22	6·75	90	—	—	2

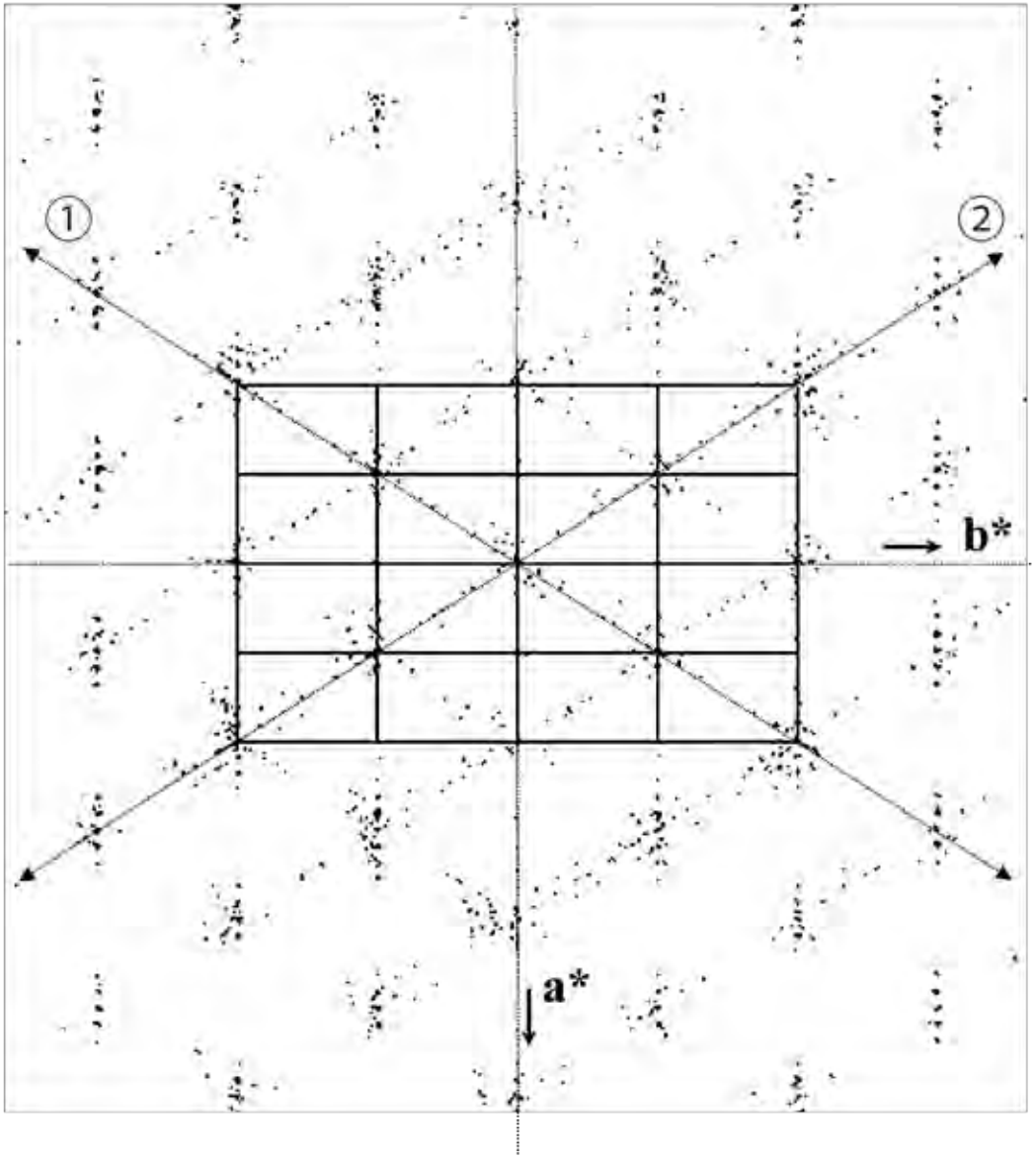
The phases of Na_2CO_3

α	β	γ	δ
≈ 757K	≈ 628K	≈ 170K	
$P6_3/mmc$	C2/m	**q** vs. T C2/m(α0γ)0s	**q** = ⅙ **a*** + ⅓ **c*** (C2/m(⅙0⅓)0s) $P2_1/n$
a = 5.21Å b = 6.47	a = 9.01 b = 5.23 c = 6.34 β = 96.06°	a = 8.92 b = 5.25 c = 6.05 β = 101.35° **q** = (.182,0,.322)	a = 19.91 b = 5.23 c = 17.99 β = 119.01°

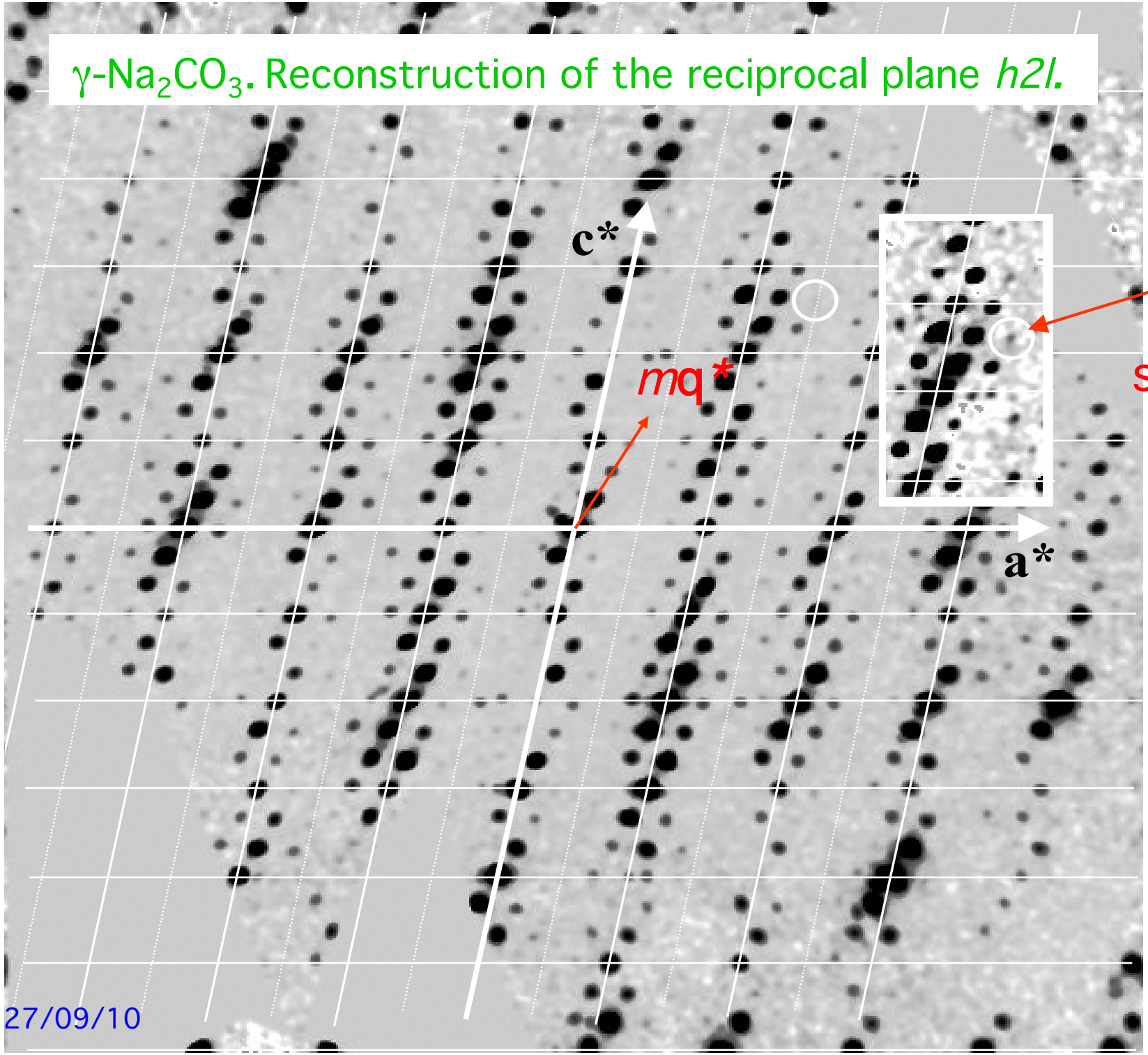
(Dušek *et al.*, Acta Cryst. 2003
Arakcheeva *et al.* Acta Cryst. 2005)

γ-Na_2CO_3. Projection of the reciprocal space along **c***

As is often the case in diffraction, the examination of the reciprocal space reveal the presence of twins or domains.
In the present case, we observe the presence of three domains.



γ-Na_2CO_3. Reconstruction of the reciprocal plane *h2l*.

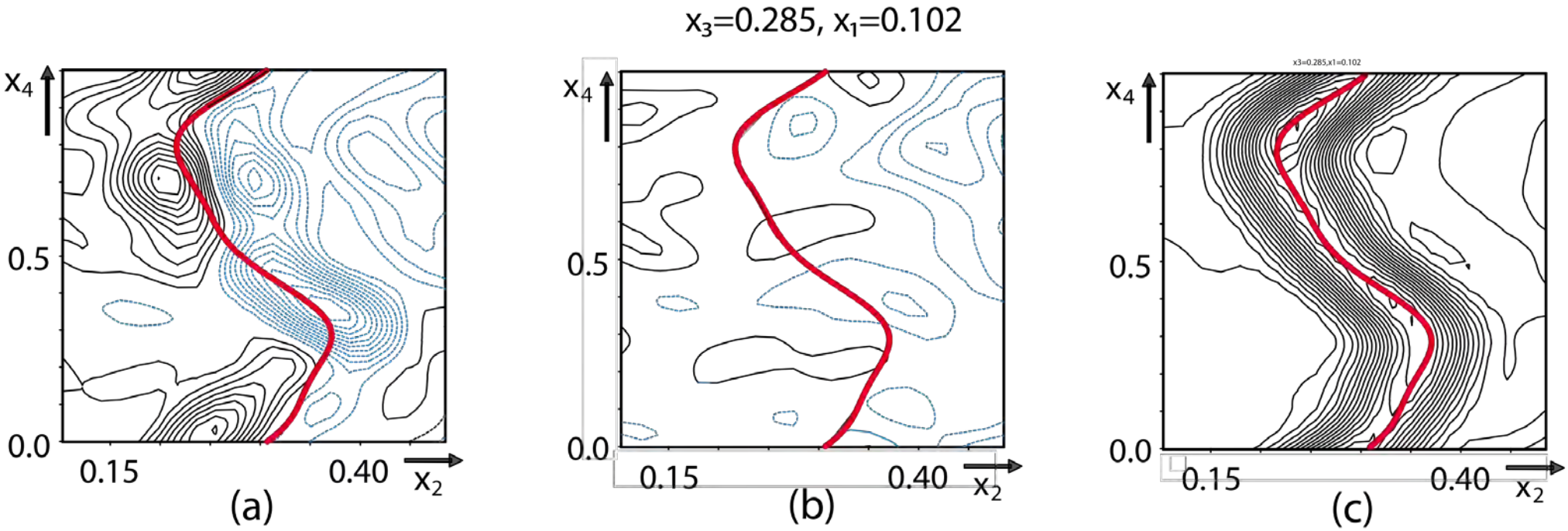


γ-Na_2CO_3. The importance of ADP modulations

ΔF map without ADP modulation for atom O1

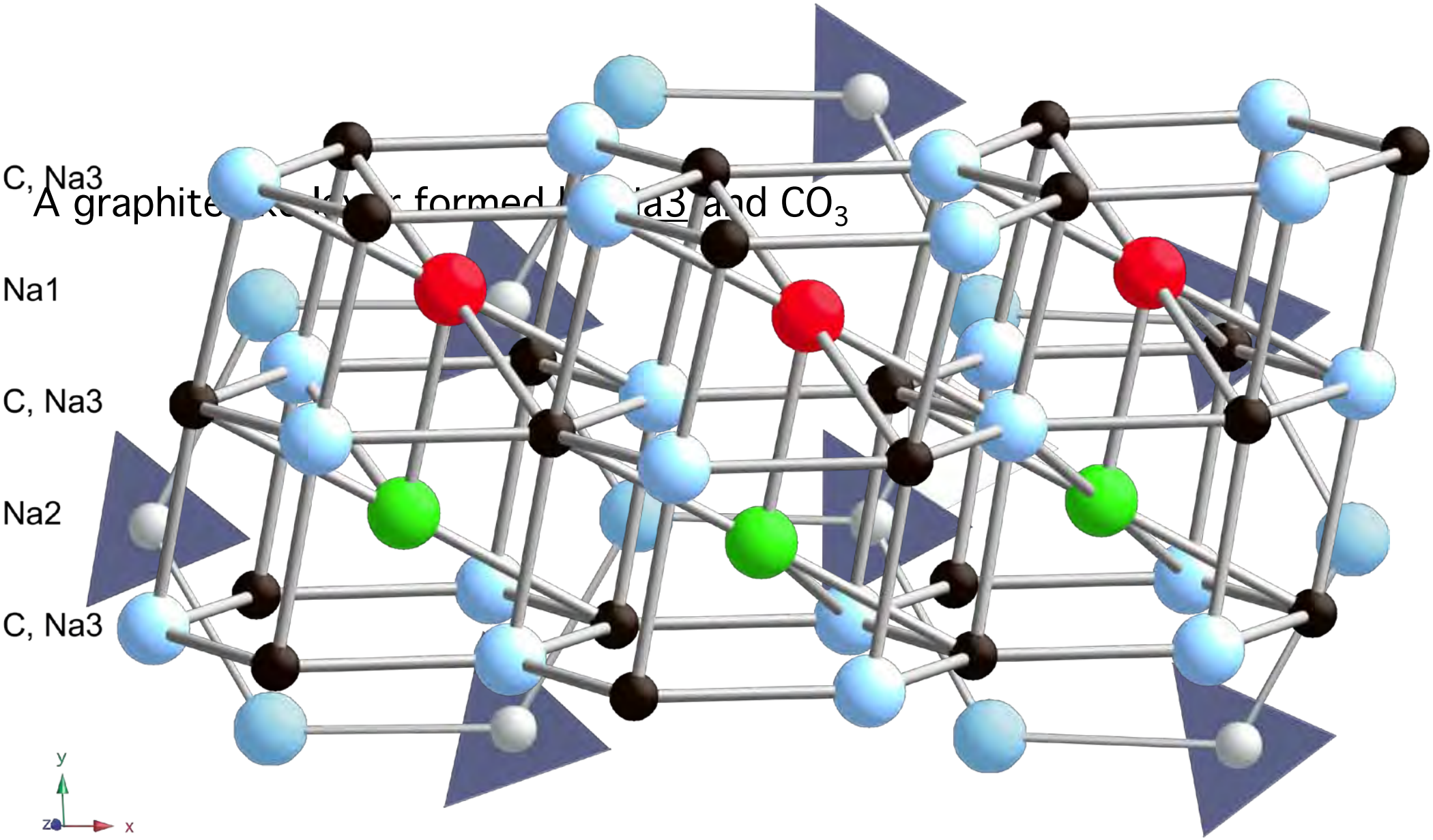
ΔF map with ADP modulation for atom O1

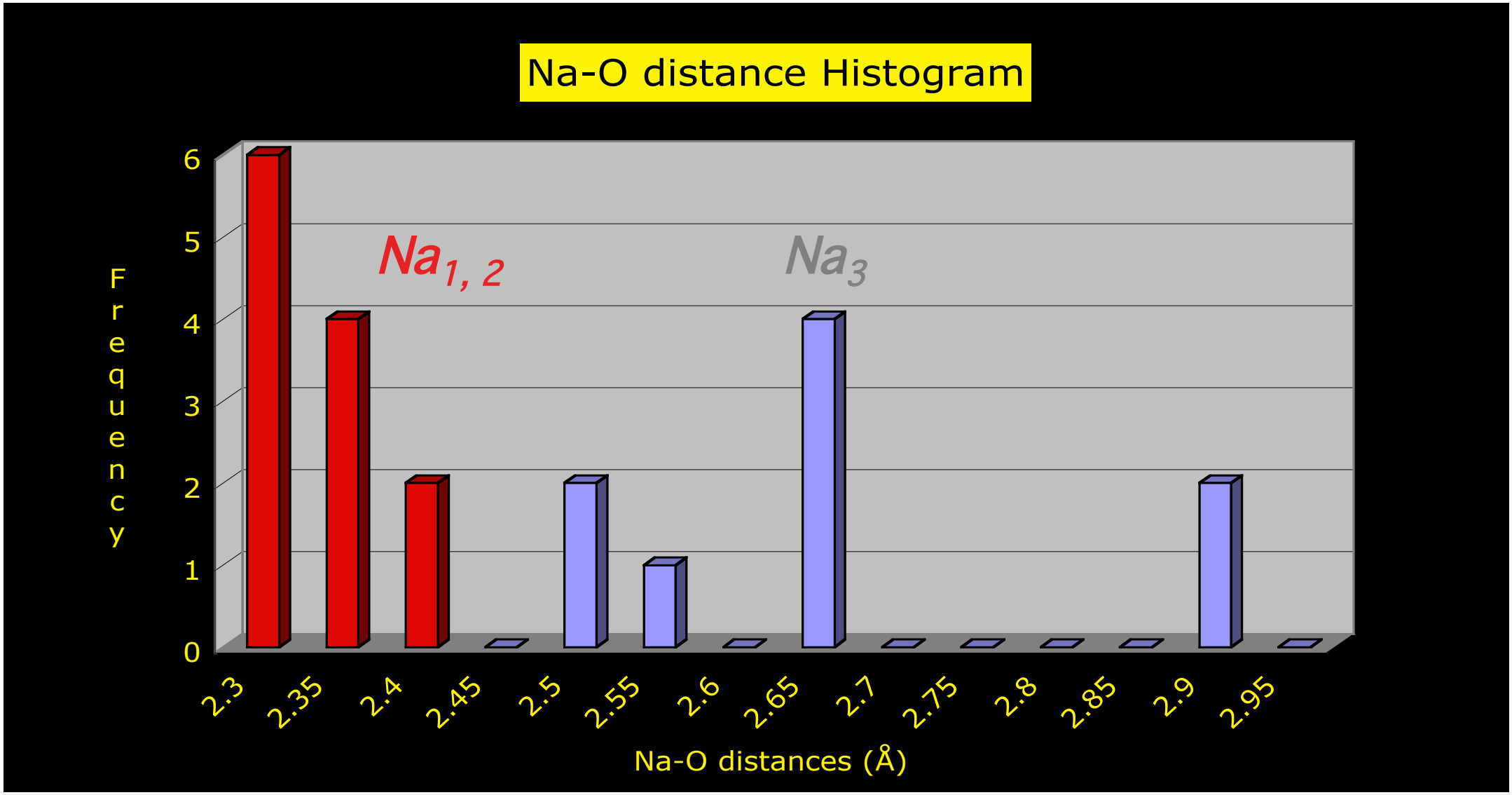
F_o for atom O1



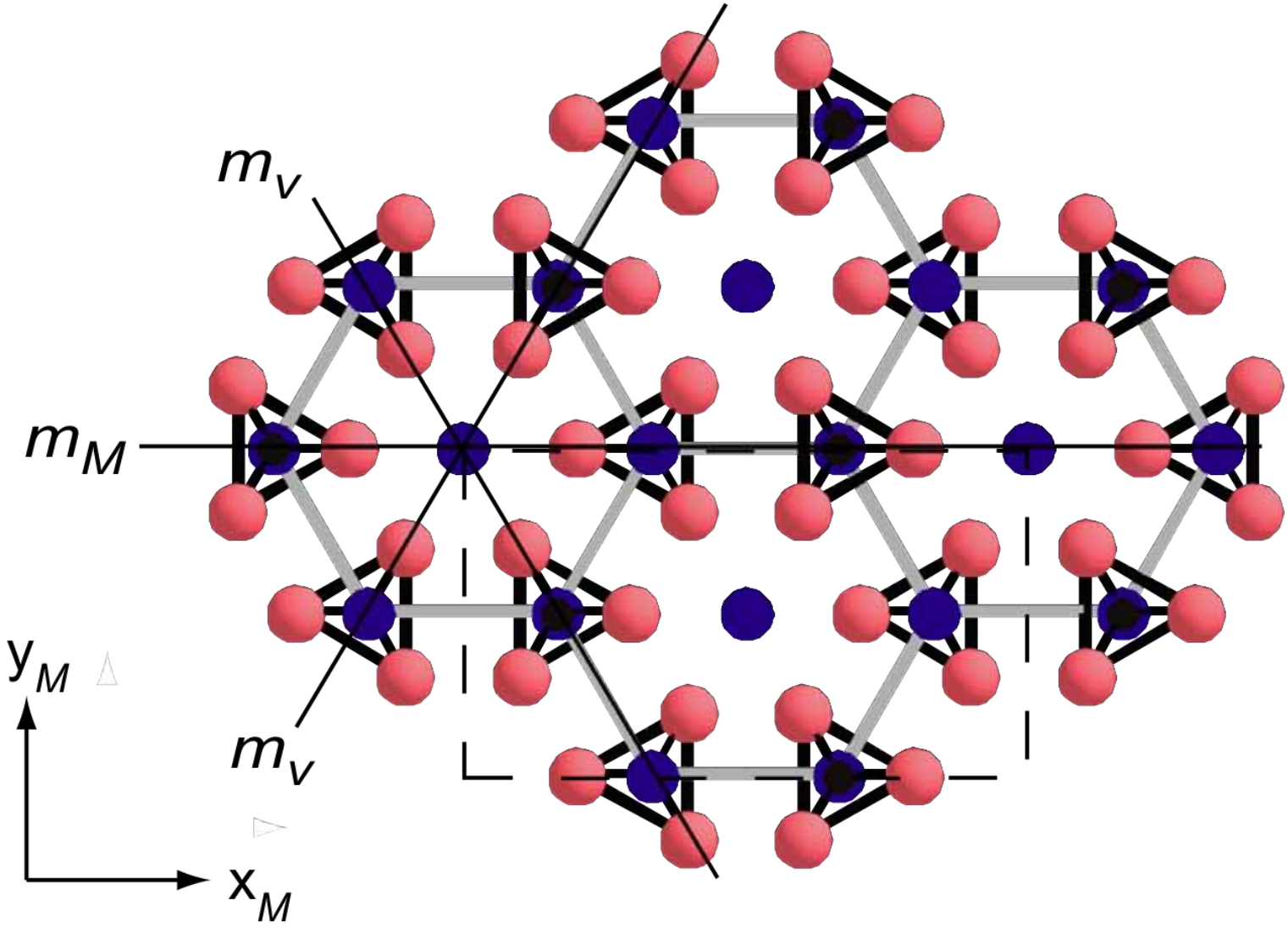
Structure description of Na_2CO_3 (low temperature phase)

A graphite-like layer formed by Na3 and CO_3




Na-O distance Histogram
Frequency
0
1
2
3
4
5
6
$Na_{1,2}$
Na_3
2.3
2.35
2.4
2.45
2.5
2.55
2.6
2.65
2.7
2.75
2.8
2.85
2.9
2.95
Na-O distances (Å)

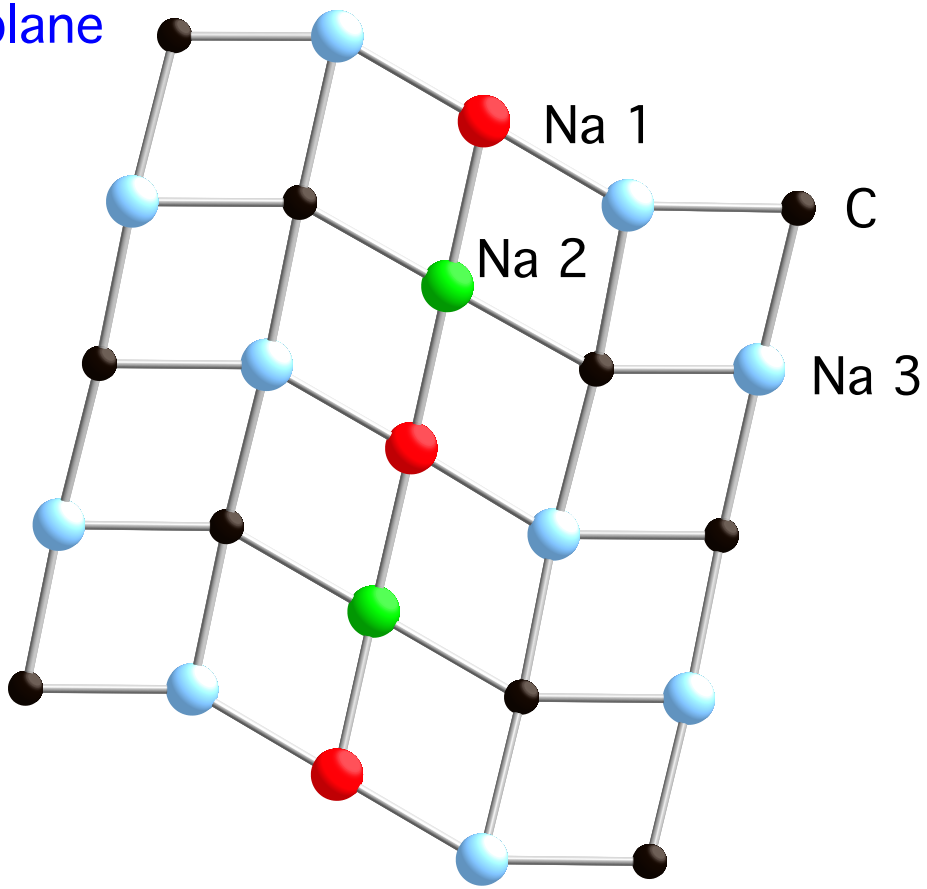
Na_2CO_3. The role of the m_M and m_v planes in the incommensurate γ-phase.

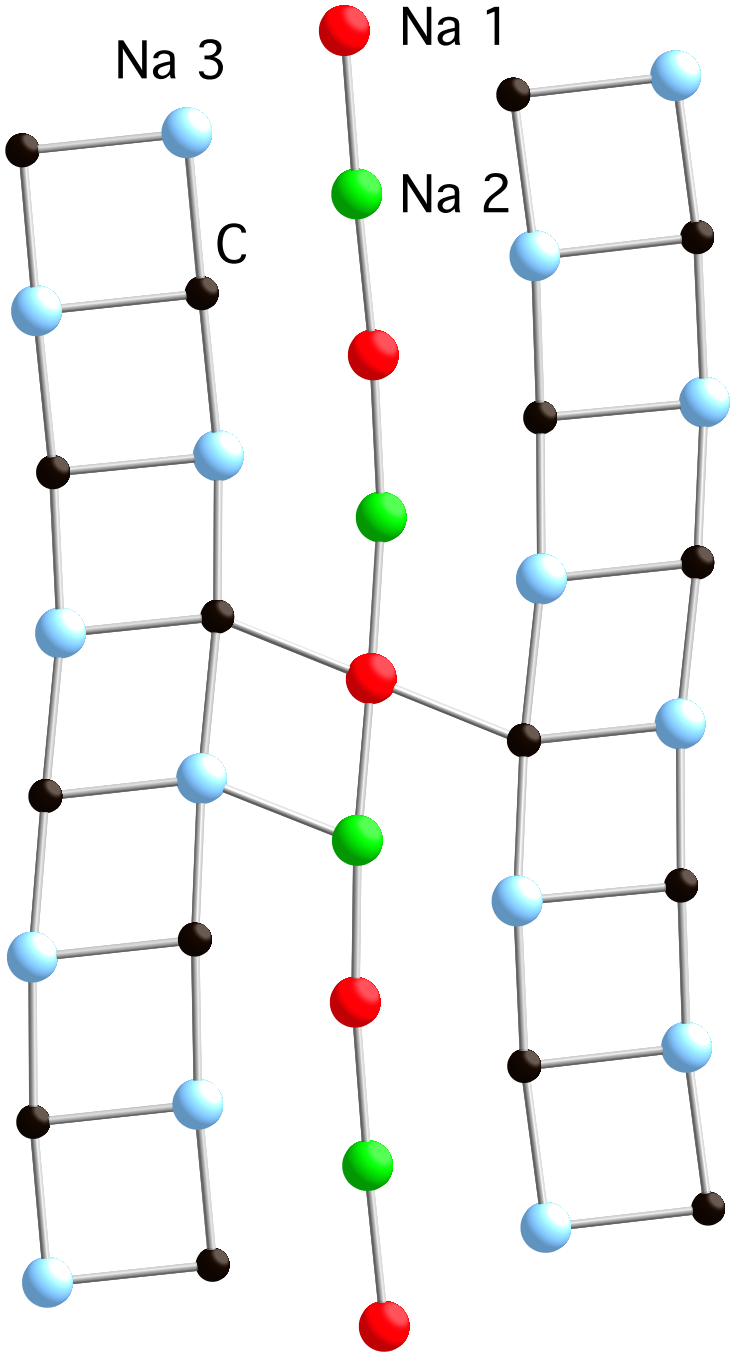


Na_2CO_3. The competing planes

M_v plane

M_m plane

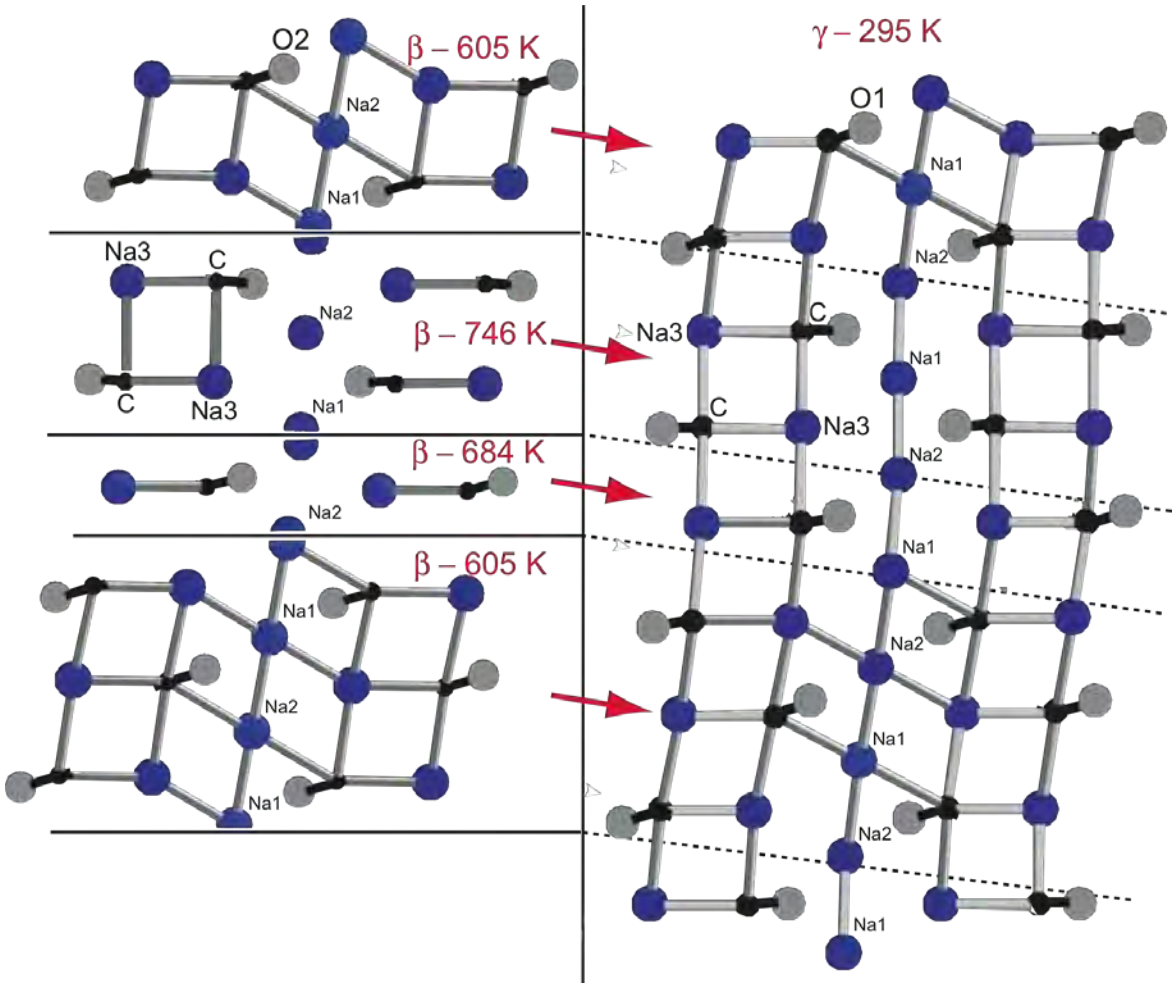




Na_2CO_3. What can you find in an incommensurate structure ?

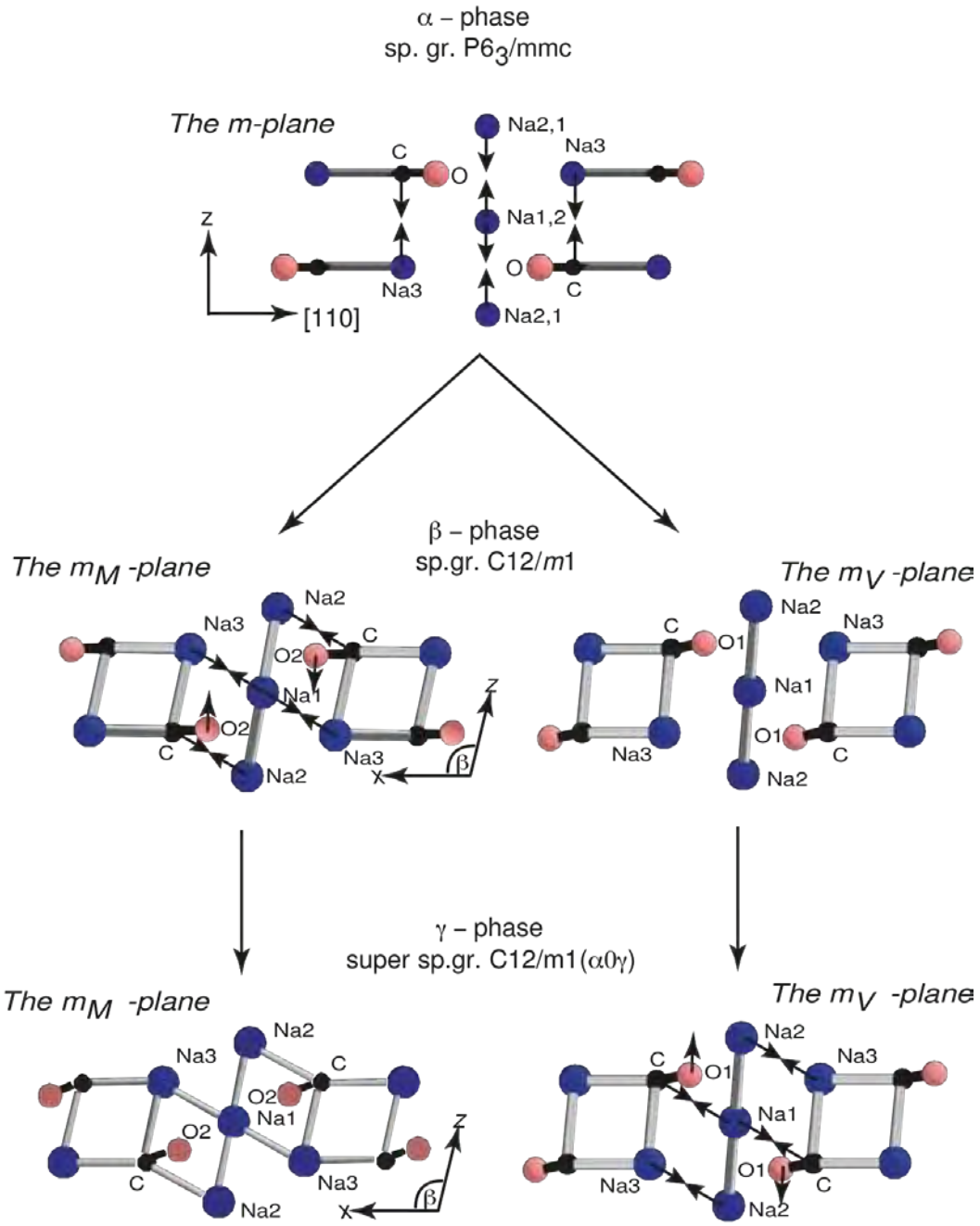
Analogy of the modulation wave and the temperature dependence in the $\{110\}_{hex}$ family of planes.

Solid lines: interatomic contact distances < 3.1 Å



Na_2CO_3. The phase transition mechanisms

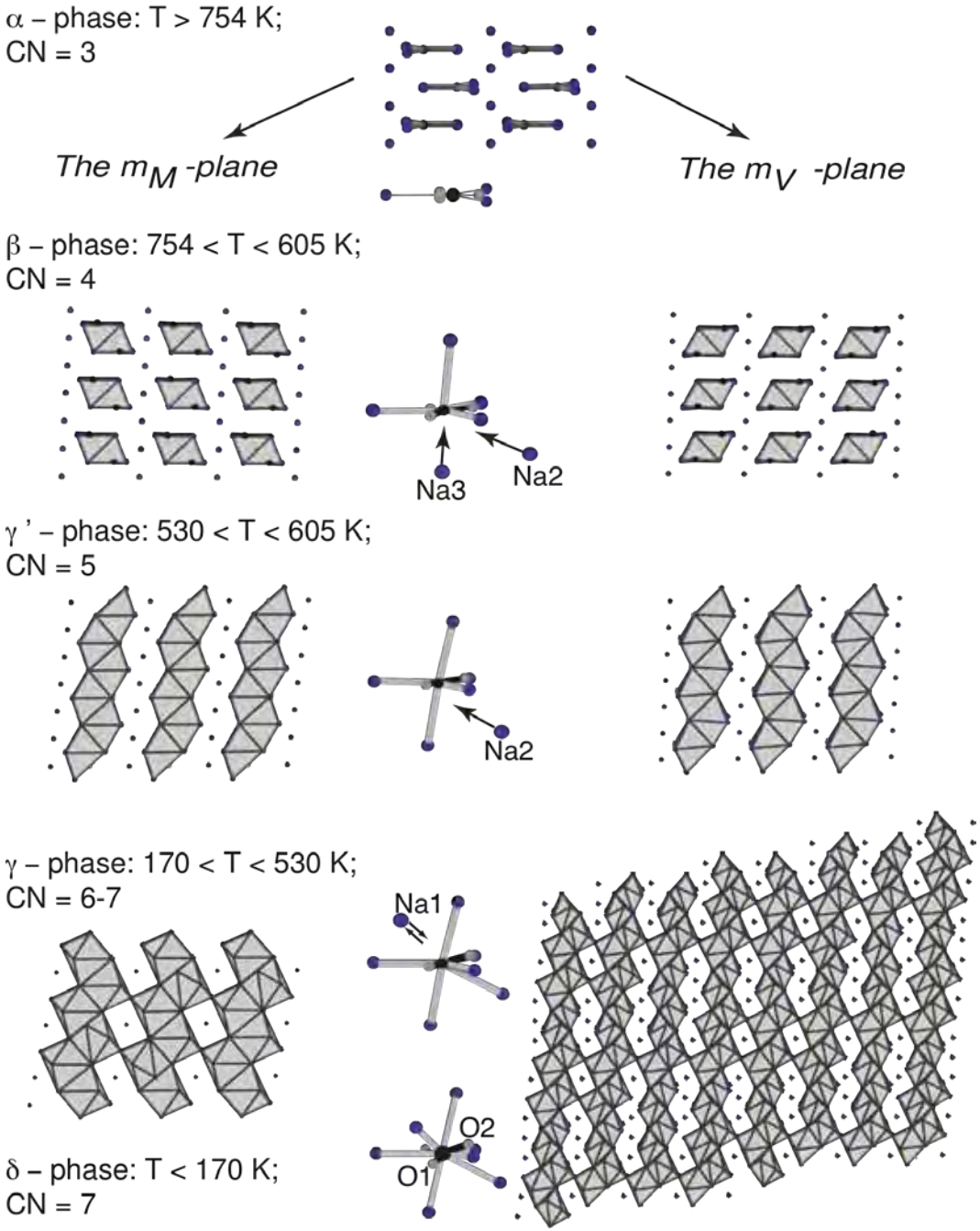
The structural transformations take place in the family of atomic planes $\{110\}_{hex}$



Na_2CO_3. The phase transition mechanisms

Evolution of the Na environment in the vicinity of the C atom.

The coordination number (CN) of the C atom is limited to the C—Na distances < 3.1 Å



What did we learn from the incommensurate nature of structure ?

- The structure of Na_2CO_3 would be better represented by the chemical formula $Na_{4/3}Na_{2/3}CO_3$ indicating the two different natures of the Na atoms
- The series of phase transitions can be much better understood in terms of next of next-next nearest neighbours
- Incommensurate structures contain structural details which can be found in other temperature modifications.
- The incommensurate character of the structure is the direct consequence of subtle chemical interactions which can be exploited in simulations of modelling.

Examples of modulated structures

- Na_2CO_3
- A member of the scheelite family, $KSm(MoO_4)_2$
- Extension of the structure type concept exemplified with the scheelite structures
  - Applications: structure property relations
- The complex structure of metallic elements
  - Barium, Rubidium
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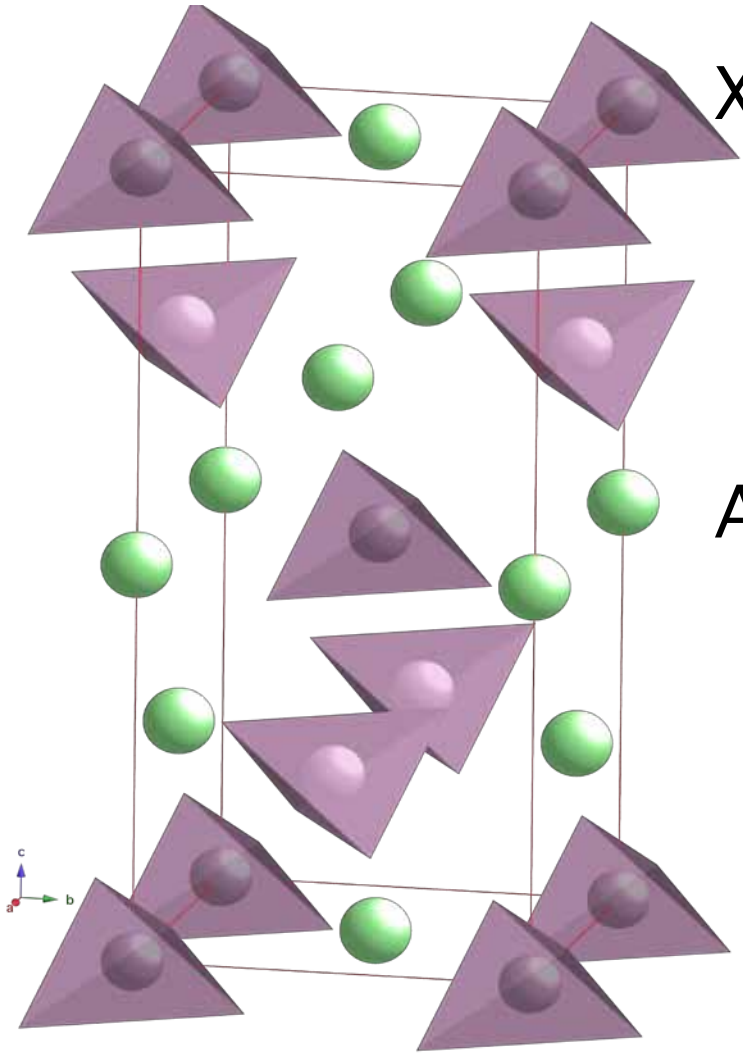
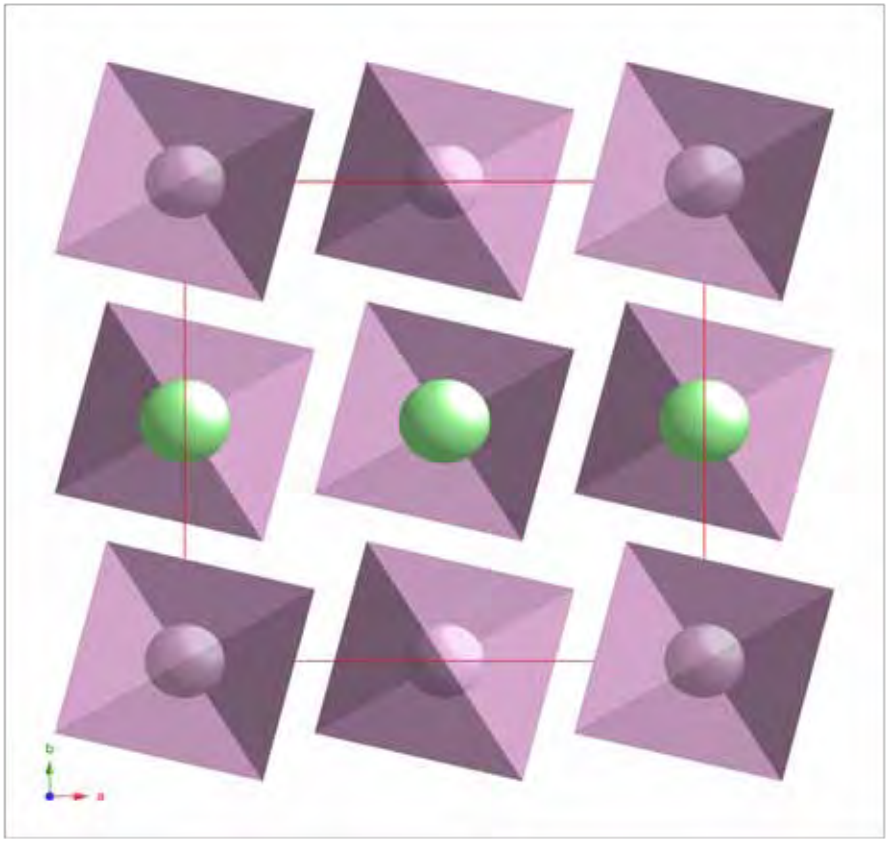
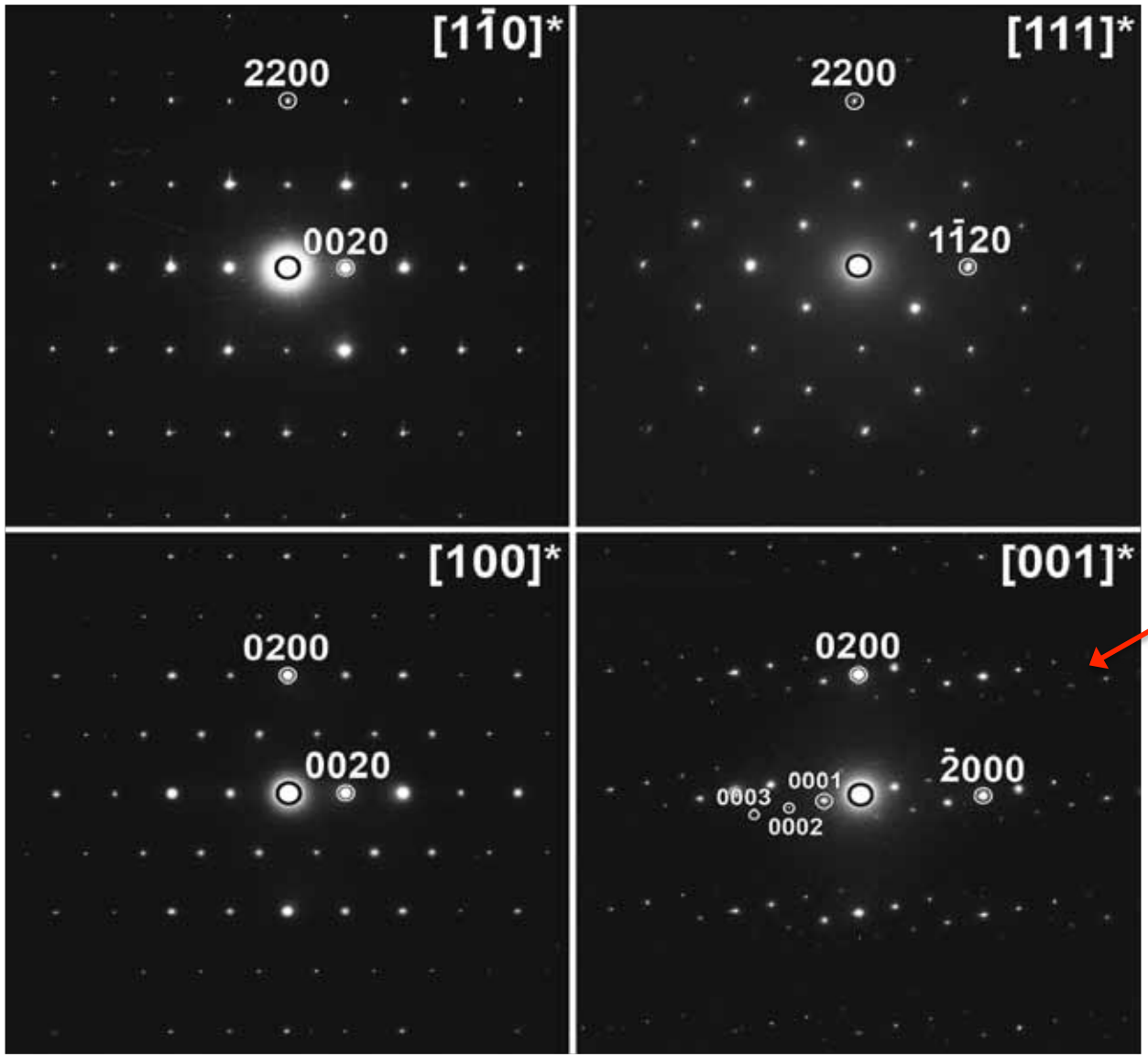
The incommensurately modulated structure of a scheelite: $KSm(MoO_4)_2$ (Arakcheeva *et al*. 2008)



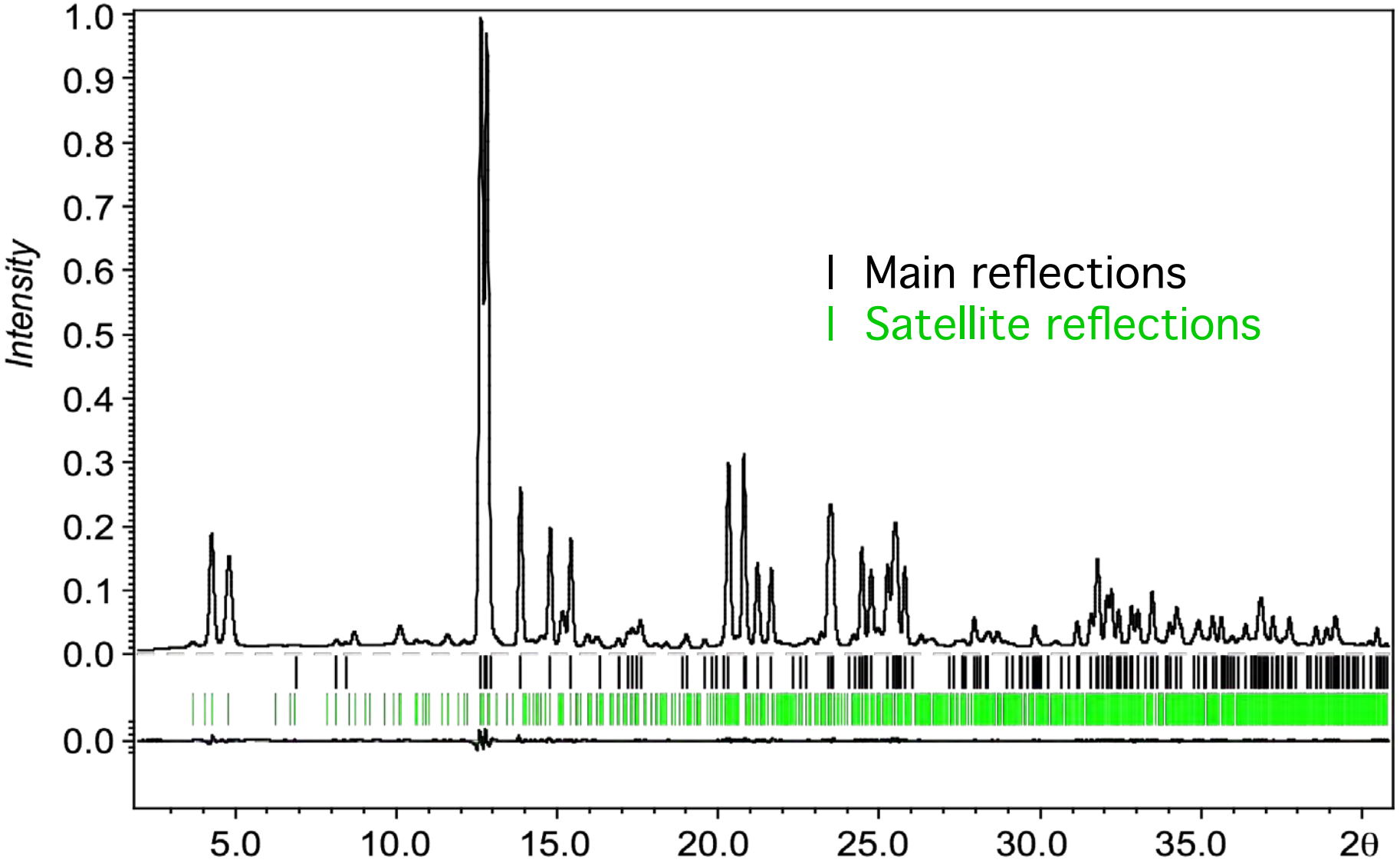


Electron diffraction pattern of $KSm(MoO_4)_2$



Satellites in the ab plane

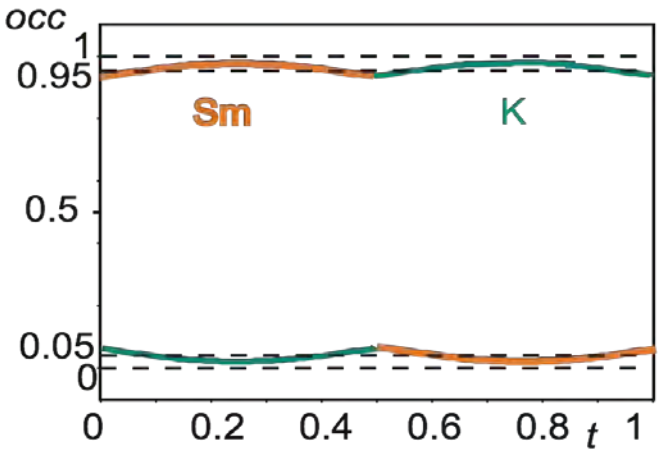
Structure refinement of the modulated structure of $KSm(MoO_4)_2$ by synchrotron powder diffraction



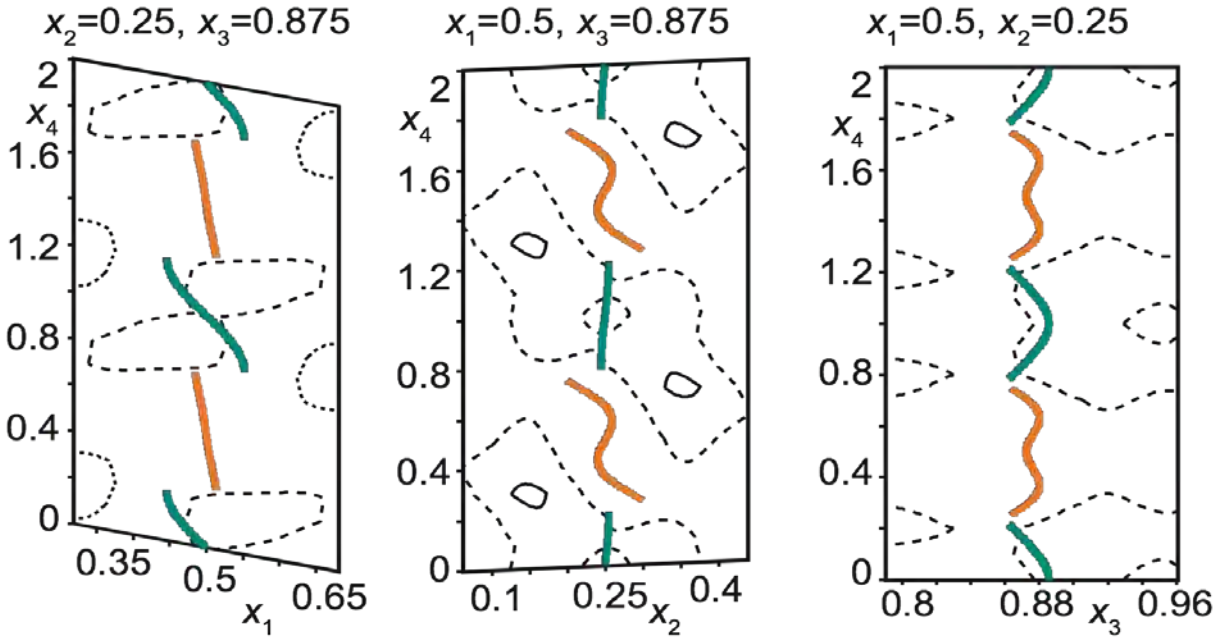
Occupation modulation functions and corresponding displacive modulations of Sm and K

The modulation functions can be selected from a pool of basic functions (harmonics, crenel, saw tooth and others. They can also be combined.

Here, the occupation function of Sm and K results from a combination of crenel and harmonics.

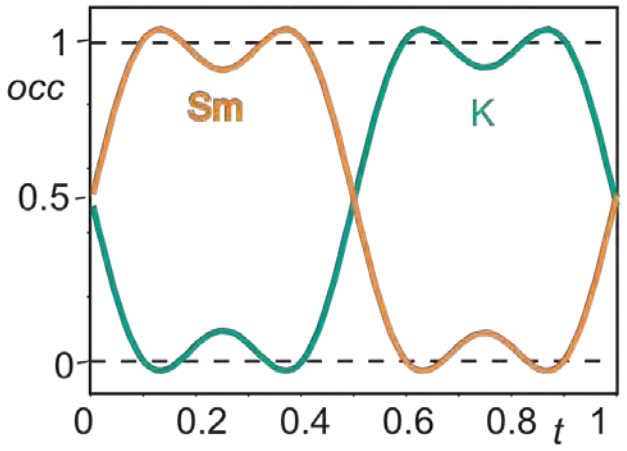


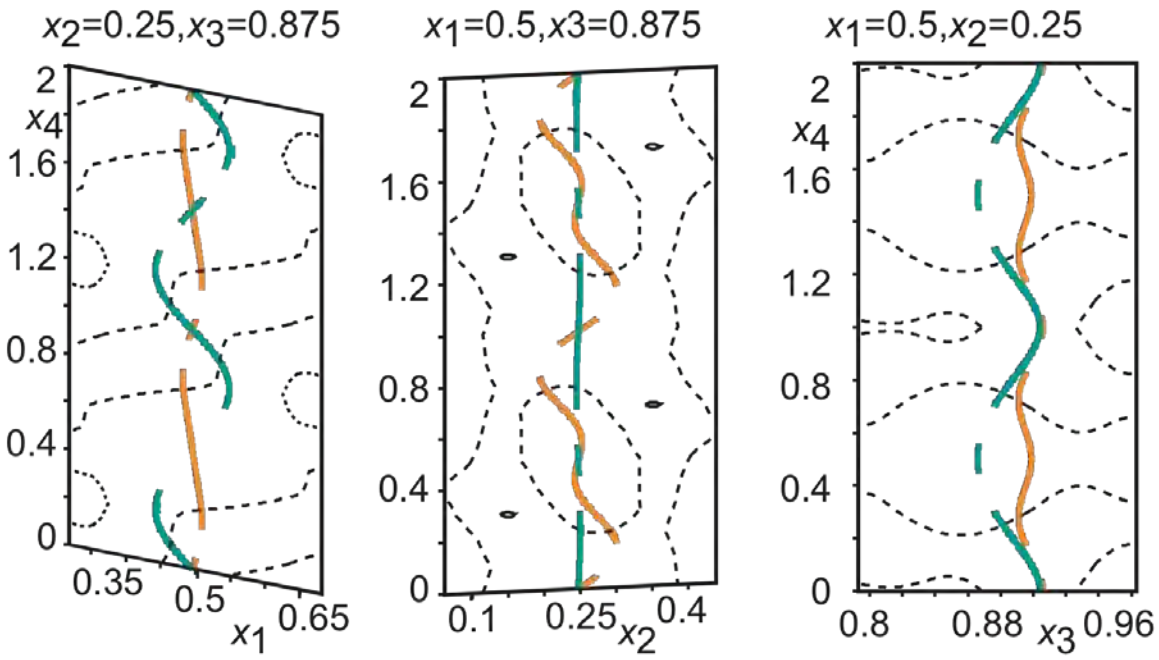
ΔF sections



Occupation modulation functions and corresponding displacive modulations of Sm and K

Here, the occupation function of Sm and K are modelled with harmonics.
Occupation and ΔF sections shows some overlap.

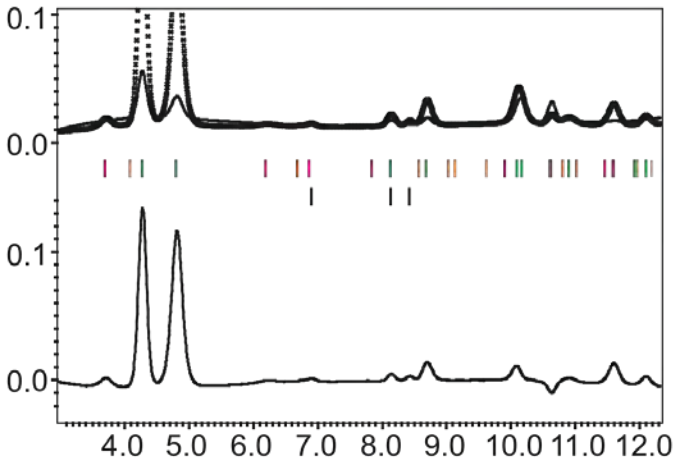




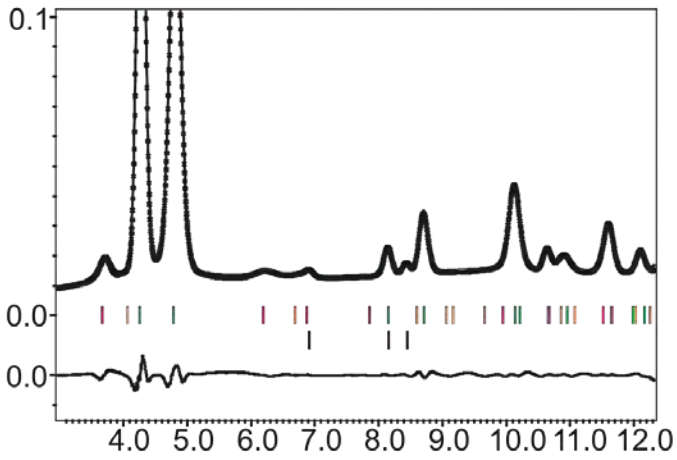
Criteria for the selection of the best model

The Crenel and the harmonic models do not perfectly fit. There are still some residual peaks on the lower part of the powder diffraction diagrams.

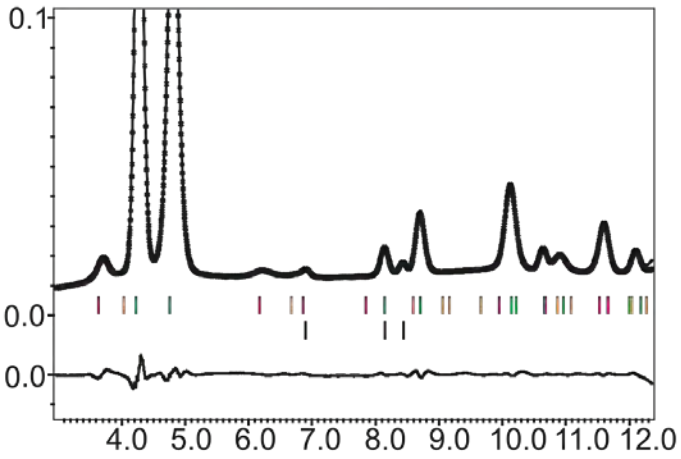
K and Sm are randomly distributed on the *A* position



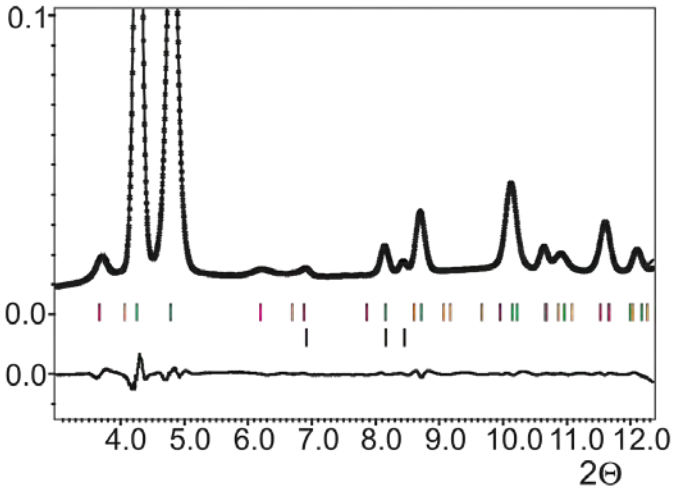
Crenel-I approximation of the $A = (K_{1/2}Sm_{1/2})$ position occupation



Harmonic approximation of the $A = (K_{1/2}Sm_{1/2})$ position



Crenel-II approximation of the $A = (K_{1/2}Sm_{1/2})$ position occupation



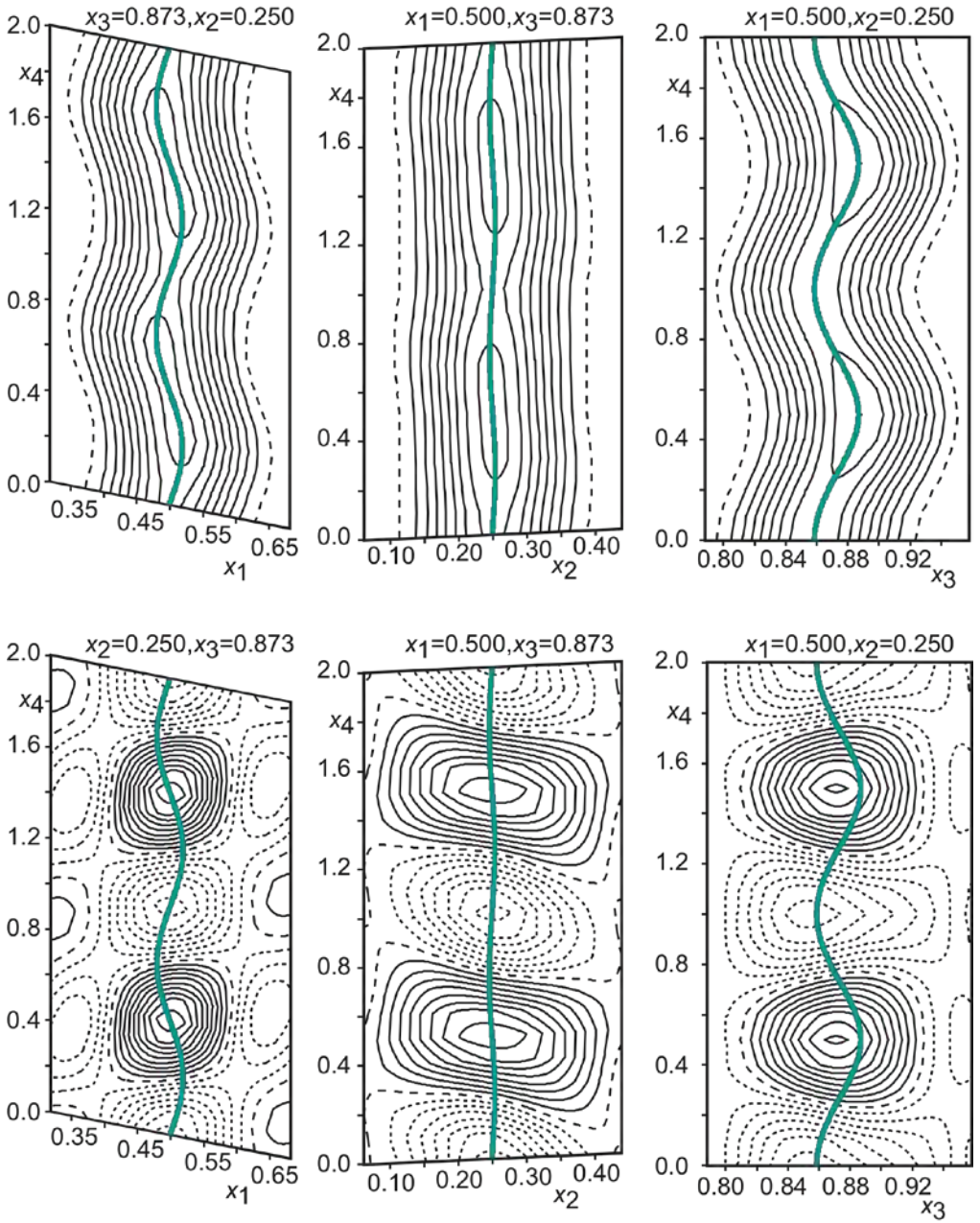
Criteria for the selection of the best model

The vicinity of the A = ($K_{½}Sm_{½}$) position in the structural model with randomly distributed K and Sm atoms.

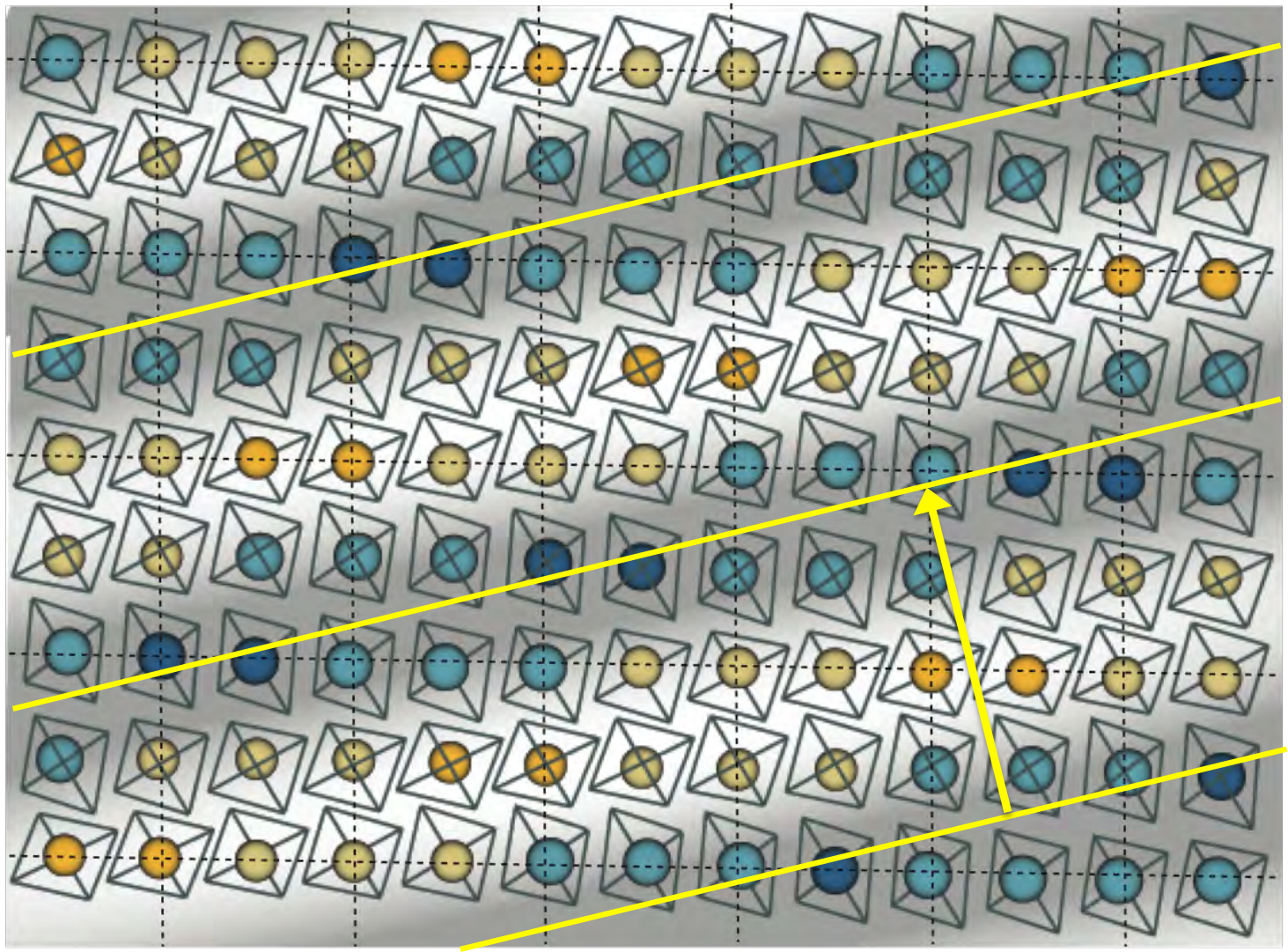
The sections represent electron density (top) and residual electron density (bottom) maps.

The model must obviously be improved to decrease the residual electron density.

Side question: What can we deduce from the shape of the three sections ?



And the final results...

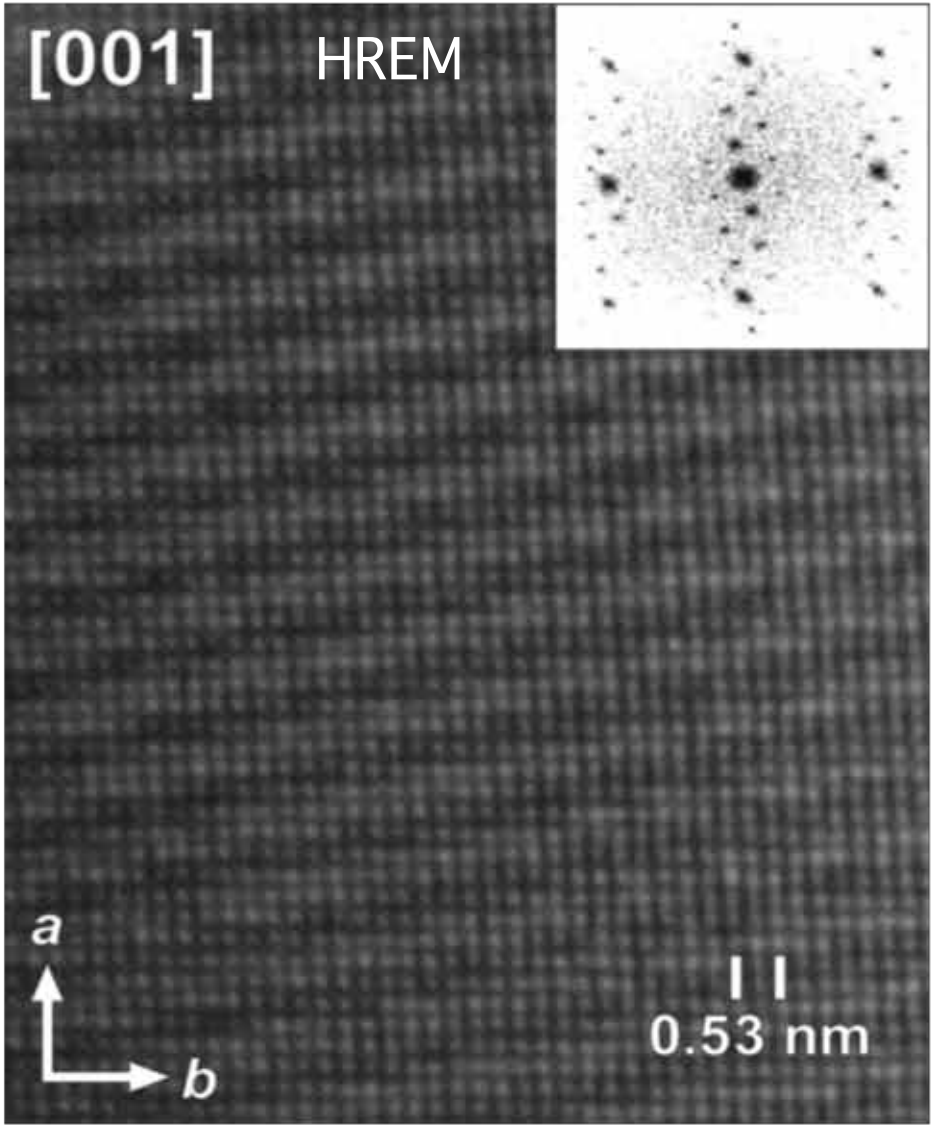


$Sm[MoO_4]$

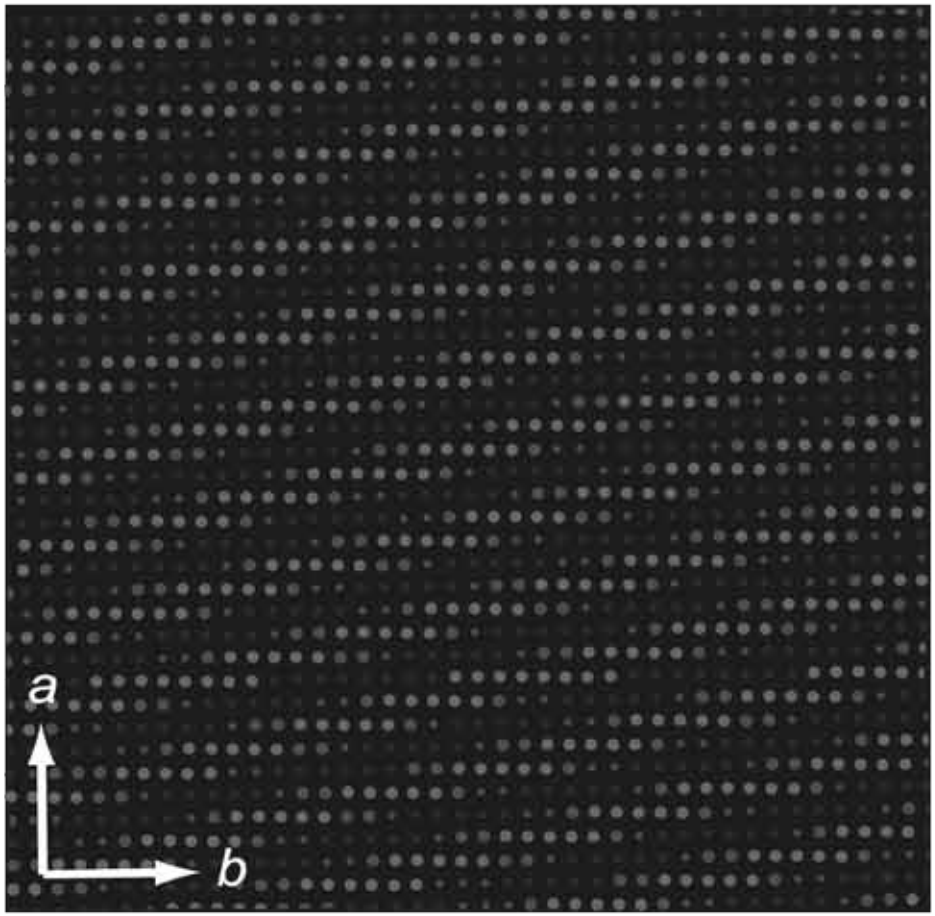
$K[MoO_4]$

Additional periodicity given by the vector // q with magnitude 1/q

Comparison of the HREM image and corresponding Fourier transform with the X-ray model



X-ray structure solution



Incommensurately modulated crystals and applications

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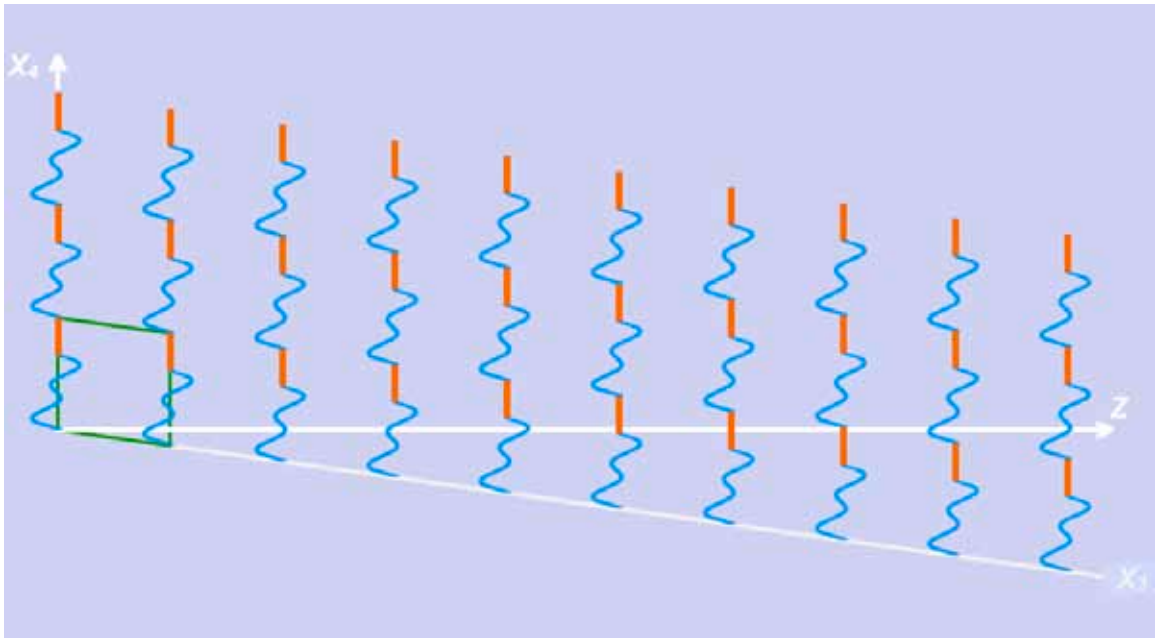
Extension of superspace for the description of families of compounds

The model of superspace gives also a very efficient method to describe families of compounds with common building blocks (also called modular structures).
We use the property of varying the modulation vector and the variable *t.*



A single (3+1)D model *e.g.* can thus generate a multiplicity of structures, some commensurate and some incommensurate. We shall exploit this property with examples from the family of sheelite structures.

The scheelite family $(A', A'')_{n-\delta A}[(X', X'')O_4]_{n-\delta X}$ (Arakcheeva *et al.* 2008)

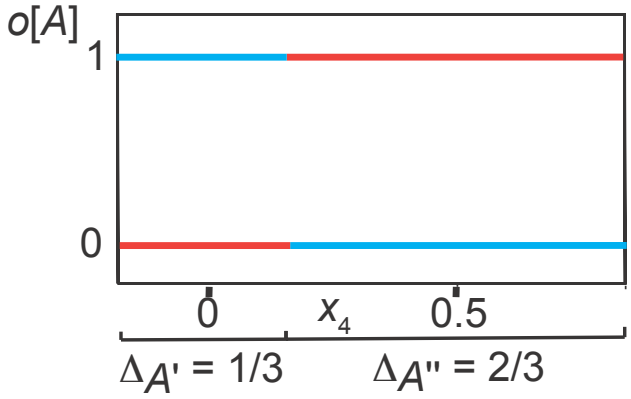
Compound	Space group; independent atomic sites	Superspace group: I2/b(ab0)00 SSG; lattice constants a ≈ b ≈ 5.5 Å, c ≈ 2a γ ≈ 90°; N = 4 independent atomic sites	
		Modulation vector q = $\alpha a^* + \beta b^*$ and t_0 for commensurate members	$\Delta_{A,X}$ parameters of the crenel occupation functions
Incommensurate members			
$KNd[MoO_4]_2$	-; 4	$q = 0.5779a^* - 0.1475b^*$	$\Delta_K = \Delta_{Nd} = 1/2$
$KSm[MoO_4]_2$	-; 4	$q = 0.5688a^* - 0.1288b^*$	Harmonic approximation
$KEu(MoO_4)_2$	-; 4	$q = 0.5641a^* - 0.1335b^*$	$\Delta_K = \Delta_{Eu} = 1/2$
$KLa[MoO_4)_2]$	-; 4	$q = 0.3507a^* + 0.6222b^*$	$\Delta_K = \Delta_{La} = 1/2$
Commensurate members			
$RbBi[MoO_4]_2$	$P2_1/a$; 12	$q = 0a^*+1/2b^*$; $t_0 = 0$	$\Delta_K = \Delta_{Nd} = 1/2$
$K_2Th[MoO_4]_3$	A2/a; 10	$q = 0a^*+2/3b^*$; $t_0 = 0$	$\Delta_K = 2/3$, $\Delta_{Th} = 1/3$
$Eu_2\square[WO_4]_3$	A2/a; 9	$q = 2/3a^*+2/3b^*$; $t_0 = 0$	$\Delta_{Eu} = 2/3$, $\Delta_\square = 1/3$
$Bi_2\square\ [MoO_4]_3$	$P2_1/a$; 17	$q = 2/3a^*+1/3b^*$; $t_0 = 0$	$\Delta_{Bi} = 2/3$, $\Delta_\square = 1/3$
$La_2\square\ [MoO_4]_3$	A2/a; 26	$q = 2/3a^*+8/9b^*$; $t_0 = 0$	$\Delta_{La} = 2/3$, $\Delta_\square = 1/3$
$Bi_3[(FeO_4)(MoO_4)_2]$	A2/a; 10	$q = 0a^*+2/3b^*$; $t_0 = 0$	$\Delta_{Mo} = 2/3$,$\Delta_{Fe} = 1/3$
$Na_4Zr[\square(MoO_4)_4]$	$I4_1/a$; 7	$q = 2/5a^*+4/5b^*$; $t_0 = 0$	$\Delta_{Na} = \Delta_{MoO4} = 4/5$, $\Delta_{Zr} = \Delta_\square = 1/5$
$Na_4Y[Na'(MoO_4)_4]$	$I4_1/a$; 8	$q = 2/5a^*+4/5b^*$; $t_0 = 0$	$\Delta_{Na} = \Delta_{MoO4} = 4/5$, $\Delta_Y = \Delta_{Na'} = 1/5$

The occupation functions of various Scheelite

A single superspace model describes the family. Each member is characterised by the modulation vector, occupation and modulation functions of the independent atoms.

$A'A''_2[XO_4]_3$ composition

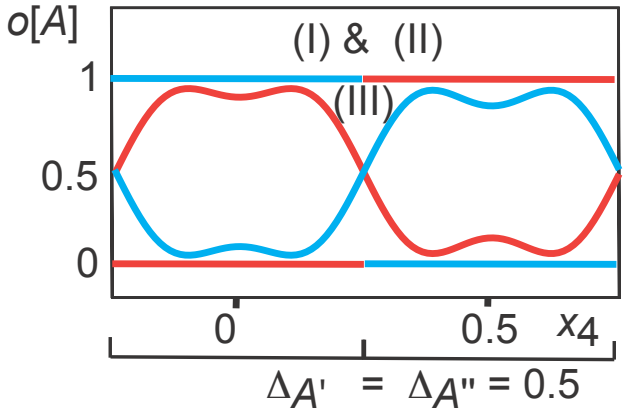
$K_2Th[MoO_4]_3$
$\square La_2[MoO_4]_3$
$\square Eu_2[WO_4]_3$
$\square Bi_2[MoO_4]_3$



A'
A''

$A'A''[XO_4]_2$ composition

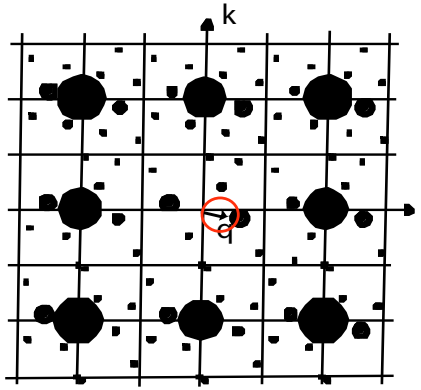
(I) $KNd[MoO_4]_2$
(II) $RbBi[MoO_4]_2$
(III) $KSm[MoO_4]_2$



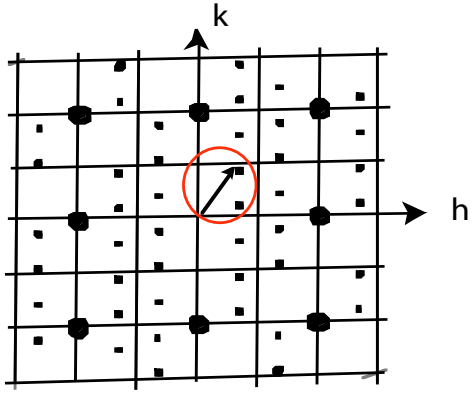
The (3+1)D Scheelite family

Choice of q-vectors for the 3D members

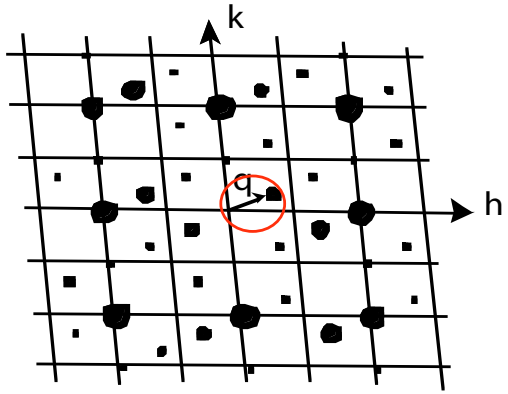
$KNd[MoO_4]_2$



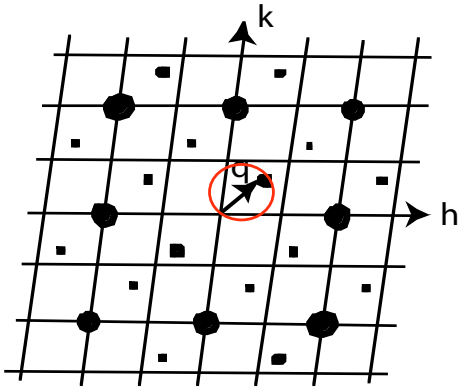
$La_2[MoO_4]_3$



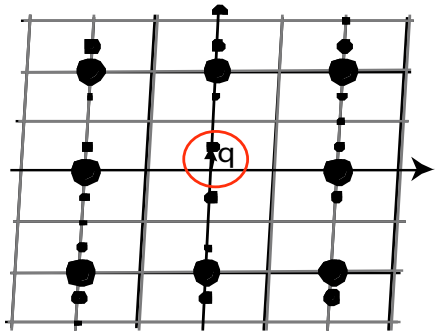
$Bi_2[MoO_4]_3$



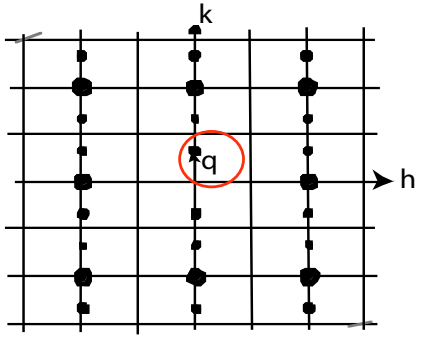
$Eu_2[WO_4]_3$



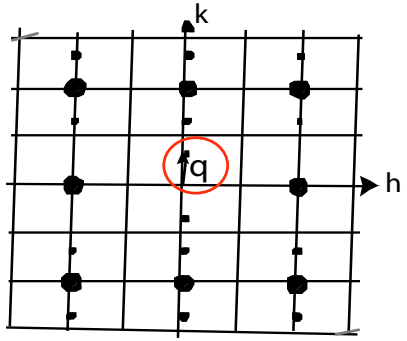
$RbBi[MoO_4]_2$



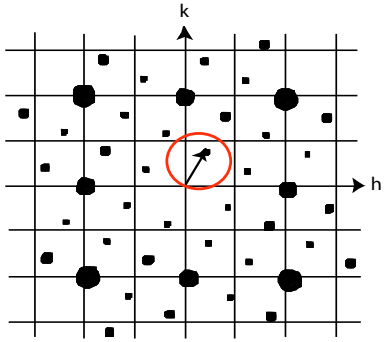
$K_2Th[MoO_4]_3$



$Bi_3[FeO_4][MoO_4]_2$



$Na_4Zr[MoO_4]_4$



The (A',A'')[(X',X'')] (3+1)D Scheelite family

One size fits all!

Illustration of the concept with a few examples.

Superspace group:
I2/b(αβ0)00

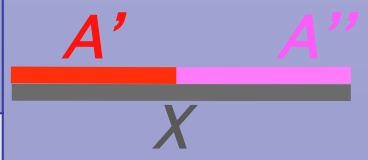
Basic structure:
Scheelite

Variables:

$$q = \alpha a^* + \beta b^*$$

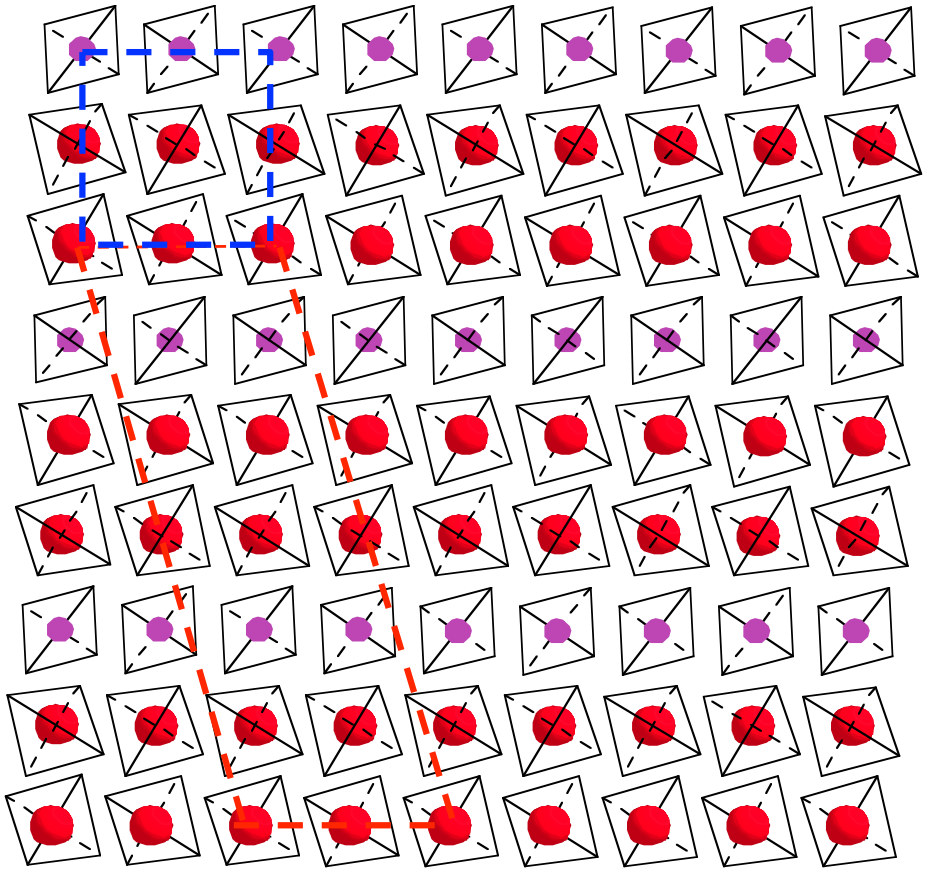
&

occupation functions of A and X

Composition	q	Occupation functions
$KNd[MoO_4]_2$ Incommensurate	$0.578a^* - 0.147b^*$	
$RbBi[MoO_4]$	$0a^*+\frac{1}{2}b^*$	
$K_2Th[MoO_4]_3$	$0a^*+\frac{2}{3}b^*$	
$\square Eu_2[WO_4]_3$	$\frac{2}{3}a^*+\frac{2}{3}b^*$	
$\square Bi_2[MoO_4]_3$	$\frac{2}{3}a^*+\frac{1}{3}b^*$	
$\square La_2[MoO_4]_3$	$\frac{2}{3}a^*+\frac{8}{9}b^*$	
$Bi_3[FeO_4][MoO_4]_2$	$0a^*+\frac{2}{3}b^*$	
$Na_4Zr[MoO_4]_4$	$\frac{2}{5}a^*+\frac{4}{5}b^*$	
$Na_4Y[Na(MoO_4)_4]$		

$K_2Th[MoO4]_3$

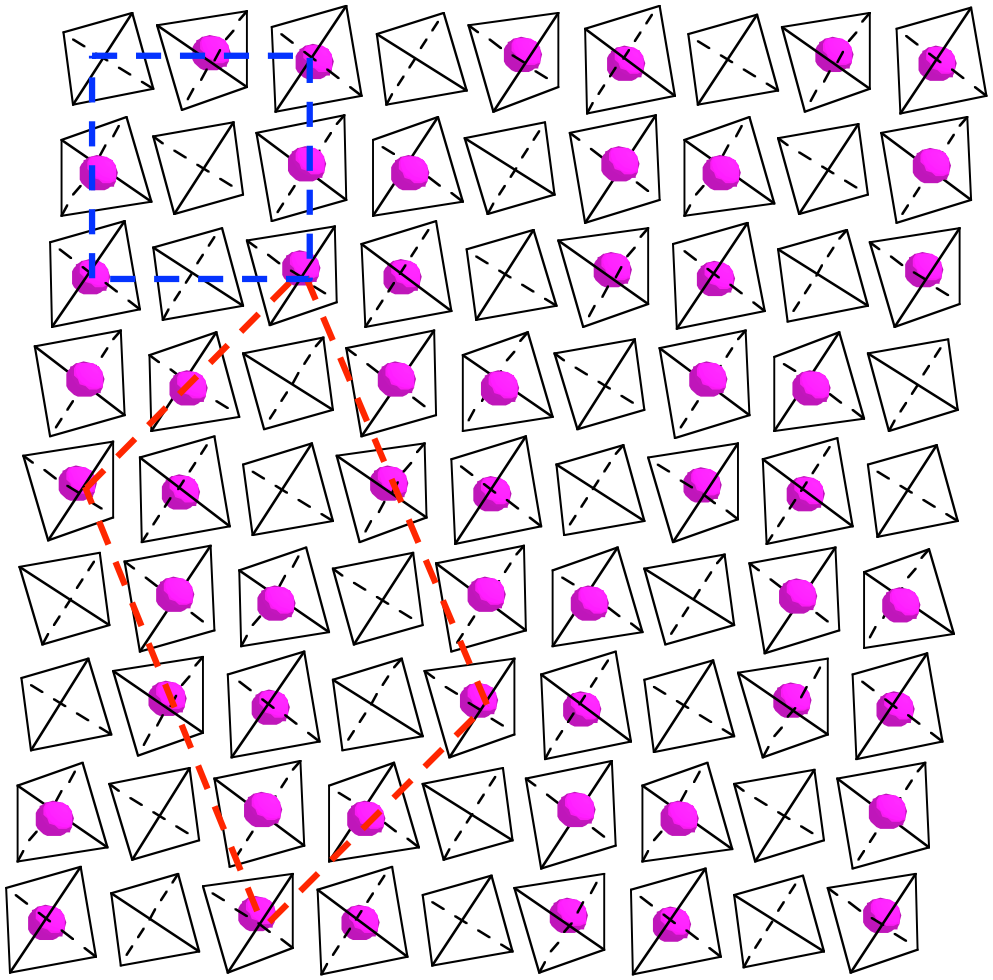
Projection on the ab-plane



$q = 0a^* + ⅔b^*$

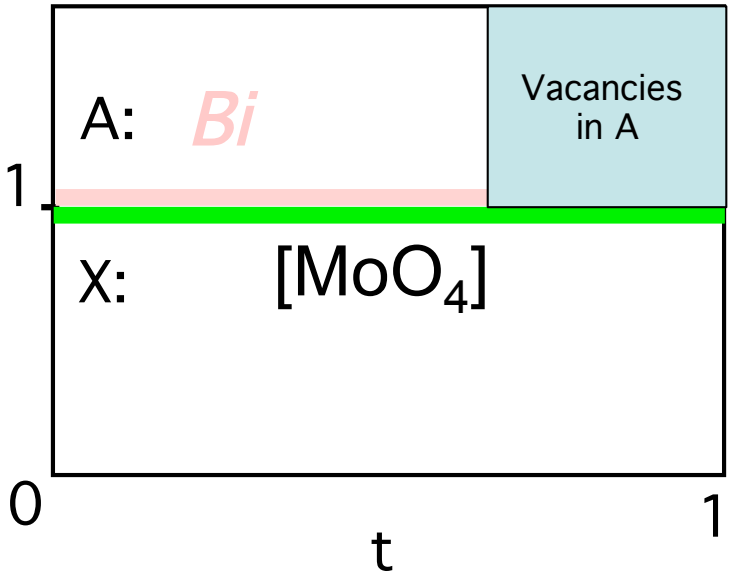
Occupation function

$Bi_2[MoO_4]_3$

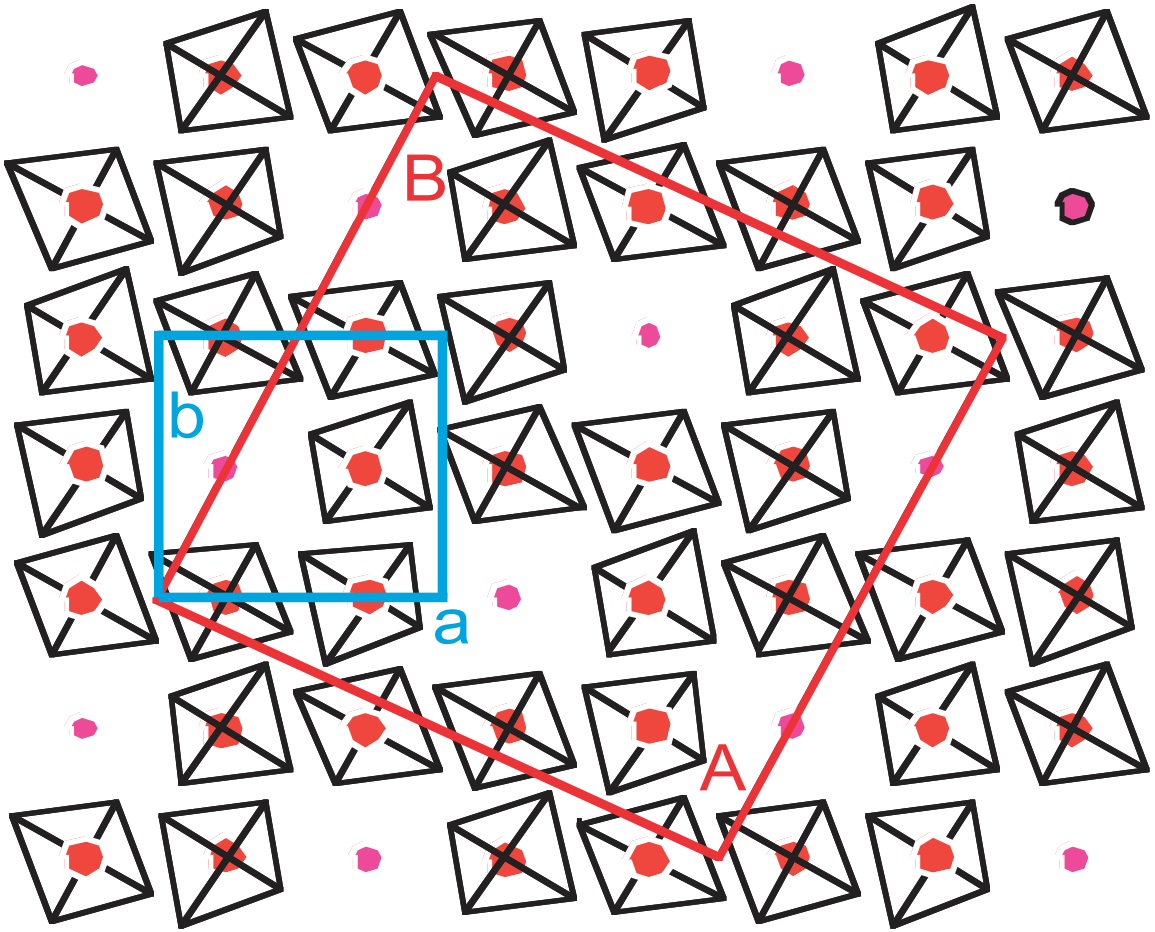


$q = \frac{2}{3}a^* + \frac{1}{3}b^*$

Occupation function

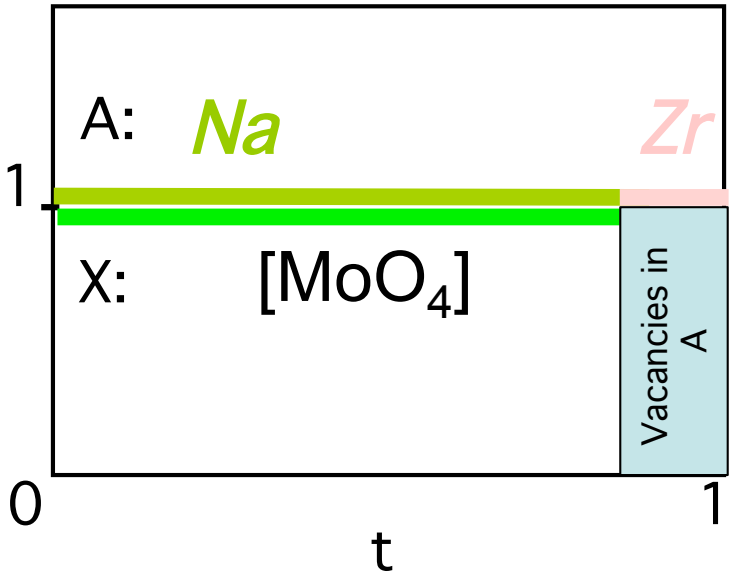


$Na_4Zr[\square MoO_4]_4$

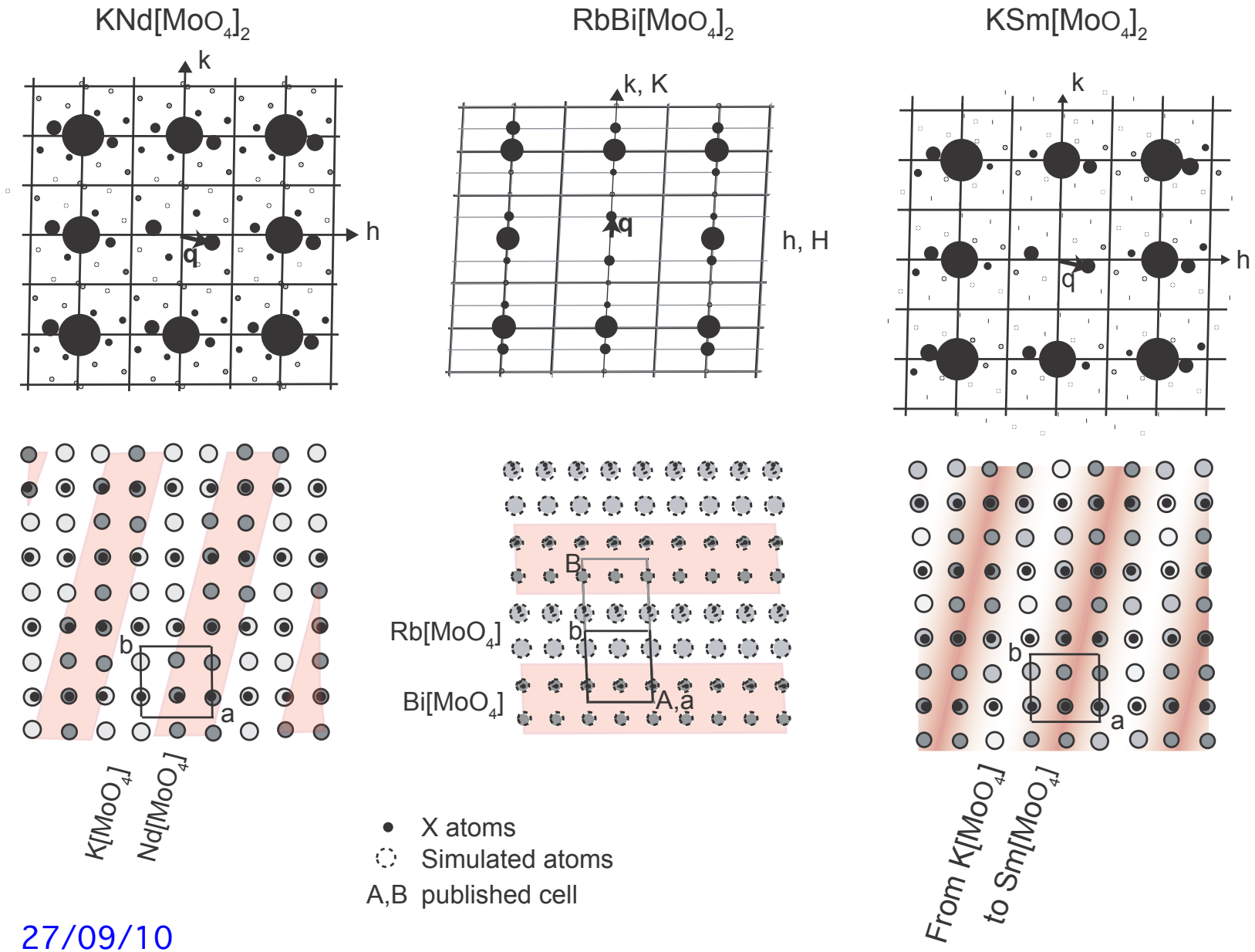


$q = 2/5a^* + 4/5b^*$

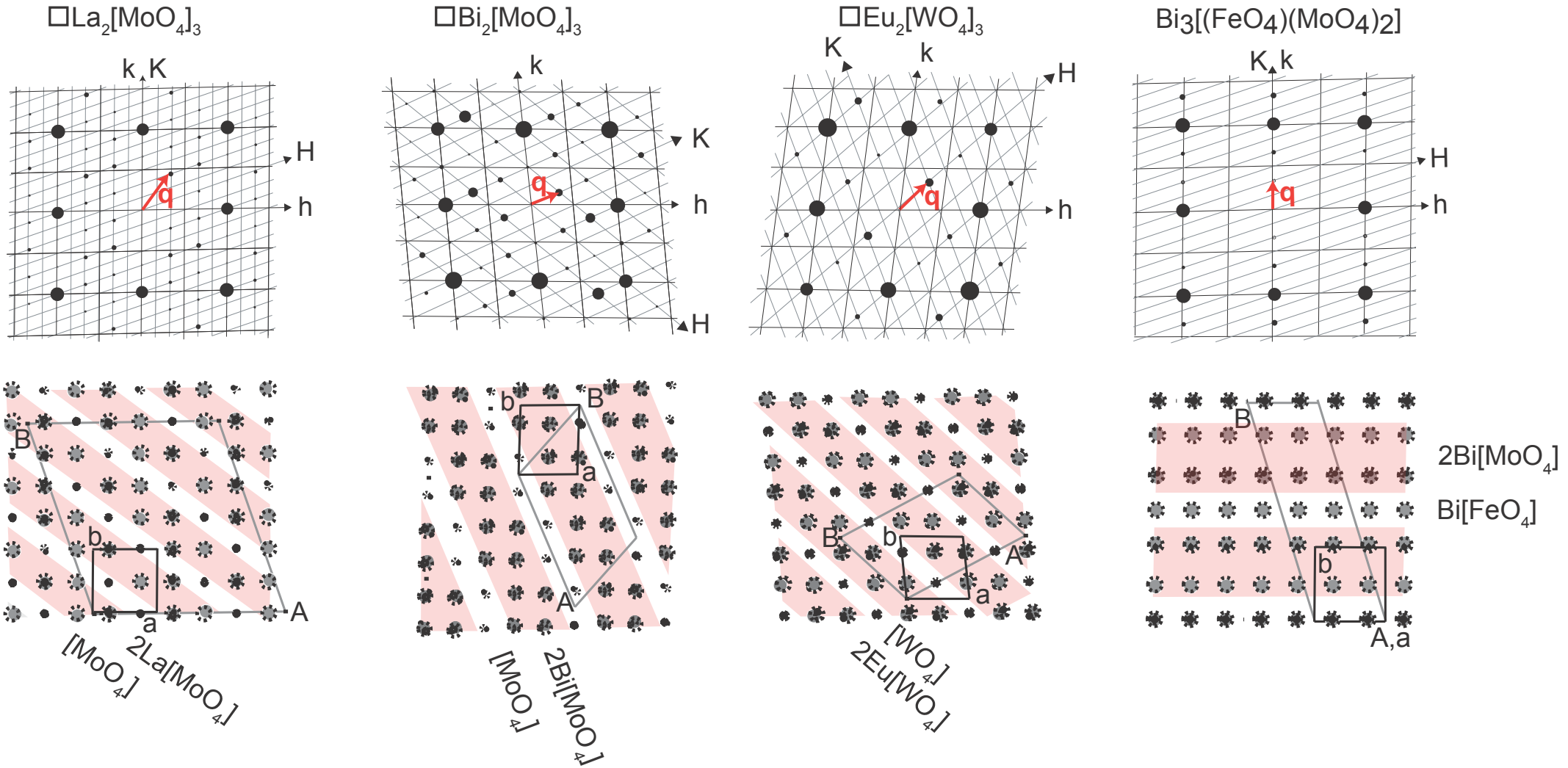
Occupation function



The q-vector defines the wave of composition



The q-vector defines the wave of composition

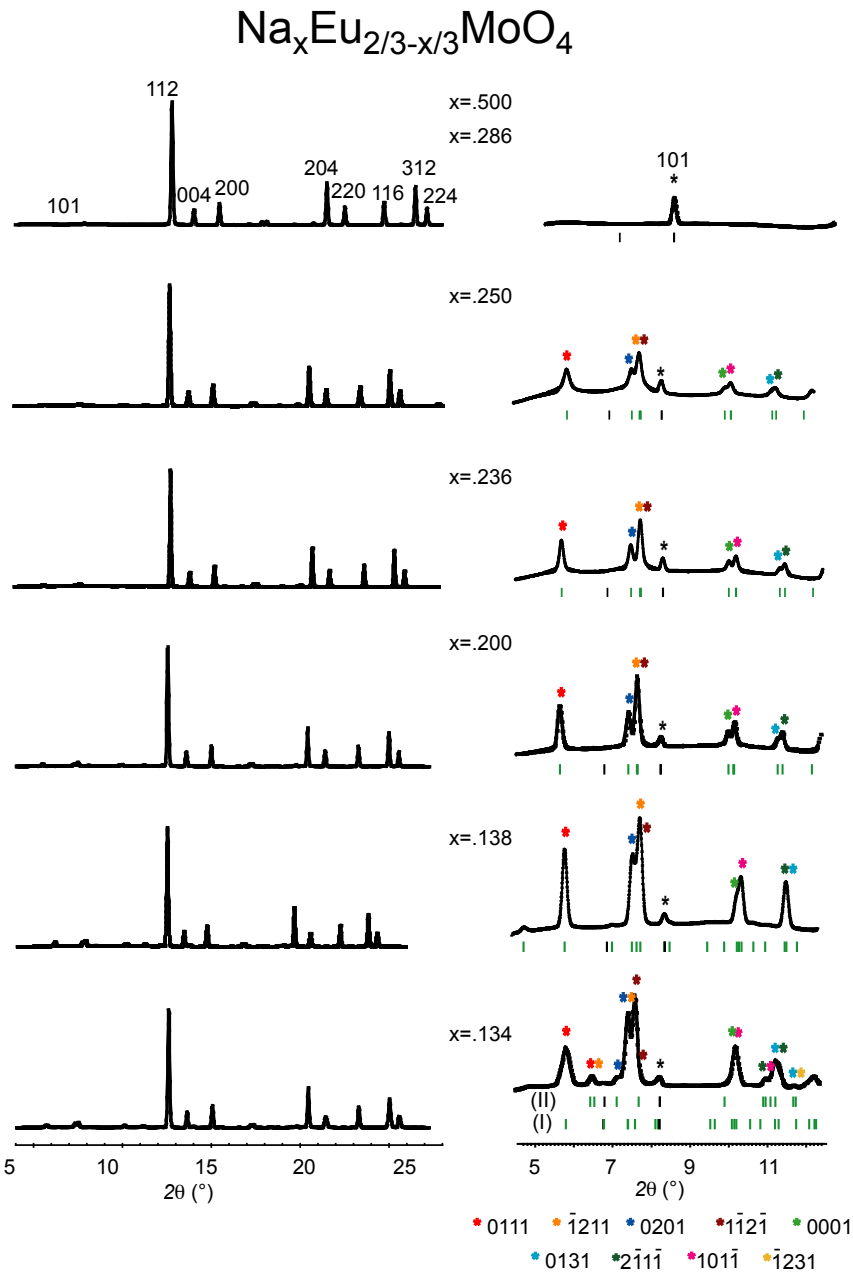


Application of the superspace concept: structure property relations (luminescence)
(A. Arakcheeva, private communication)

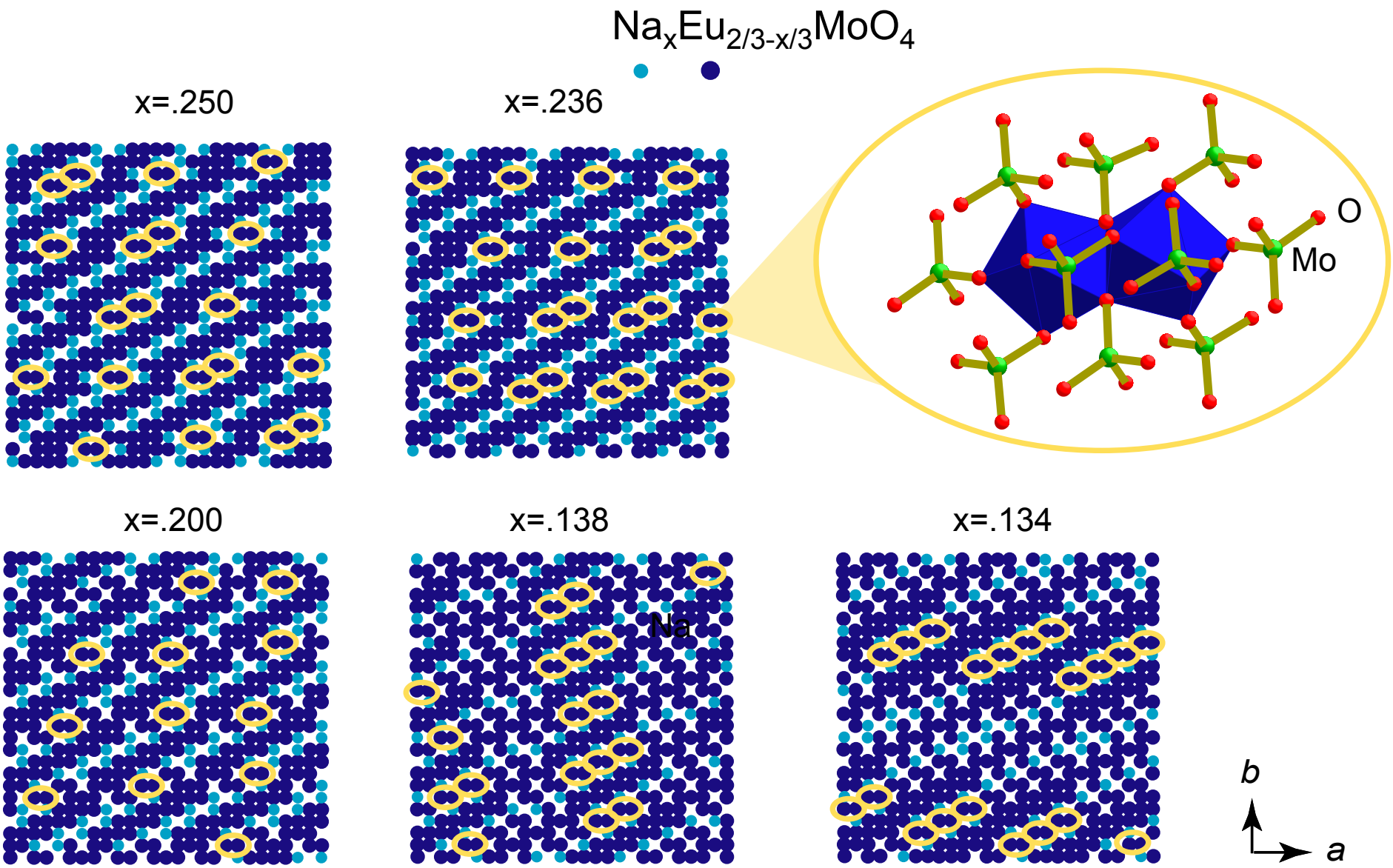
Most of the Scheelite structures listed in the PDF (ICDD) database are average structures. A large number of them are incommensurately modulated.

The presence of satellites reflections are barely recognisable on conventional powder diagrams. They are evident from synchrotron data.

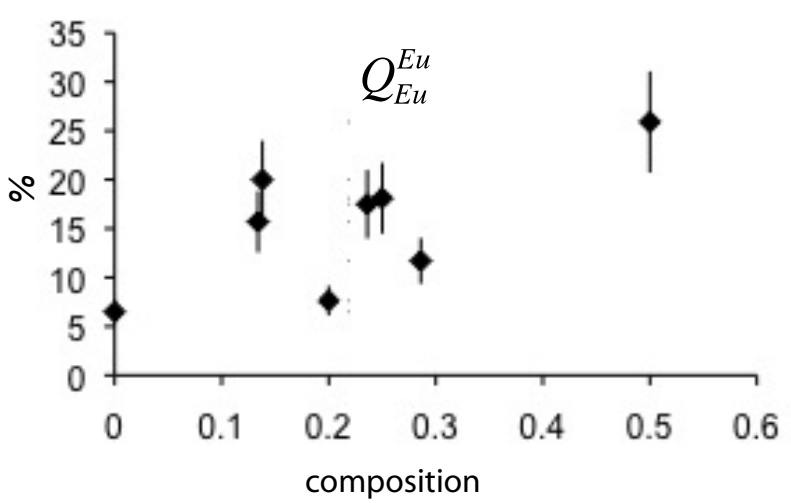
The resolution of their structure in superspace shed some new light on their structure property relation.

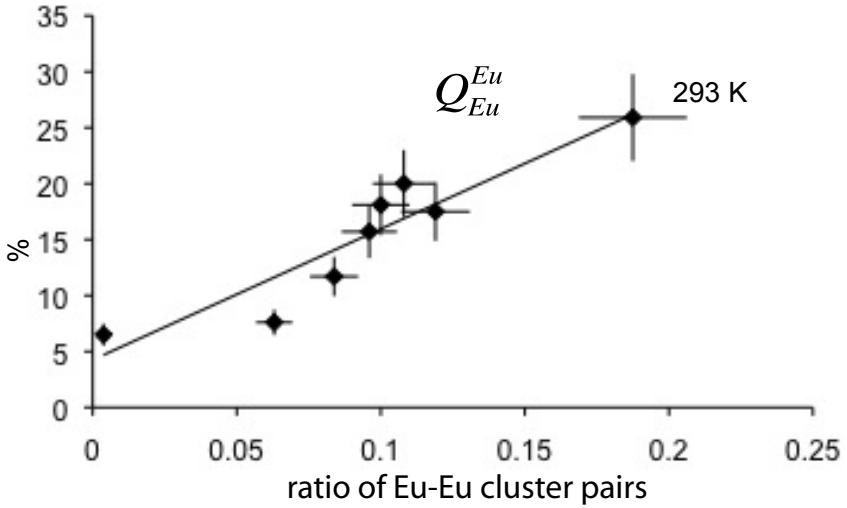


Some more with structure property relations (luminescence)



Some more with structure property relations (luminescence)





Superspace and structure-property relations

- The superspace concept is particularly efficient in order to reveal fine details in complex structures
- Neglecting to account for “small” peaks in diffraction patterns or by considering them as “impurities” is tantamount to average the structure and consequently disregard all fine details of the structure.
- The relation between structure and properties has often been overseen due to the fact that the superspace character of the structures was not recognised.

Incommensurately modulated crystals and applications

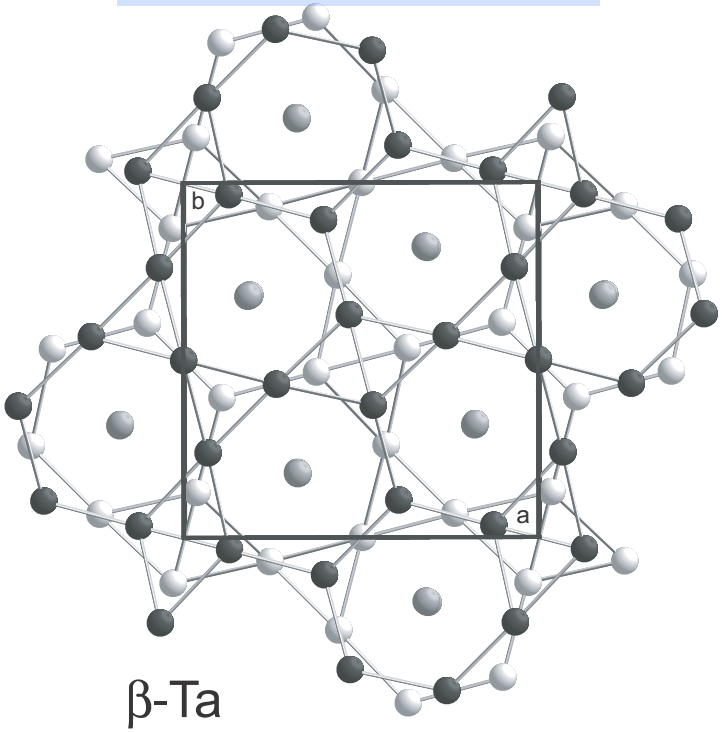
Examples of modulated structures

- Na_2CO_3
- A member of the scheelite family, $KSm(MoO_4)_2$
- Extension of the structure type concept exemplified with the scheelite structures
  - Applications: structure property relations
- The complex structure of metallic elements
  - Barium, Rubidium
  - Gallium II (2.8 GPa)

The structures of metals under high pressure

Often exhibit incommensuration by forming structures of the host-guest type. In particular self-hosting structures in the case of elements.

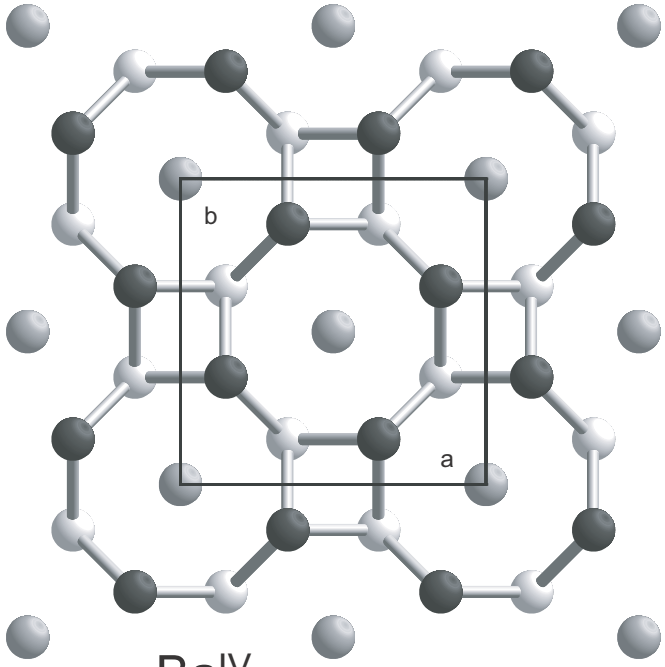
Normal pressure commensurate



β-Ta

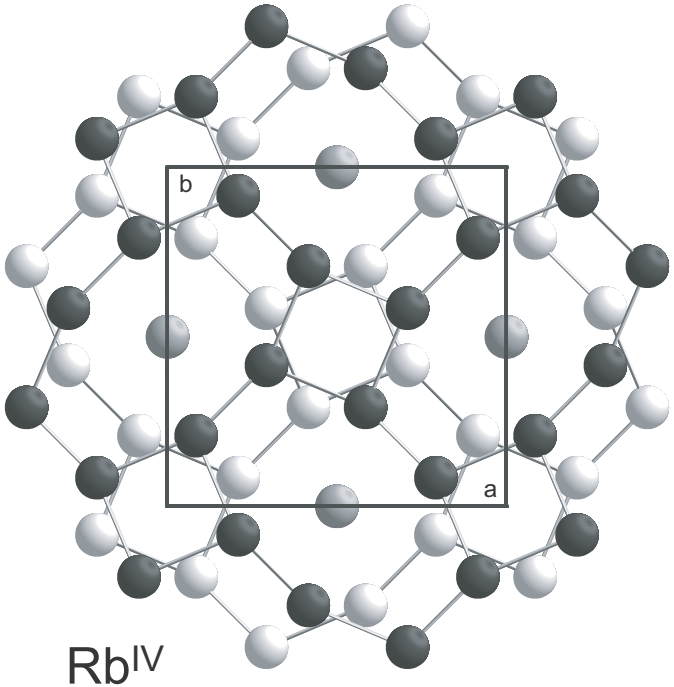
Arakcheeva *et al.* 2005

12.6<Ba^{IV}<45 GPa
I4/mcm(00γ)0000



Ba^{IV}

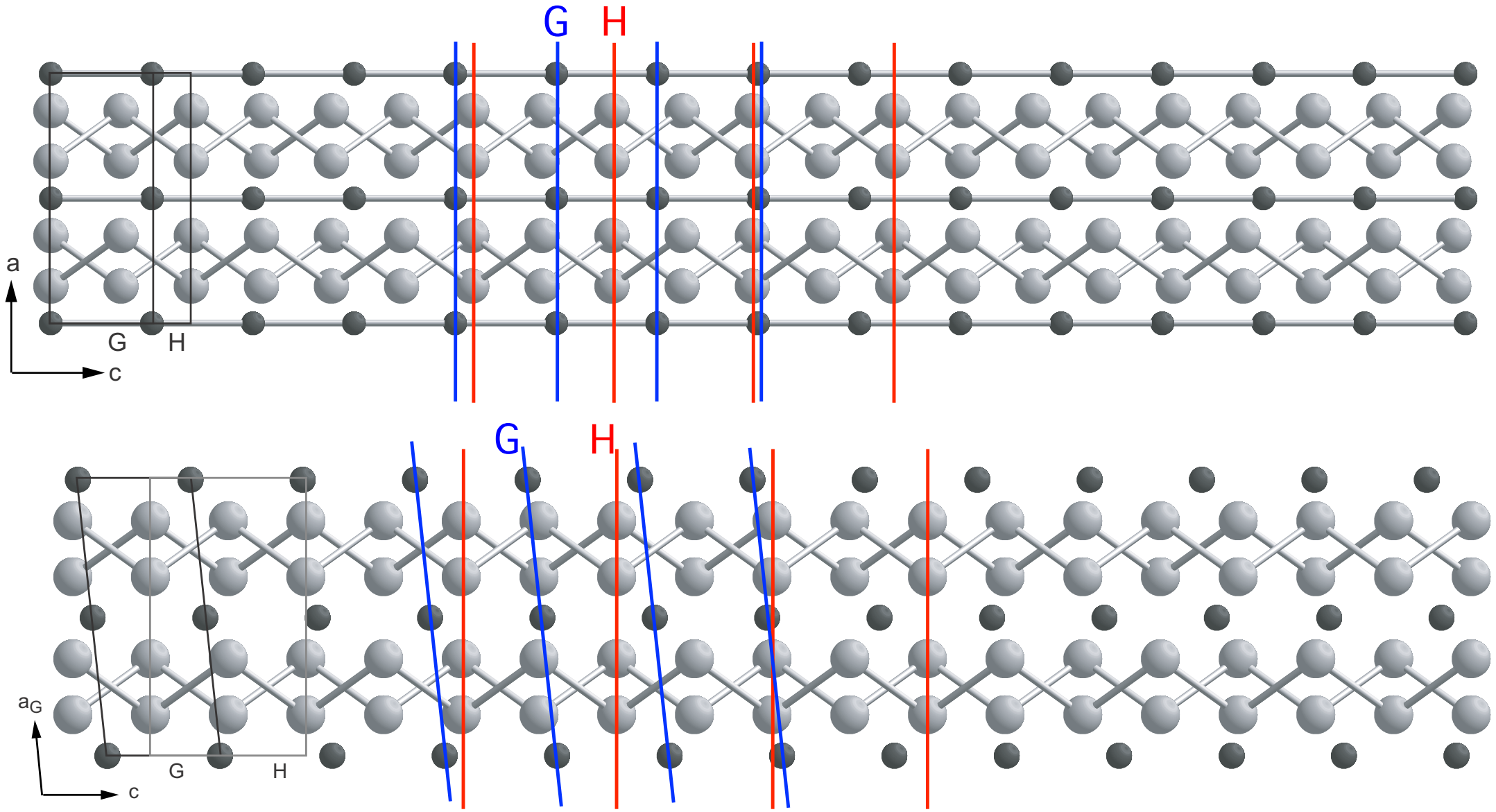
17<Rb^{IV}<20 GPa
incommensurate



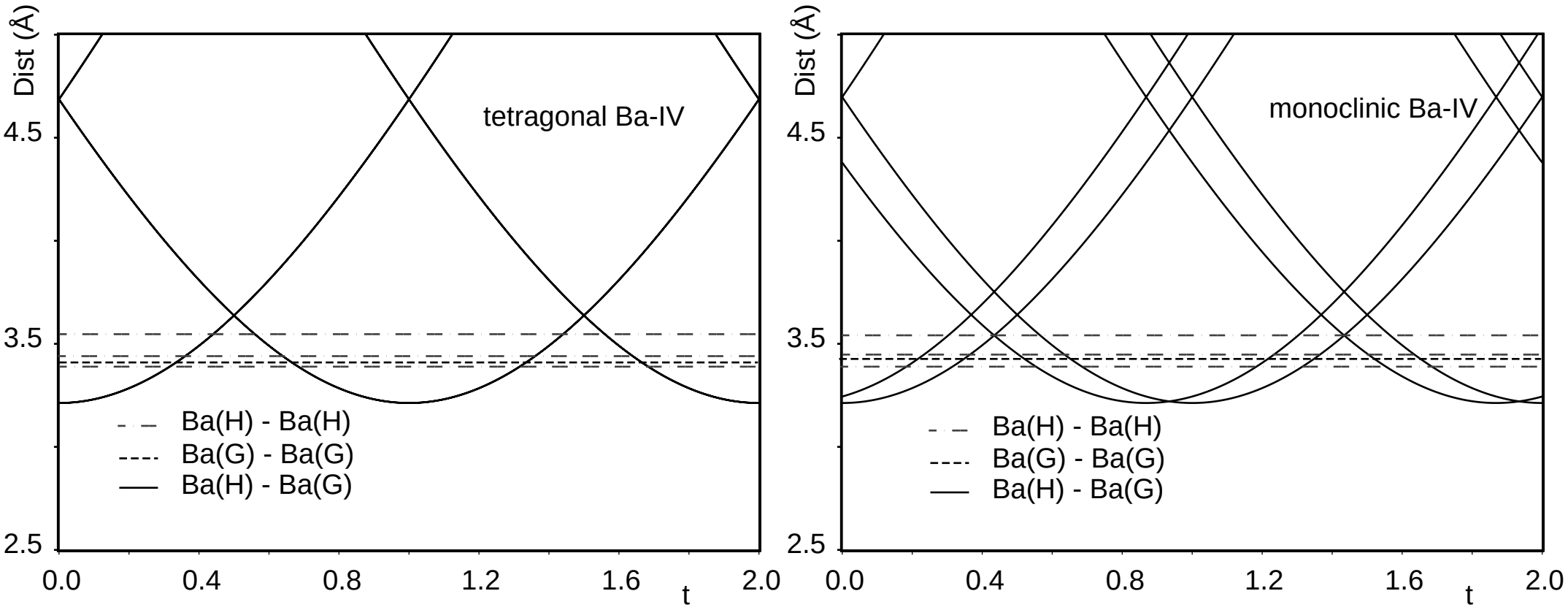
Rb^{IV}

McMahon *et al.* 2004

Ba^{IV} exists in two variants, tetragonal (top) and monoclinic (bottom)

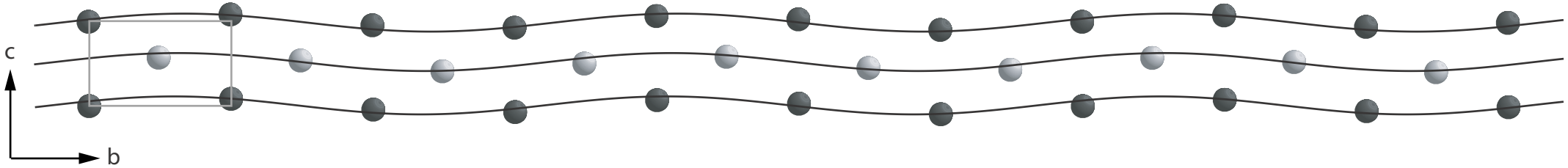


Ba-Ba distances in Ba^{IV}

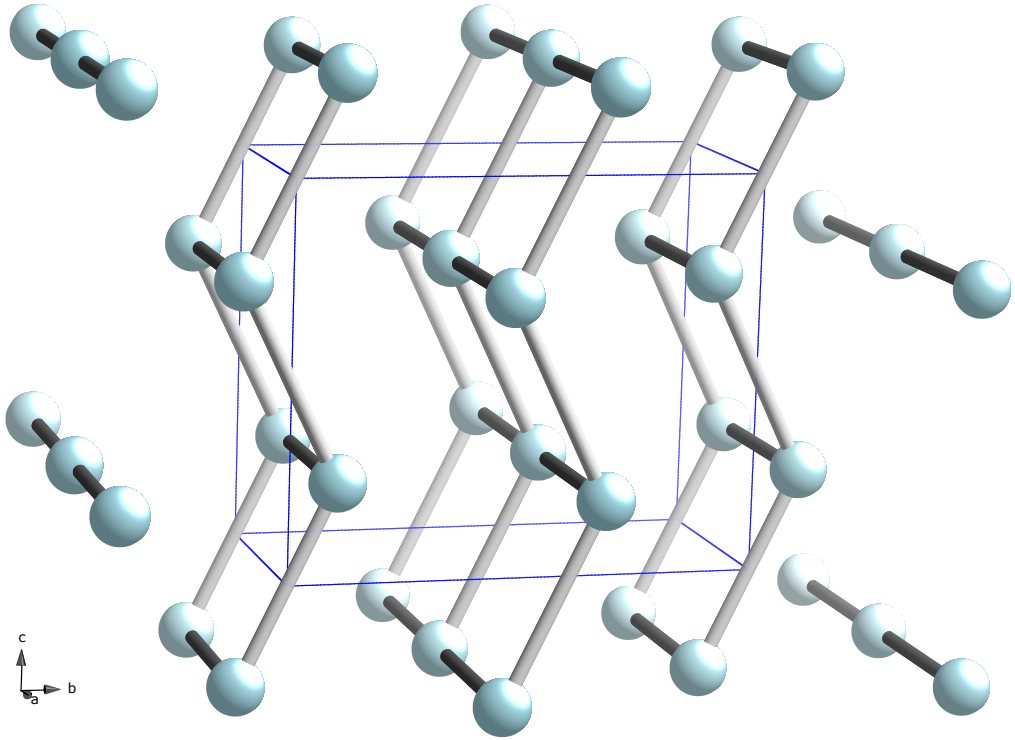


Many more examples of incommensurate structures of metallic elements exists

7< Te^{III} < 11 GPa
X2/m(0β0)s0, X=(½½½½)
Hejny *et al.* 2003



α-U < 37 K
? P2/m11(½βγ) ?
Marmeggi *et al.* 1982
van Smaalen *et al.* 1987
q=(½, .176, .182)
Main modulation along a



Structure modulations in metals under high pressure

PRL 97, 115501 (2006) PHYSICAL REVIEW LETTERS week ending 15 SEPTEMBER 2006

Apparently Complex High-Pressure Phase of Gallium as a Simple Modulated Structure

J. M. Perez-Mato,[1,*] Luis Elcoro,[1] Mois I. Aroyo,[1] Hannelore Katzke,[2] Pierre Tolédano,[3] and Zunbeltz Izaola[1]

[1]*Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo 644, 48080 Bilbao, Spain*

[2]*Institute of Geosciences, Crystallography, University of Kiel, 24098 Kiel, Germany*

[3]*Department of Physics, University of Picardie, 80000 Amiens, France*

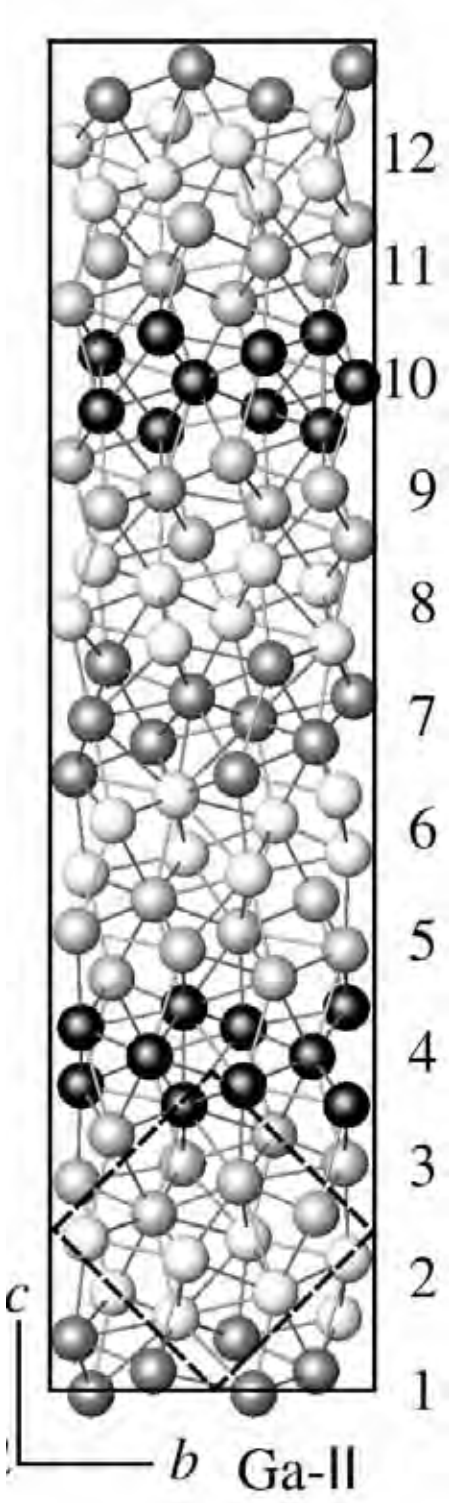
(Received 4 July 2006; published 13 September 2006)

The phase of gallium GaII, with symmetry $C222_1$ and 104 atoms per unit cell, has been recently reported as an example of *structural complexity* under high pressure. It is shown here that this phase is a simple modulated distortion of an average structure of *Fddd* symmetry with all atoms structurally equivalent. The modulation can be described with only 4 parameters and satisfies symmetry properties described by a centrosymmetric superspace group. The structural distortion is dominated by a frozen transversal mode associated with a single irreducible representation of *Fddd*, with a wave vector on the line Q, at an edge of the Brillouin zone. The average structure can be related with an hcp configuration through simple sliding of hcp layers, reminiscent of the hcp-bcc Bürgers mechanism.

Gallium II (Degtyareva *et al.* 2004)

TABLE I. Refined atomic coordinates of Ga-II ($oC104$) at 2.8(1) GPa and RT in space group $C222_1$. The refined lattice parameters are $a = 5.976(1)$ Å, $b = 8.576(1)$ Å, $c = 35.758(3)$ Å. The number of nearest-neighbor (nn) distances is given in ranges (i) 2.65–2.7 Å, (ii) 2.7–3.1 Å, and (iii) 3.1–3.3 Å. These ranges are selected for comparison with Cs-III and Rb-III [7,8], and the upper bound of 3.3 Å is set at the first minimum in the distribution of contact distances.

		Atomic coordinates ($\times 10^4$)			No. of nn distances		
	Site	x	y	z	(i)	(ii)	(iii)
Ga1	4b	5000	1802(9)	2500	2	8	0
Ga2	8c	6956(9)	4684(7)	2716(2)	2	8	0
Ga3	8c	5804(9)	7858(8)	2861(2)	0	10	0
Ga4	8c	2772(9)	5622(7)	3081(2)	0	10	0
Ga5	8c	−341(7)	7809(6)	3292(2)	1	9	0
Ga6	8c	8482(8)	4567(6)	3430(2)	1	9	0
Ga7	8c	5632(9)	6919(6)	3666(2)	0	10	0
Ga8	8c	2324(8)	4838(7)	3851(2)	0	9	1
Ga9	8c	6129(10)	2914(7)	4003(2)	1	9	0
Ga10	8c	8276(10)	5660(7)	4250(2)	1	8	1
Ga11	8c	−30(9)	2613(7)	4435(2)	1	7	2
Ga12	4a	2460(9)	0	5000	0	8	2
Ga13	8c	1052(10)	3090(7)	5170(2)	0	8	2
Ga14	8c	3574(8)	5518(7)	5409(2)	1	8	1



Gallium II (Perez-Mato *et al.* (2006)

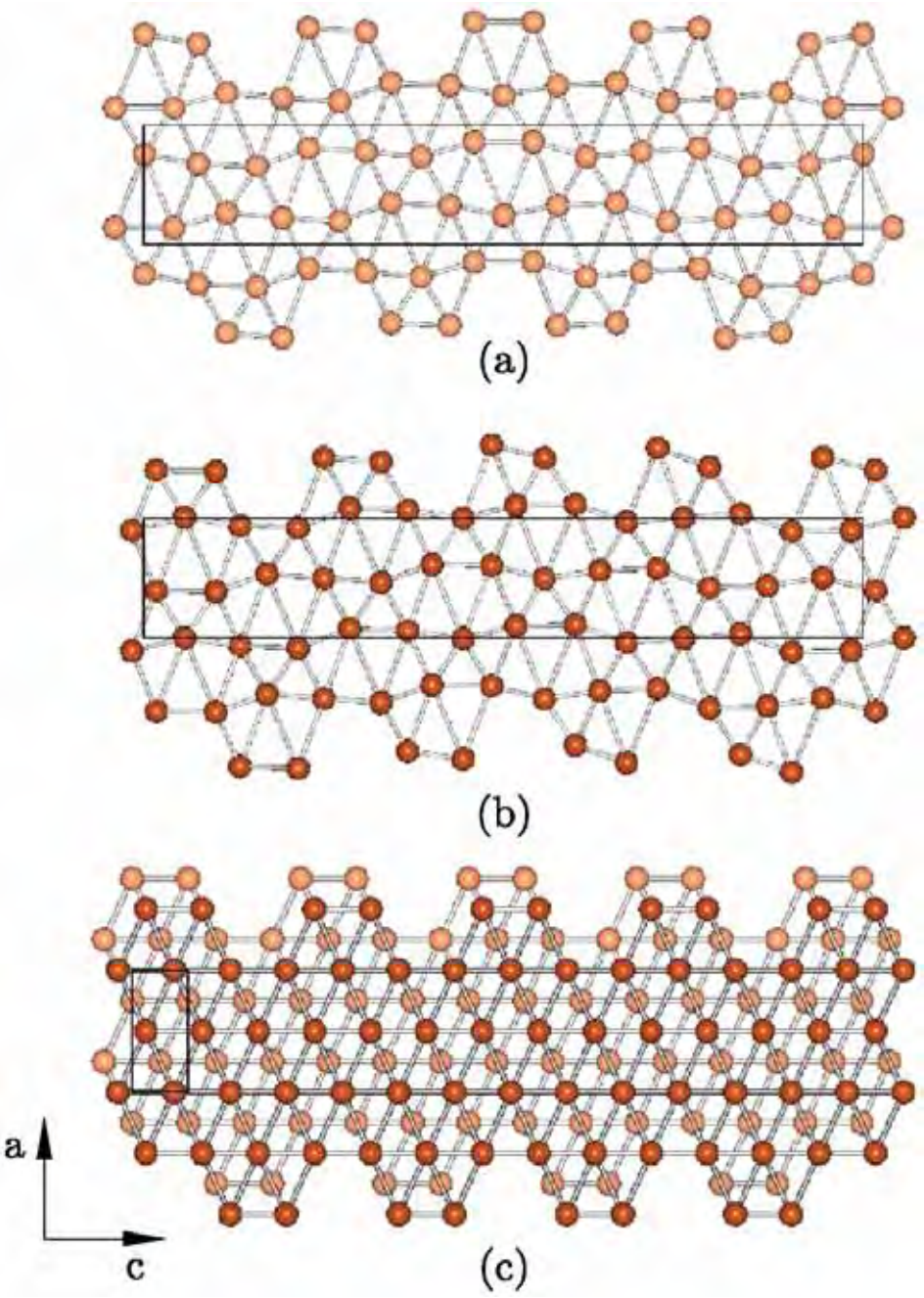
Analysis of the “complex” structure

- four hexagonal layers normal to b.
- Two are related by the C centring.
- The two independent layers (a) and (b) looks very similar.

Construction of an ideal structure

- Smaller cell c_{aver}=c/13 (c).

Could this structure be interpreted as a modulated structure?

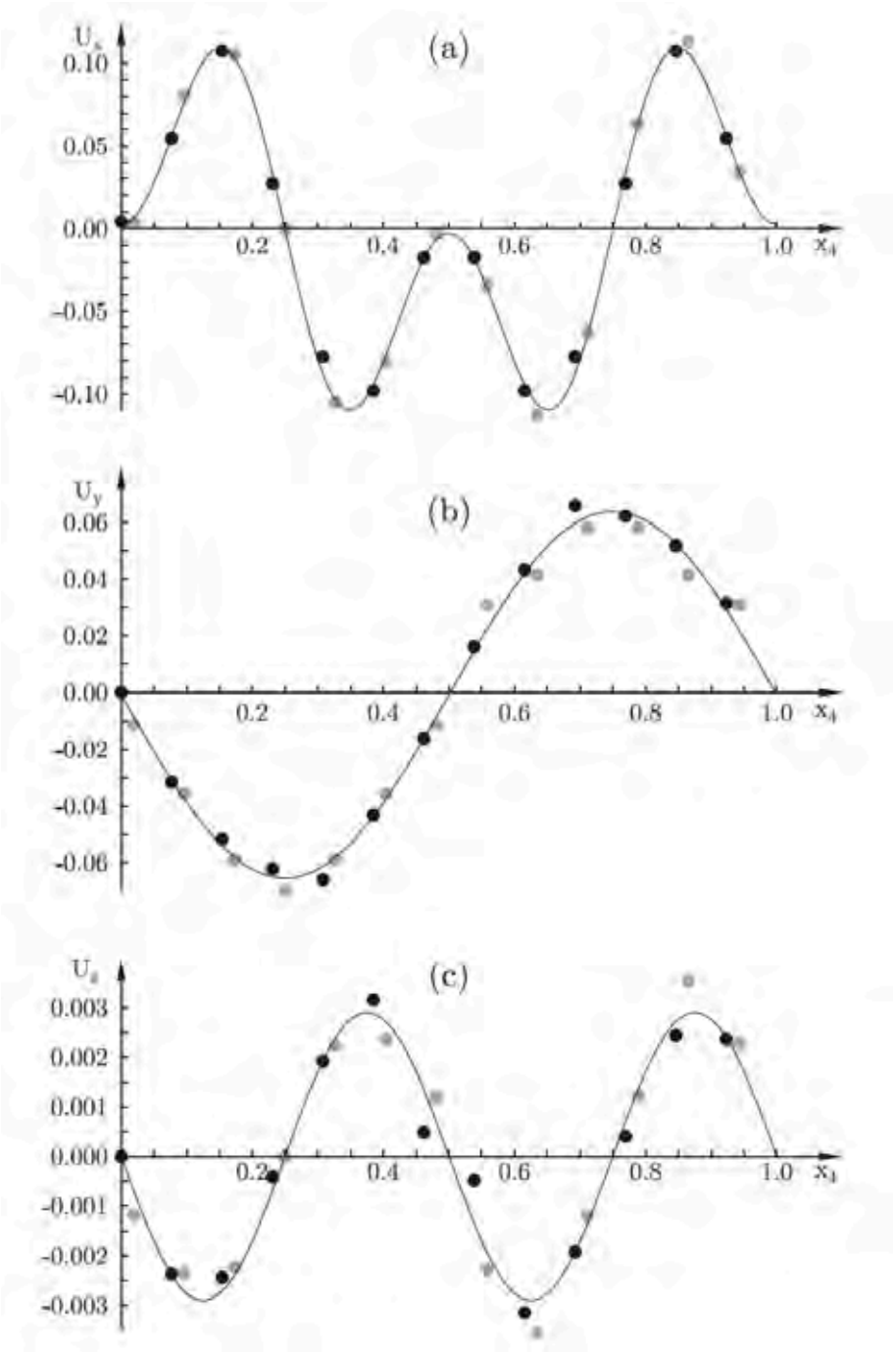


Gallium II (Perez-Mato *et al.* (2006)

Atomic displacement in relative units

- along (a), (b) and (c)
- grey and black points are related to the two independent layers
- fit the same type of modulation
- $u_x(x_4) = A\cos 2\pi x_4 + B\cos 6\pi x_4$
- $u_y(x_4) = A\sin 2\pi x_4$
- $u_z(x_4) = A\sin 4\pi x_4$
- $\mathbf{q} = n/13\ \mathbf{c}^*_{aver}$, best choice with n=9

The structure is better described as a modulated structure in superspace group *Fddd*(00γ)0s0 with 4 independent parameters (instead of 38 in the original paper.



Questions