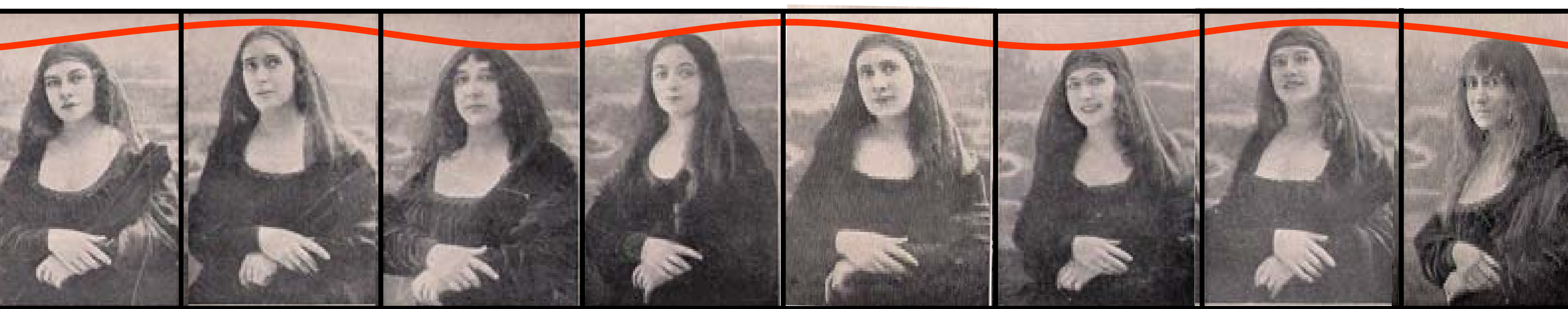
Crystal Chemistry of Modulated Structures



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Examples

1 $Zn_{3-x}Sb_2$

2 Stistaite

3 Onoratoite

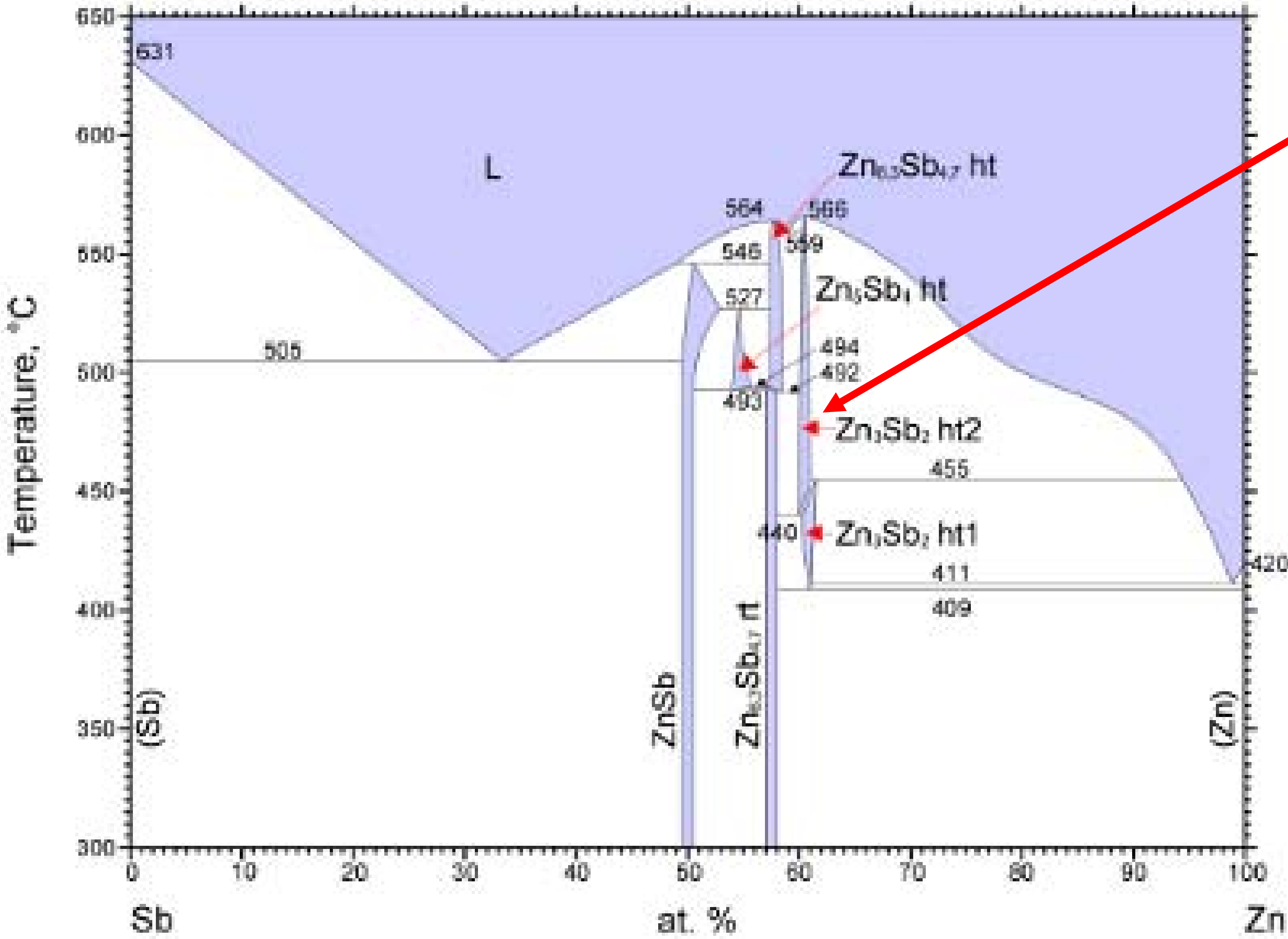
4 $Ba_2Cu_2Te_4O_{11}Br_2$ and $Ba_2Cu_2Te_4O_{11-d}(OH)_{2d}Br_2$

5 $Ca_{28}Ga_{11}$

6 $Re_{13}(Cd/Zn)_{\sim 58}$

7 $ReGe_{2-x}$

$Zn_{3-x}Sb_2$



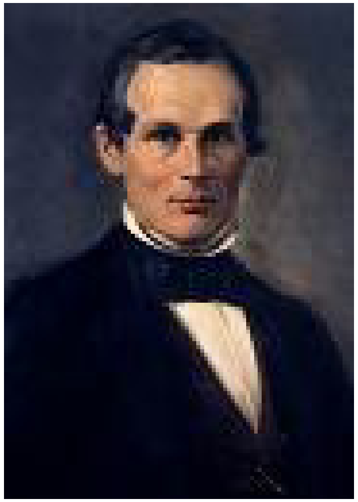
650
600
550
500
450
400
350
300
Temperature, °C
631
L
564
566
559
545
527
505
494
492
493
Zn_3Sb_2 ht2
455
440
Zn_3Sb_2 ht1
420
411
409
(Sb)
ZnSb
(Zn)
0
10
20
30
40
50
60
70
80
90
100
Sb
at. %
Zn

Modulated structure

Orthorhombic:

7.2834, 15.3976, 25.0555 Å

$q \approx (0.385\ 0\ 0)$



Anders Jöns Ångström

1814-1874

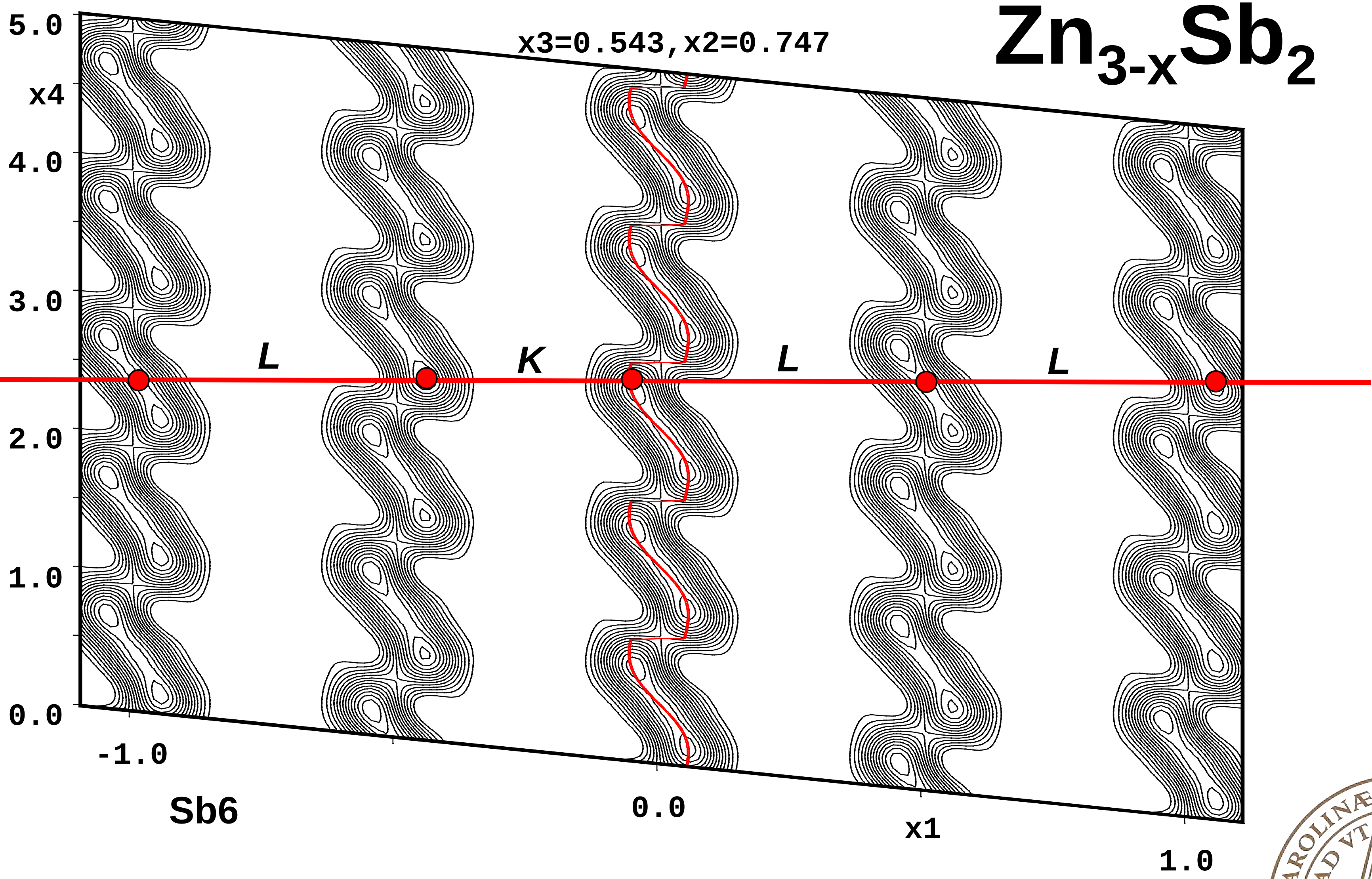
$Pnaa(\alpha 00)0s0$

Five boring Sb positions, one exciting Sb

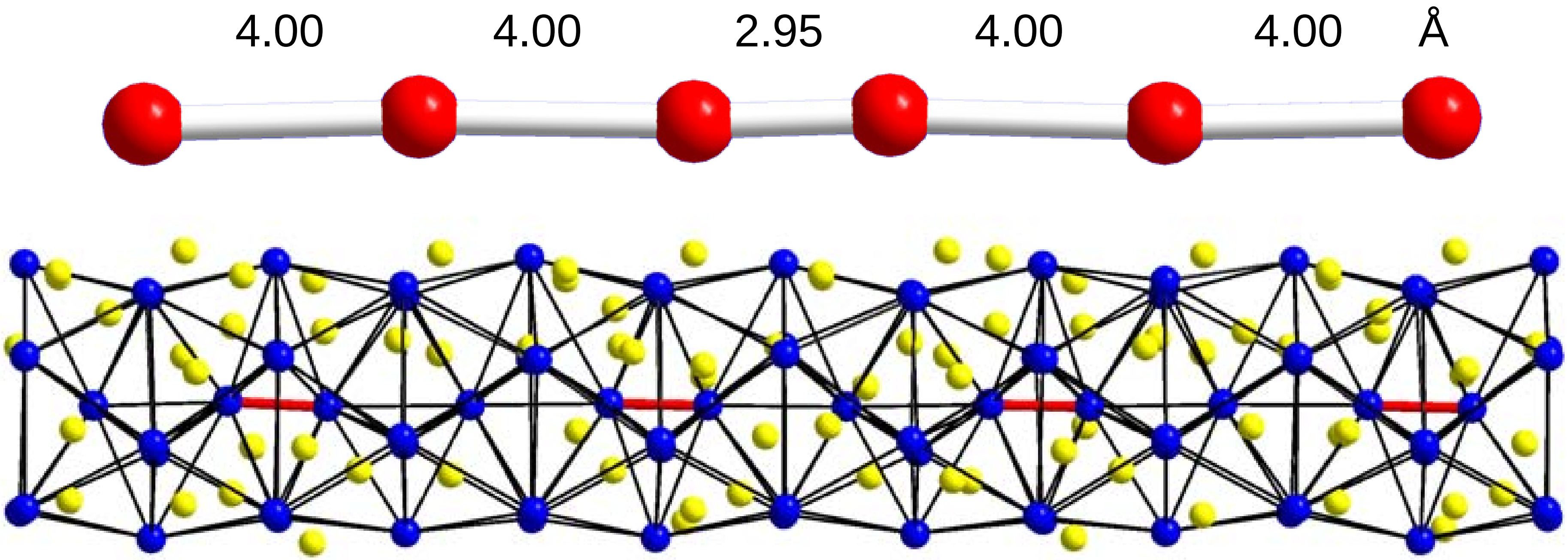
Zn all over the place!

What is going on ?

$Zn_{3-x}Sb_2$

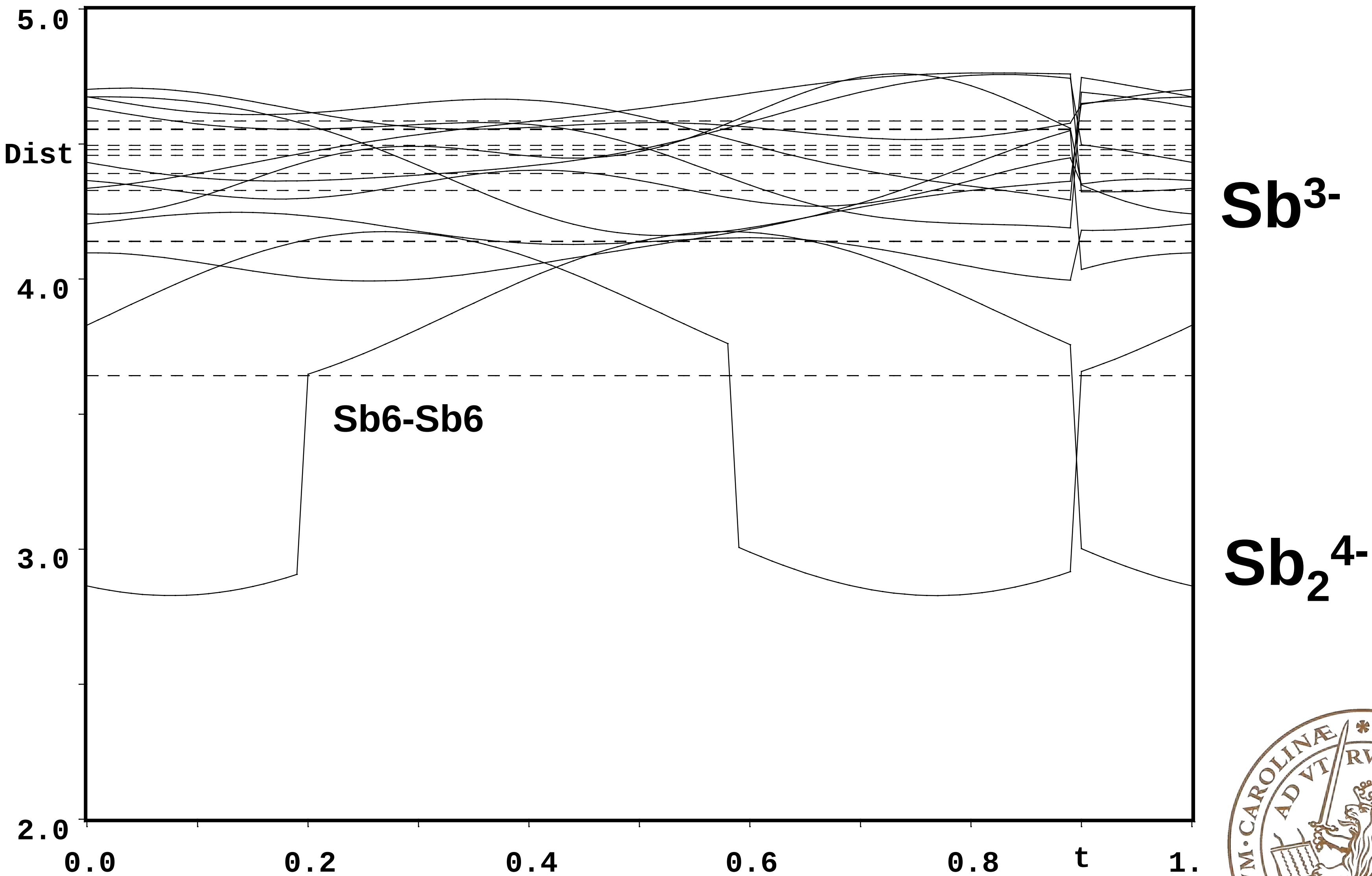


Sb^{3-}, Sb_2^{4-}



Zintl-pair formation in a pentagonal column

Sb-Sb distances



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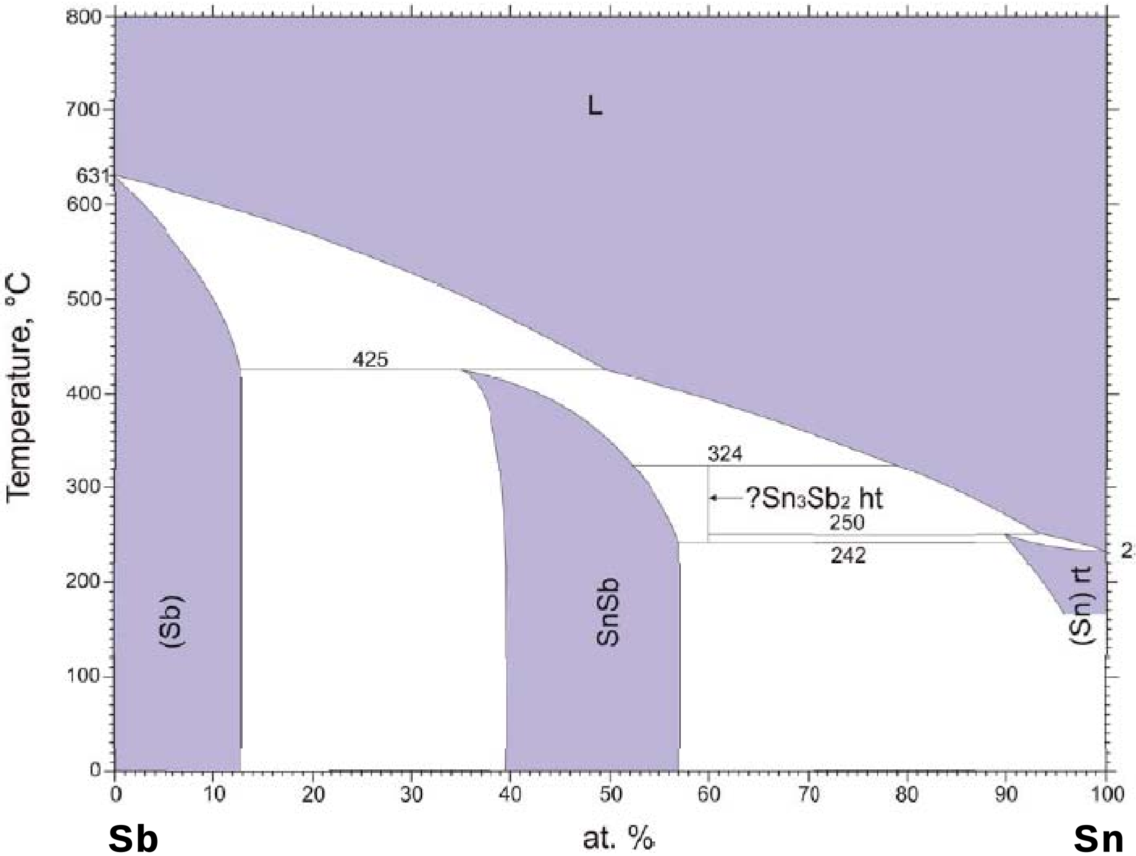
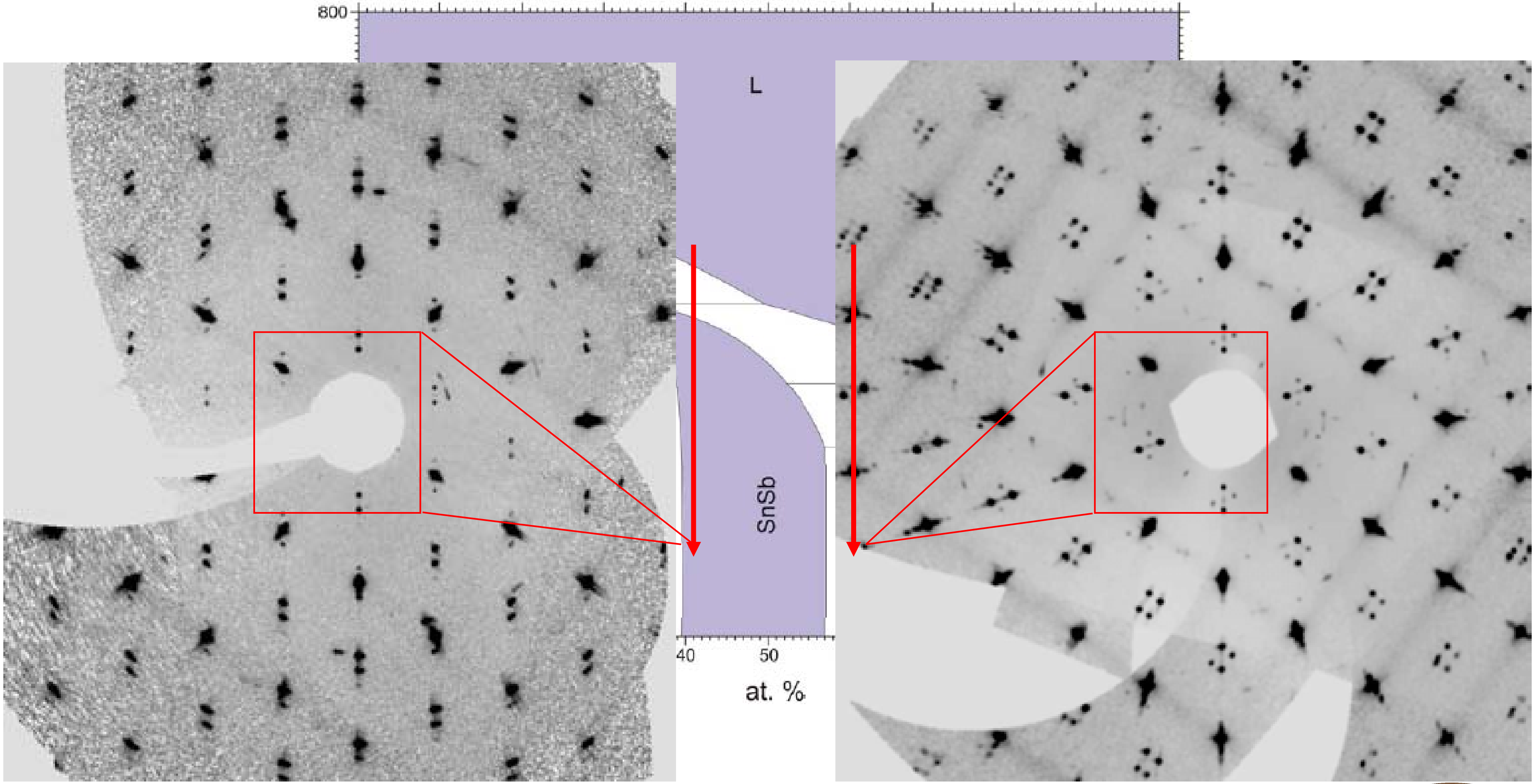
7 $ReGe_{2-x}$

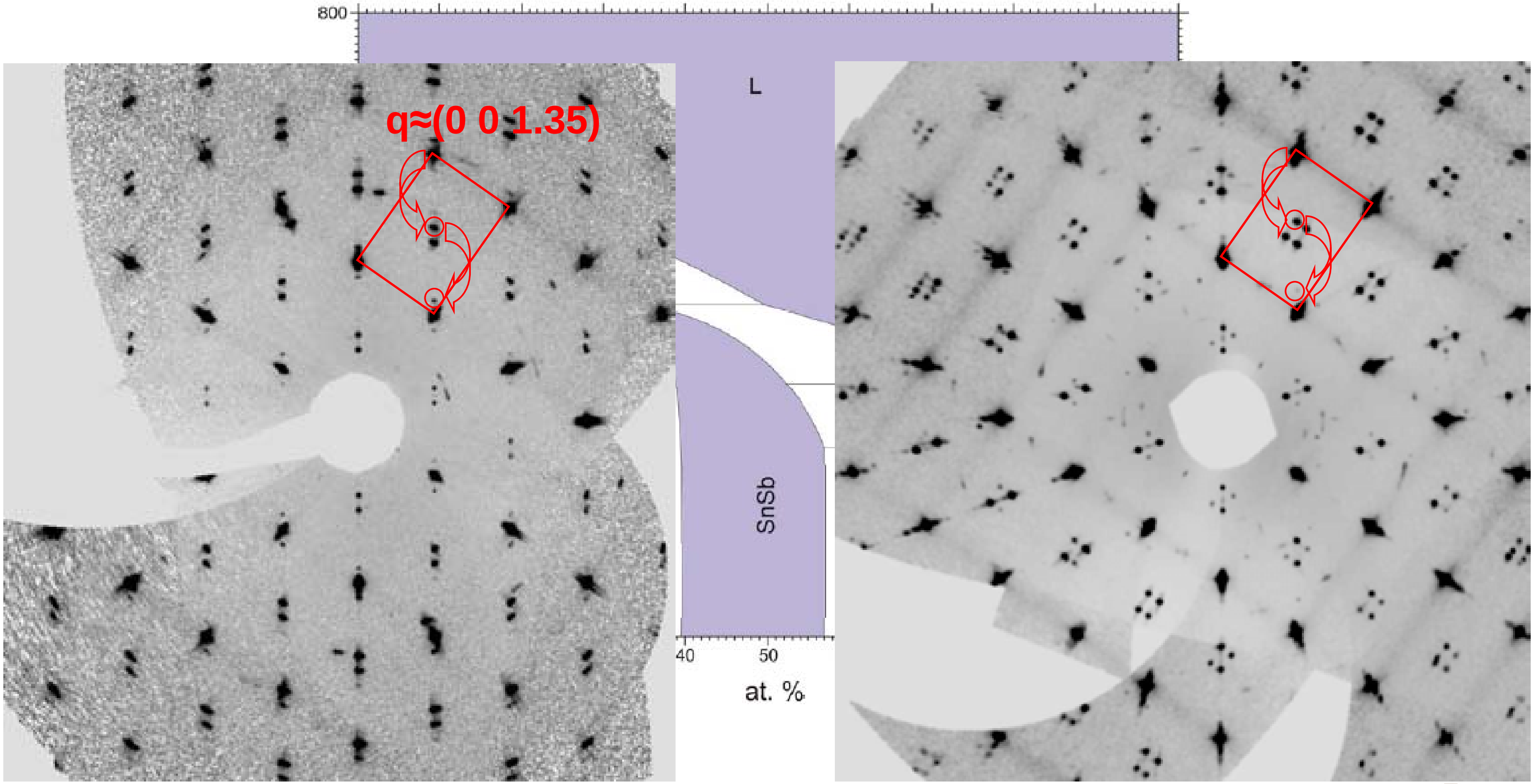
How exciting is Sb-Sn?



Diffraction from Sb-Sn

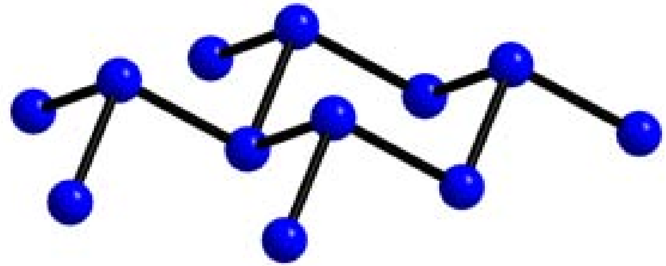


Diffraction from Sb-Sn



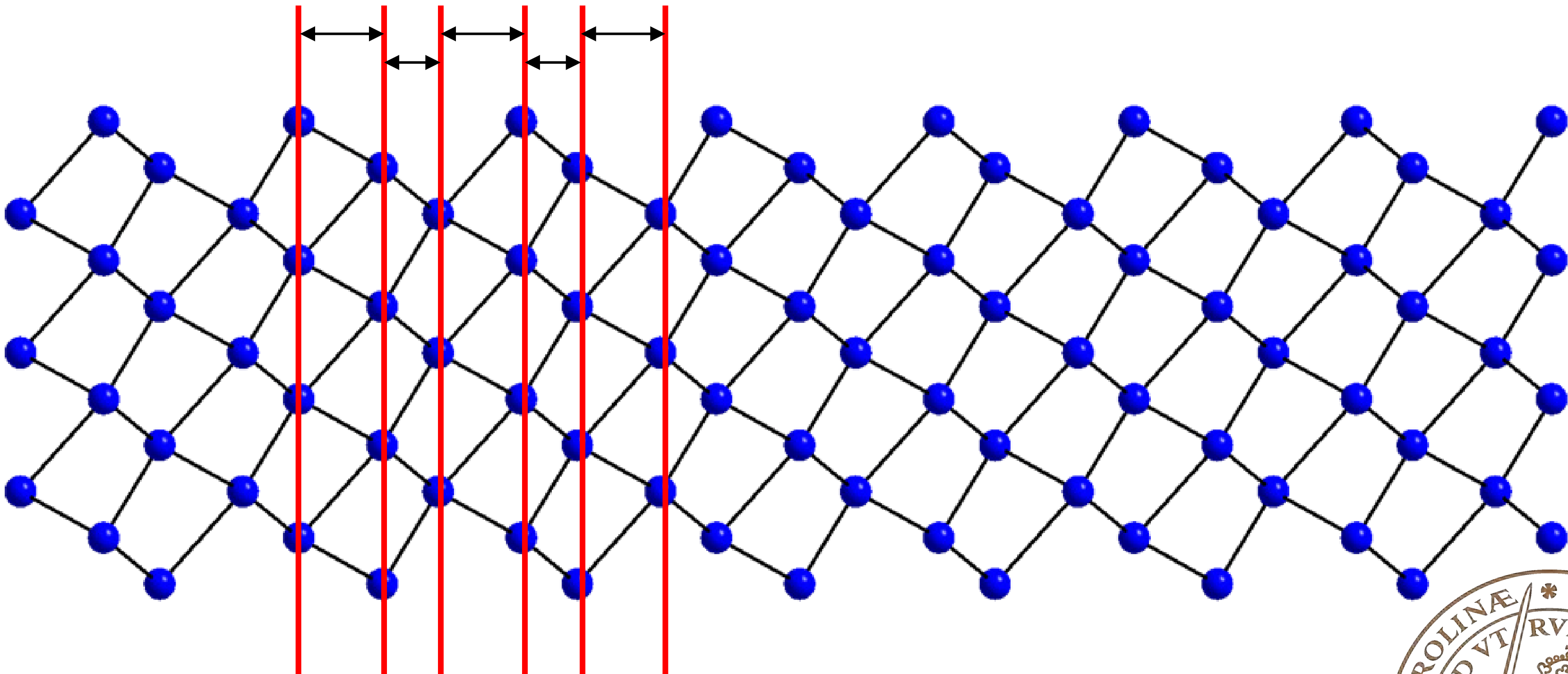
Questions of crystal chemistry:

1) What is the structure of Stistaite?
2) What is all the garbage in Sn-rich Stistaite?



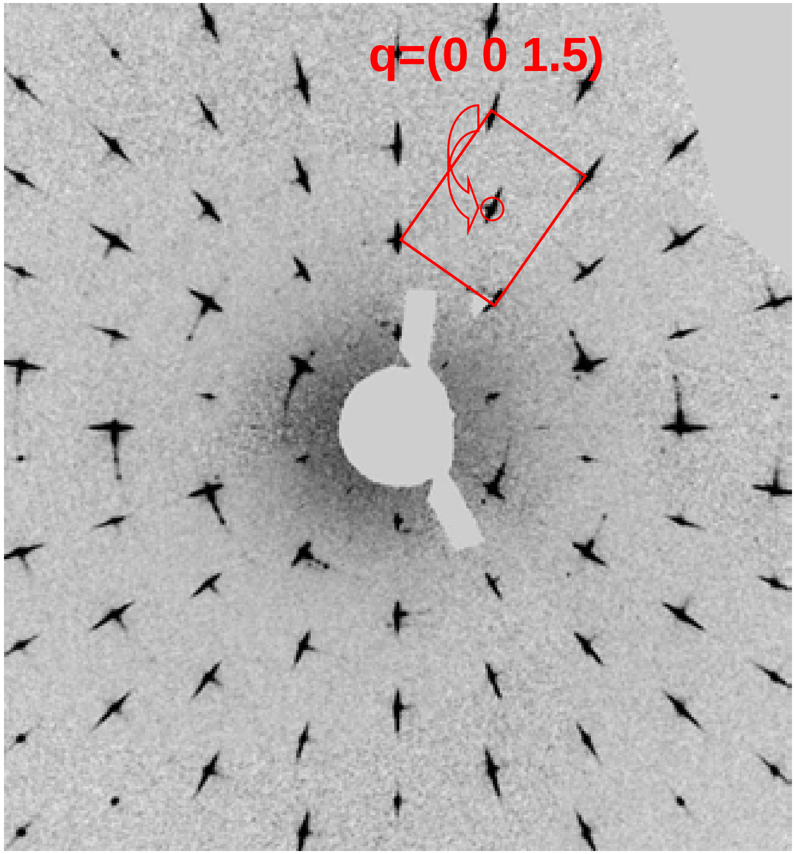
1) What is the structure of Stistait?

Das Urstoff Sb! Each Sb is 3-bonded to yield a full octet



Das Urstoff Sb - diffraction

Sb is a doubled PC struture. The effect is very strong, an it is difficult to distinguish between main reflections and satellites. The effect is purely displacive.



Symmetry/Cell

R-3m(00γ)00

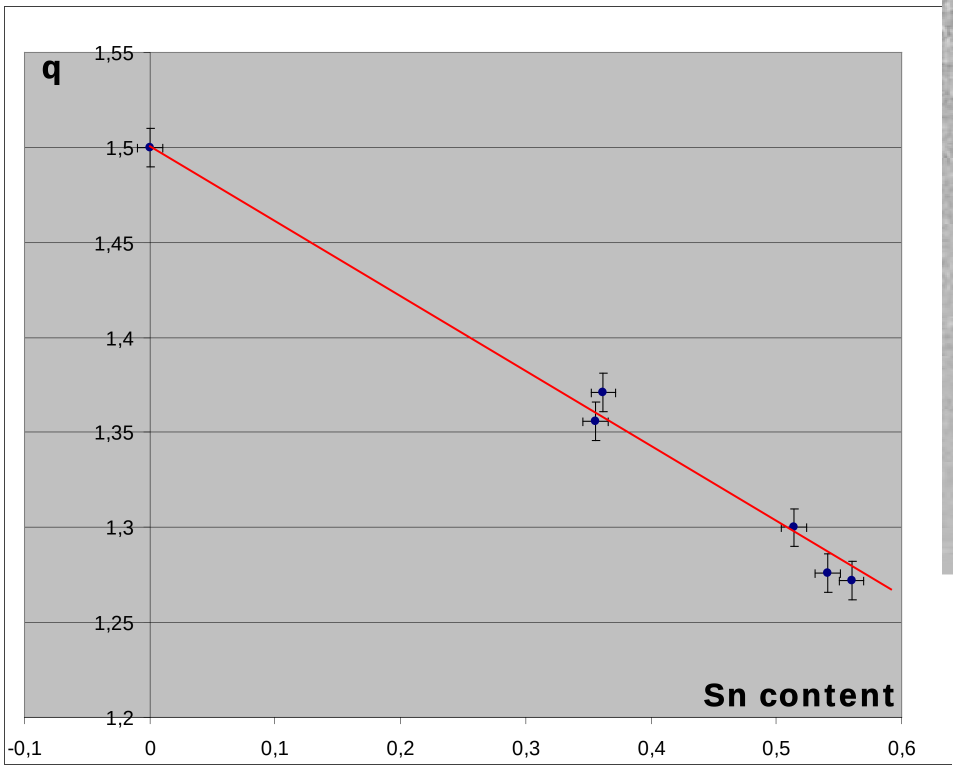
Sb :a=4.310 c=5.640 q=(0,0,1.50)

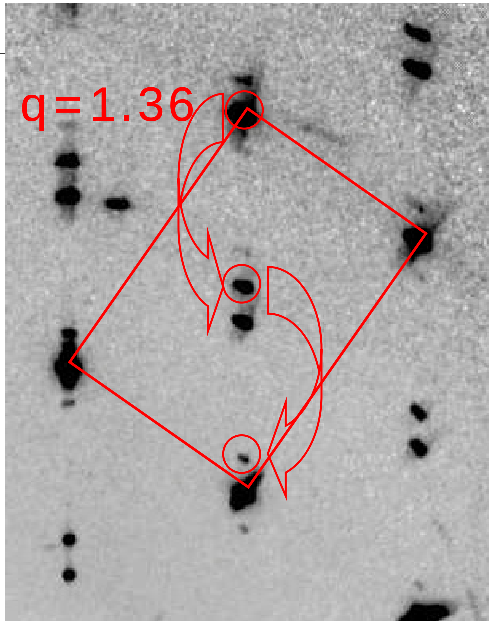
Sb_2Sn :a=4.329 c=5.412 q=(0,0,1.37)

Sb_3Sn_4:a=4.340 c=5.312 q=(0,0,1.29)

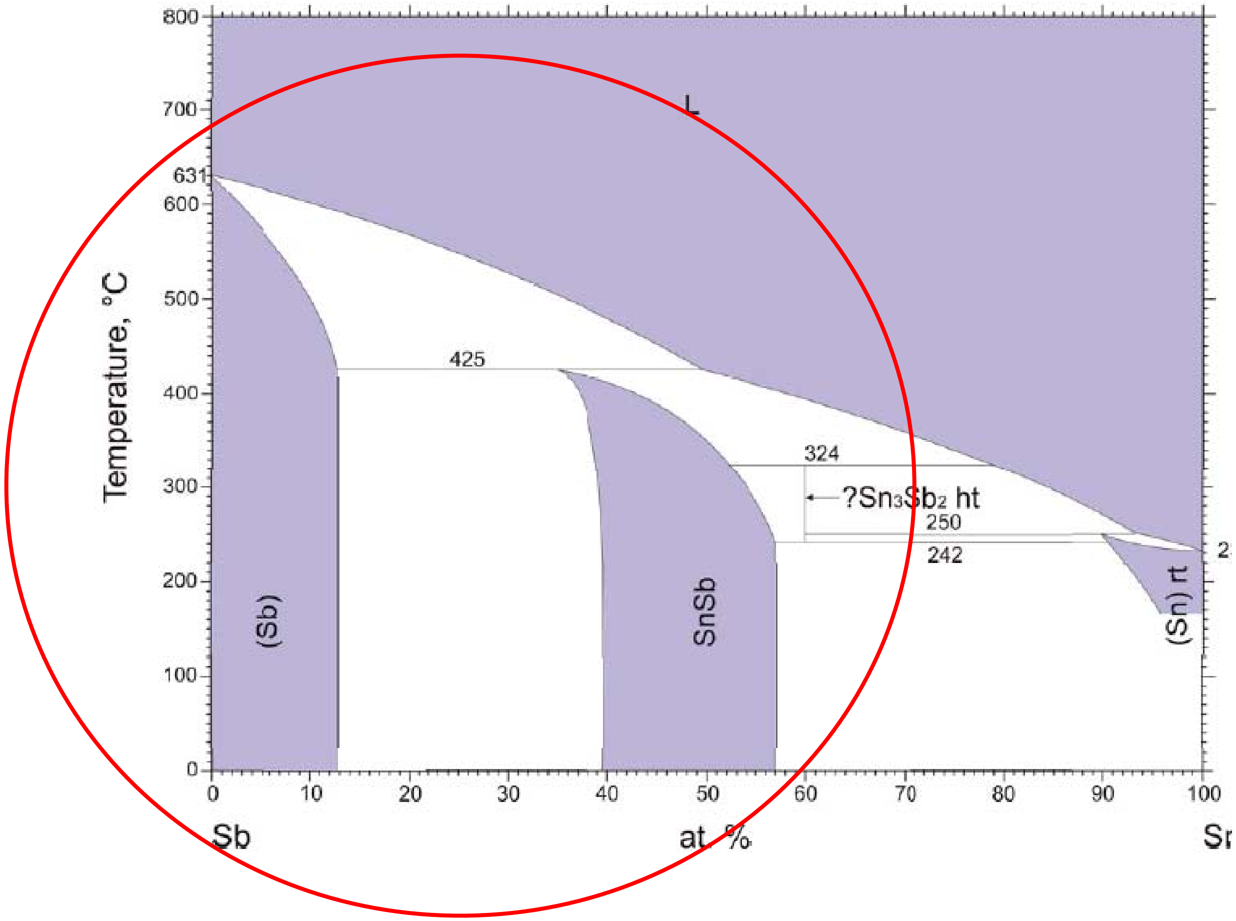
$\gamma=3/2(1-[Sn]/4)$ $[Sn]=4(1-2\gamma/3)$

It’s could be all the same

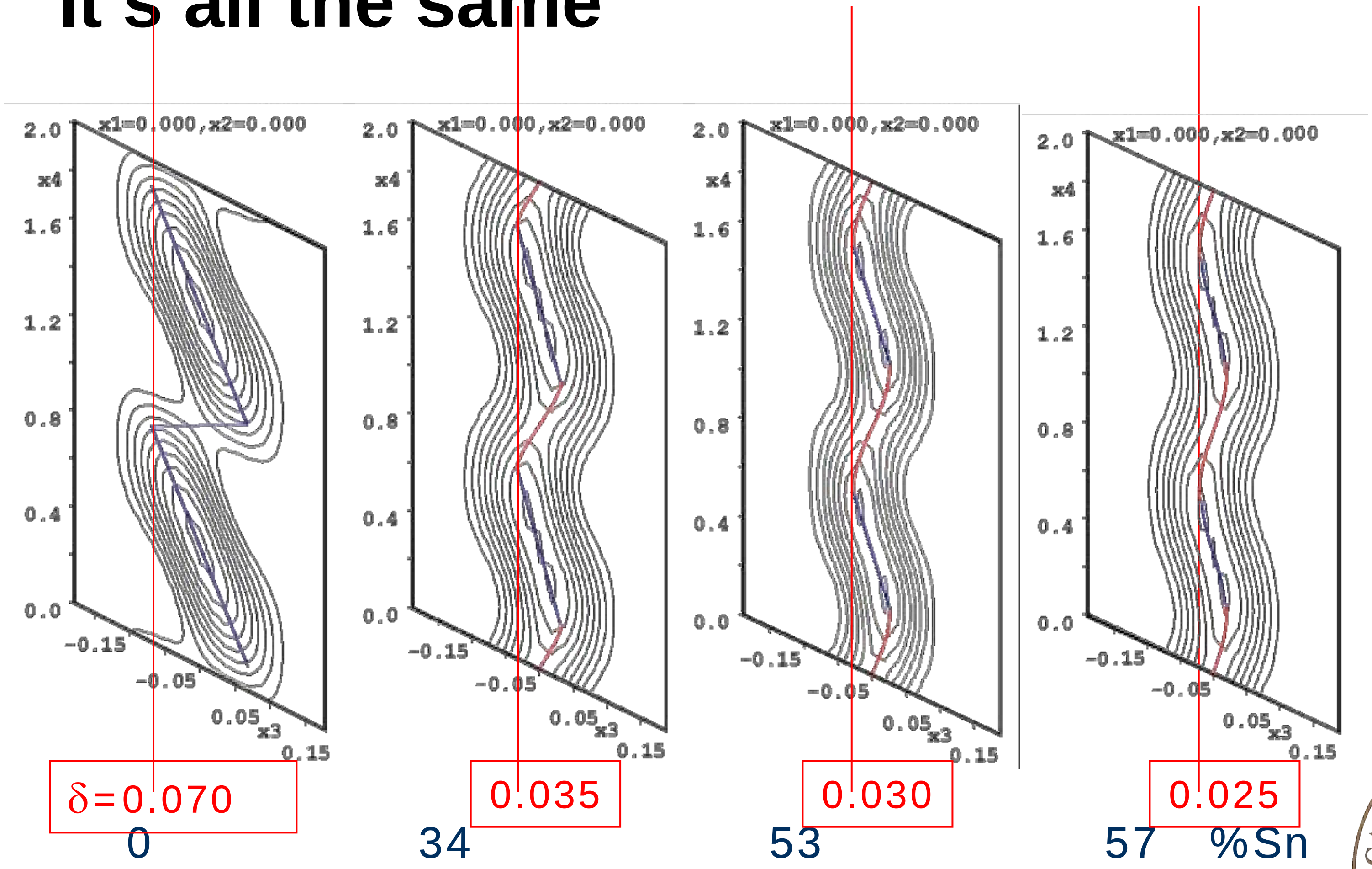




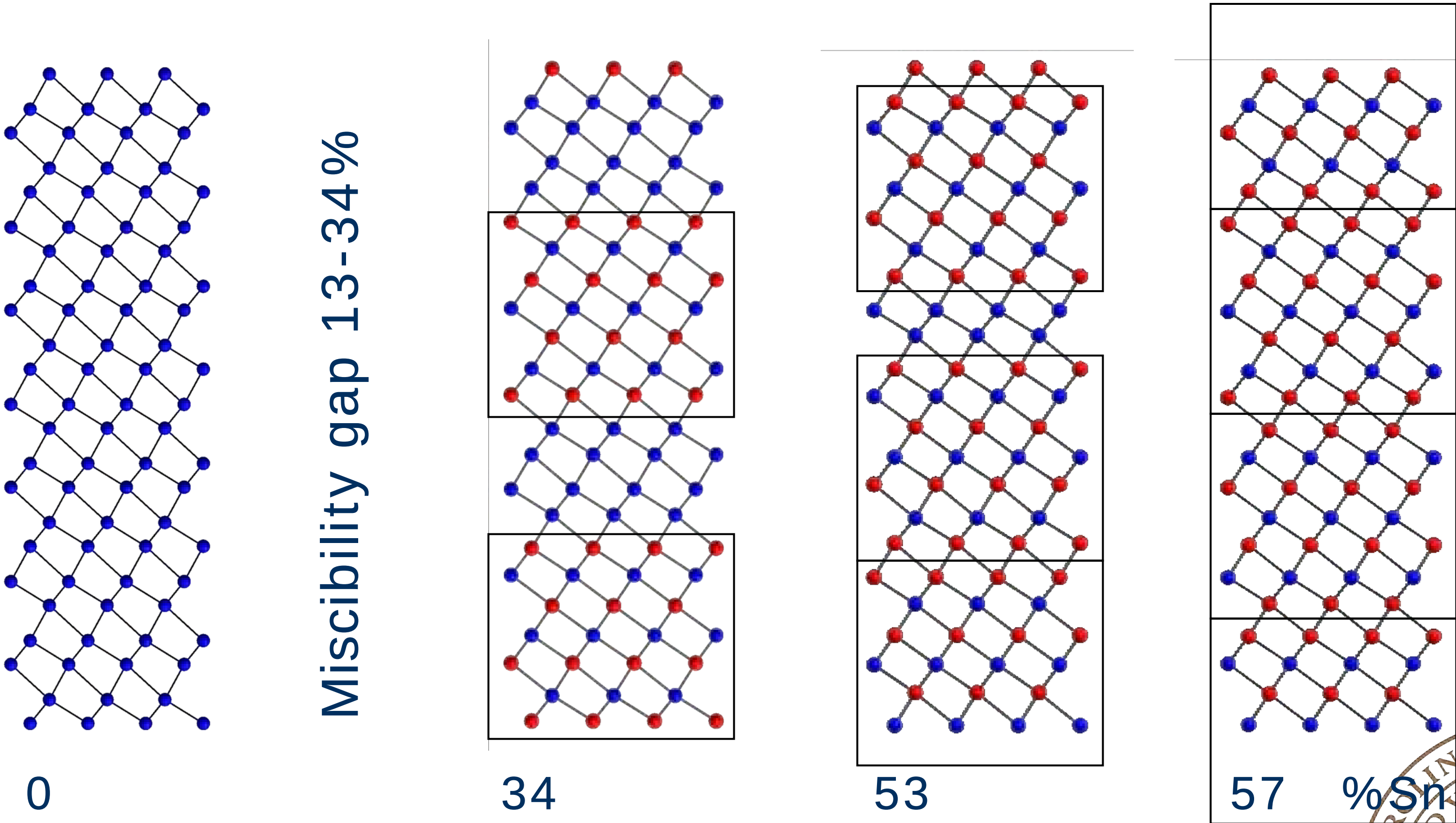
One discontinuous phase



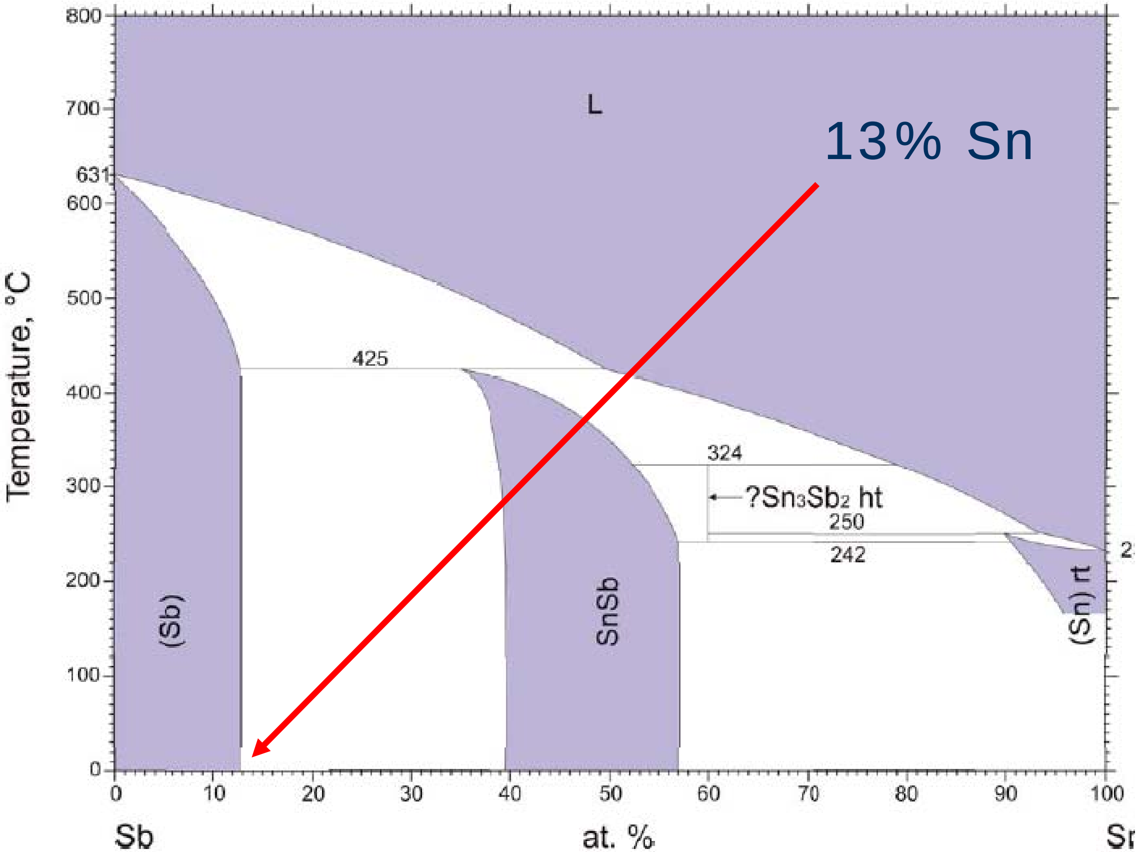
It’s all the same



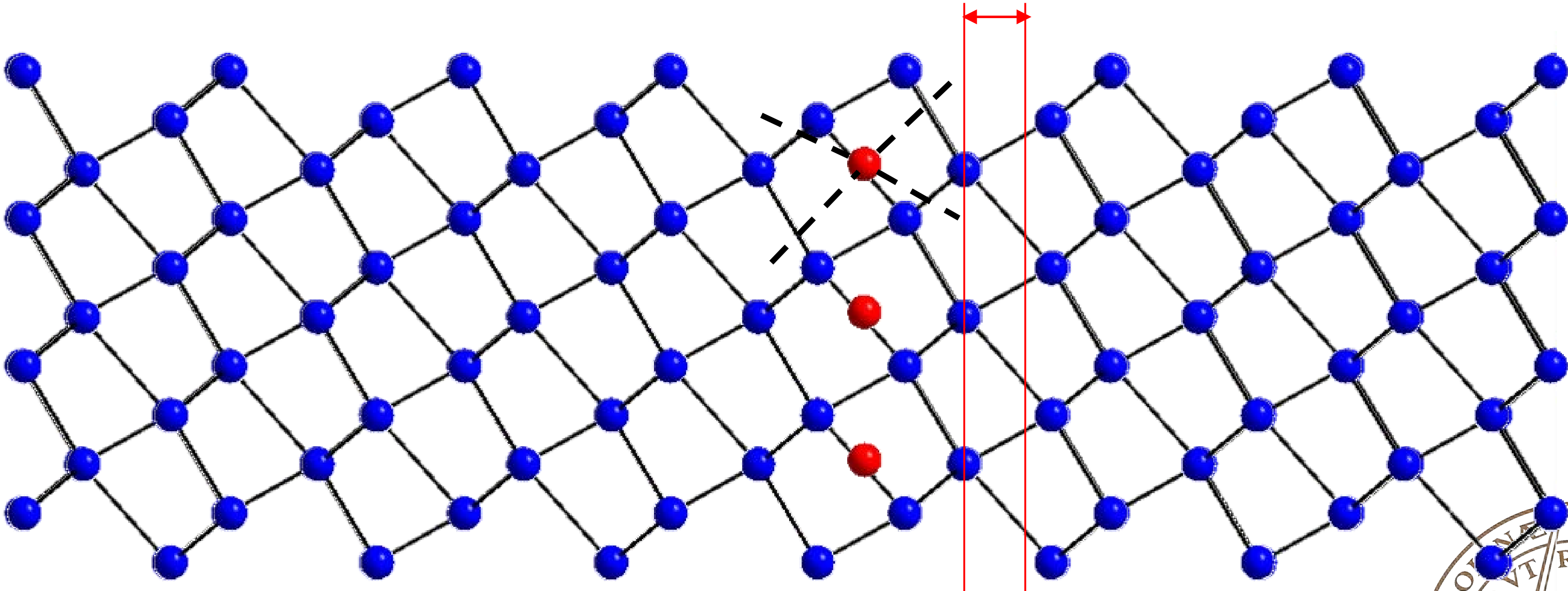
It’s all the same



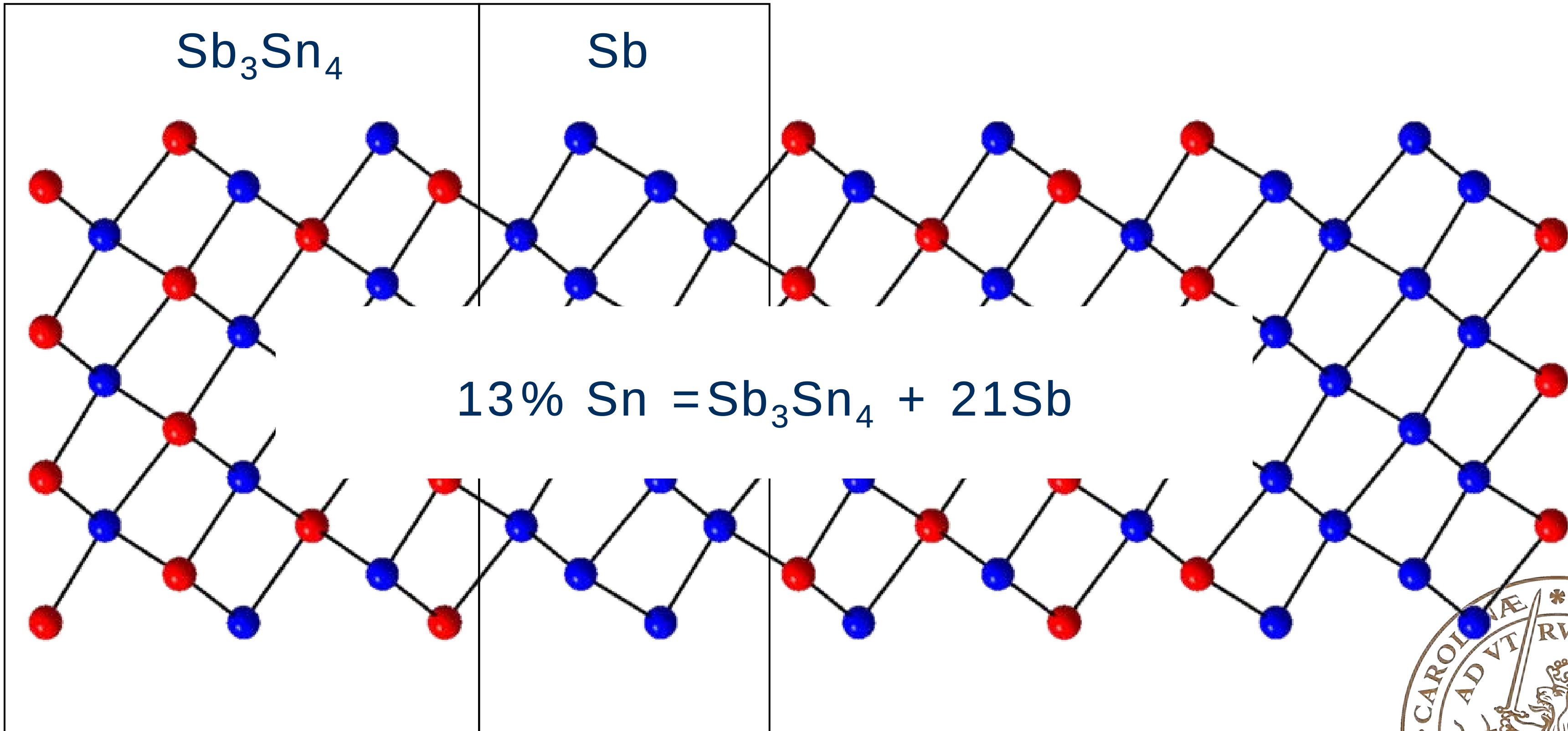
Solid solution



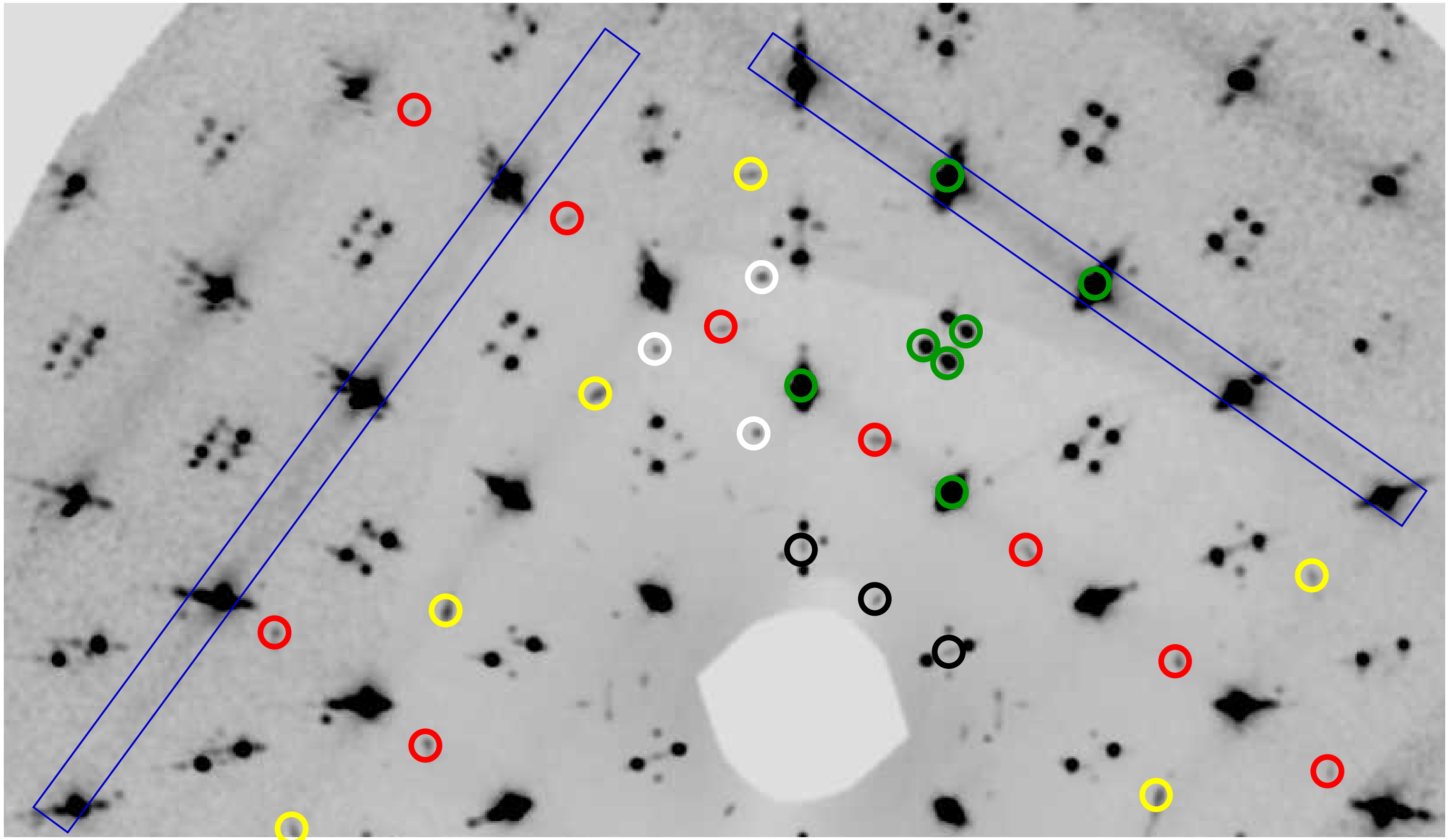
Solid solution



Solid solution

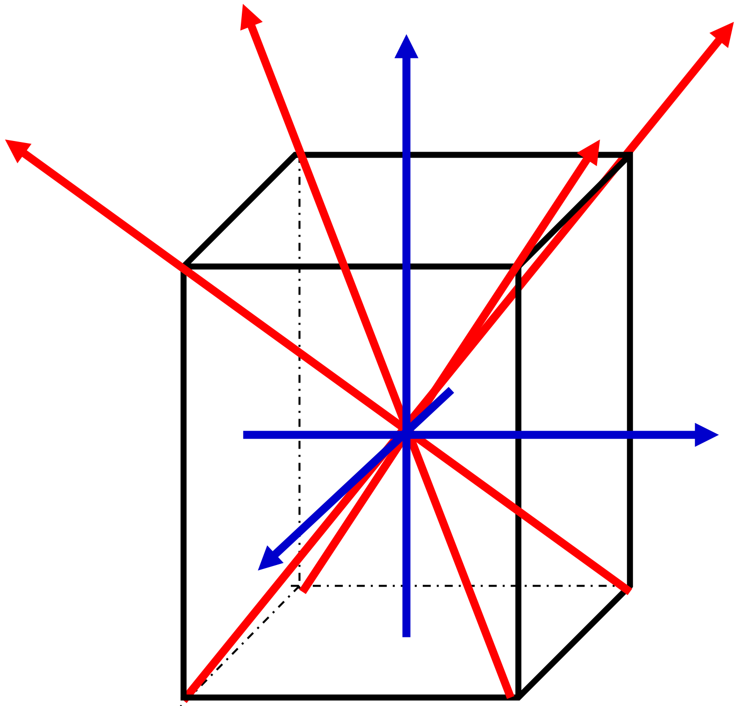


2) What is all the garbage in Sn-rich Stistaite?
Twin'n'Sn!



Stistaite
α-Sn
α-Sn
Strain
λ half

Composite diffraction pattern



Sn
SbSn

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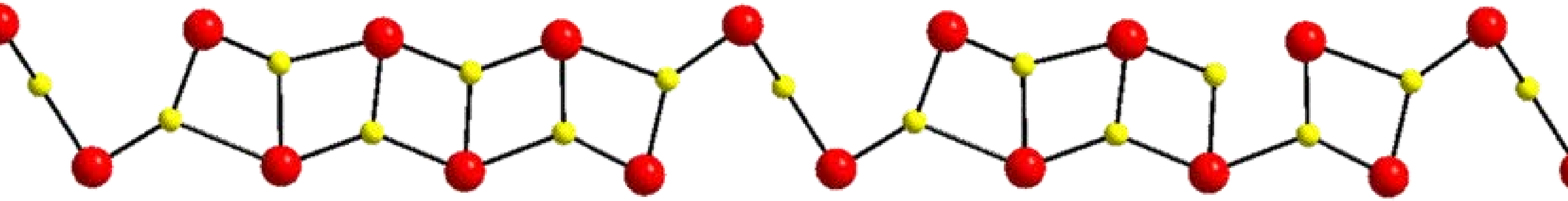
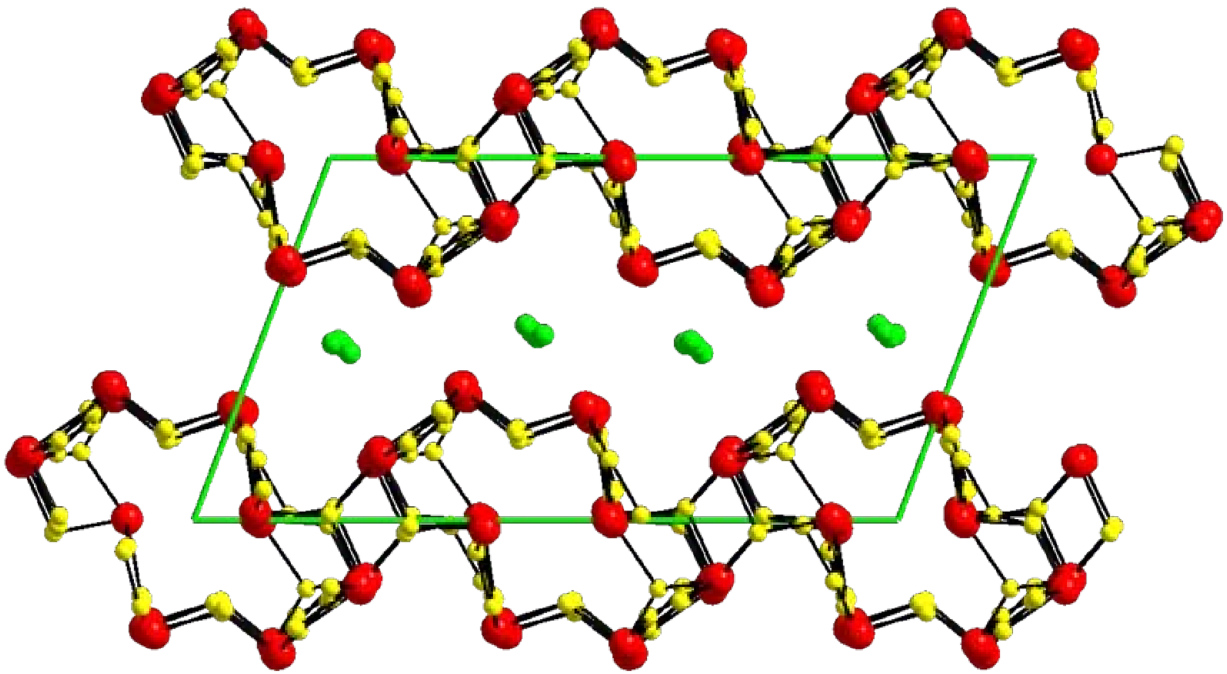
Onoratoite



In each column, oxygen vacancies order to form a fourfold superstructure along b.

Cl-onoratoit has $q = 0\ \frac{1}{4}\ 0$ while for I-onoratoit $q \approx \frac{1}{2}\ \frac{1}{4}\ {}^{1}/_{6}$

Onoratoite



Onoratoite

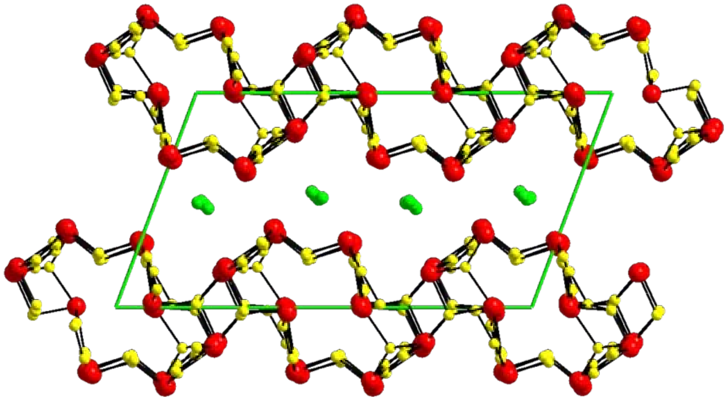
Strategy for structural solution:

Take super structure from Cl-Onoratoite, covert to modulated structure q=(¾ ¼ 0)

Reduce symmetry to triclinic, use parameters as starting model for I-Onoratoite q≈(0.5 0.25 0.16)

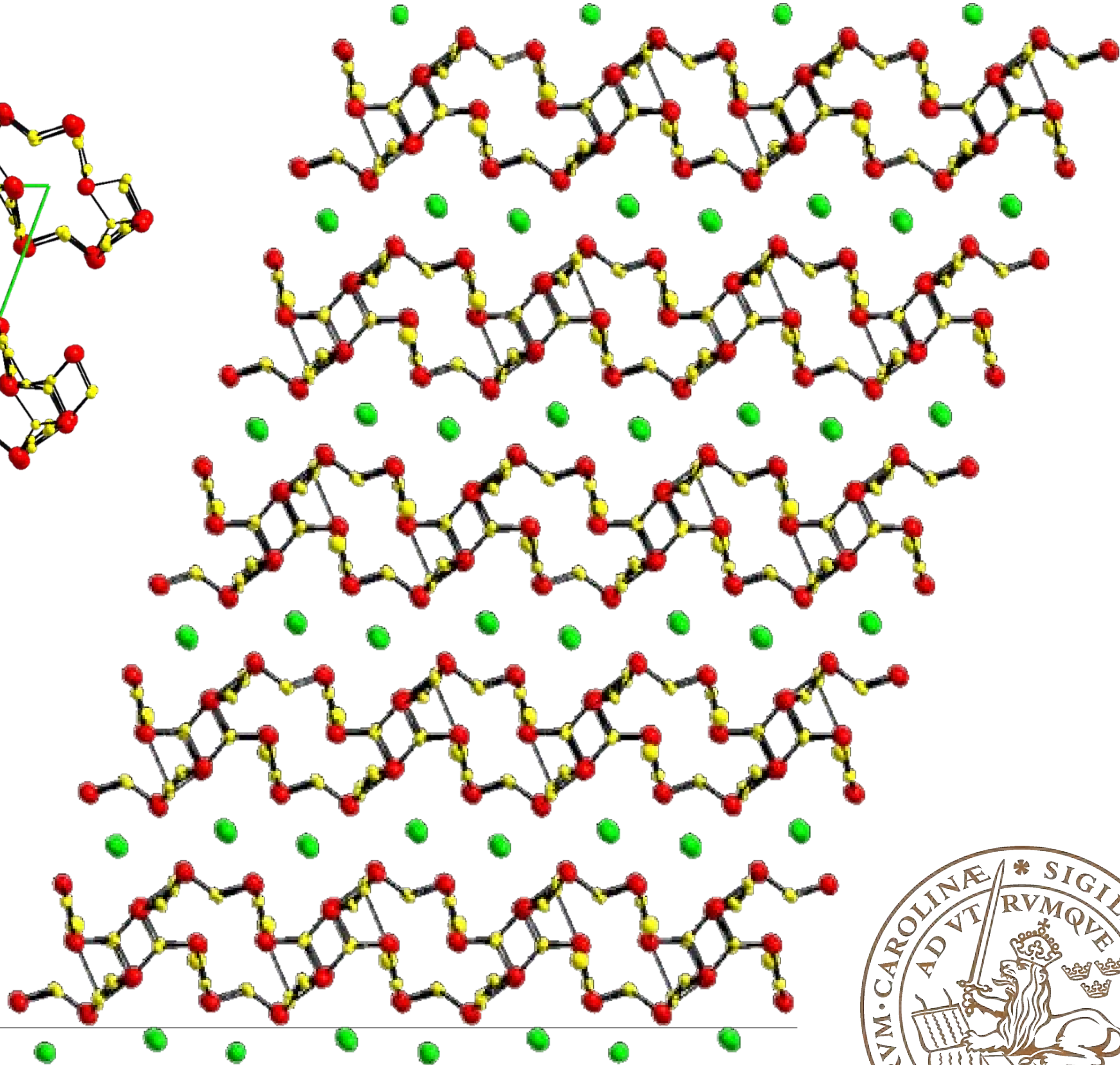
Refine. Very small change.

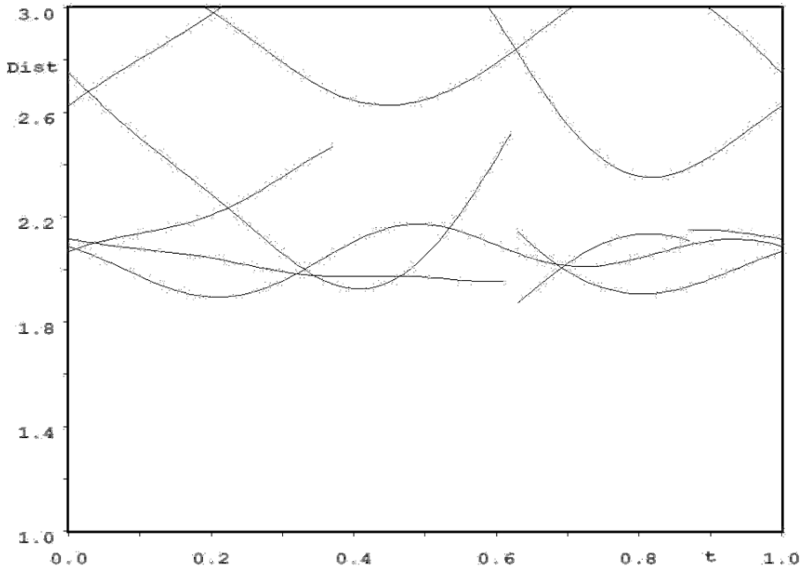
Onoratoite

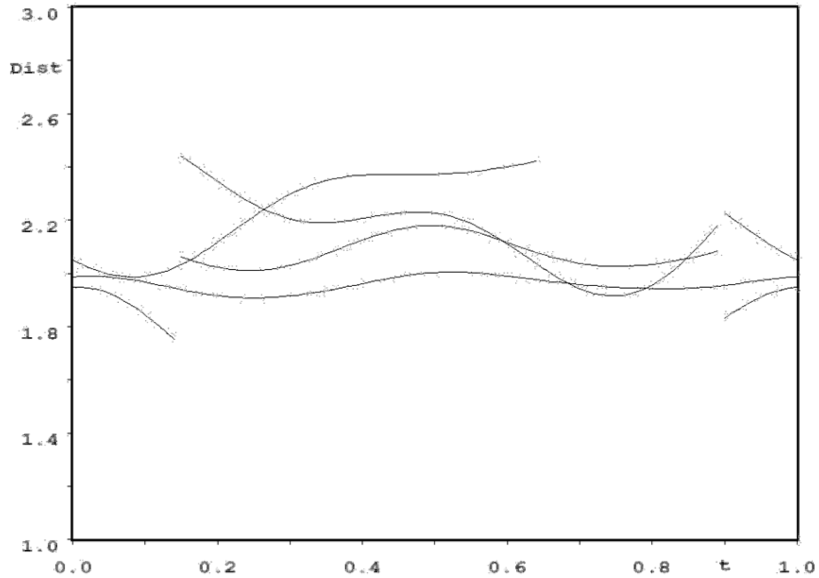


Cl

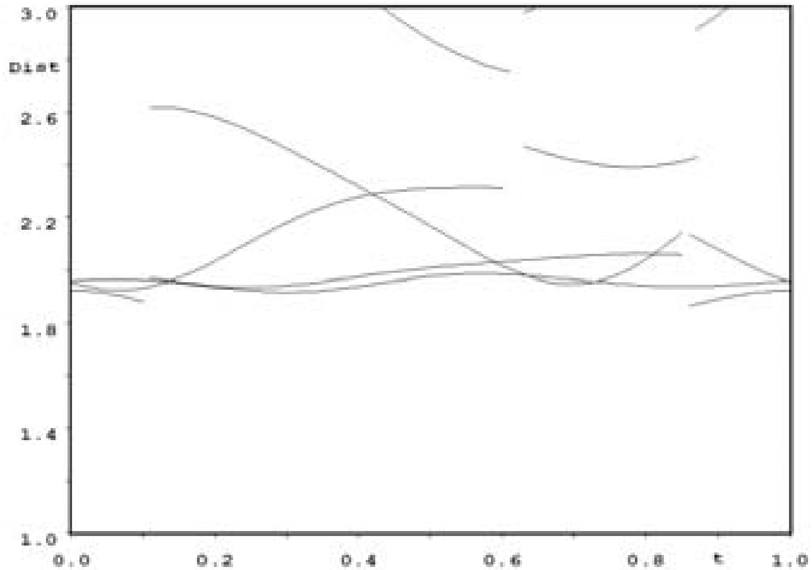
I

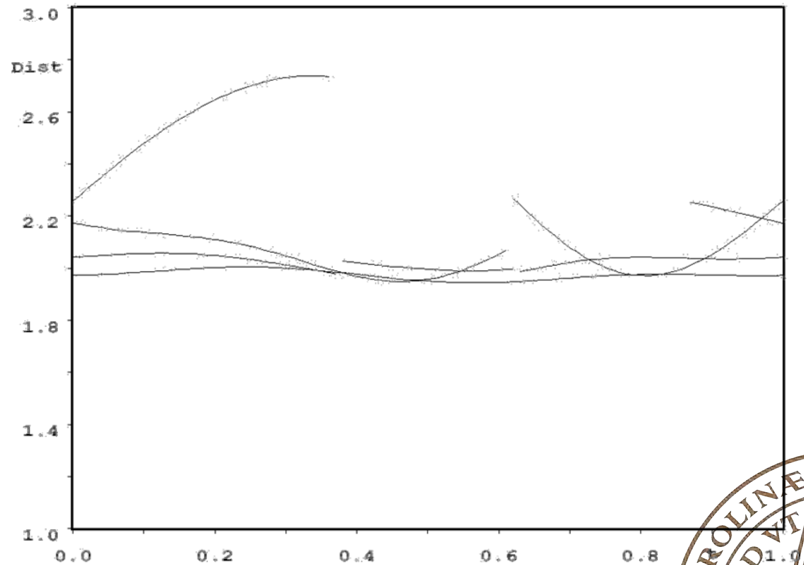


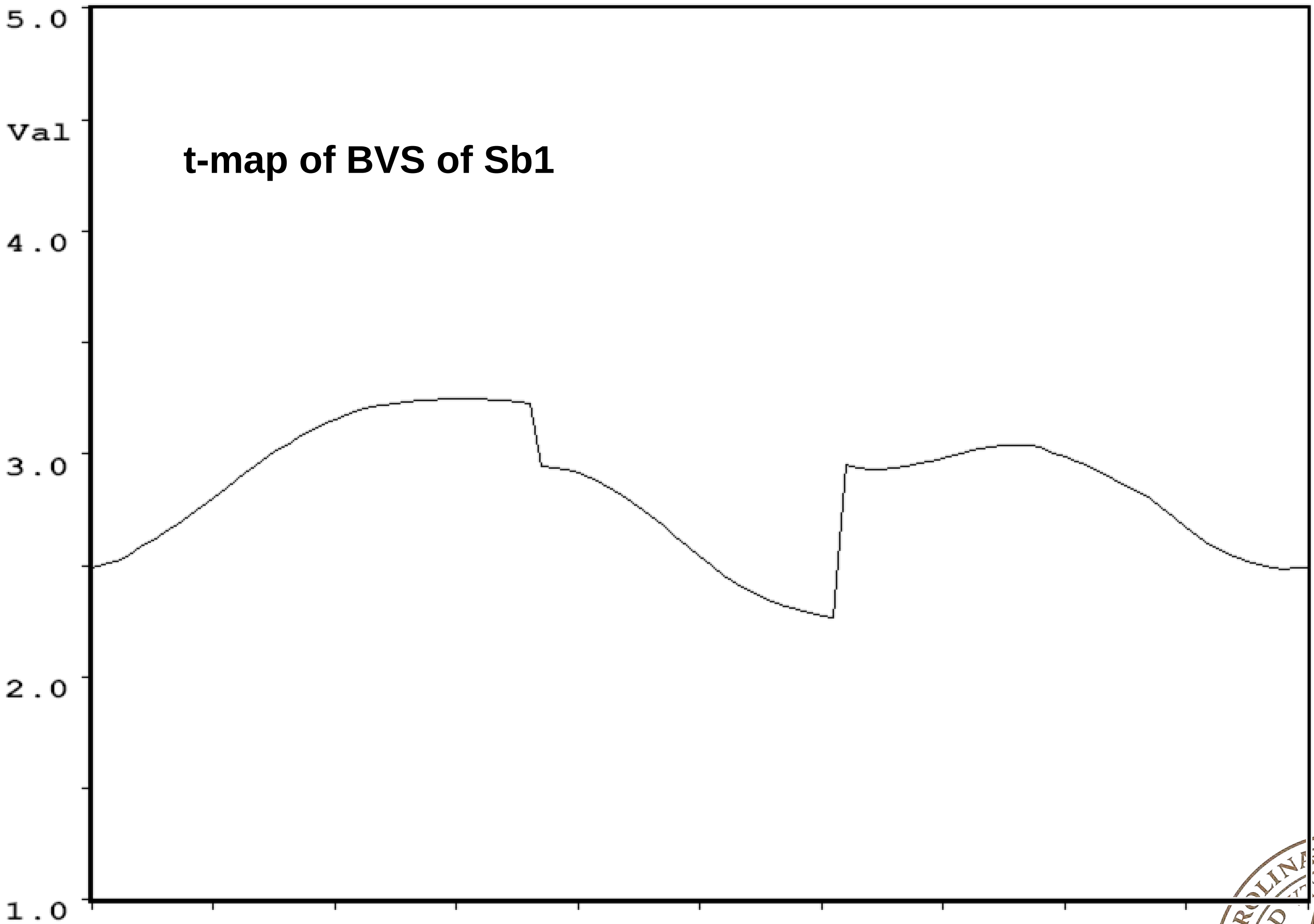




t-map of Sb-O distances






5.0
Val
t-map of BVS of Sb1
4.0
3.0
2.0
1.0

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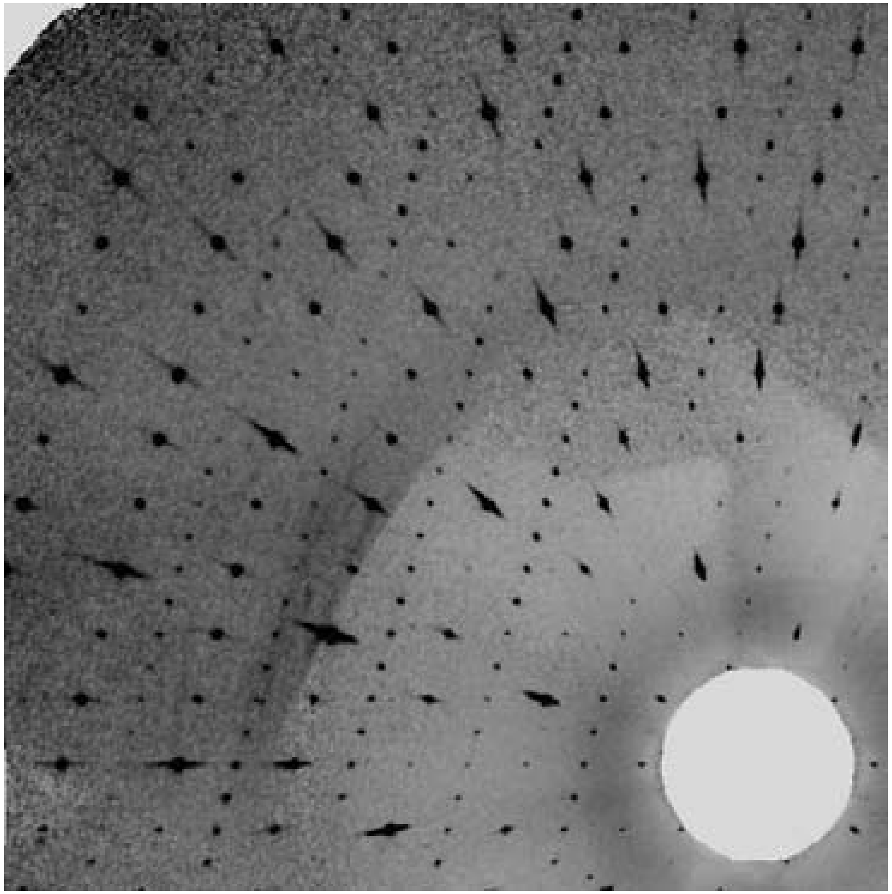
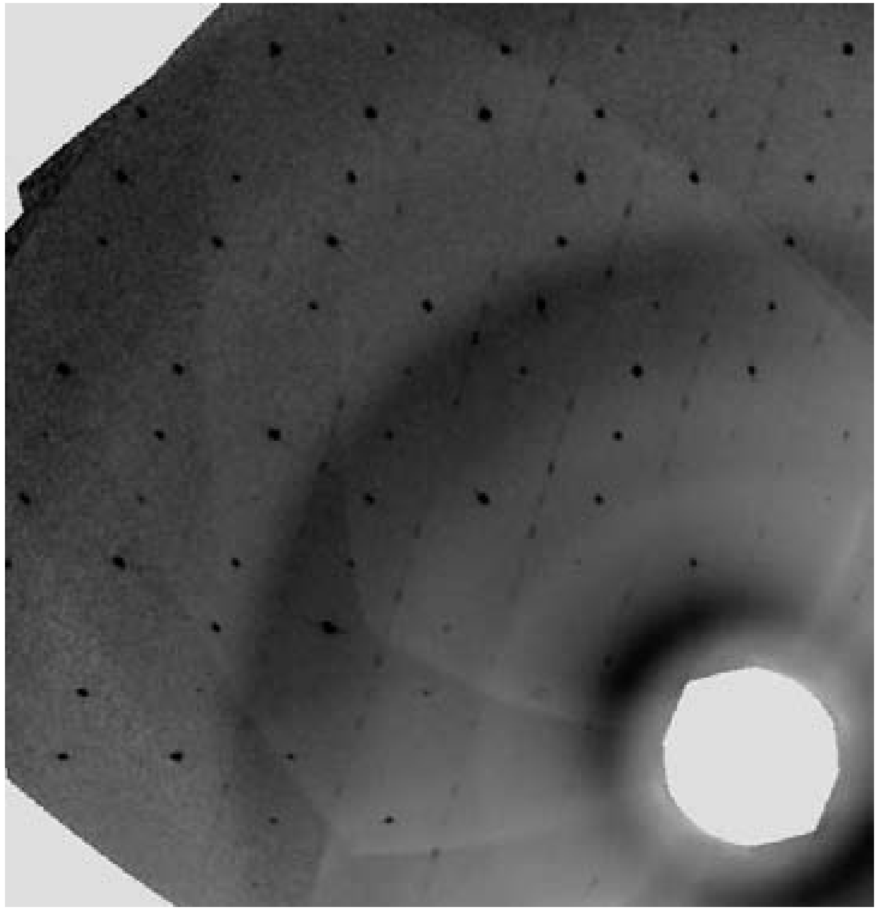
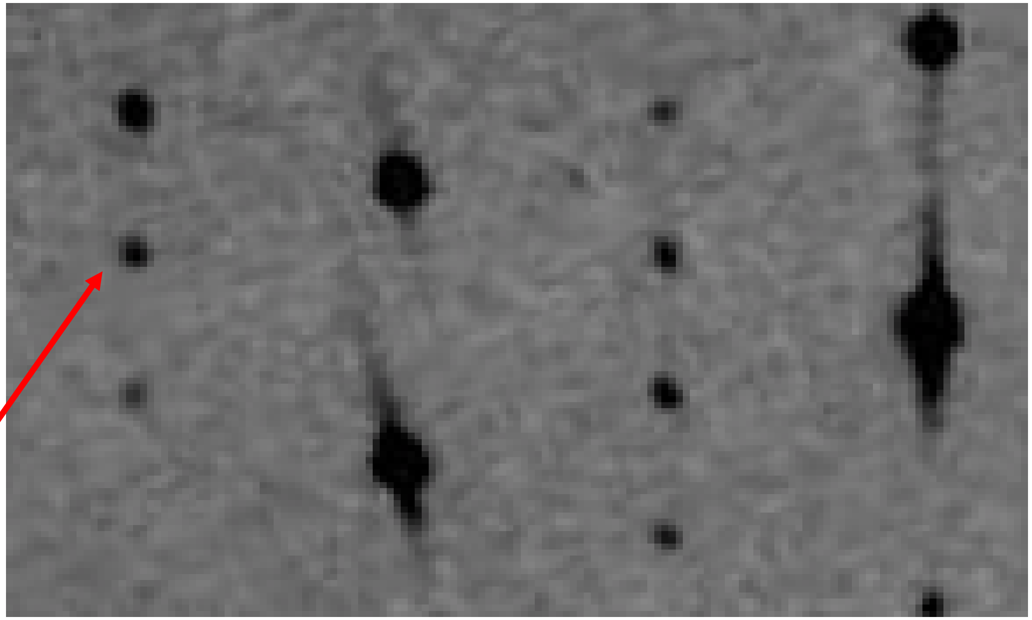
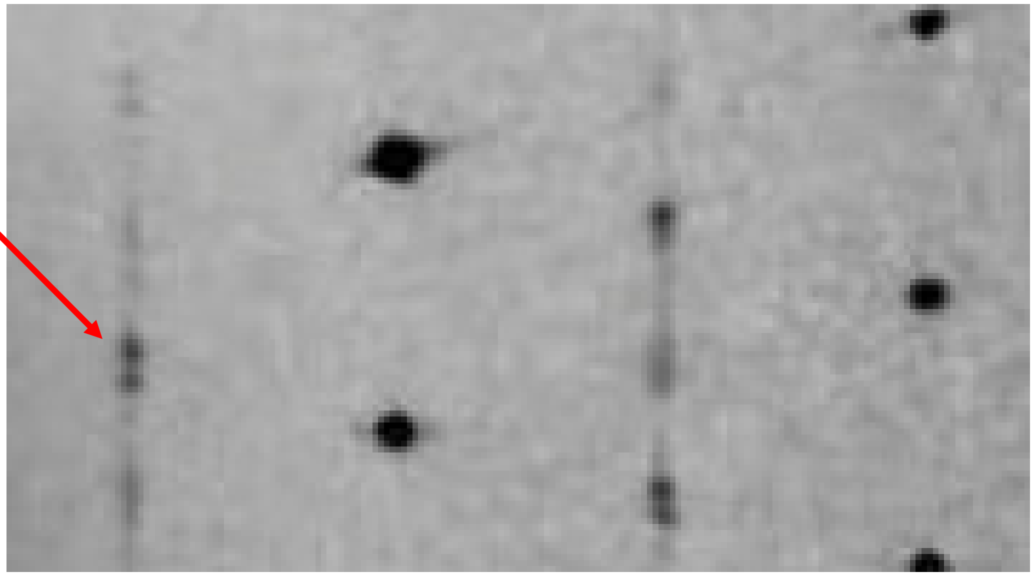
 

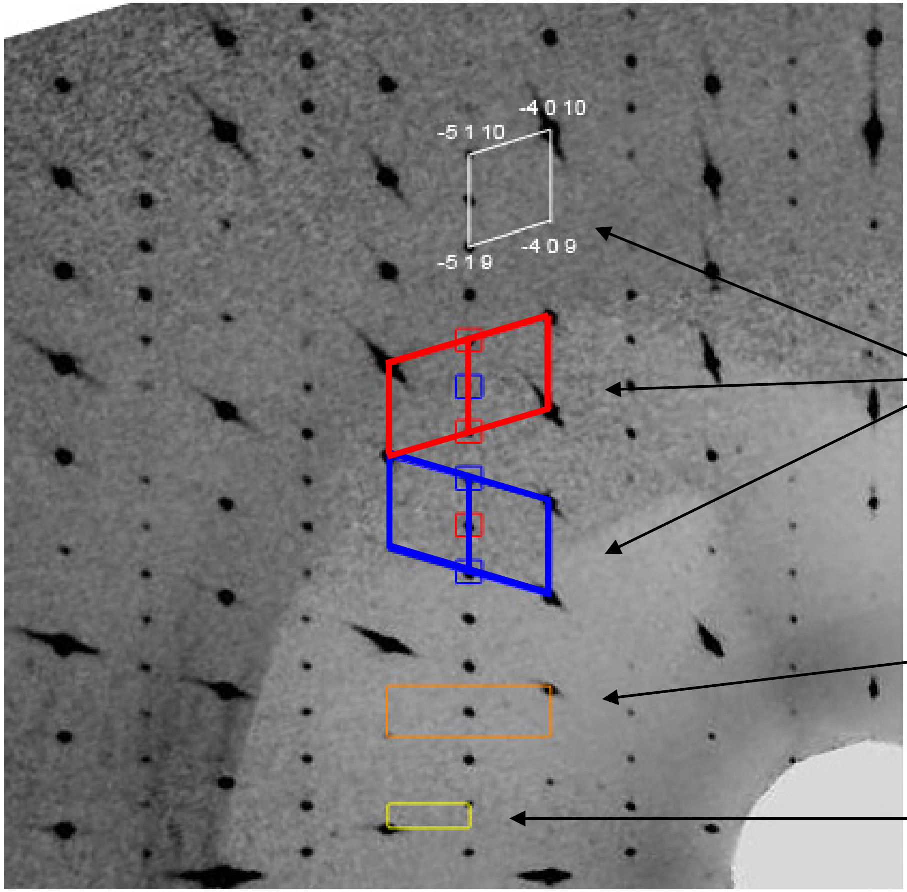
Projections h0l +h1l. Normal left. Modulated right

Note the splitting below





Interpretation of the pattern for the normal compound

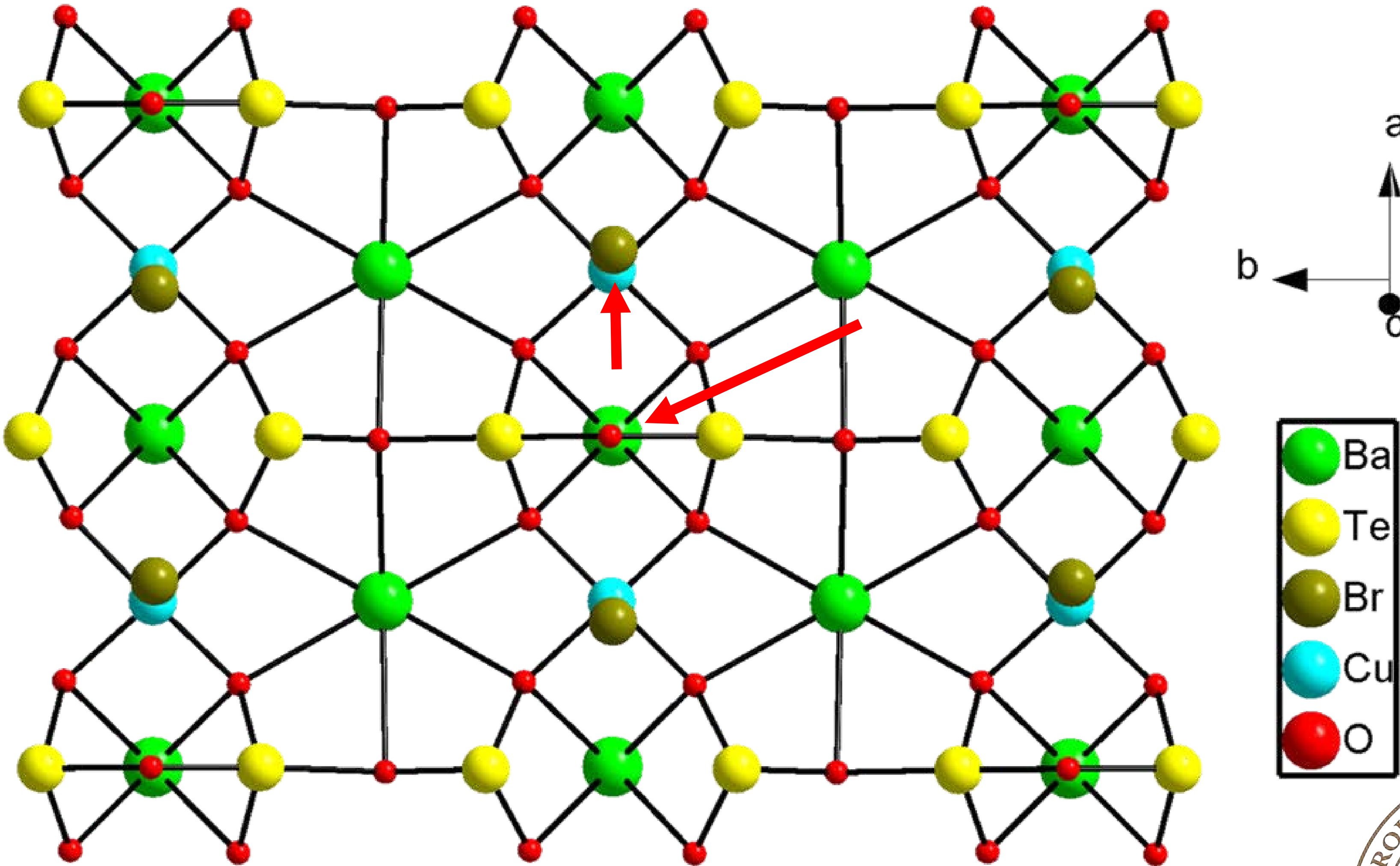


Twinned cell used in refinement, C2/m =>C-1

Twin induced superstructure, Fdd2

Fundamental cell, Bmmb

Cause of super structure – O11- Effect Br



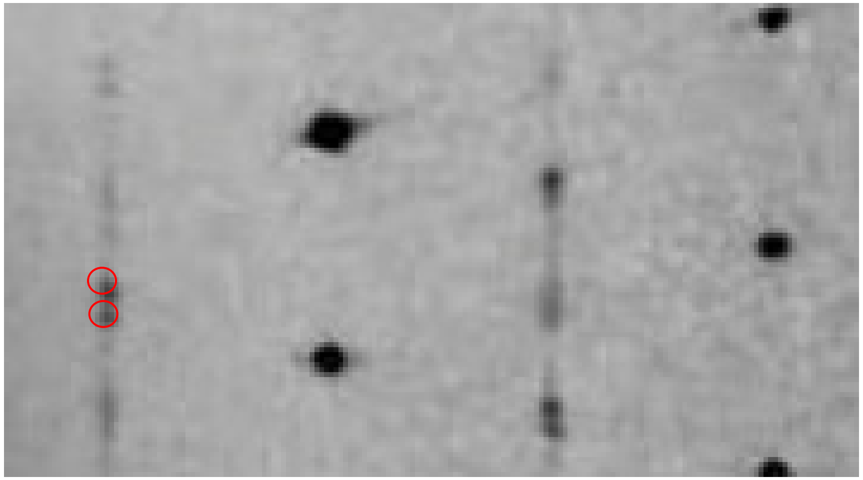
But…

The compound is (slightly) unstable in air, and a sample left in contact with moisture loses the sharp super structure reflections to diffuse streaks.

A sample sealed under ambient conditions shows an incommensurate modulation,

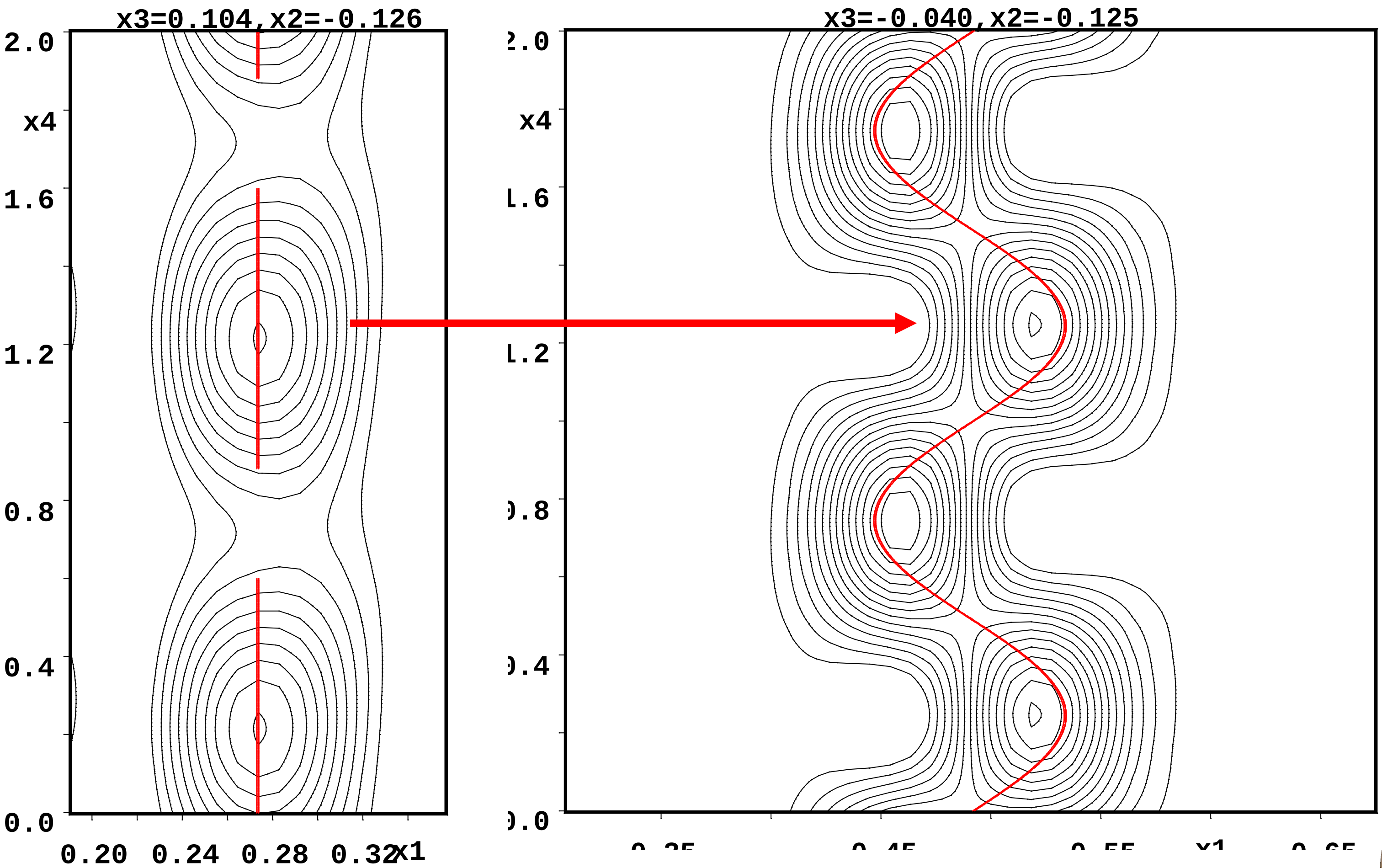
$$q \approx (0\ 0\ 1/16)$$

instead of the superstructure reflections.

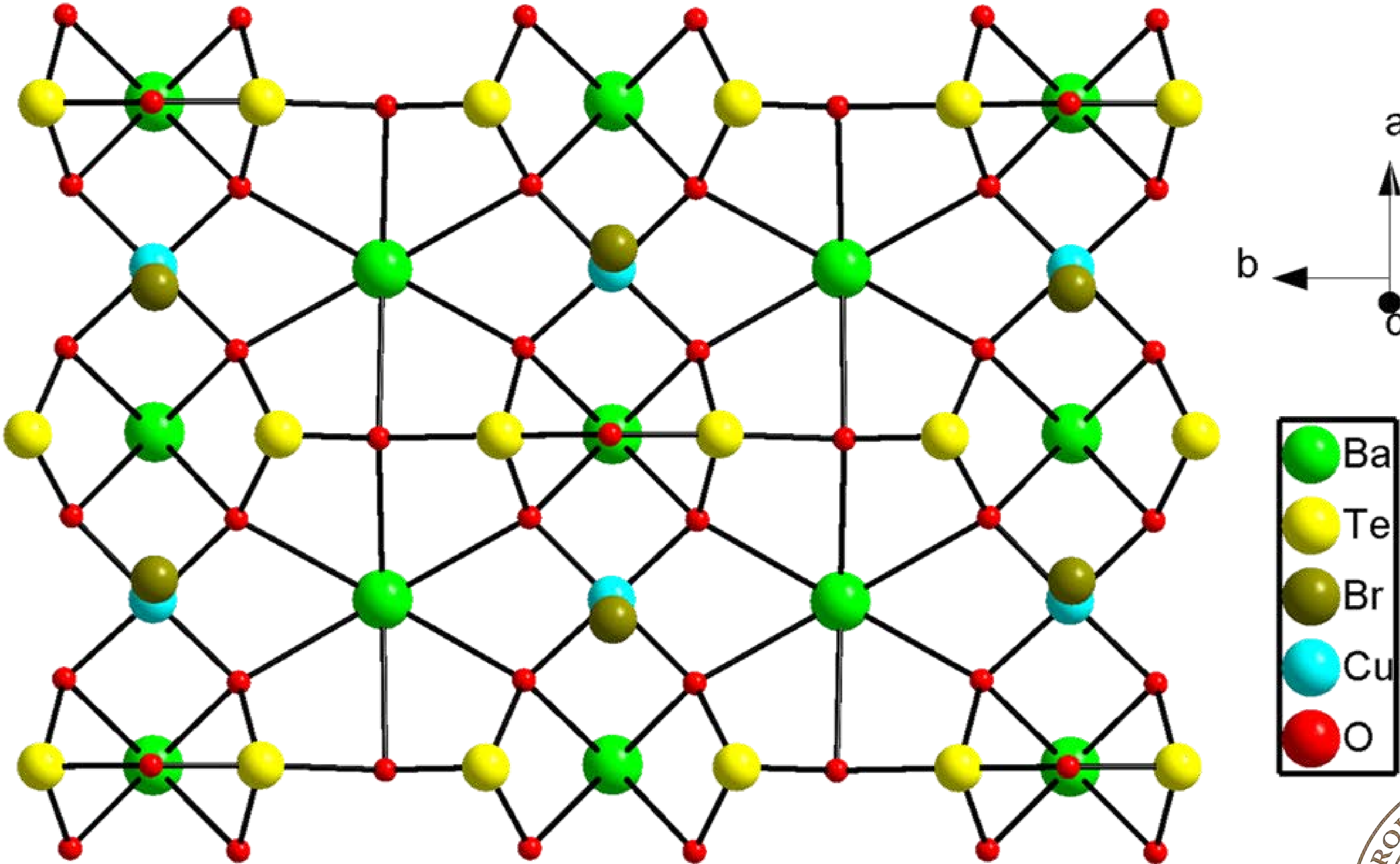


Modulation

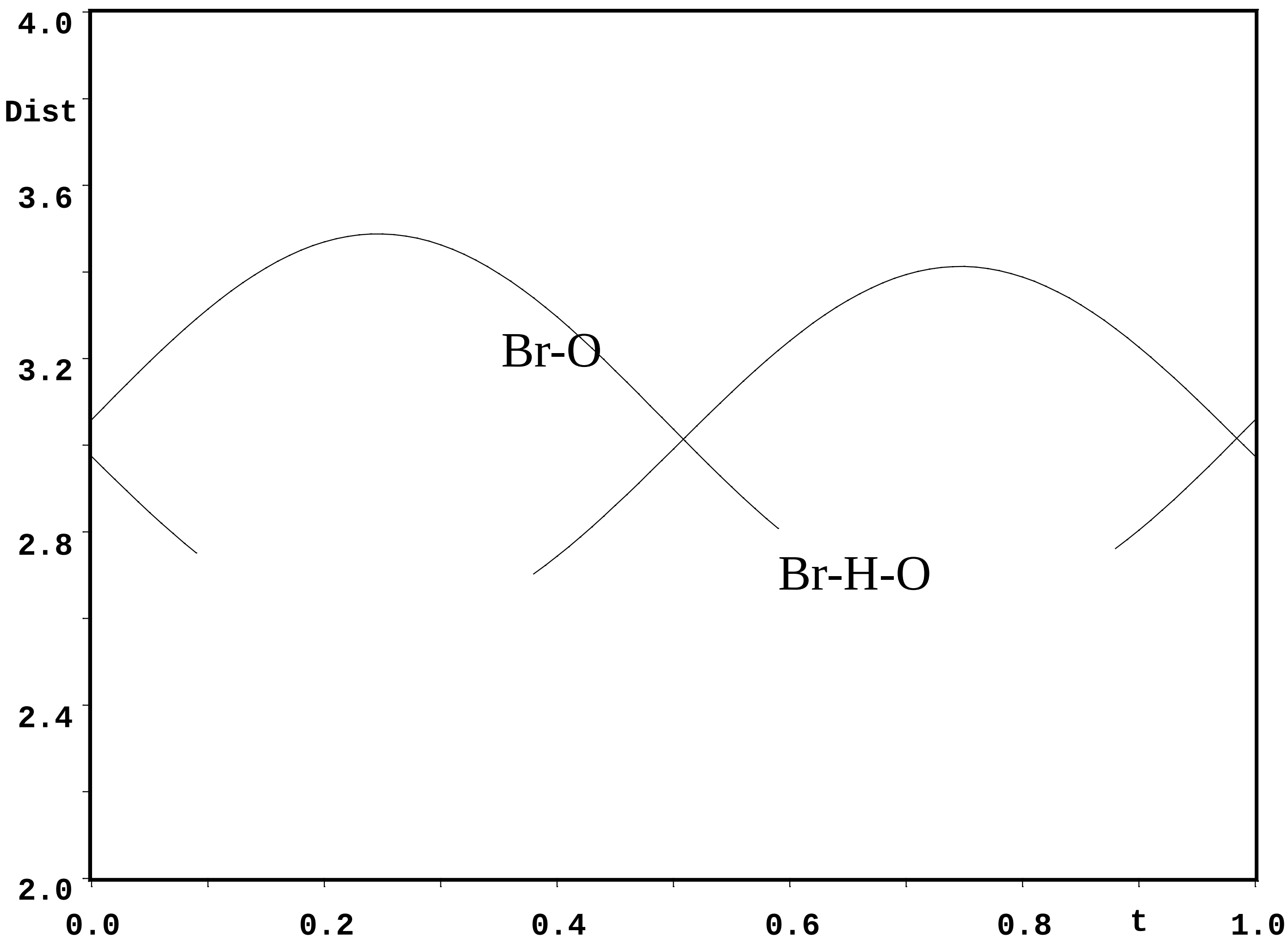
O11 **Br**



Exchange of O for OH



Distances Br-O



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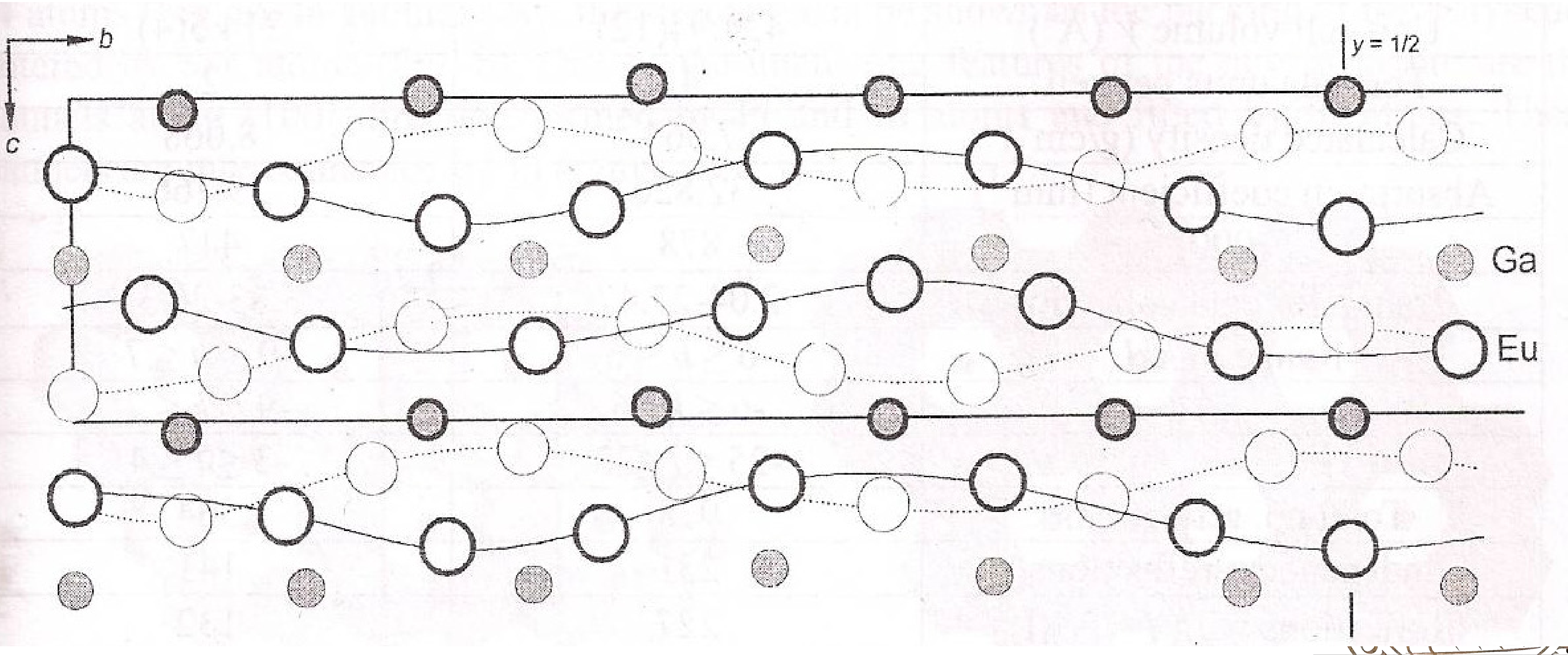
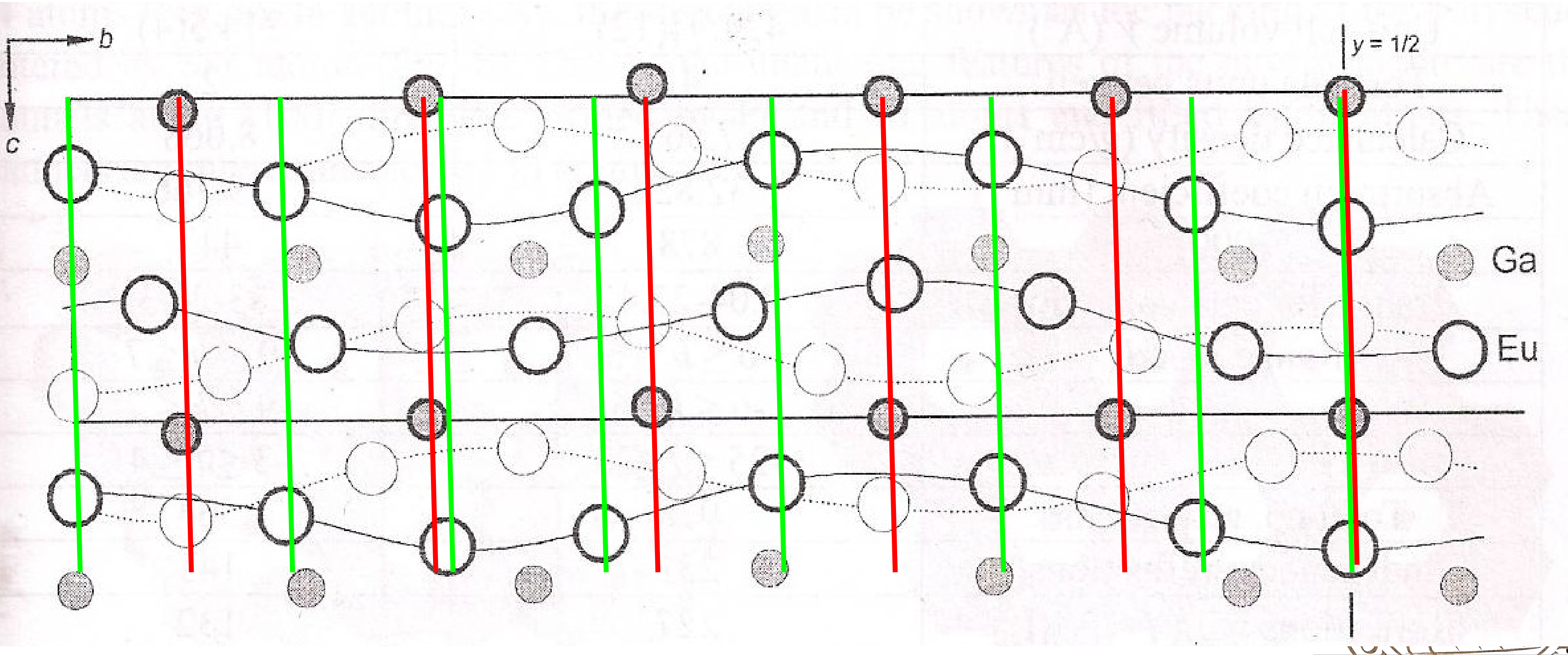
Memories of Lviv (Lvov, Lwow, Lemberg, Leopolis)



$Ca_{28}Ga_{11}$

Imm2, a=5.324Å, b=61.445Å,c=7.488Å

15 Ca positions, 6 Ga positions



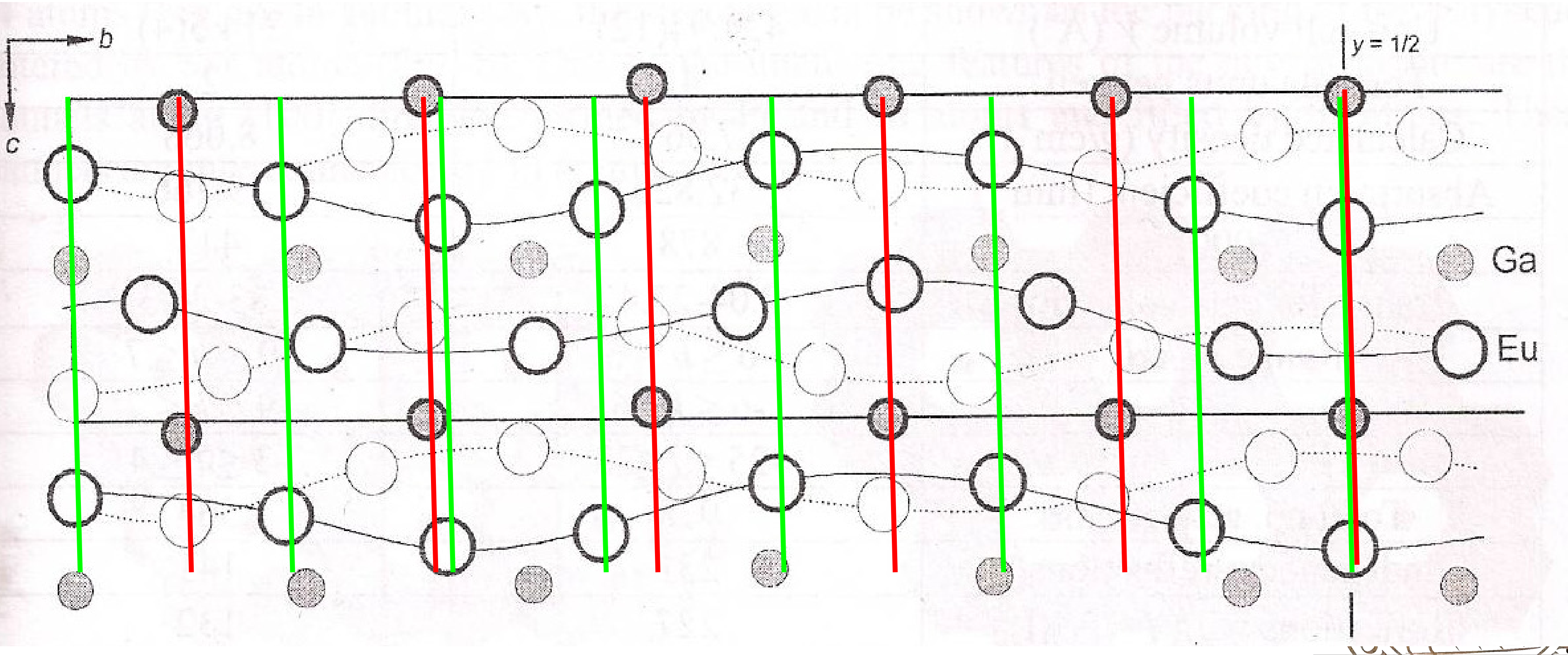
Composite?

Yes, a single Ga position and one Ca.

Xmmm(0β0)00s, β=0.2727=3/11

a=5.324Å, b=4.7265Å,c=7.488Å, 38 parameters (60)

$Ca_{28}(Ga,Ge)_{11-x}$?



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Hexagonal Approximants in the $Re_{13}(Cd/Zn)_{\sim 58}$ Systems

The Good, The Bad and the Ugly

$CeCd_{\sim4.5}$

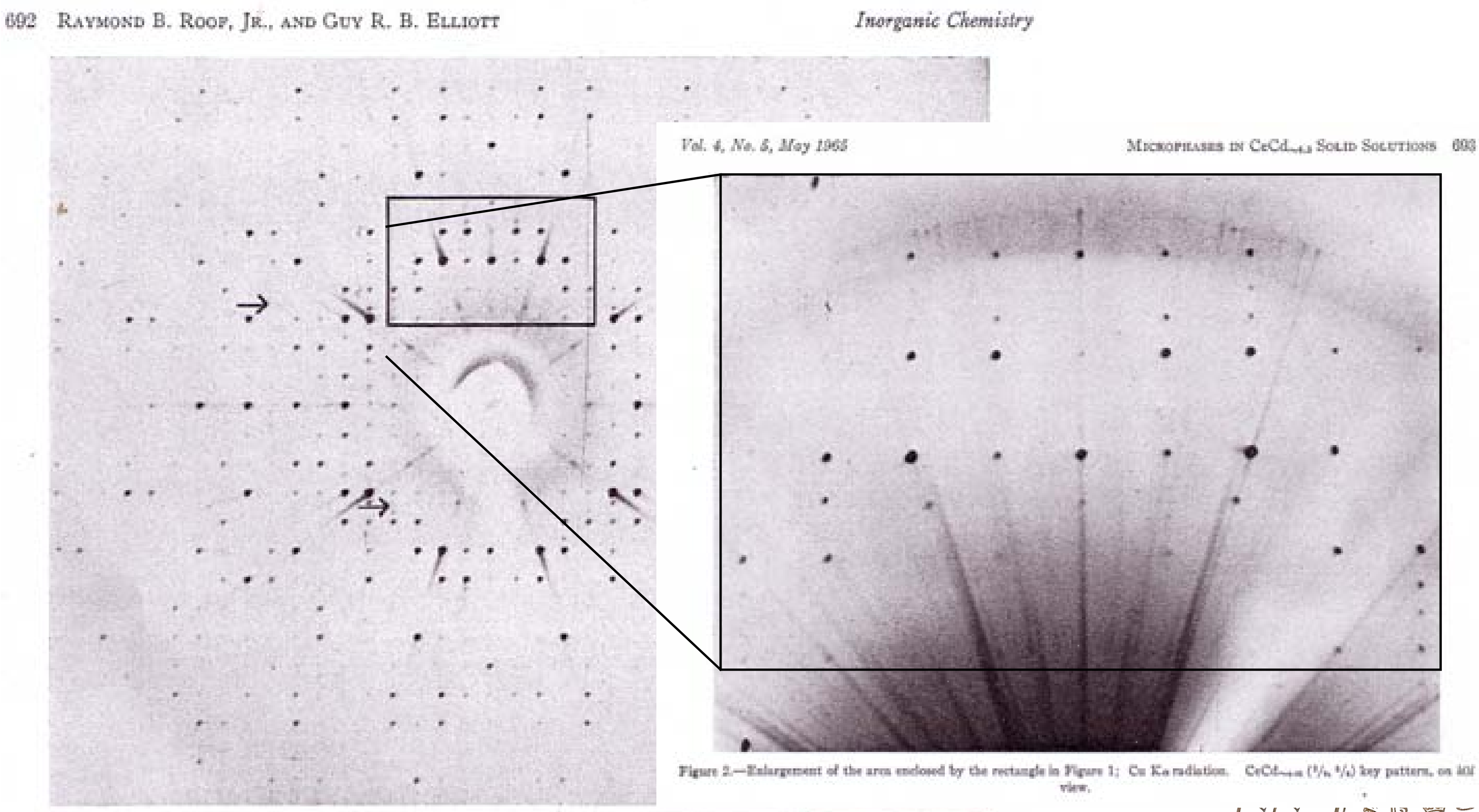
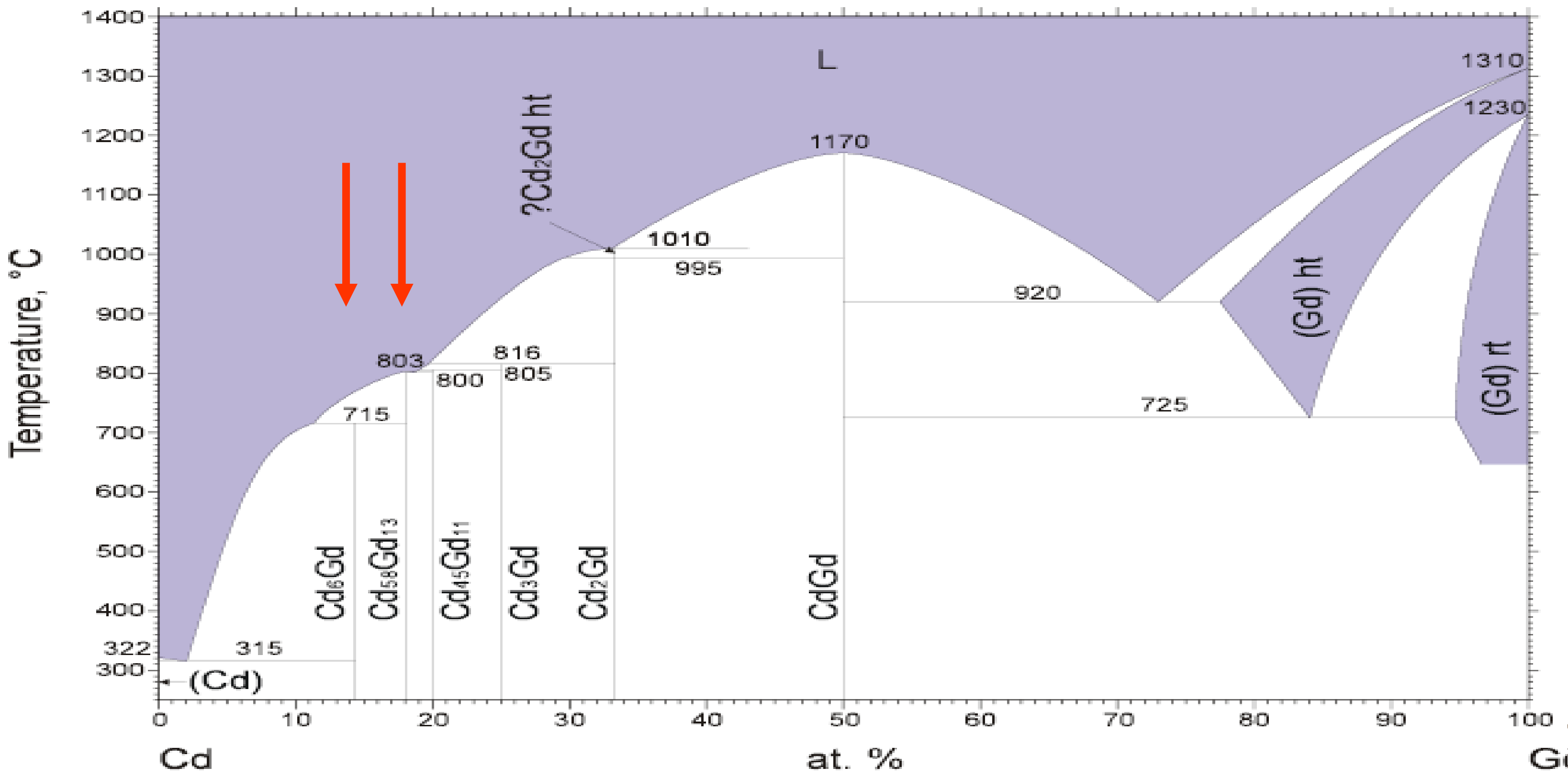


Figure 2.—Enlargement of the area enclosed by the rectangle in Figure 1; Cu Kα radiation. $CeCd_{\sim4.5}$ (¹/₈, ¹/₈) key pattern, on *h0l* view.

Figure 1.—Superlattice spots on an *h0l* view of the parent lattice for a crystal of $CeCd_{\sim4.5}$; Mo Kα radiation.

Typical Constitution Diagram



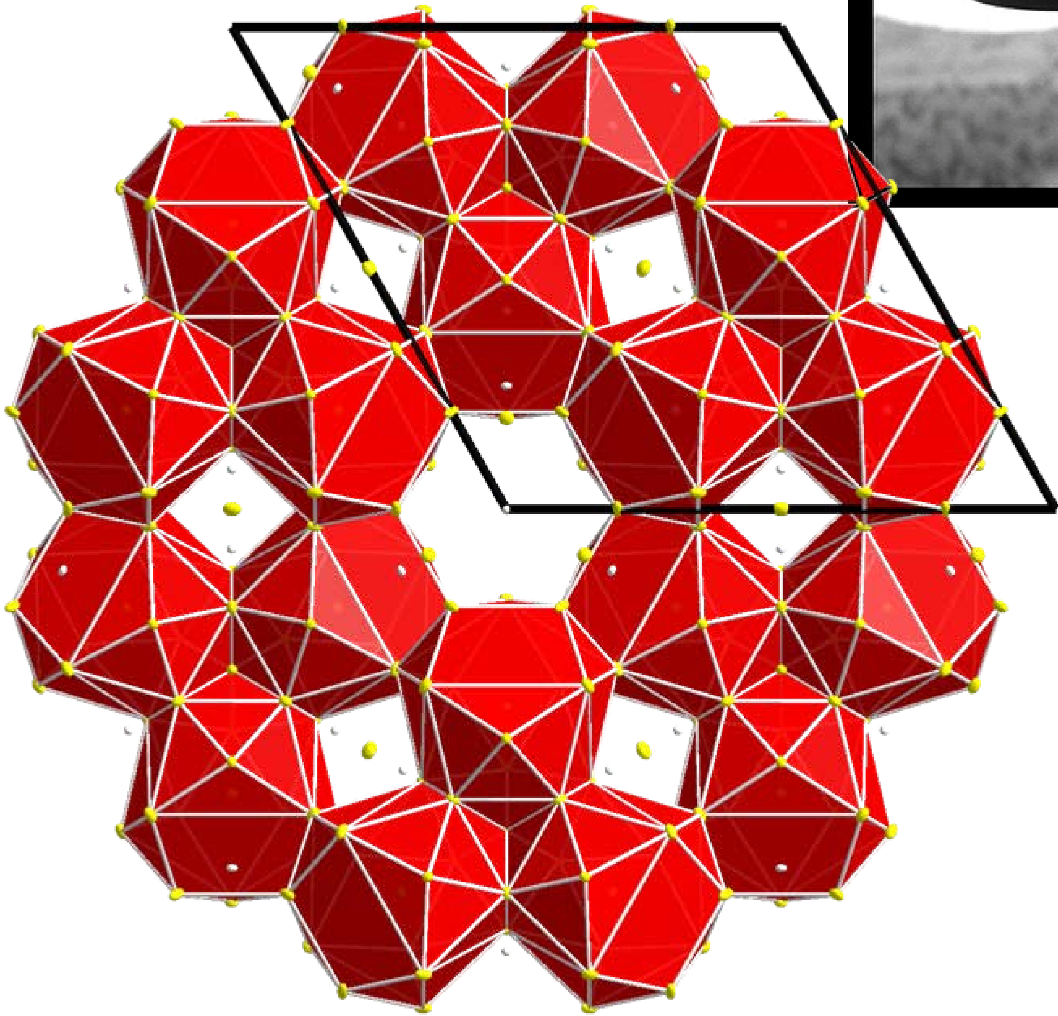
Hexagonal structures Zn

Note:

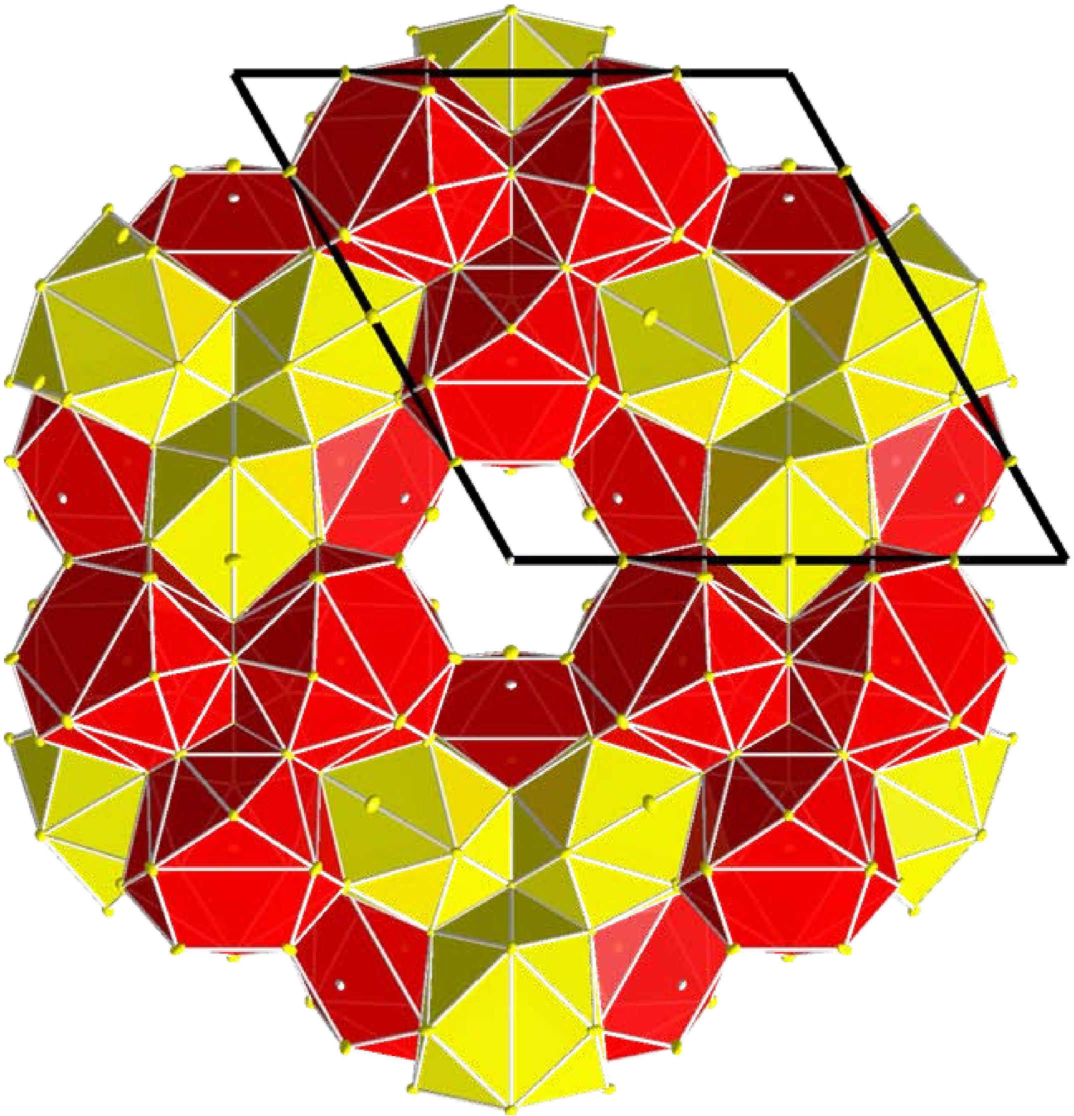
S.G. determination from satellites, absences and/or failure to refine

RE	**Radius**	**S.G**
Eu	204	-------
Yb	194	$P6_3/mmc$ (+ Pc)
La	188	?
Pr	183	$P6_3/mmc$
Ce	182.5	$P6_3/mmc$
Nd	182	$P6_3/mmc$
Pm 181	?????	
Y	181	?
Sm 180	$P6_3/mmc$	
Gd	180	$P6_3/mmc + P2_1$
Tb	178	$P6_3mc + P2_1$
Dy	177	Pnma
Ho	177	Pnma + Inc
Er	176	$Pc2_1n$
Tm	175	$Pc2_1n$
Lu	173	$Pc2_1n$

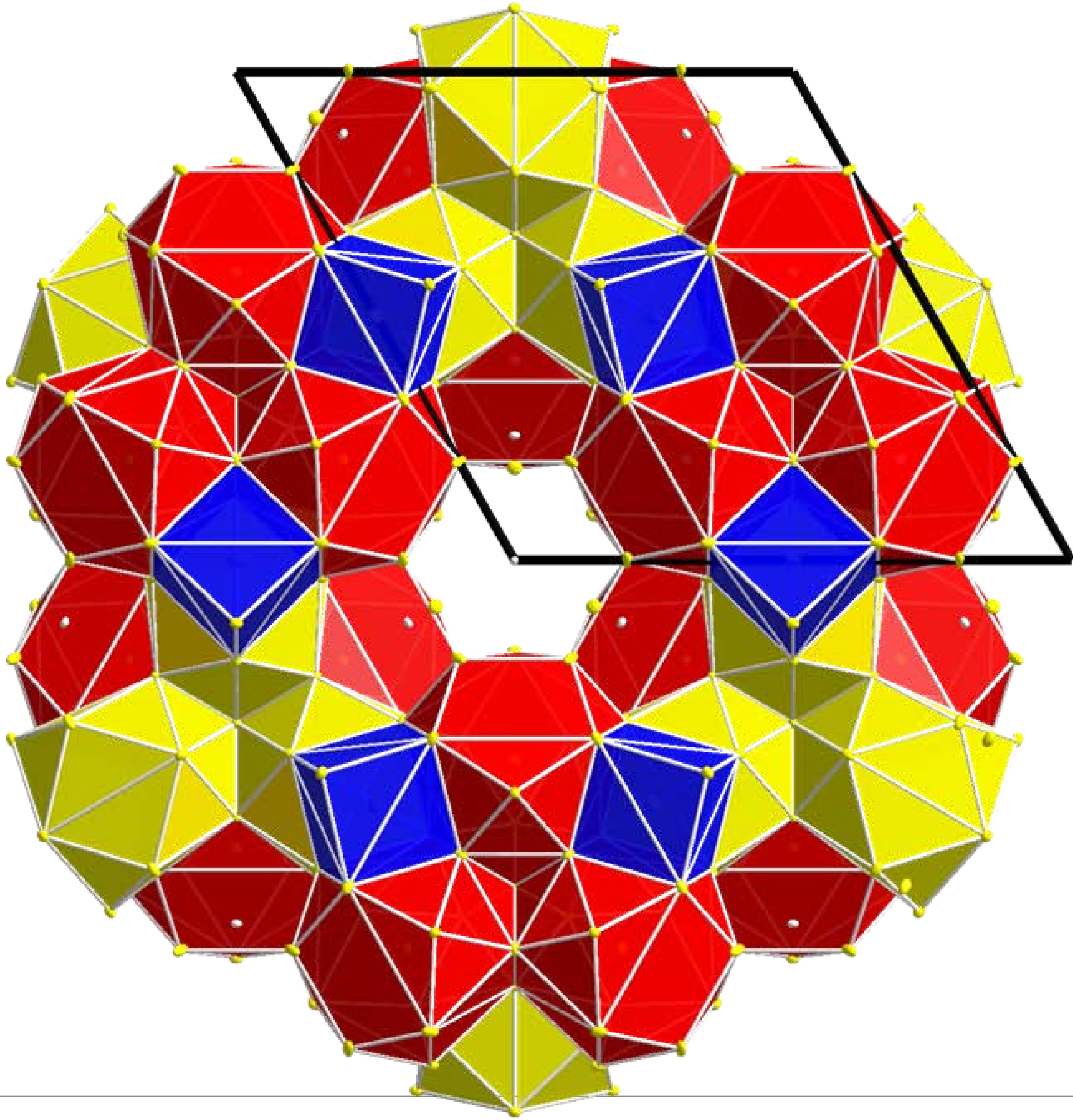
Complex basic structure



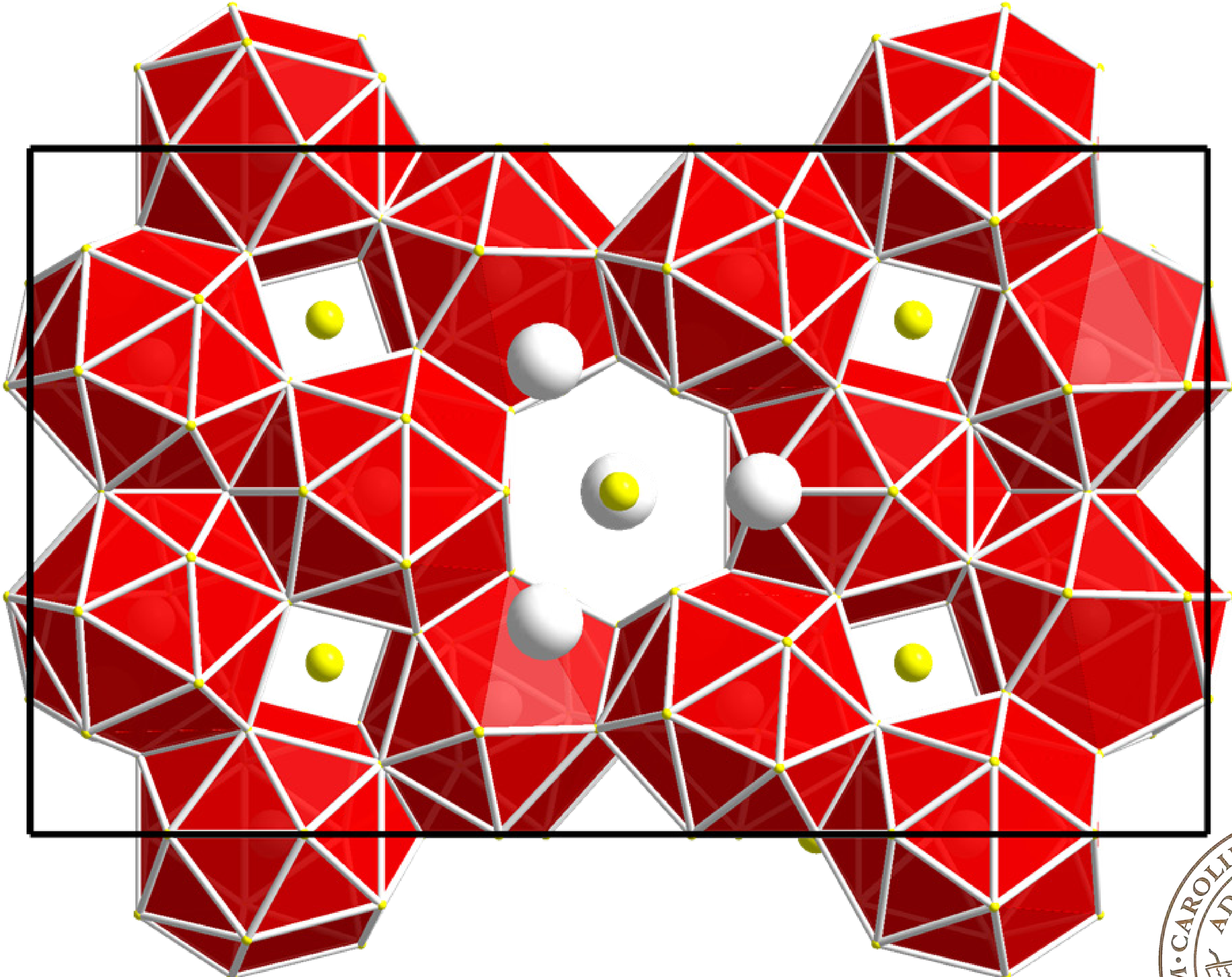
Complex basic structure



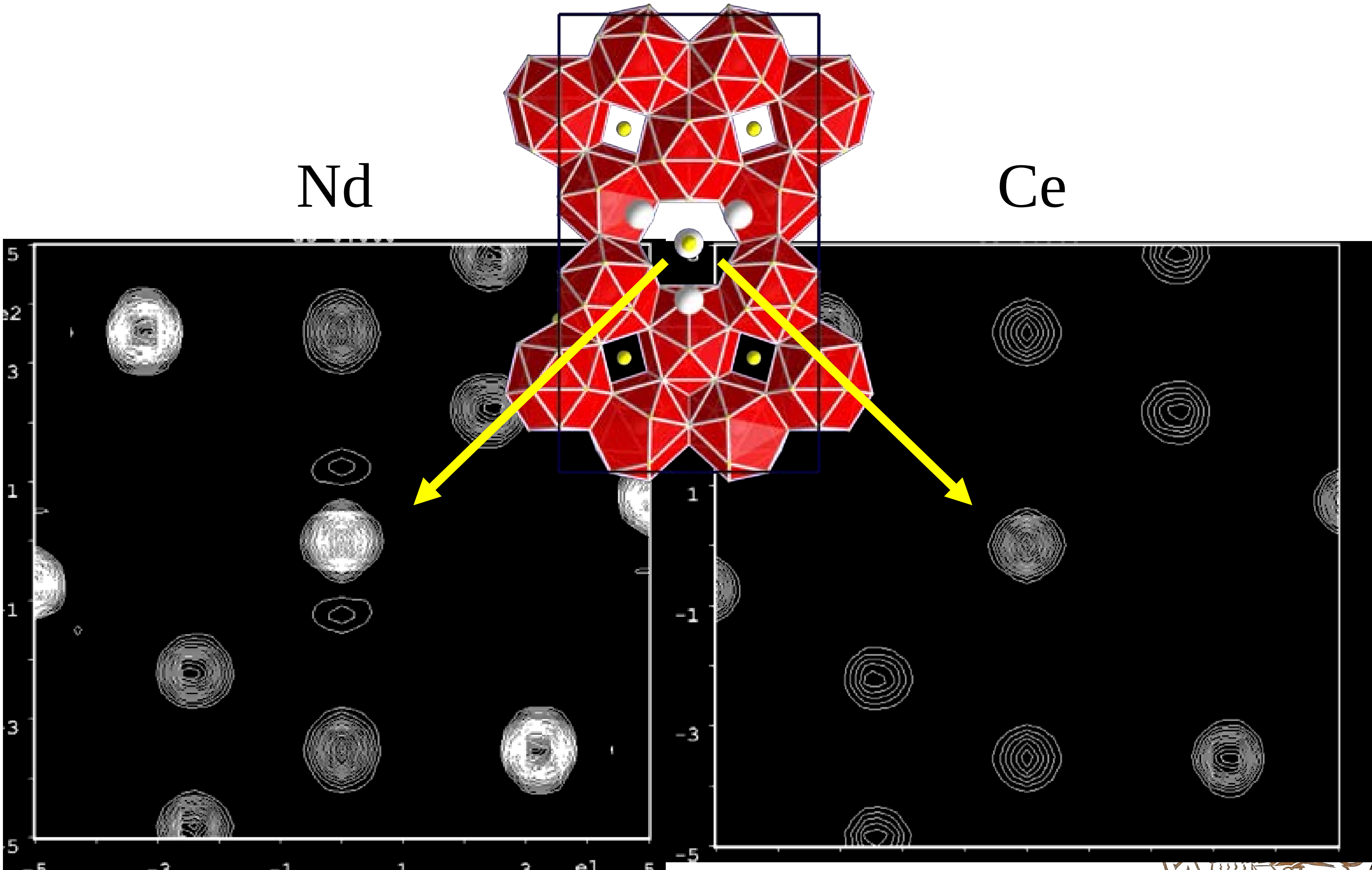
Complex basic structure



Complex basic structure



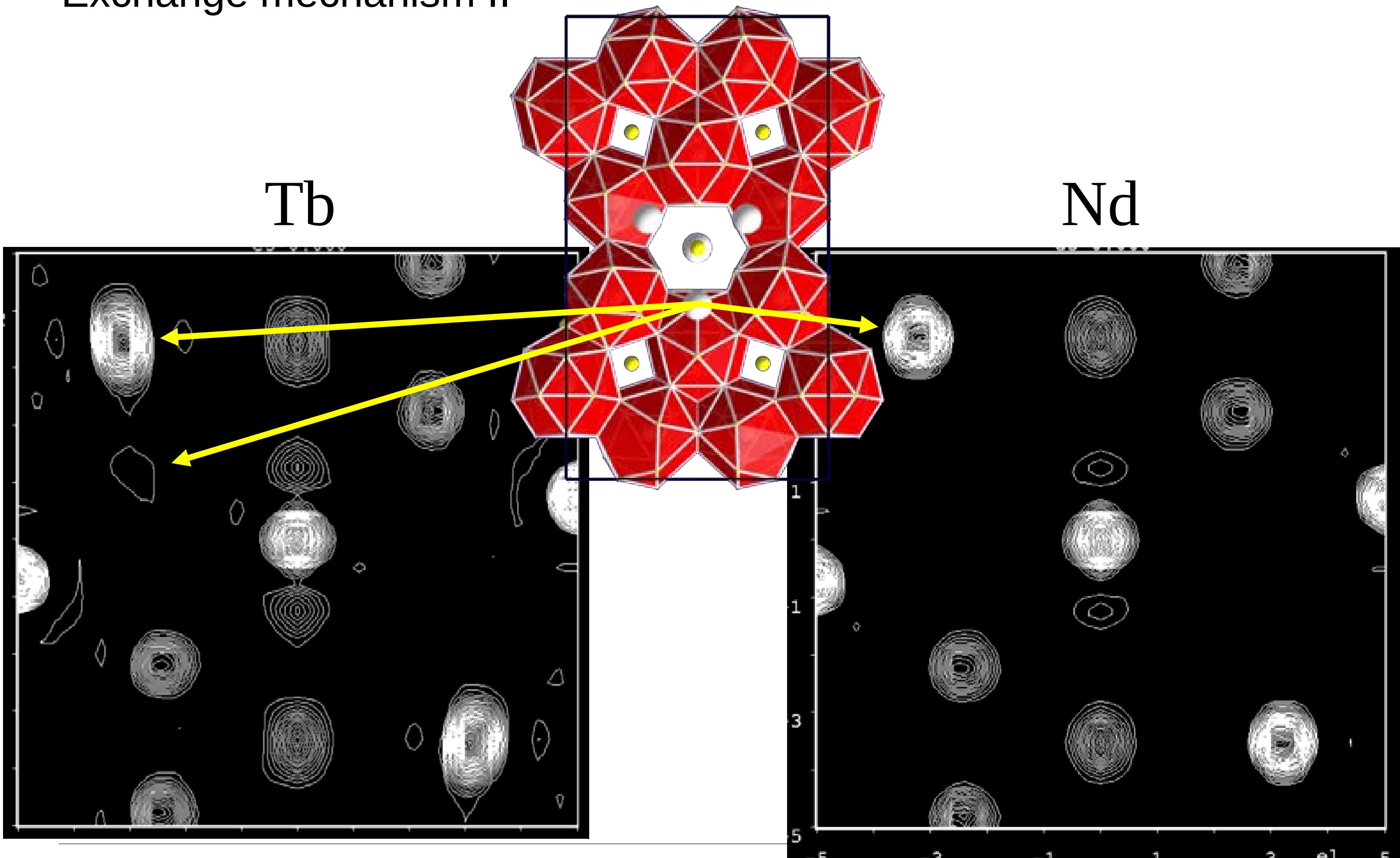
Exchange mechanism I



Exchange mechanism I

For Ce and Pr no exchange is found. For Nd it is found to some degree to make the composition $Nd_{12.8}Zn_{58.4}$.
For Yb, Sm, Gd and Tb it is found together with exchange mechanism II

Exchange mechanism II



Exchange mechanism II

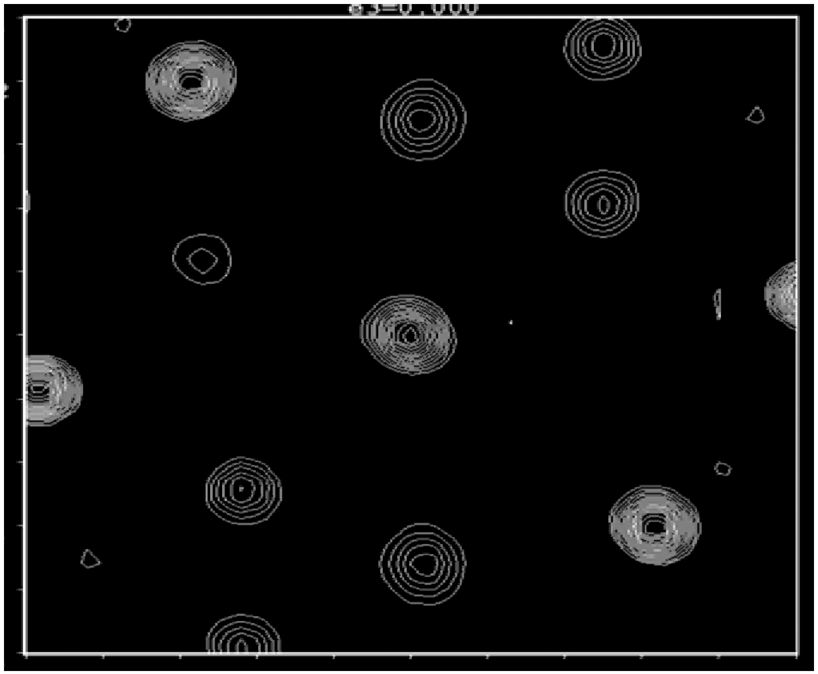
Mechanism II causes the symmetry lowering $P6_3/mmc$ to $P6_3mc$

It boosts Zn content further.

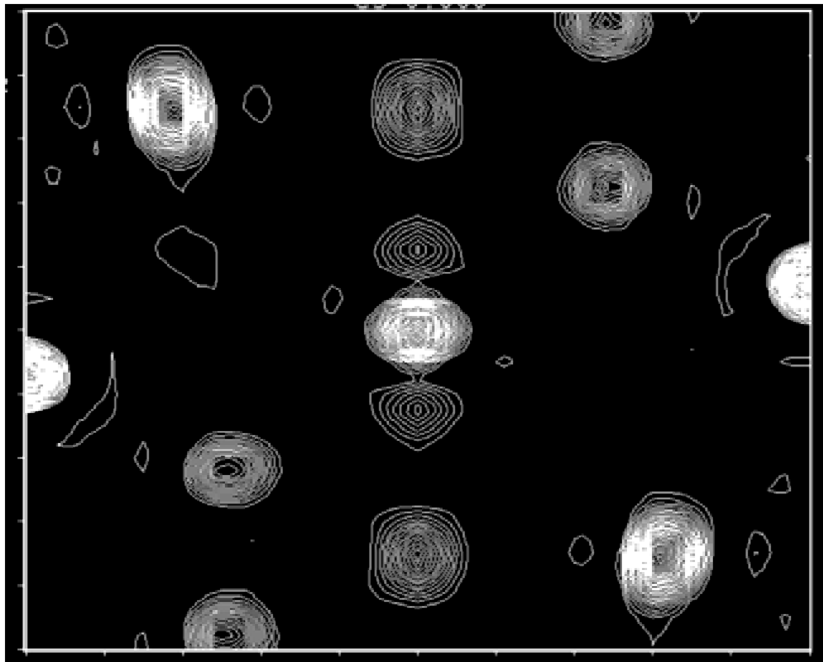
As occupancy of this position approaches 1/3, the next ordering kicks in

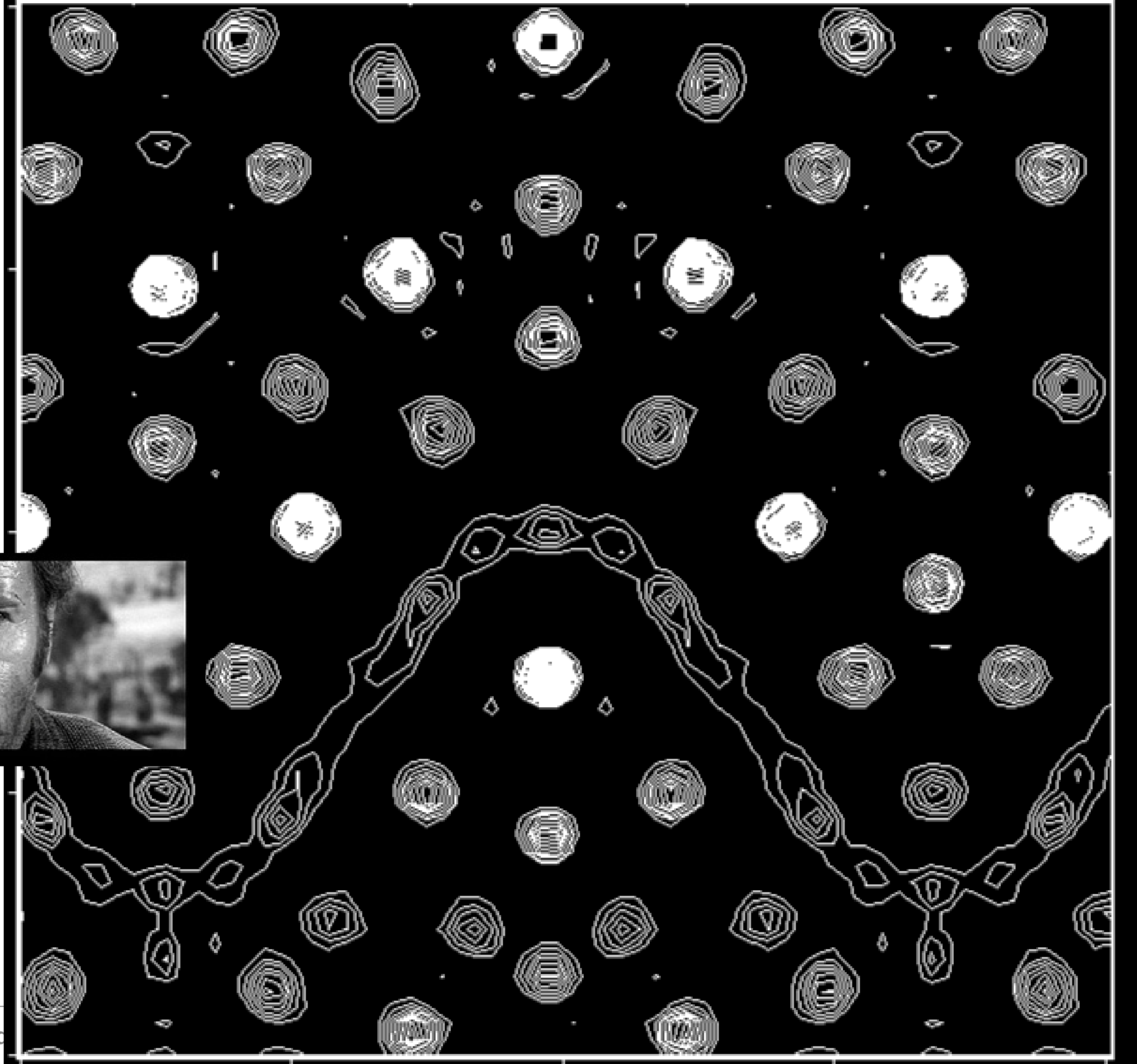
For fully ordered mechanism II, symmetry is reduced to $P2_1$. This applies to Gd and Tb. For Er, Tm, Lu addititonal disorder allows $Pc2_1n$.

Er



Tb (I)



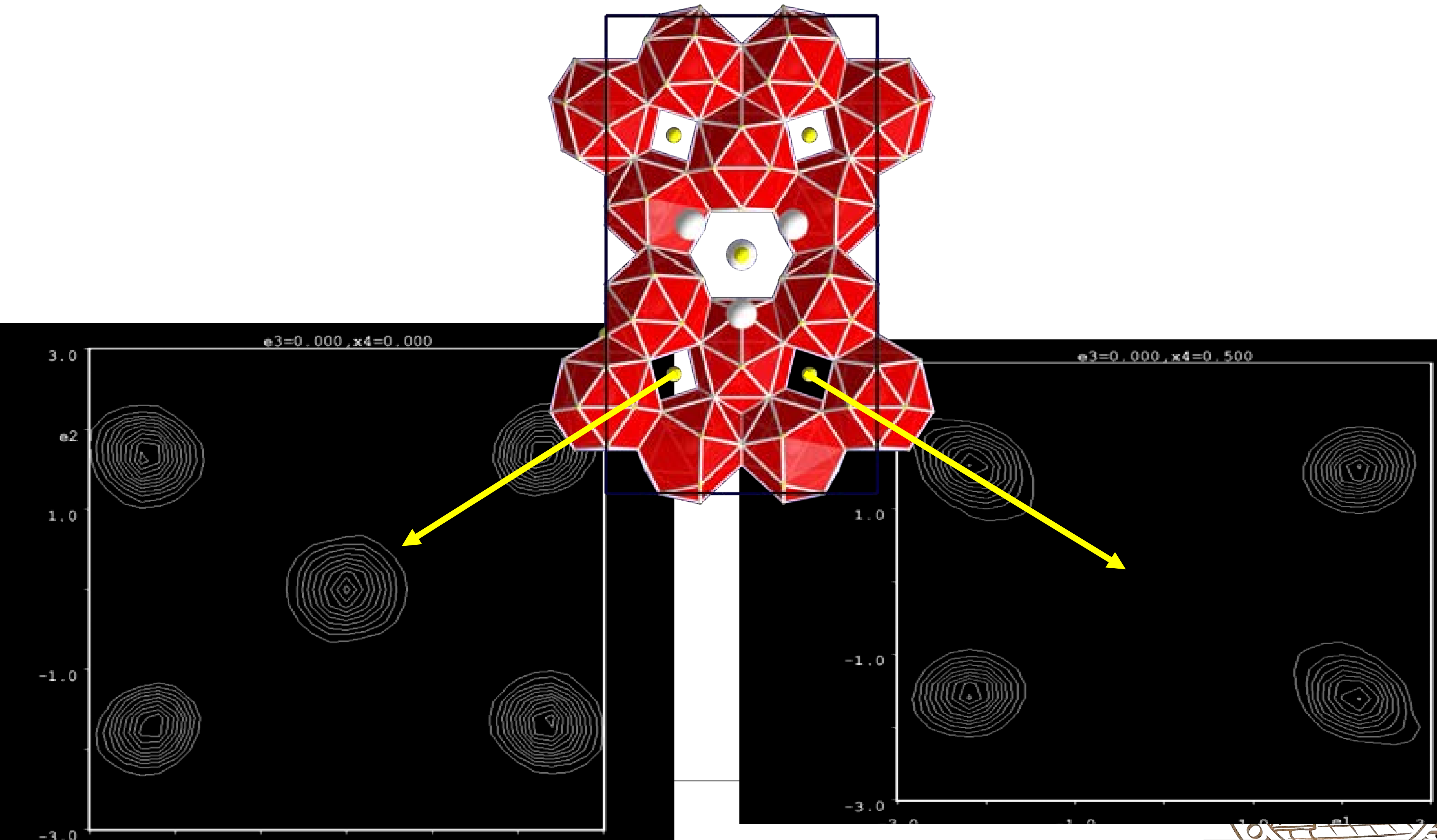


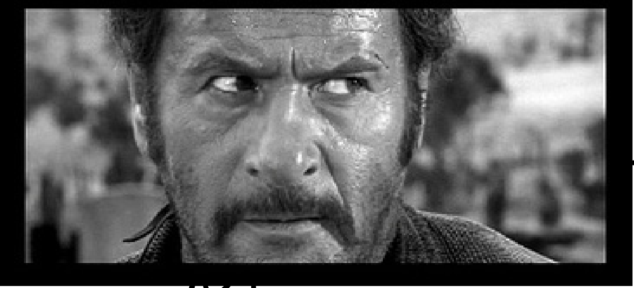
Special cases

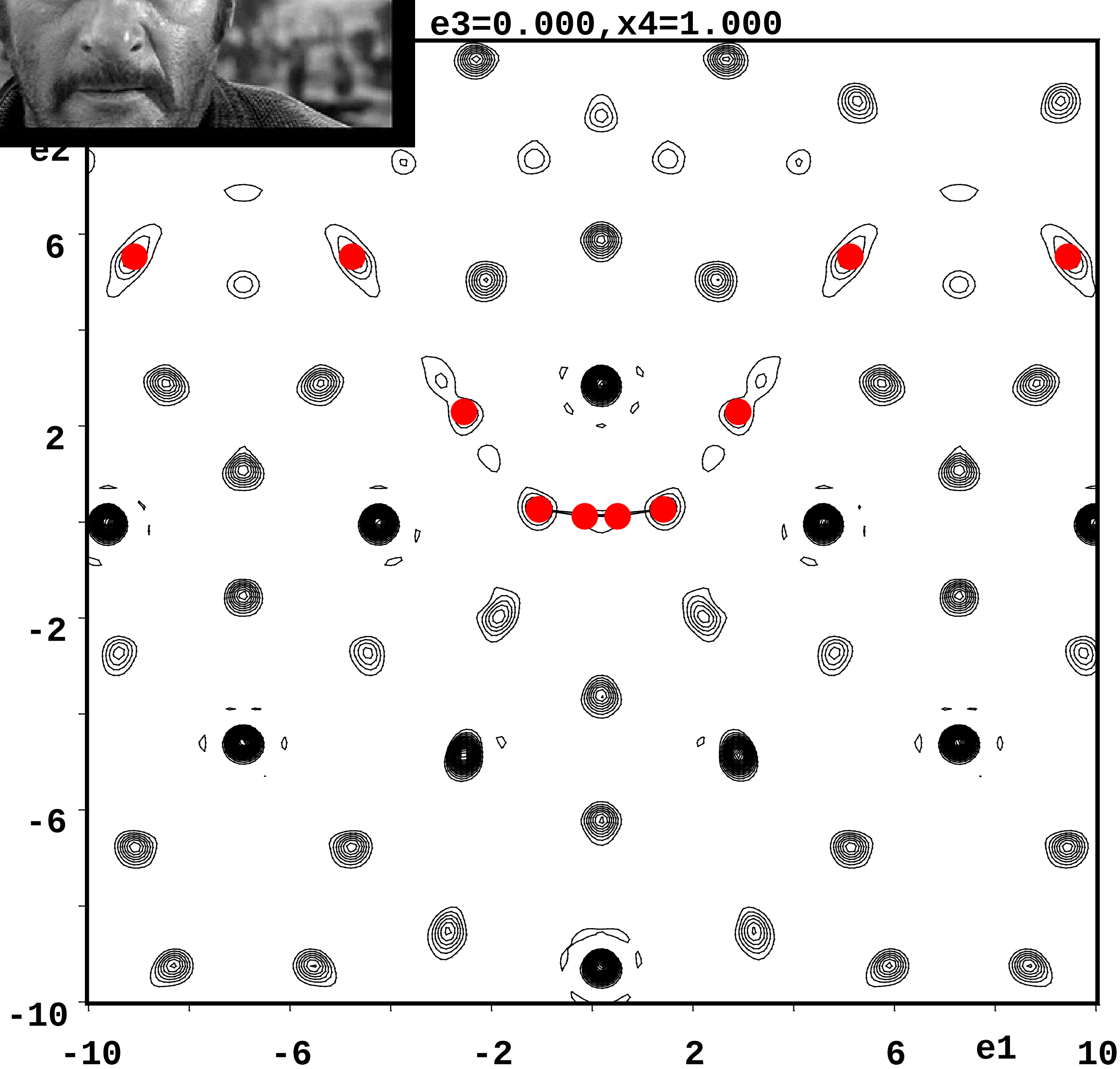
Dy shows neither of the above mechanisms, but has an ordering all of its own.

Ho is very similar to Er and Tm but the additional disorder in the latter is resolved

Dy and exchange mechanism III

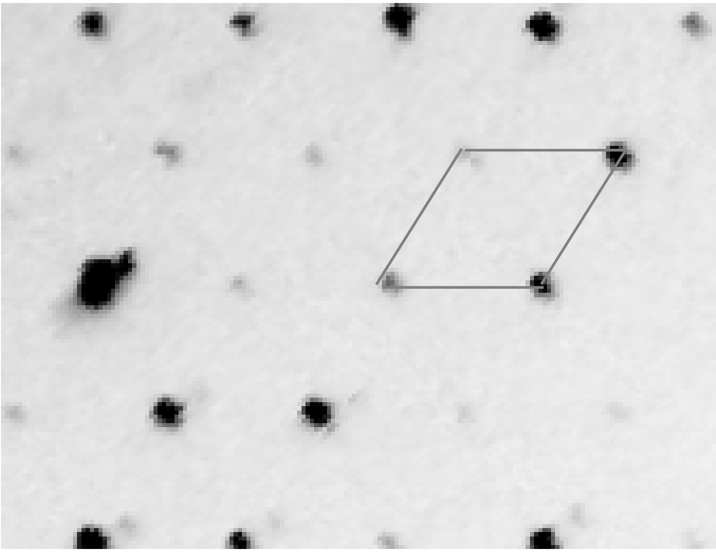


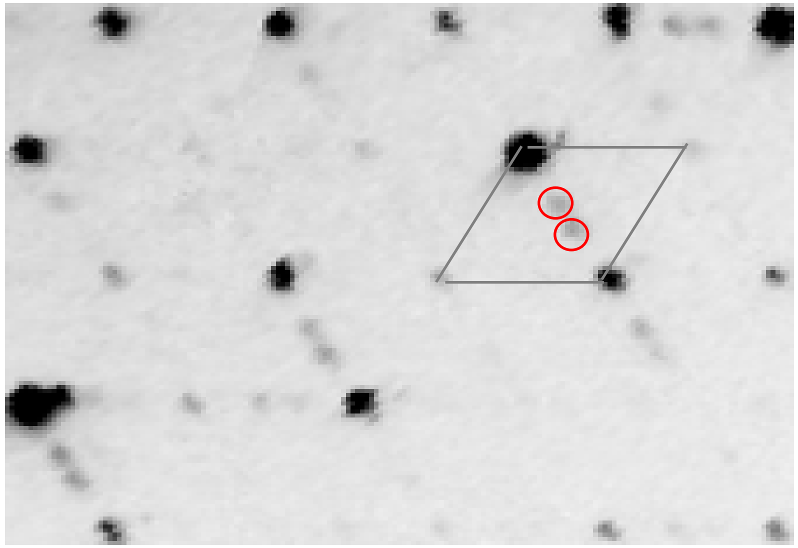



e3=0.000,x4=1.000
e2
6
2
-2
-6
-10
-10
-6
-2
2
6
e1
10

Back to the Bad

Remember $Ce_{13}Cd_{58}$





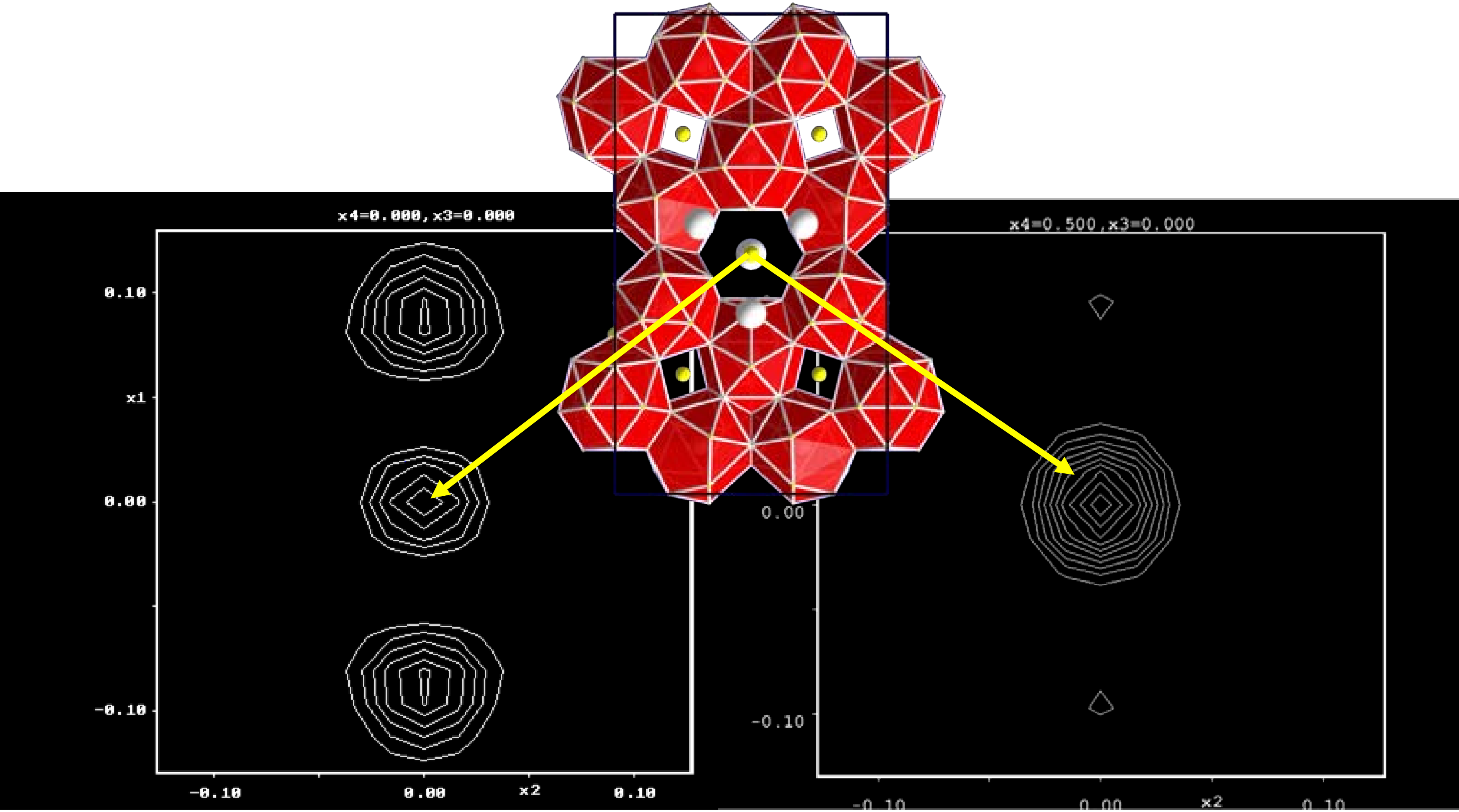
hk0

hk1

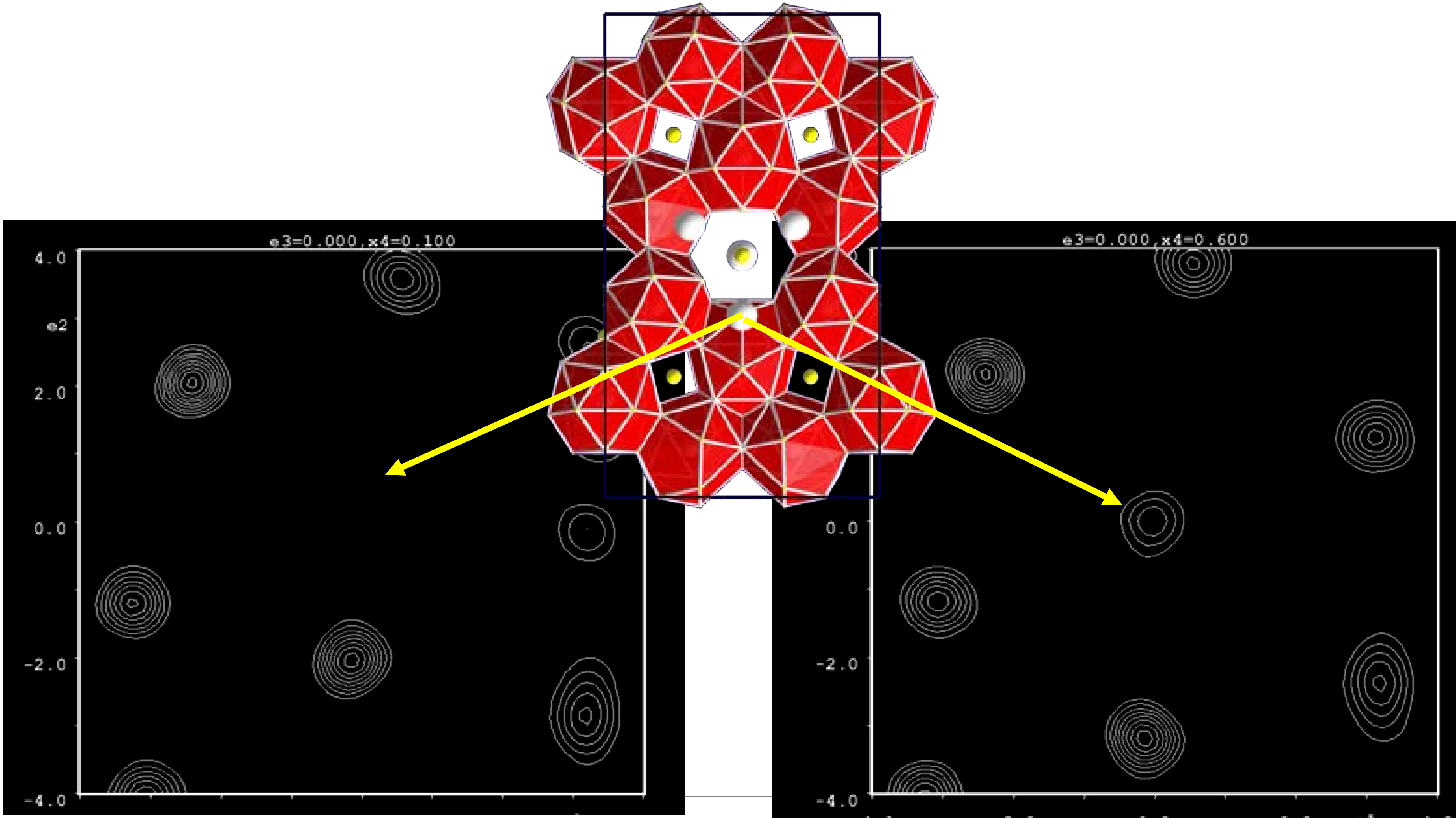
This structure contains 32 independent positions.

The superspace group is Amma(00g)s00

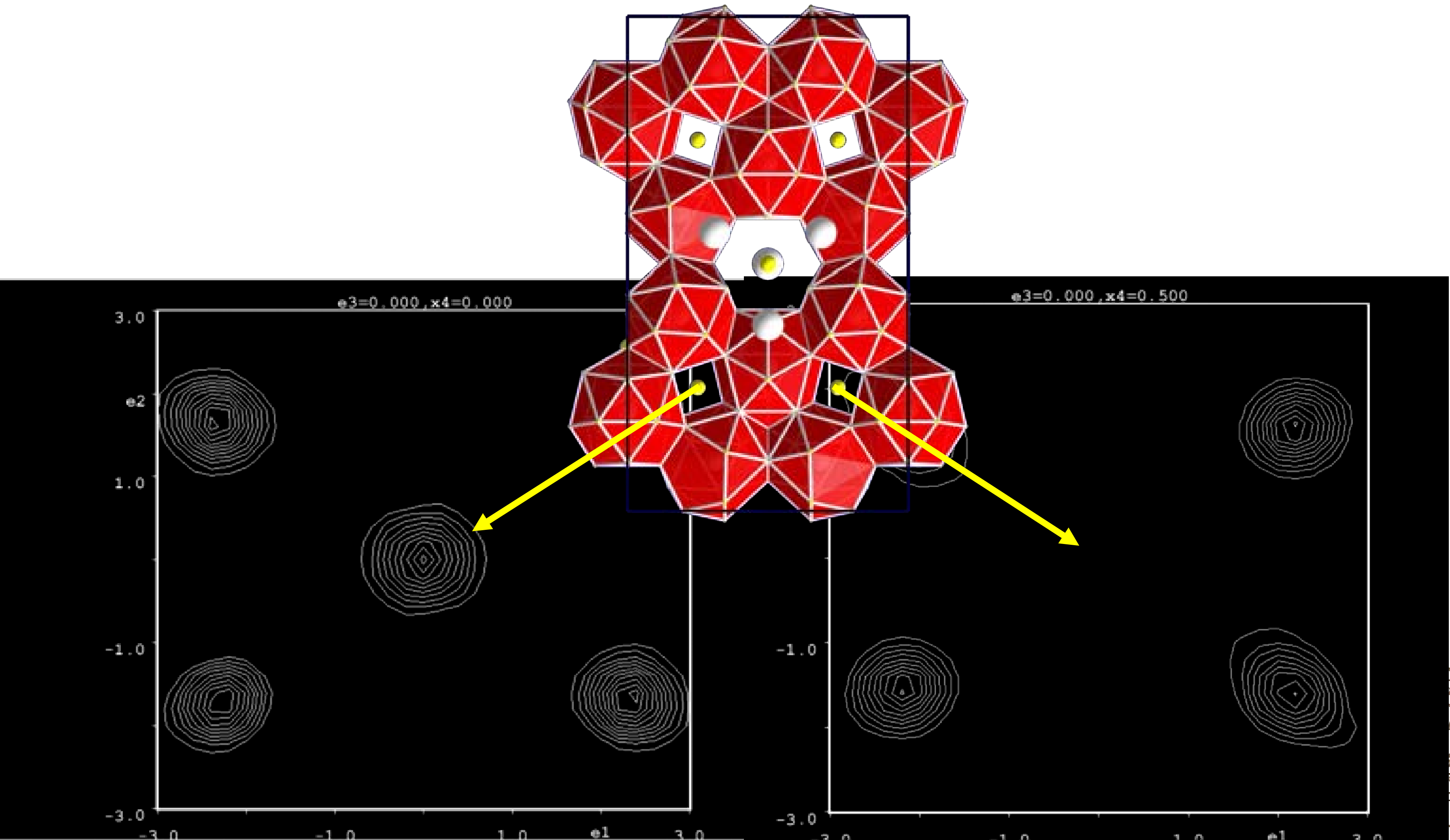
Exchange mechanism I



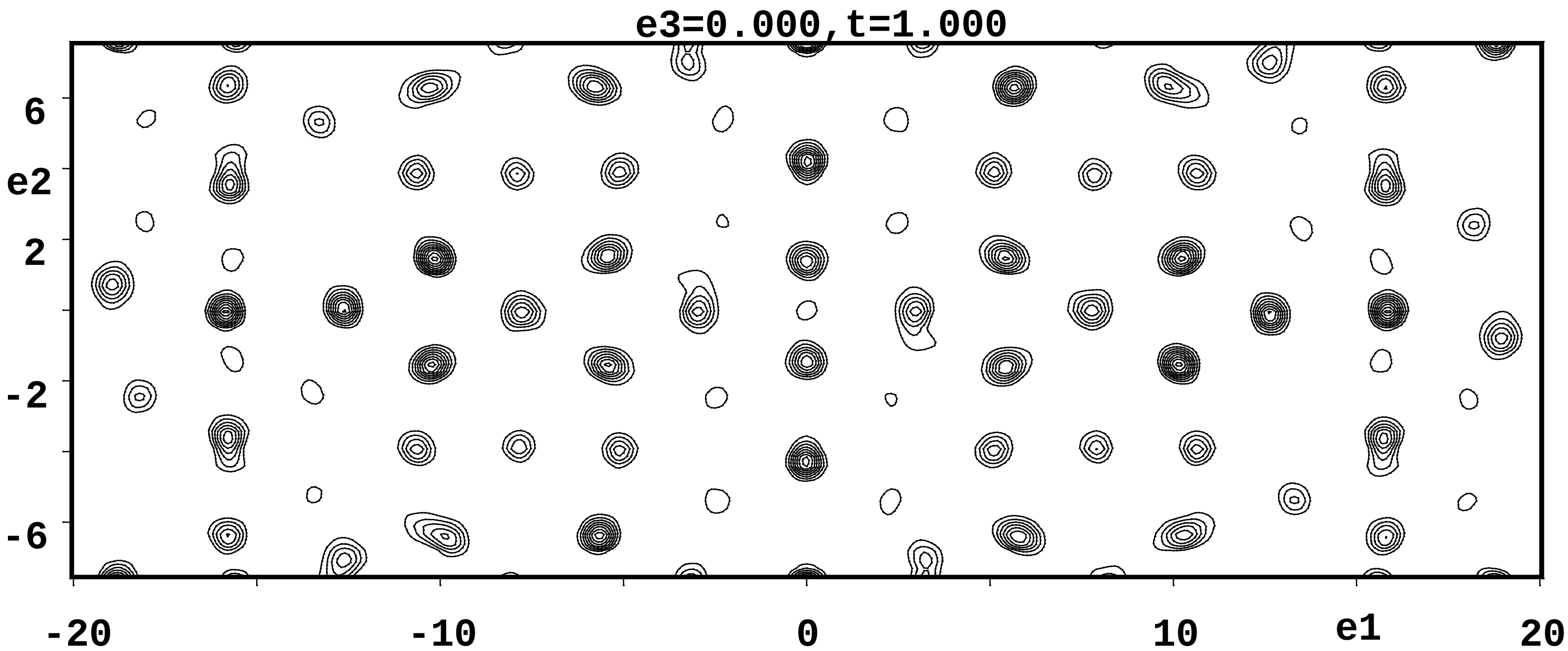
Exchange mechanism II



Exchange mechanism III



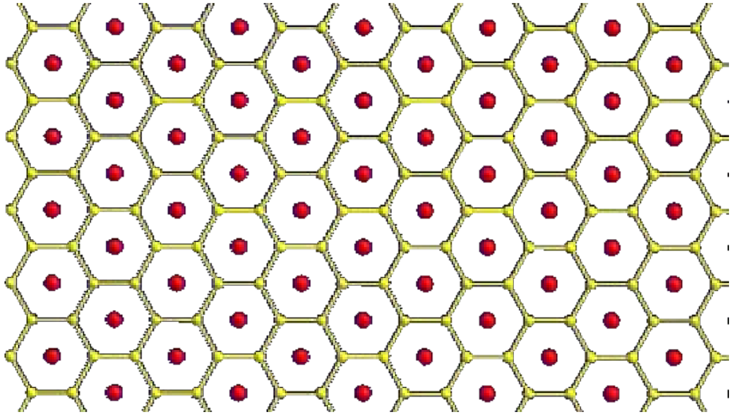
Put it all together



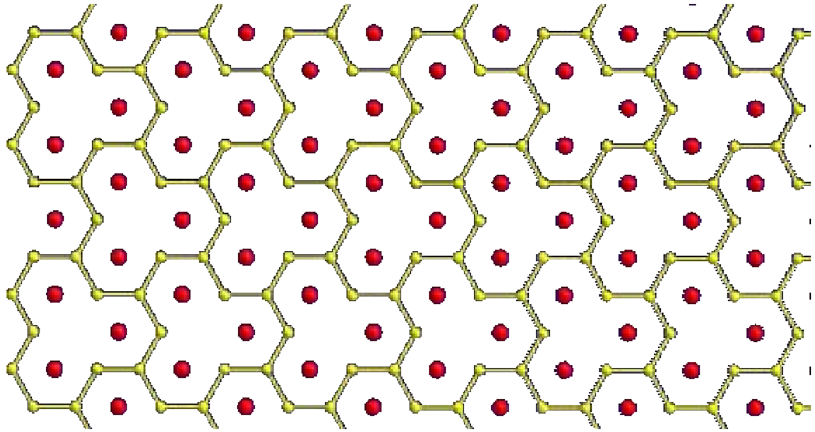
Examples

1 $Zn_{3-x}Sb_2$
2 Stistaite
3 Onoratoite
4 $Ba_2Cu_2Te_4O_{11}Br_2$ and $Ba_2Cu_2Te_4O_{11-d}(OH)_{2d}Br_2$
5 $Ca_{28}Ga_{11}$
6 $Re_{13}(Cd/Zn)_{\sim 58}$
7 $ReGe_{2-x}$

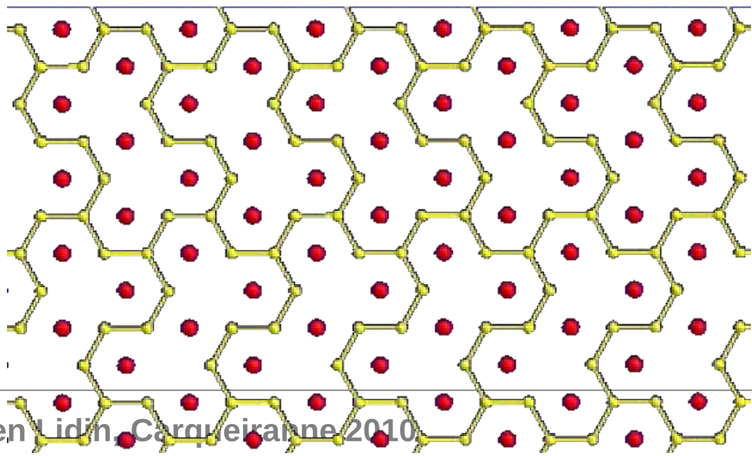
More AlB_2:XY_{2-q}



AlB_2 – P6/mmm - Cmmm



Yb_3Ge_5 – $P6\bar{2}m$ – Cm2m
q= (1/3 0 0)



R_5X_8 – Pbam
q=(2/5 0 0)

ReGe$_{2-x}$

The centering condition should allow for the C-centering of the parent AlB_2, but also for the primitive cell of the 5:8 compound.

α=0: hklm ⬄ hkl => h+k=2n

α=1/3: hklm ⬄ 3h+m k l => 3h+m+k=2n

α=2/5: hklm ⬄ 5h+2m k l => 5h+2m +k =?

This shows that the m component is involved in the centering: h+k+m=2n

$ReGe_{2-x}$

The a-glide ⊥ b is present even without the C-centering.
This must be generated by an s-glide ⊥ b =>
The superspace group is Xmmm(α00)0s0.

In many known compounds the q-vector takes the form q=(α0γ) =>
The super space group must then be a subgroup of Xmmm(α00)0s0 => X2/m(α0γ)0s

Composition

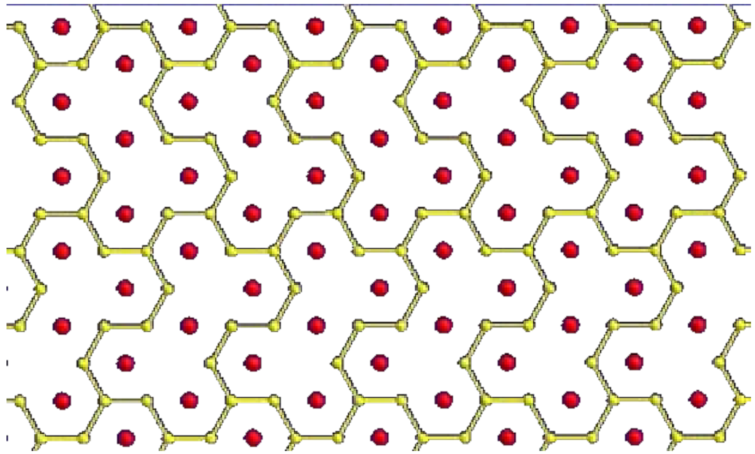
The commensurate cases indicate that the composition is given by the q-vector according to $ReGe_{2-\alpha x}$.

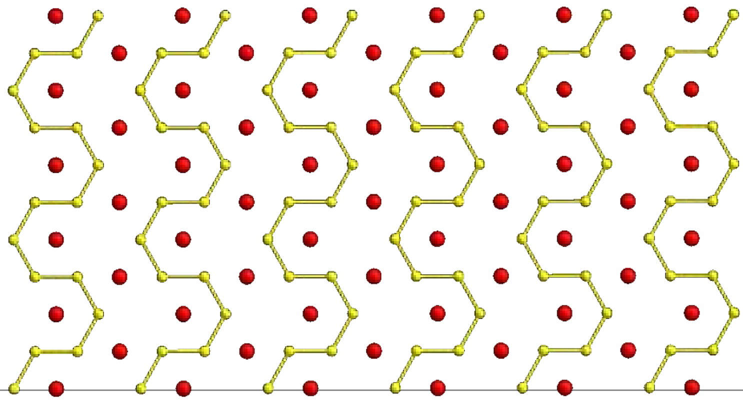
Every second Ge atom is removed from a number of rows deteremined by q_x.

The limiting case is represented by Tm_2Ge_3 and Lu_2Ge_3, $q_x=½$.

Limiting case

R_5X_8 – Pbam
q=(2/5 0 0)

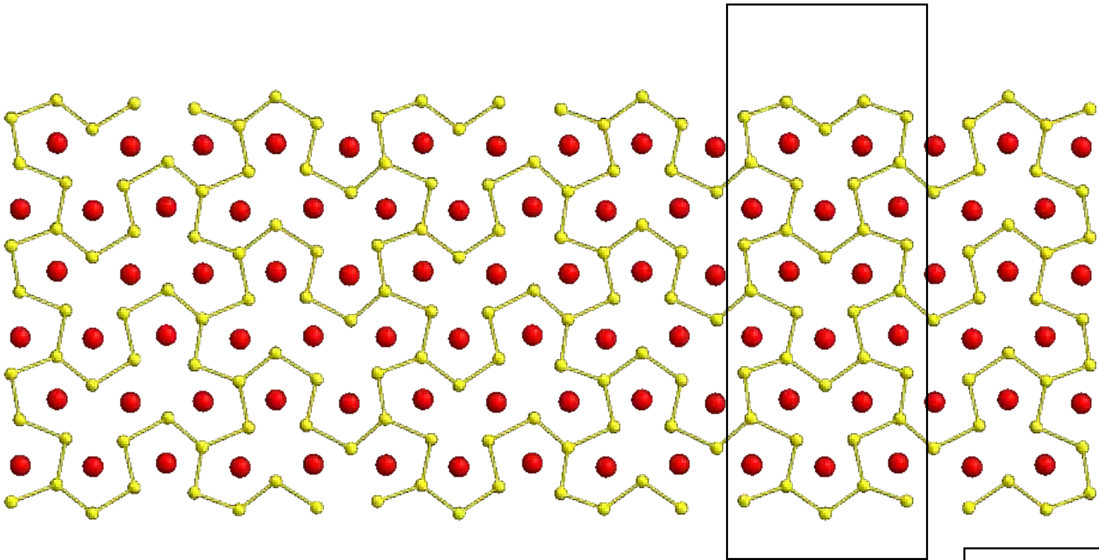




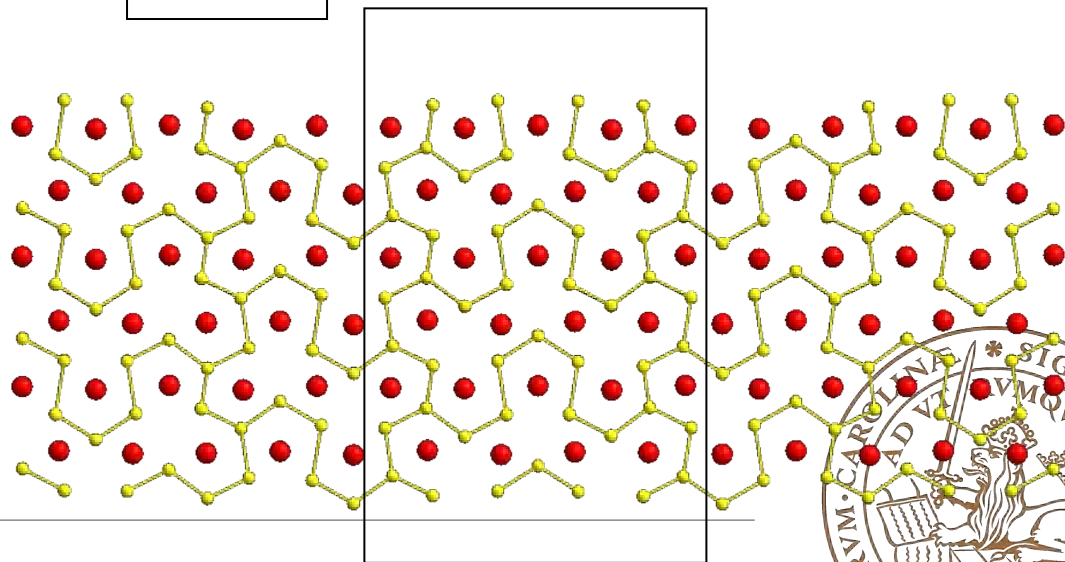
Tm_2Ge_3 – Pbam
q=(½ 0 0)

Example – Lviv

Example – $DyGe_{2-x}$



q<0.4



q>0.4