

# **cobaltates de sodium**

## **Nax-Co-O<sub>2</sub>**

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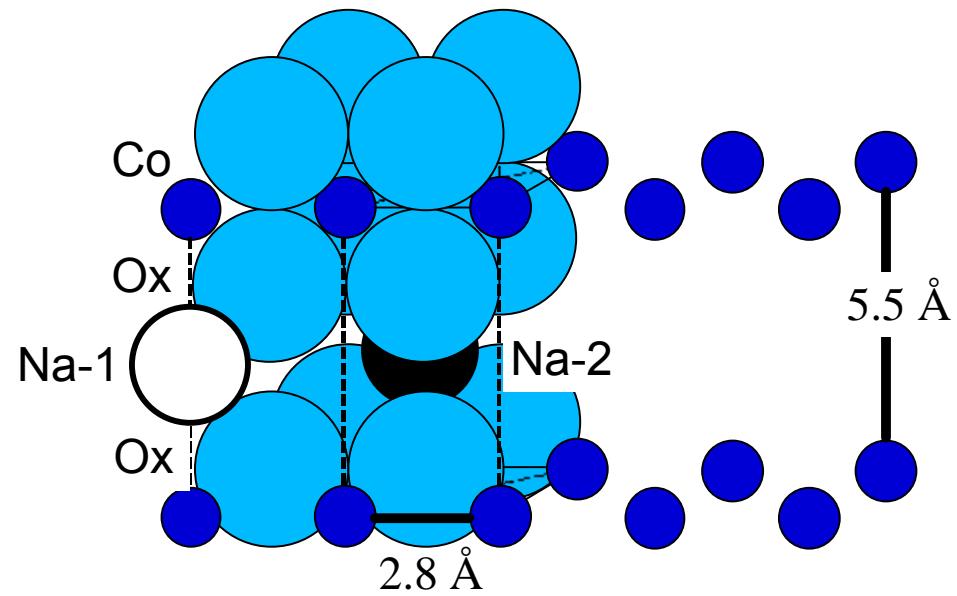
(\*) SPEC Saclay

(\*\*) Kazan State University

# Quelques caractéristiques du système **Nax-Co-O2**

- 1) Structure hexagonale des sites cobalt  
**sans pollution par des impuretés**
- 2) Structure cristalline simple : un seul motif **Nax-Co-O2** par bloc élémentaire
- 3) Diagramme de phase exceptionnellement étendu  
 $x(\text{Na})$  en principe entre  $\approx 0$  et 1  
état électronique du cobalt entre **S = 0 and 1/2**
- 4) Un diagramme de phase magnétique particulièrement riche  
Avec une phase **supraconductrice**
- 5) Propriétés de **super conducteur ionique**

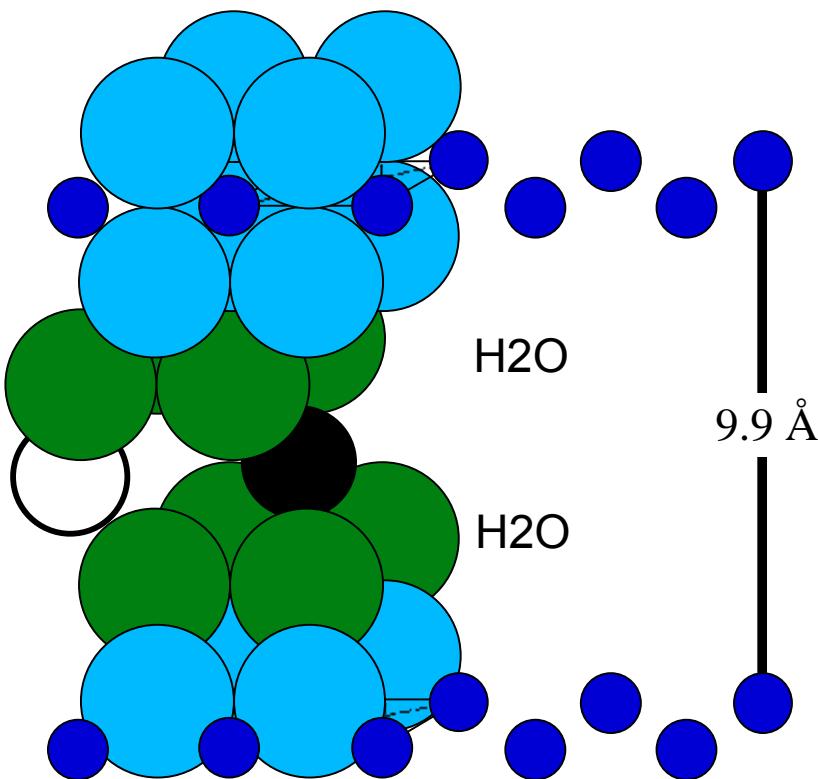
'hexagonal'



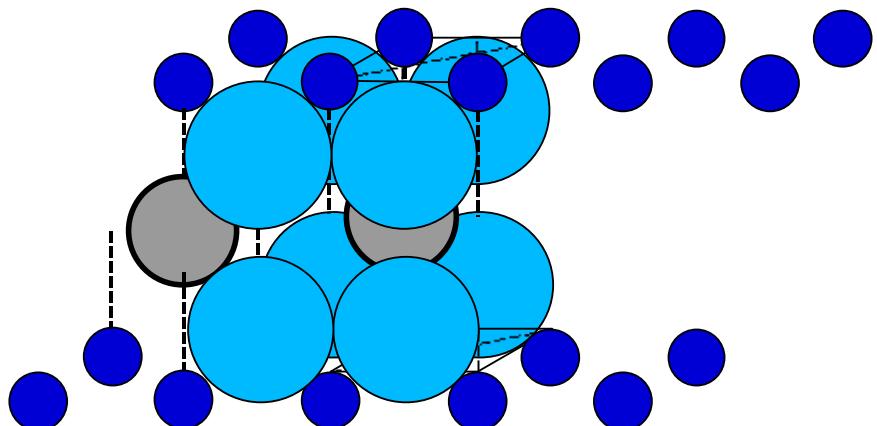
H<sub>2</sub>O

9.9 Å

H<sub>2</sub>O



Hydraté  
'supra'



'rhomboédrique'

Nax-Co-O<sub>2</sub>

1 > x > 0.40

c 5.2 Å 5.6 Å

# Composés résultant d'une combinaison des deux oxydes Co-O(1.5-2) et Na(2)-O

Le paramètre déterminant est le **degré d'oxydation du cobalt** dans les conditions de la synthèse

Ce **degré d'oxydation** ne dépend que des conditions de l'élaboration :

- { Température : une T plus élevée correspond à un degré d'oxydation inférieur
- Nature de l'atmosphère : oxydante, neutre, réductrice

Mais ne dépend pas de la **composition nominale** du mélange de départ

Difficulté : les excès d'oxyde de sodium ne sont pas toujours faciles à détecter

*Changements 'spontanés' de composition*

Exemple de difficultés :

Le diagramme de phases est séquencé en **domaines distincts**  
séparés par des **gaps de composition**

Certaines compositions difficiles à préparer directement  
→ méthode : partir de deux compositions calibrées encadrant la cible

*Publication procédant de cette méthode  
mais retraitant toutes les compositions dans les mêmes conditions*

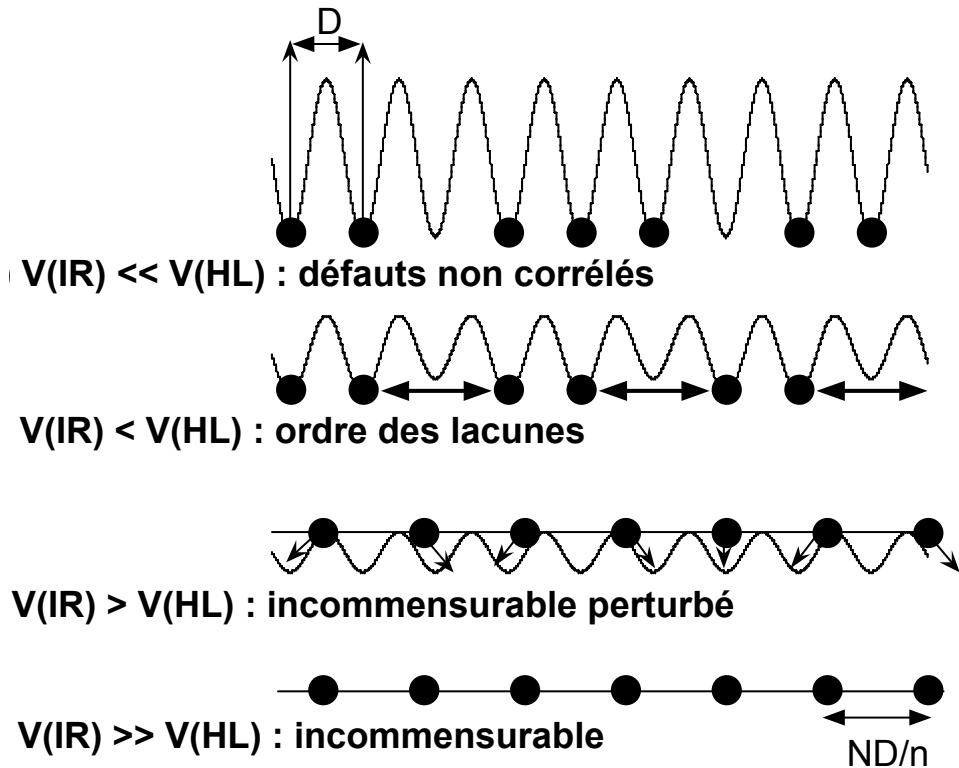
*RESULTAT : toujours le même degré d'oxydation du cobalt  
donc la même concentration en sodium ( $\pm$ impuretés)*

*Donc : les propriétés ne varient pas avec la concentration en sodium ( ? )*

# SUPER IONIC CONDUCTOR

## V(HL) HOST LATTICE

## V(IR) INTER IONIC REPULSION



DISORDER

ION ORDERING

DISTORTED  
INCOMMENSURABILITY

INCOMMENSURATE  
*super ionic*

# Dans un matériau SUPER-IONIQUE

Il existe des **canaux de conduction**

Le **potentiel est peu modulé** par le réseau hôte le long de ces canaux

Il en résulte une prédominance de la **REPULSION INTER-IONIQUE (I.R.)**

Les ions étant extrêmement **mobiles** tendent à construire des configurations dans lesquelles chaque ion occupe un **minimum du potentiel** créé par les autres ions

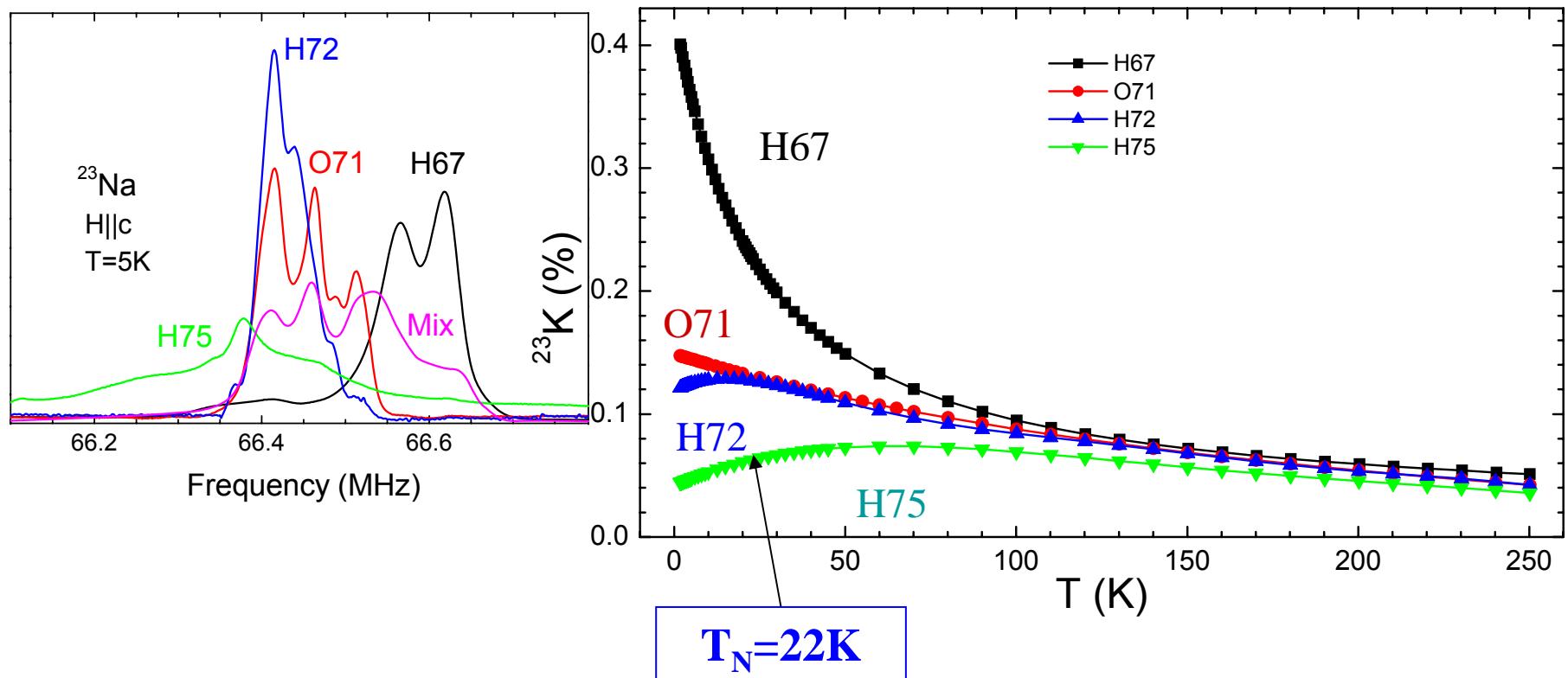
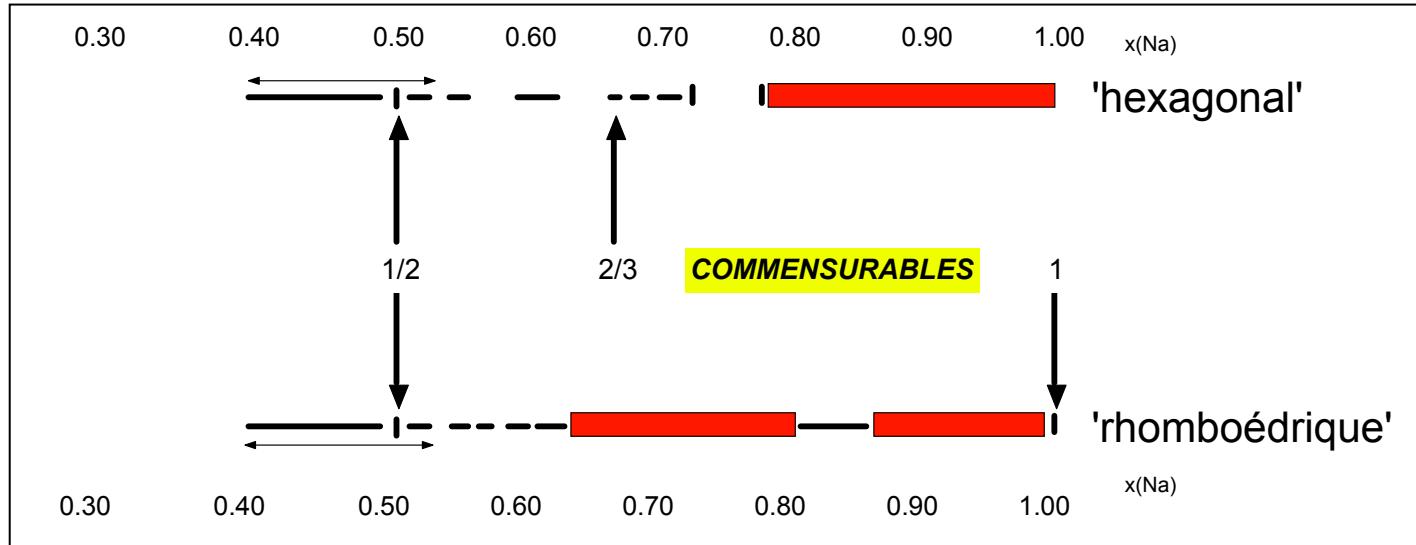
- Incommensurabilité en 1-D : Hollandite, ..
- Positions interstitielles en 2 et 3-D : Alumine  $\beta$ , Nasicon, ...

*Dans tous les cas sans référence au réseau moyen*

→ les équilibre stables n'existent que pour quelques **compositions particulières**

→ donc le diagramme de phase est **discontinu**

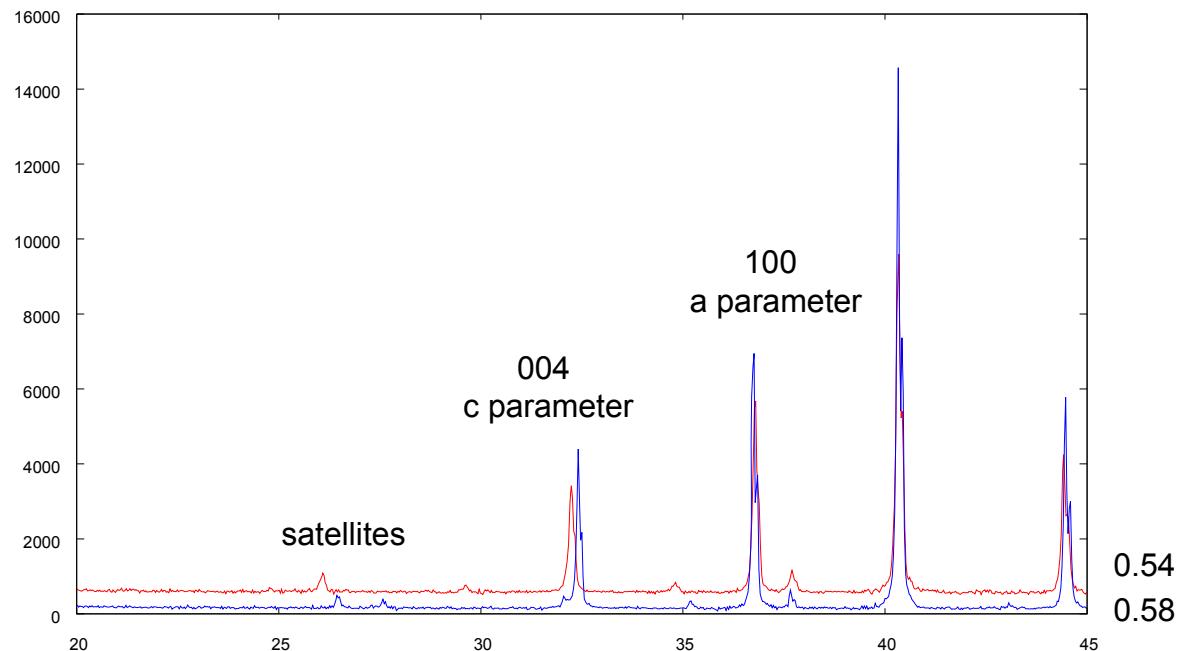
entre : **mélanges** → ordre à courte distance, séparation de phases, ...



ON X RAY DIFFRACTION PATTERNS  
SYSTEMATIC OCCURRENCE OF SATELLITE REFLECTIONS  
mostly incommensurate wave vector modulation

LONG RANGE CORRELATIONS  
AND NOT 'DISORDER' : (what is disorder ?)

INCOMMENSURABILITY IS AN ORDER IN A (3+n)D SPACE



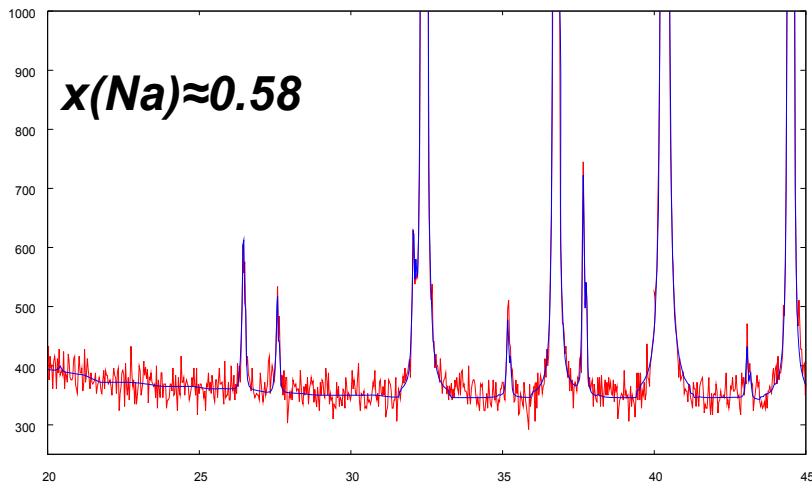
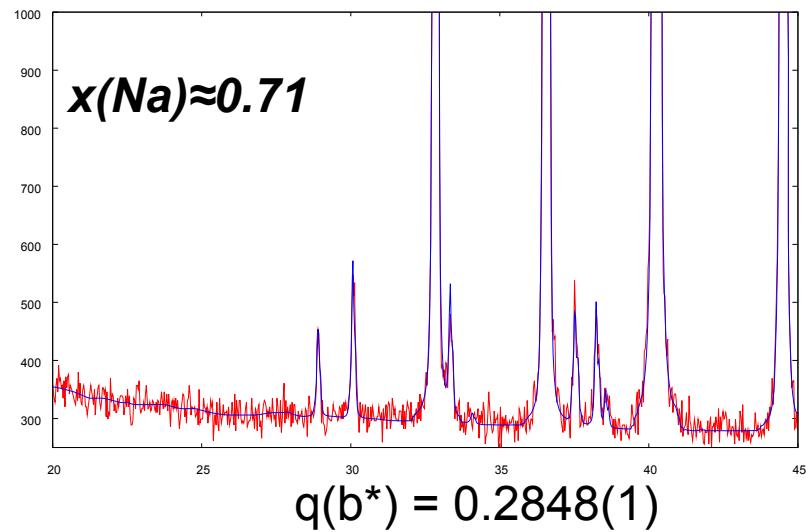
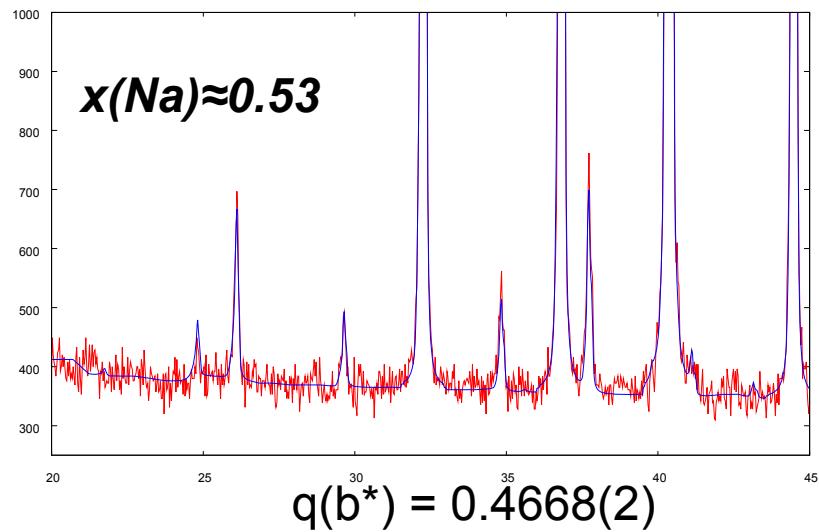
for a change 1 in  $x(\text{Na})$

sat. position  
c parameter  
a parameter

changes  
changes  
changes

1  
10-1  
10-2

*red : measured*  
*blue : calculated*



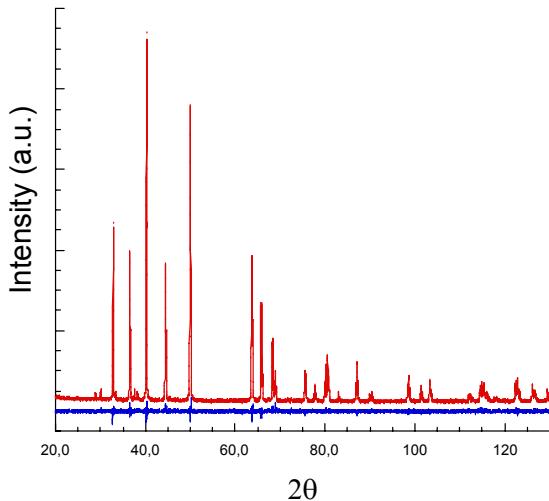
$q(a^*) = 0.0936(2)$     $q(b^*) = 0.3970(1)$     $q(c^*) = 1/2$

incommensurate wave vector modulations

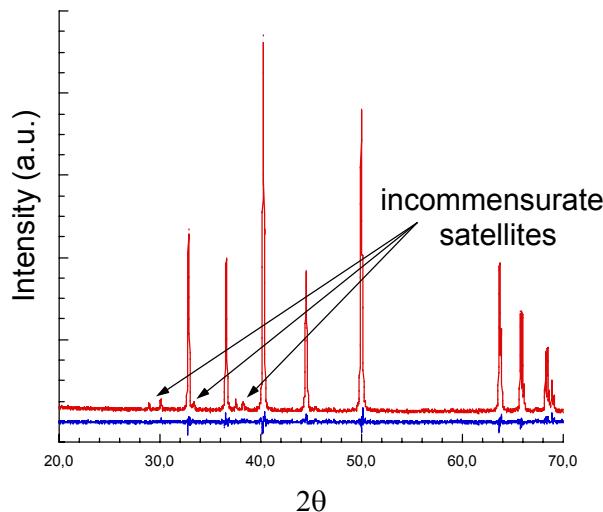
# $x(\text{Na})=0.71$

## diffraction pattern

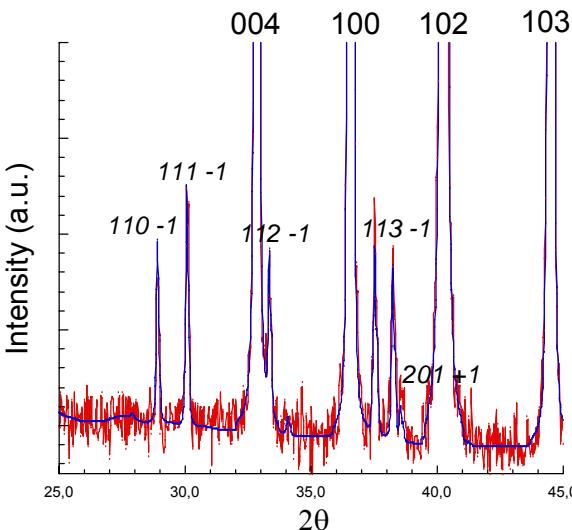
*total*



*low angle part*



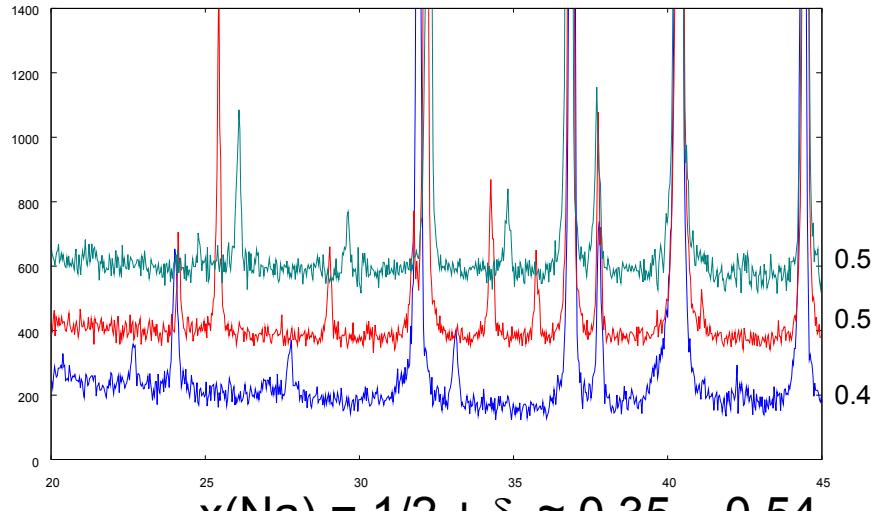
CALCULATION OF SATELLITE  
REFLECTIONS :  
POSITIONS AND INTENSITIES



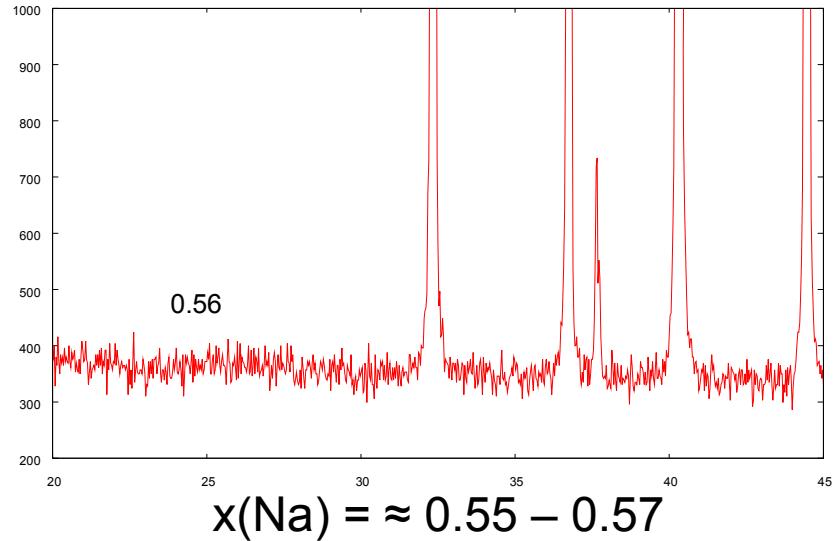
red : measured  
blue : calculated

incommensurate wave vector  
modulation :  $q(b^*) = 0.2848(1)$

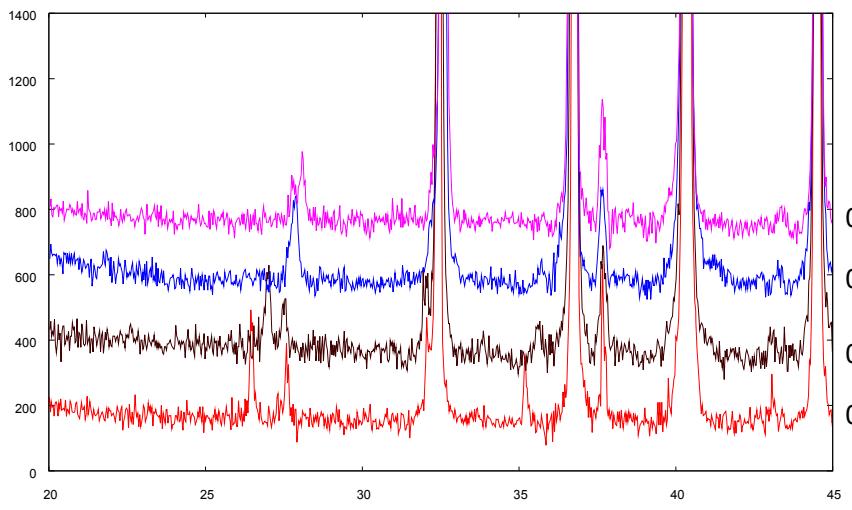
# SATELLITE REFLECTIONS



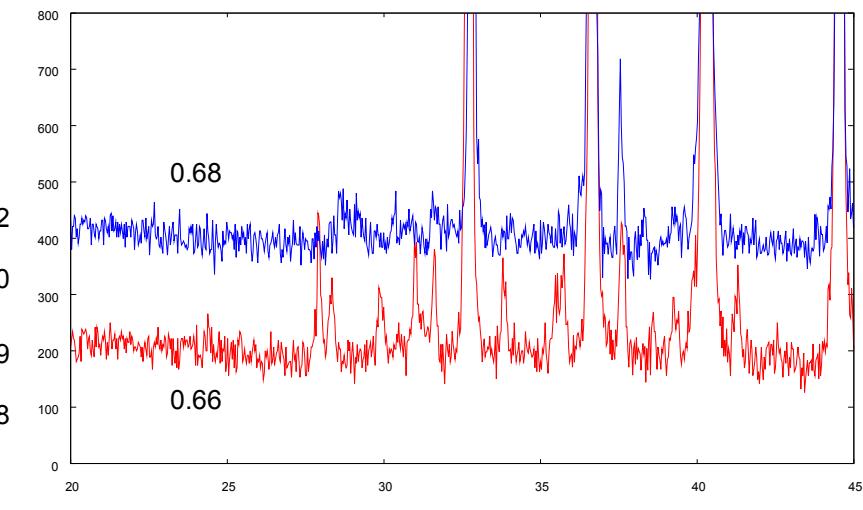
$$x(\text{Na}) = 1/2 \pm \delta, \approx 0.35 - 0.54$$



$$x(\text{Na}) = \approx 0.55 - 0.57$$



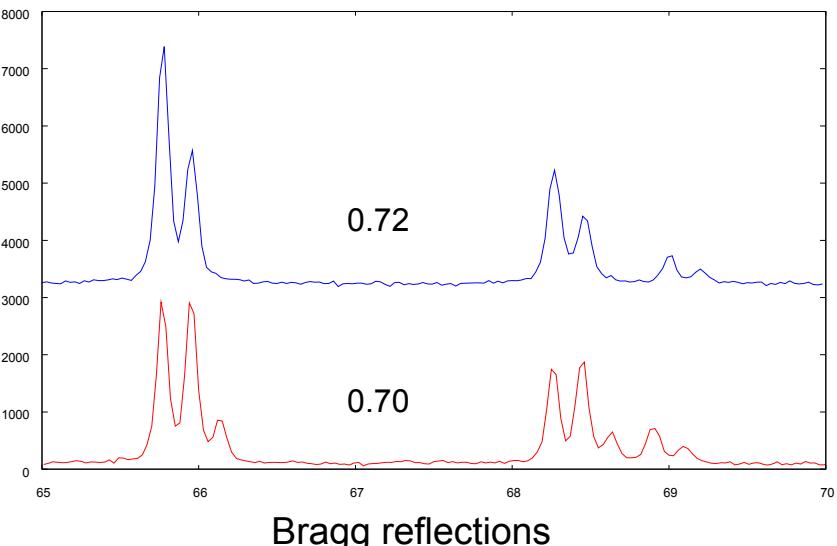
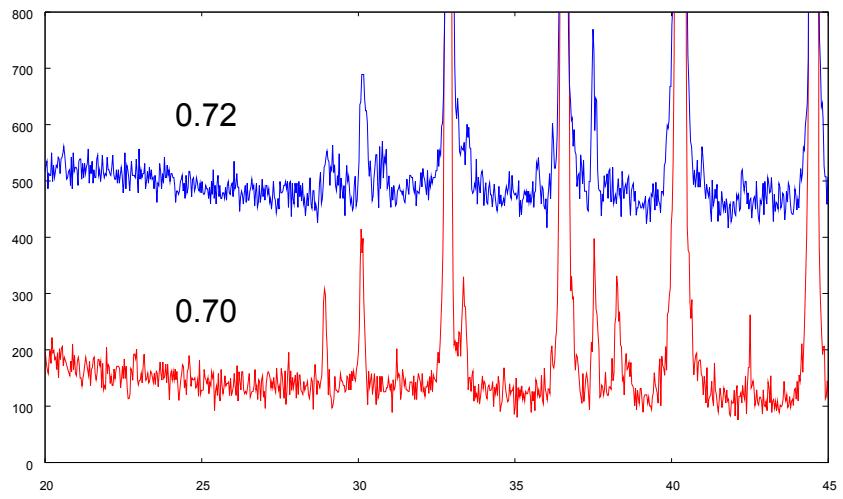
$$x(\text{Na}) = 3/5 \pm \delta, \approx 0.58 - 0.62$$



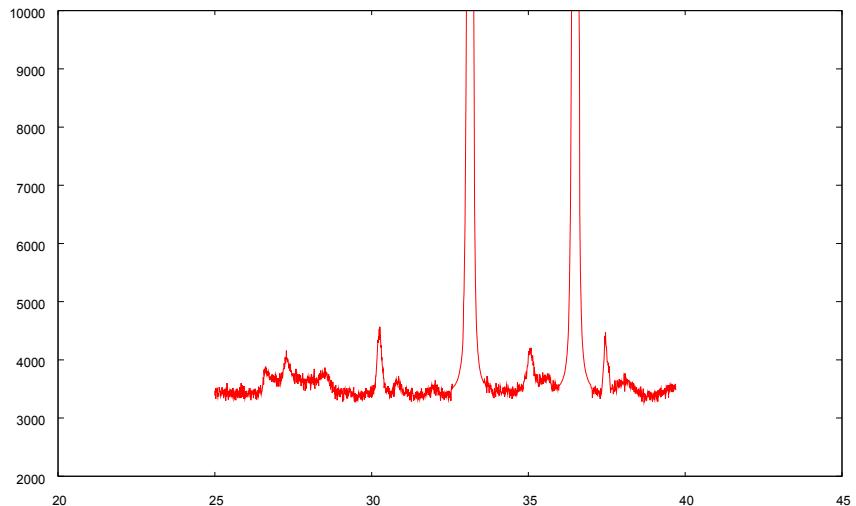
$$x(\text{Na}) = 2/3 \pm \delta, \approx 0.66 - 0.68$$

$$x(\text{Na}) = 0.72$$

$$5/7 \pm d, \approx 0.70 - 0.71$$



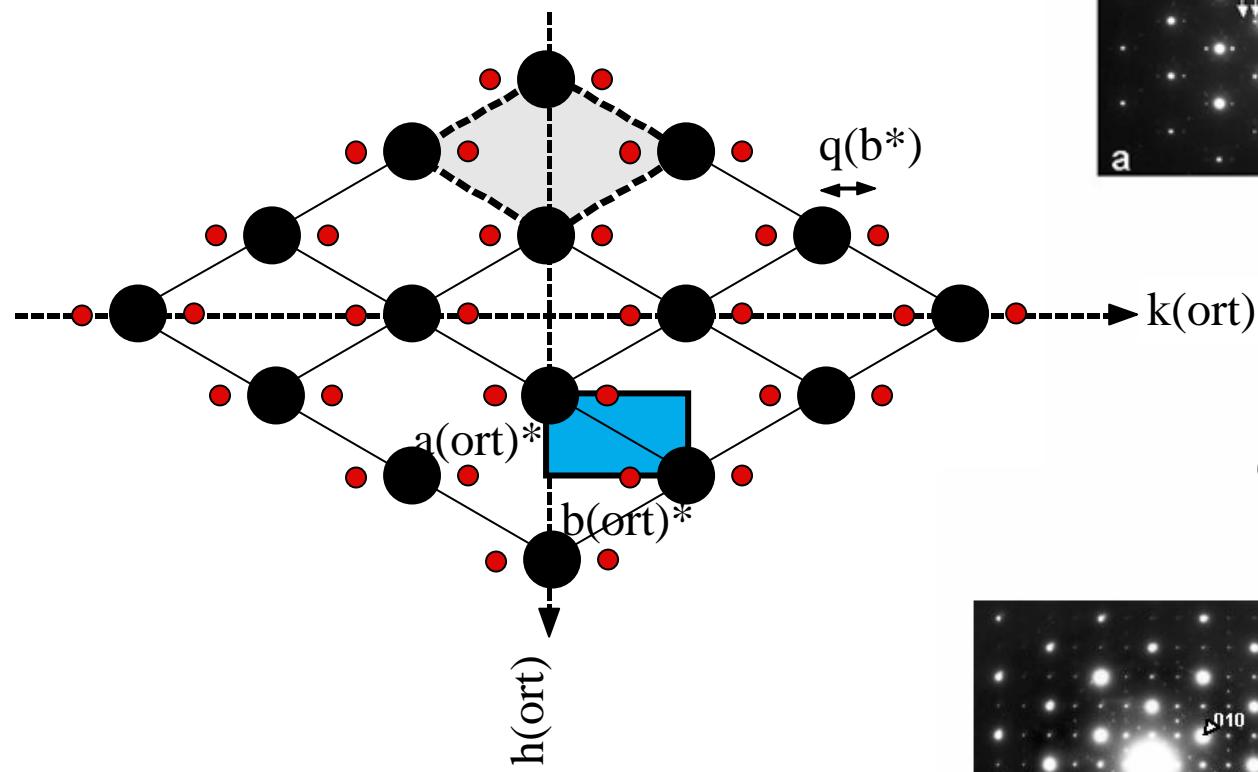
Bragg reflections  
 blue : usual hexagonal reference lattice  
 red : orthorhombic distortion



20 times longer !  
 data collection times

$x(\text{Na}) > 0.75$

Cf. Zandbergen et al.  
PRB 70, 2004



$X(\text{Na})=0.64$

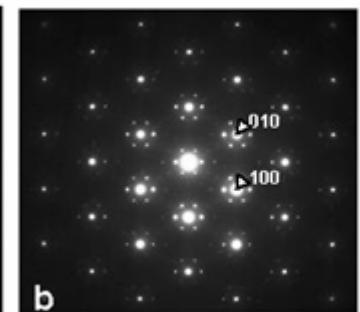
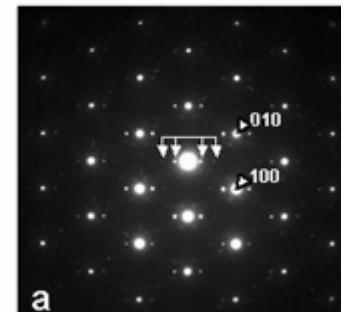
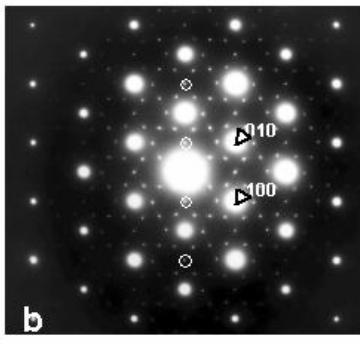
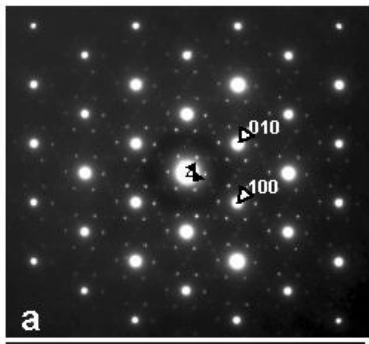
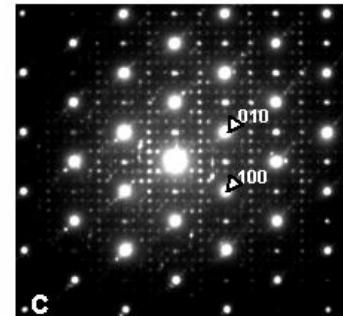
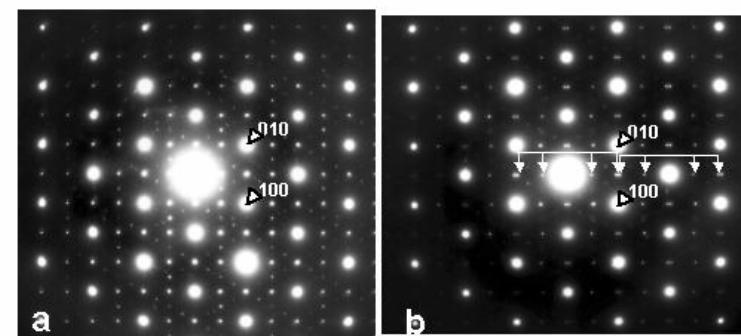
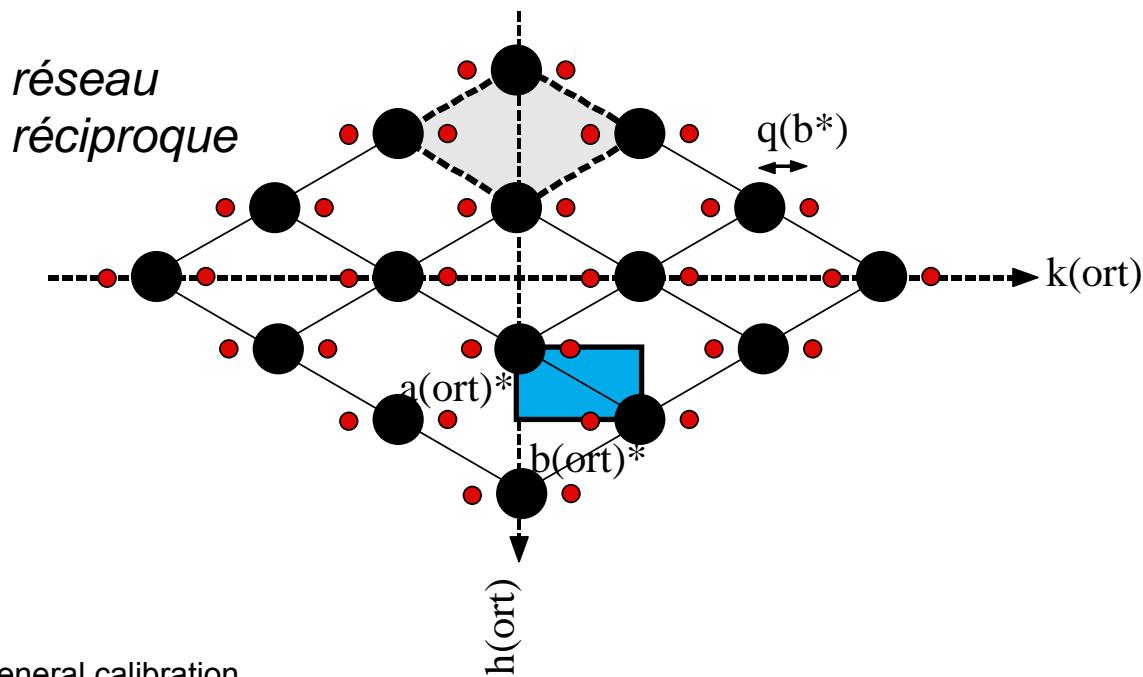


Figure 1.  $X(\text{Na})=0.7$

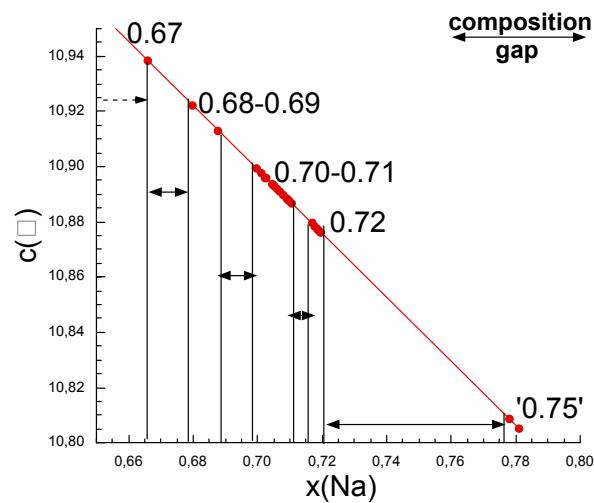
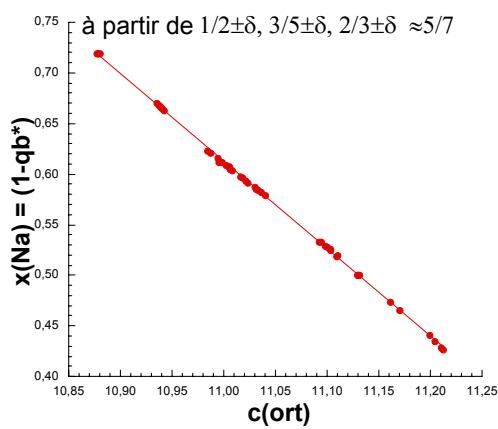
diffraction électronique



$X(\text{Na})=0.5$

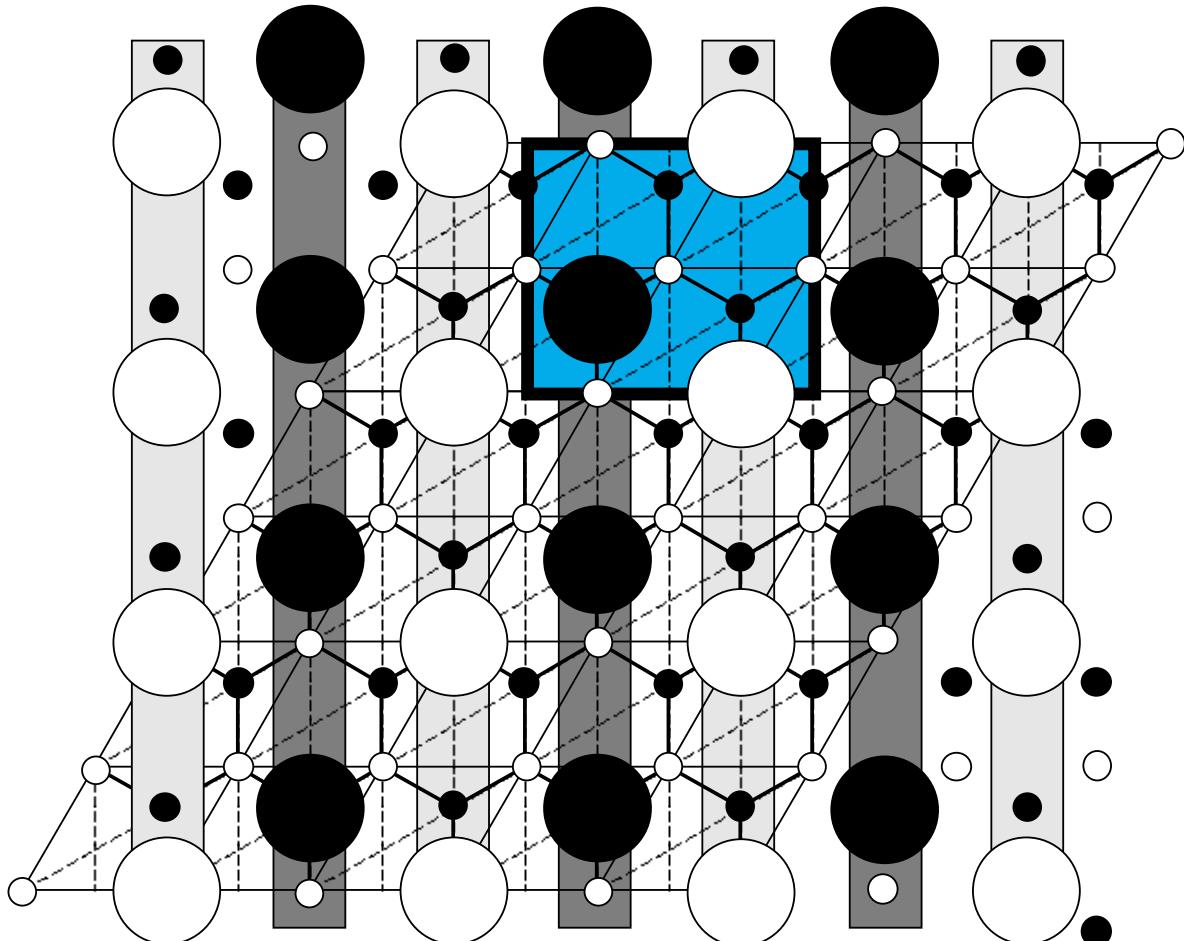


general calibration  
curve (54 points)



Dépendance linéaire entre **[c]** et **[ $1 - q(b^*) = x(Na)$ ]**

# Na<sub>1/2</sub>-Co-O<sub>2</sub>



Big circles : Na ions  
white Na-1 positions  
black Na-2 positions

*Same scale for  
Ionic radii and lattice  
constants*

blue : 2D cell

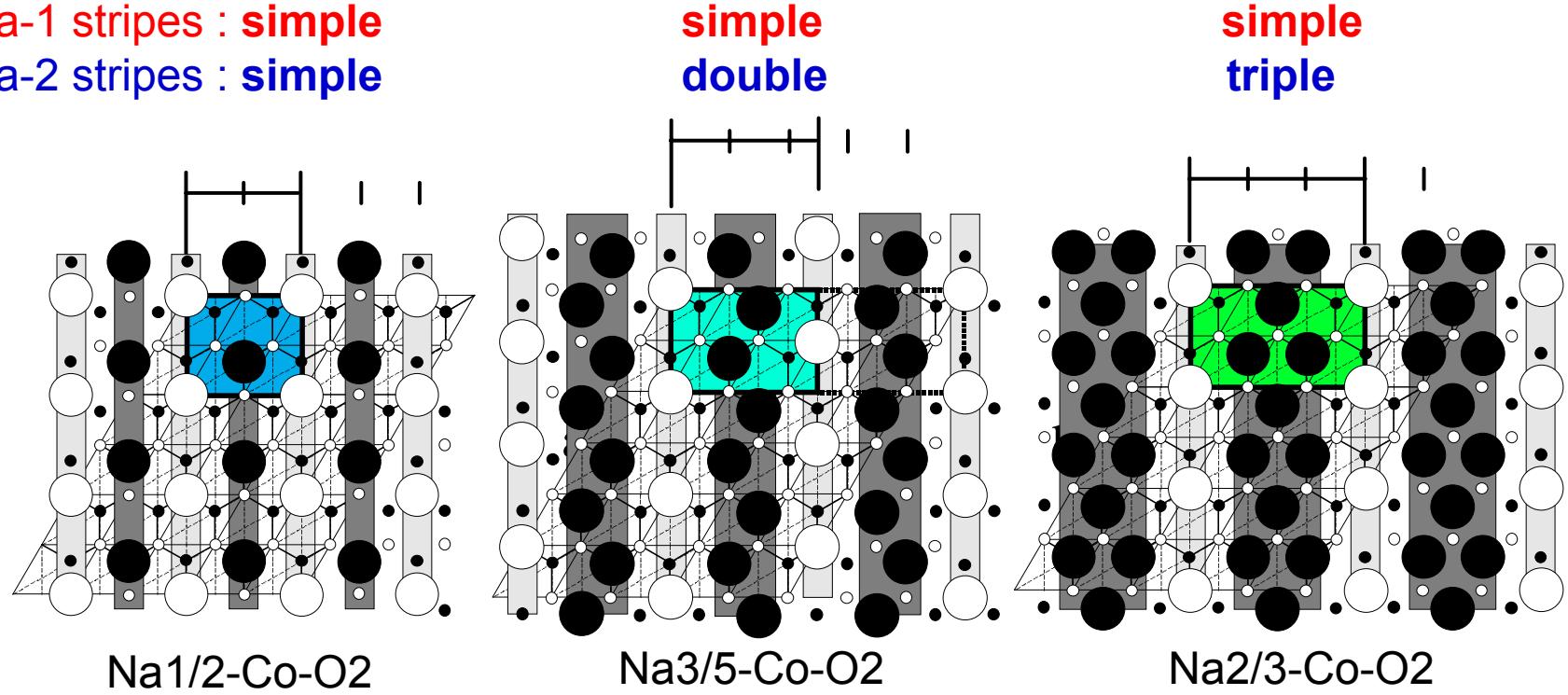
Small circles :  
forbidden positions

All positions are  
either occupied  
or forbidden



stable configuration

Na-1 stripes : simple  
Na-2 stripes : simple



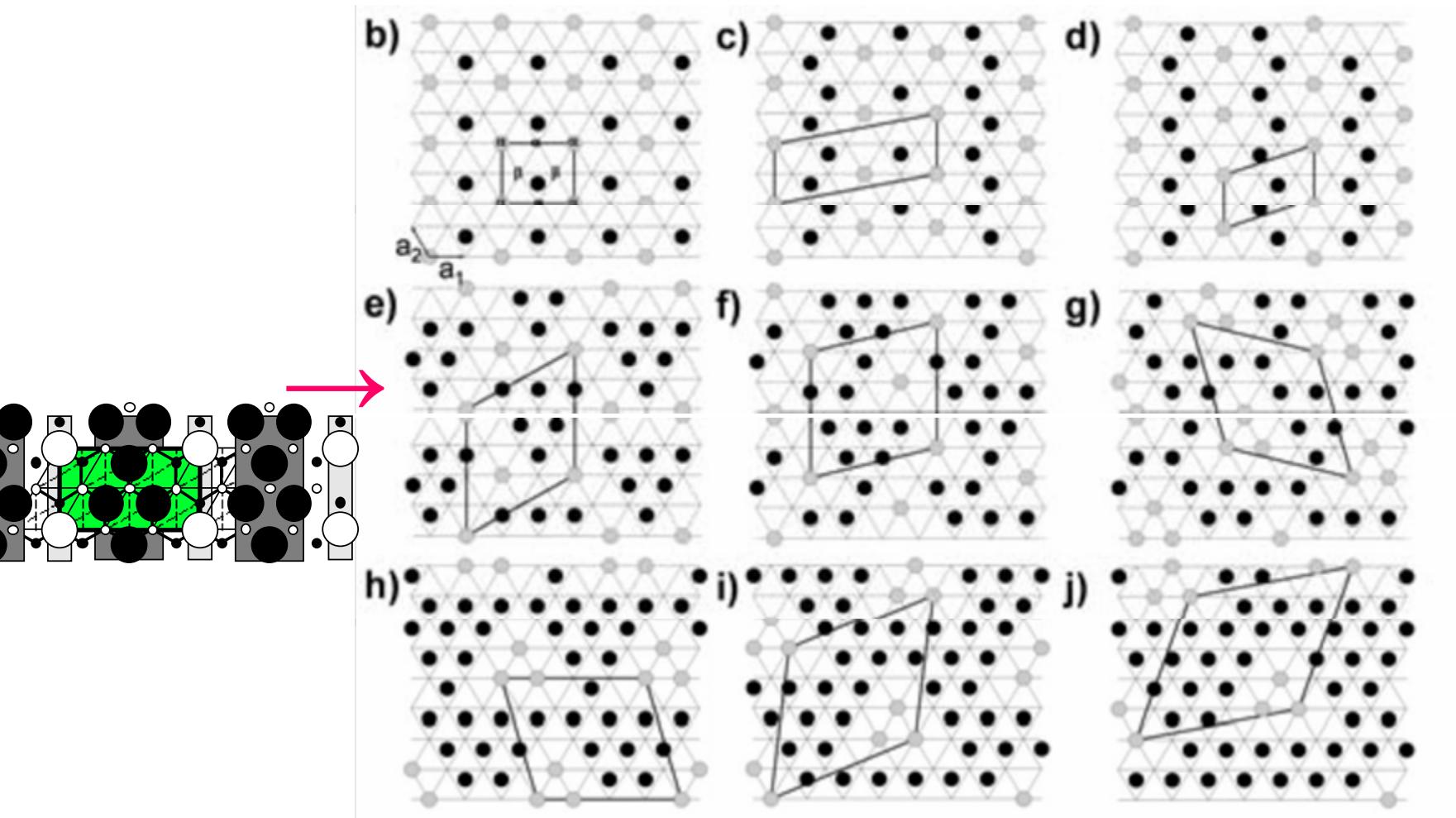
|         |                   |                     |                   |     |                   |
|---------|-------------------|---------------------|-------------------|-----|-------------------|
| cell :  | $a\sqrt{3}^*(2)a$ | $a\sqrt{3}^*(2.5)a$ | $a\sqrt{3}^*(3)a$ | ... | $a\sqrt{3}^*(p)a$ |
| n(Na)   | 2                 | 3                   |                   |     | 4                 |
| surface | $S = 4s$          | $S = 5s$            |                   |     | $S = 6s$          |

toutes sont des configurations stables

$$q(b^*) = 1/p$$

$$\rightarrow x(\text{Na}) = 1 - q(b^*)$$

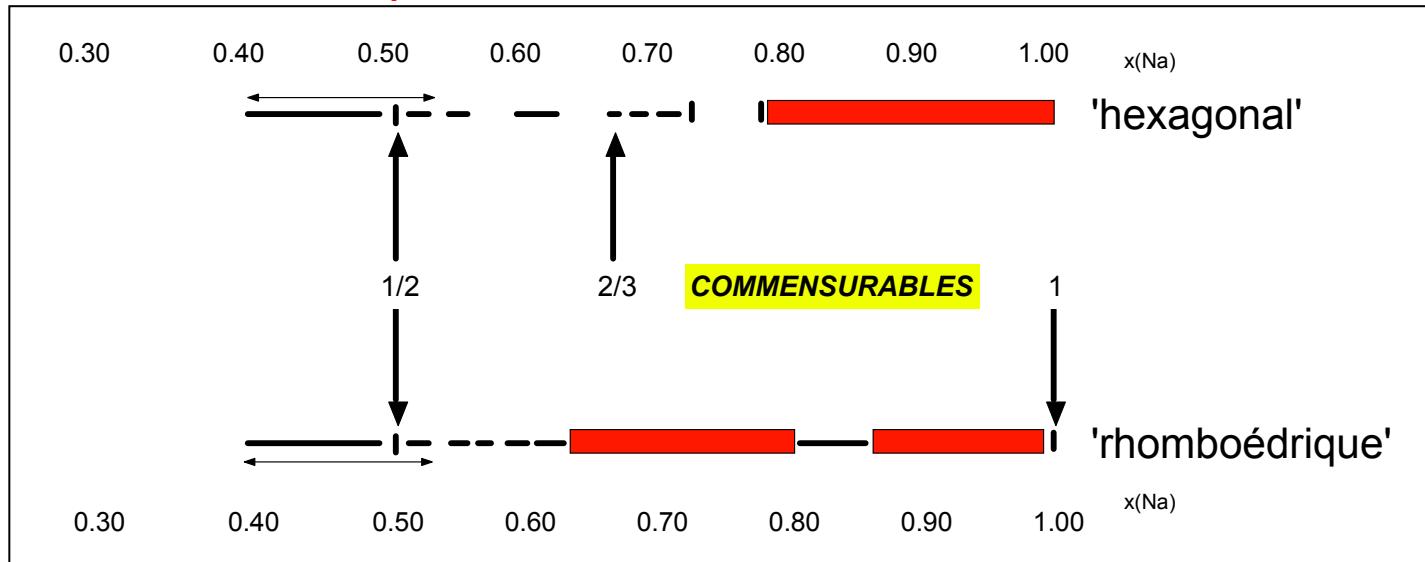
generalized gradient approximation "GGA+U "  
with the cluster expansion and Monte Carlo simulation technique



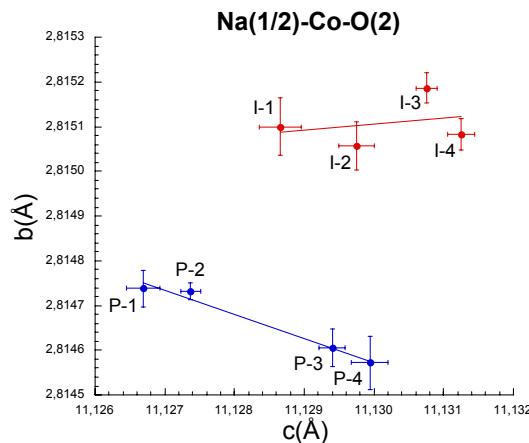
→      →

|                       |                  |                  |
|-----------------------|------------------|------------------|
| b) 0.50 (1/2),        | c) 0.56 (5/9),   | d) 0.60 (3/5)    |
| <b>e) 0.67 (4/6),</b> | f) 0.71 (5/7),   | g) 0.77 (10/13)  |
| h) 0.81 (13/16),      | i) 0.84 (16/19), | (j) 0.86 (18/21) |

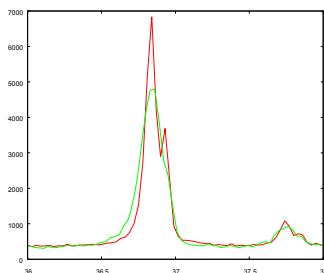
$$x(\text{Na}) = 1/2$$



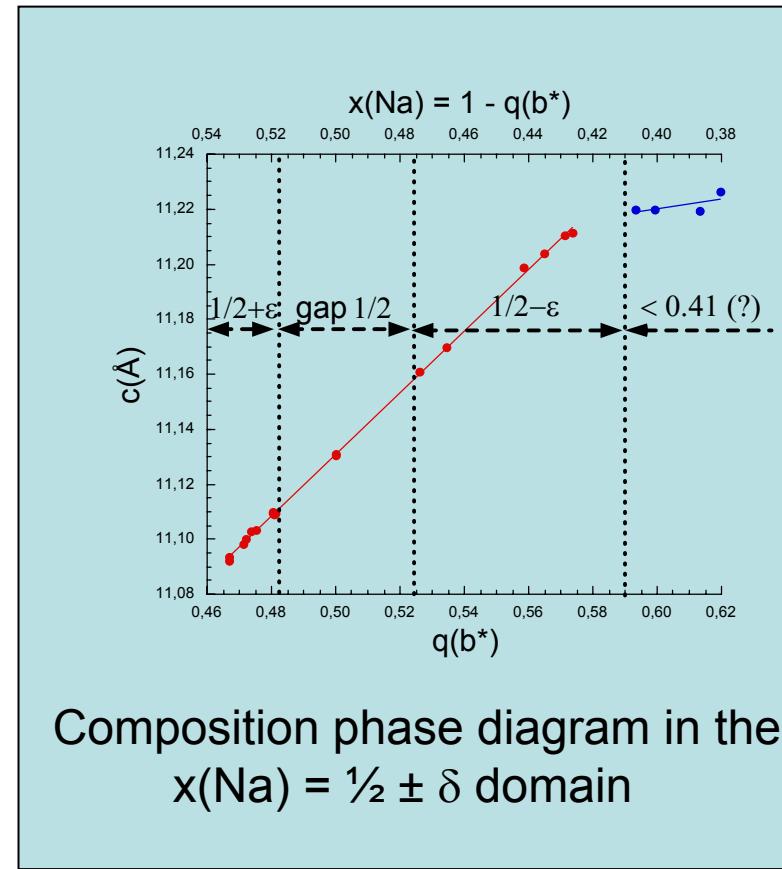
# Na<sub>1/2</sub>-Co-O<sub>2</sub>

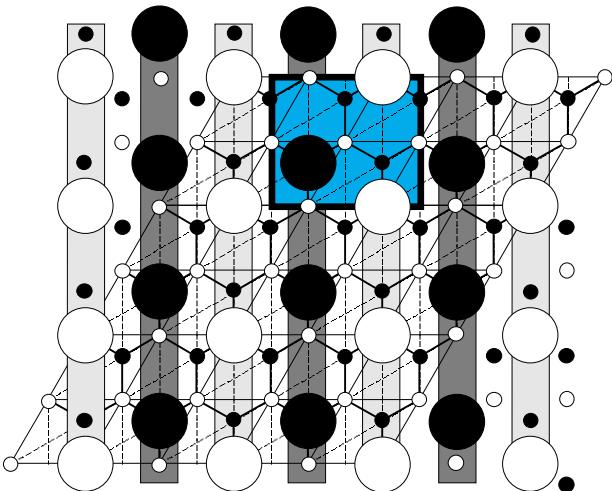


Several samples of  $x(\text{Na}) = '1/2'$   
 red : 'ideal'  
 blue: stacking faults and defects

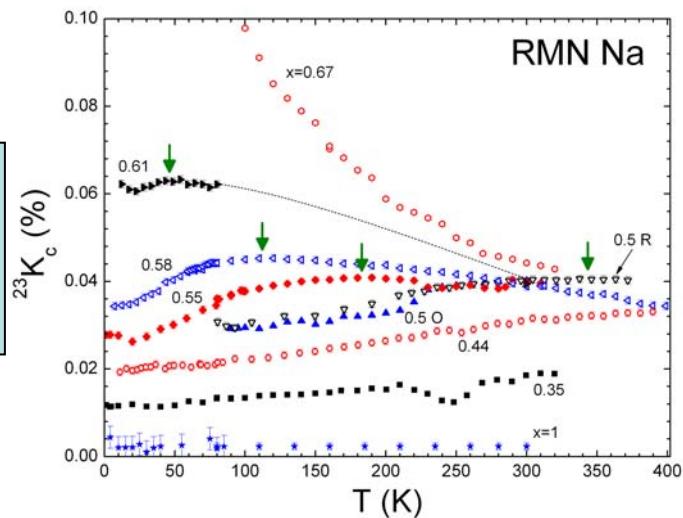
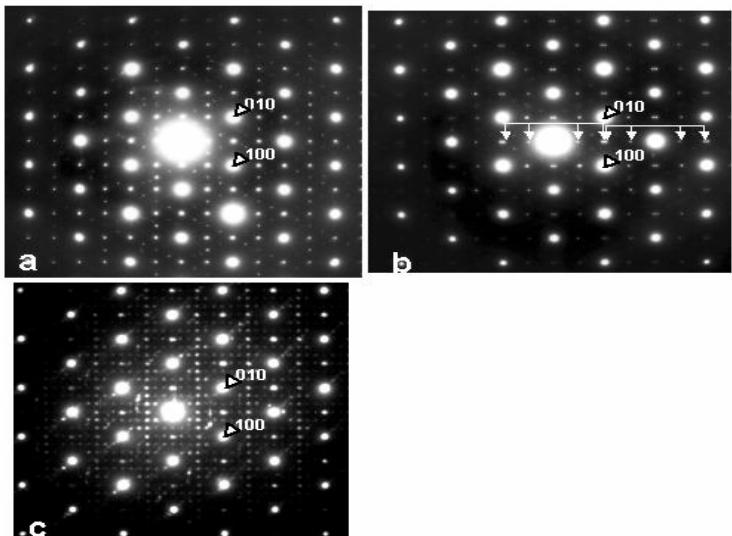


fundamental Bragg peak hexagonal 100 reflexion :  
 red : 'ideal', green : with stacking faults





Cf. Zandbergen et al.  
PRB 70, 2004



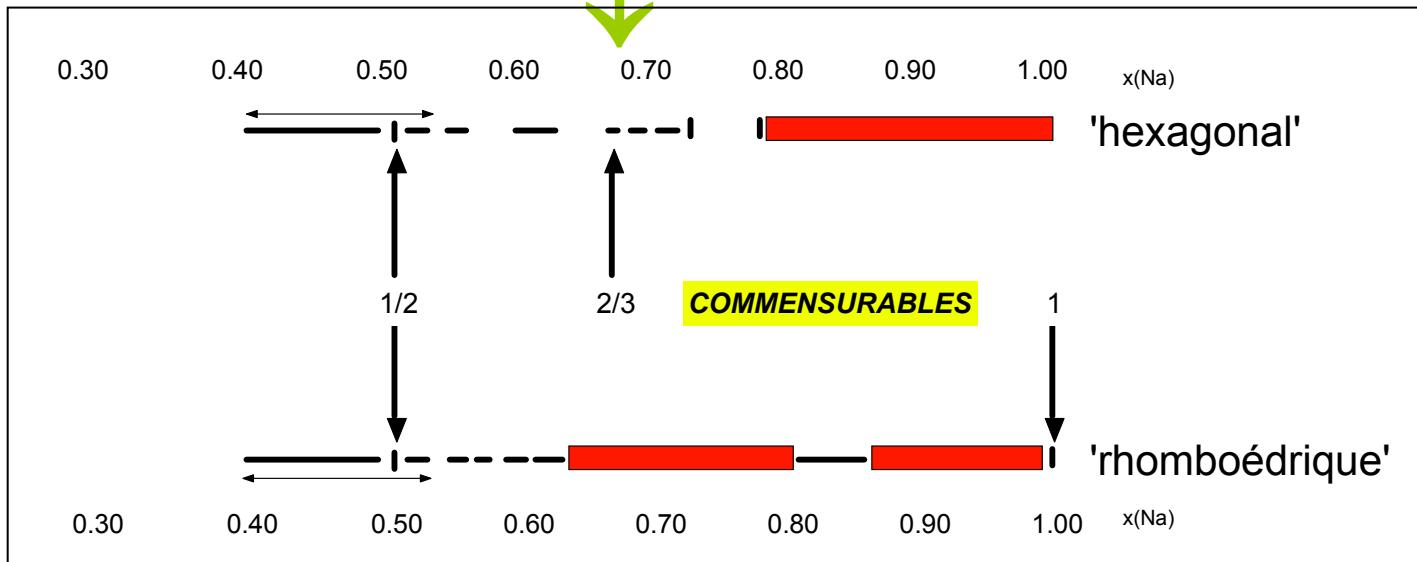
métal corrélé jusque  
seconde transition magnétique  
troisième transition

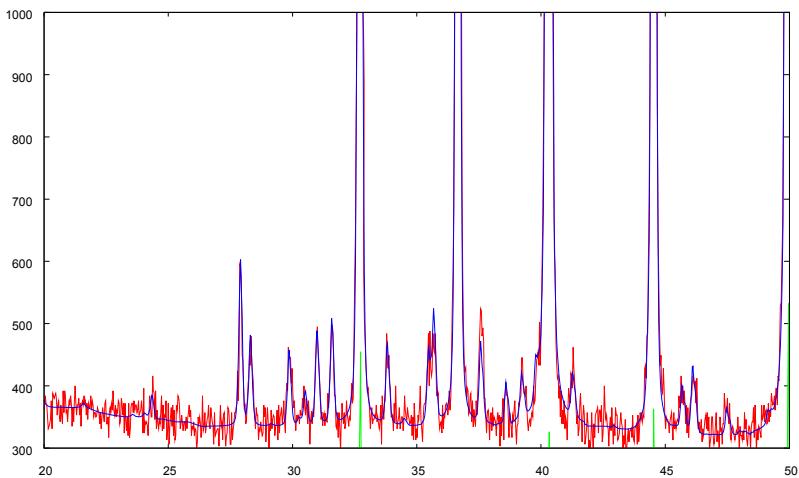
$T_N \approx 86\text{K}$   
 $T \approx 55\text{K}$   
 $T \approx 20\text{K}$

Plusieurs tentatives de diffraction de neutrons  
en traversant les transitions  
→ aucun indice de transitions structurales

Ce qui ne prouve rien  
la transition structurale est vraisemblable  
comment l'observer ?

$$x(\text{Na}) = 2/3$$

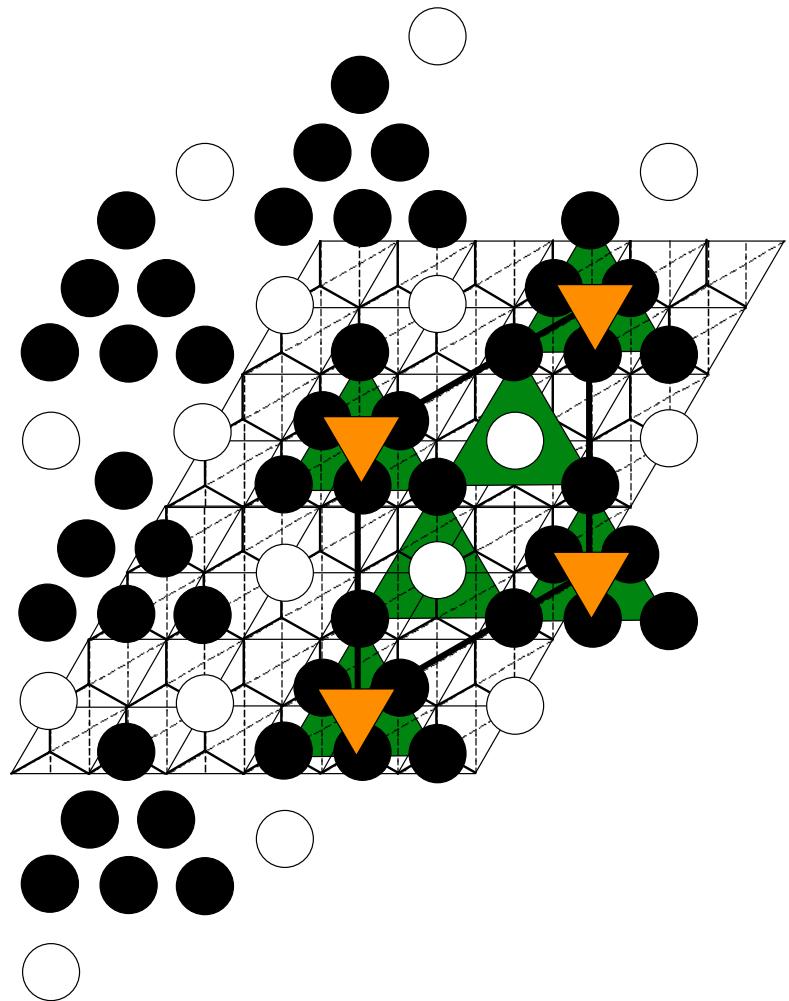
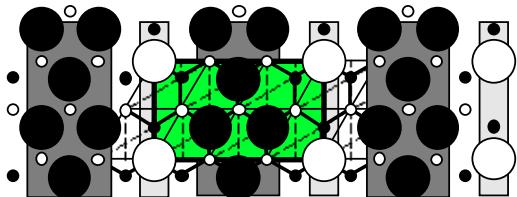


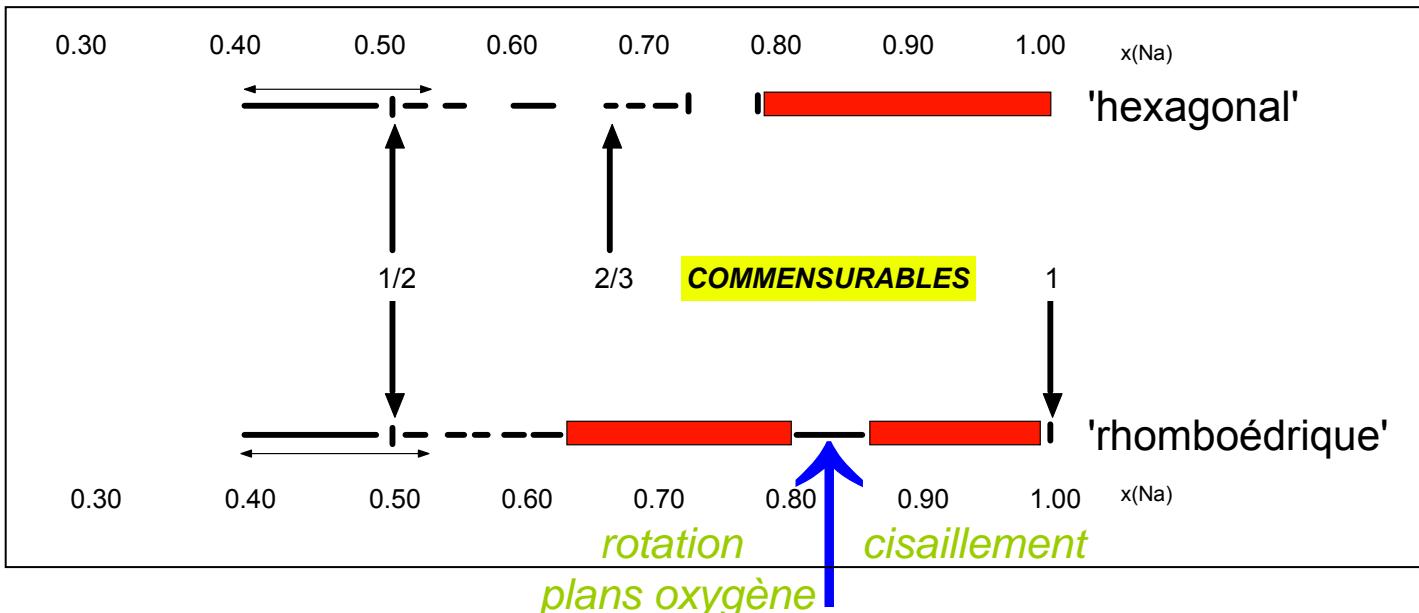


$x(\text{Na})=2/3$

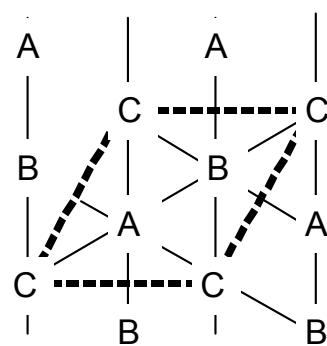
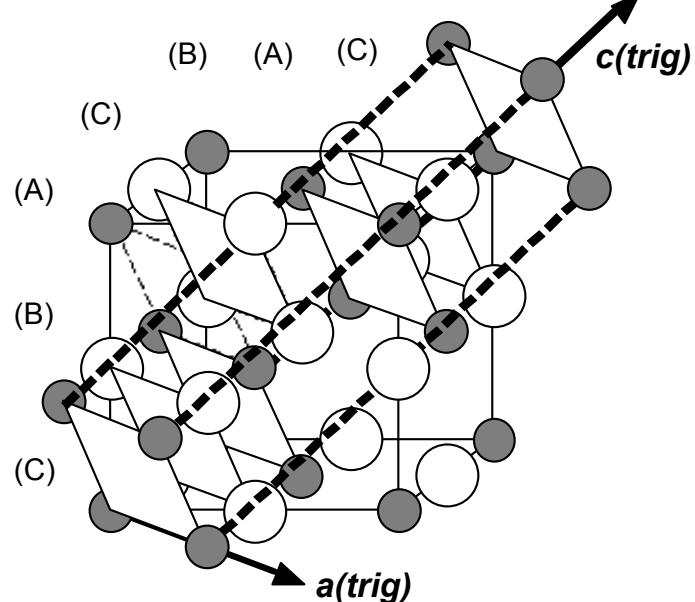
maille commensurable  
 $2a\sqrt{3} * 2a\sqrt{3} * 3c$   
groupe spatial R-3m

le réseau **nid d'abeille** des Na-1 (blancs)  
génère un réseau **Kagomé** sur les plans Co

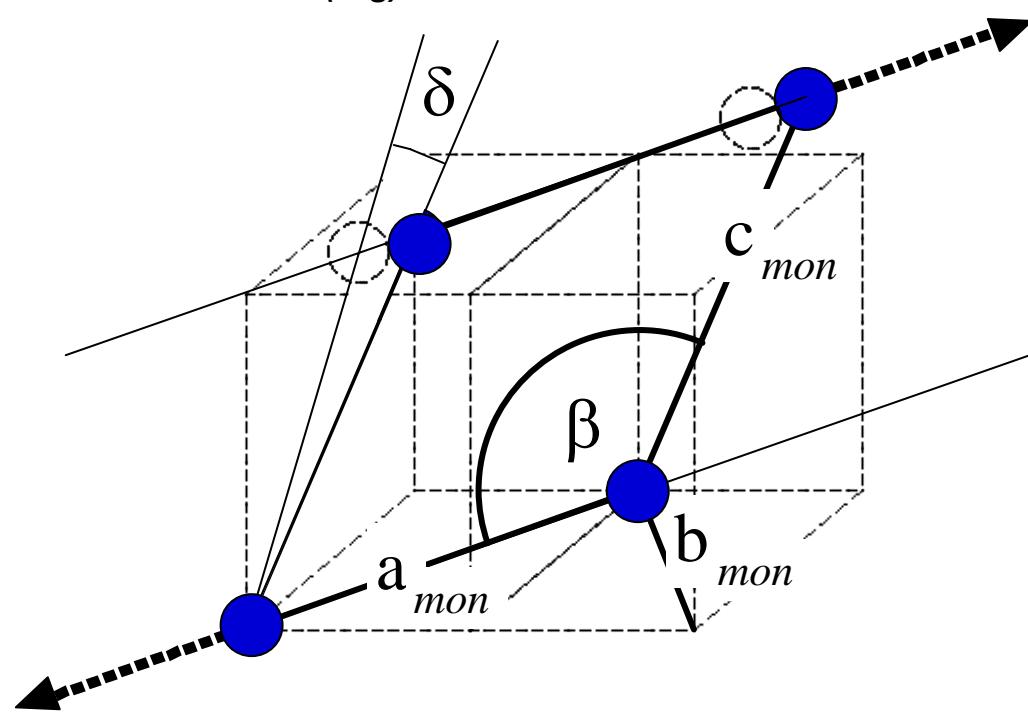
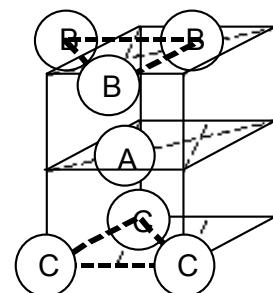




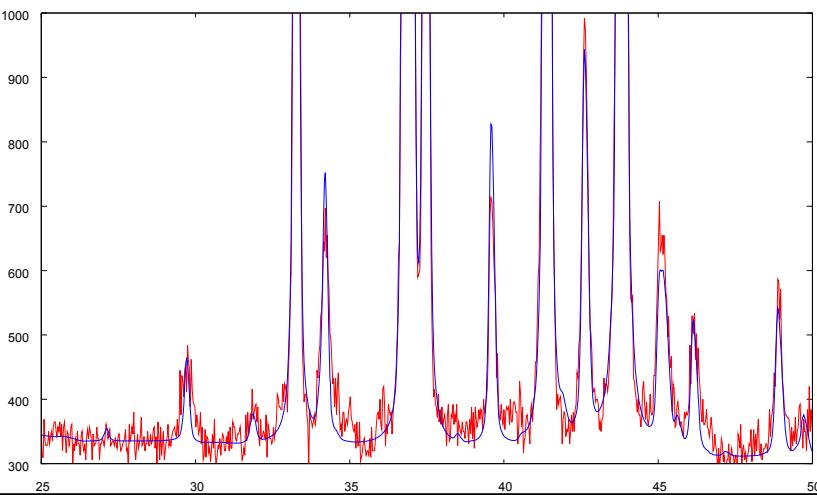
$$x(\text{Na}) = 5/6 \pm \delta$$



Na-Co-O<sub>2</sub>  
maille NaCl  
distorsion rhomboédrique

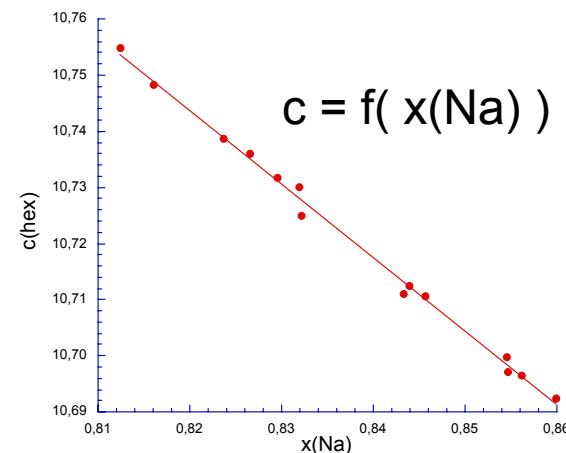
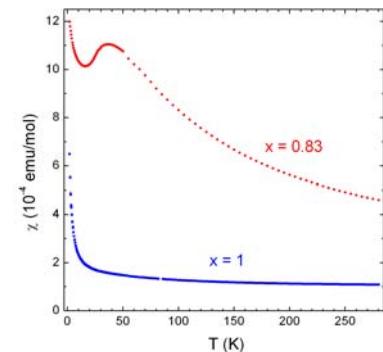
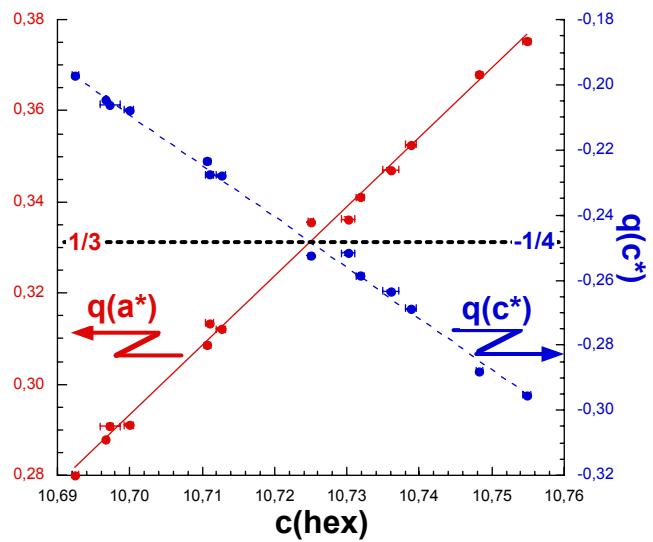


Na(0.86-0.81)-Co-O<sub>2</sub>  
monoclinique  
cisaillement du rhomboèdre

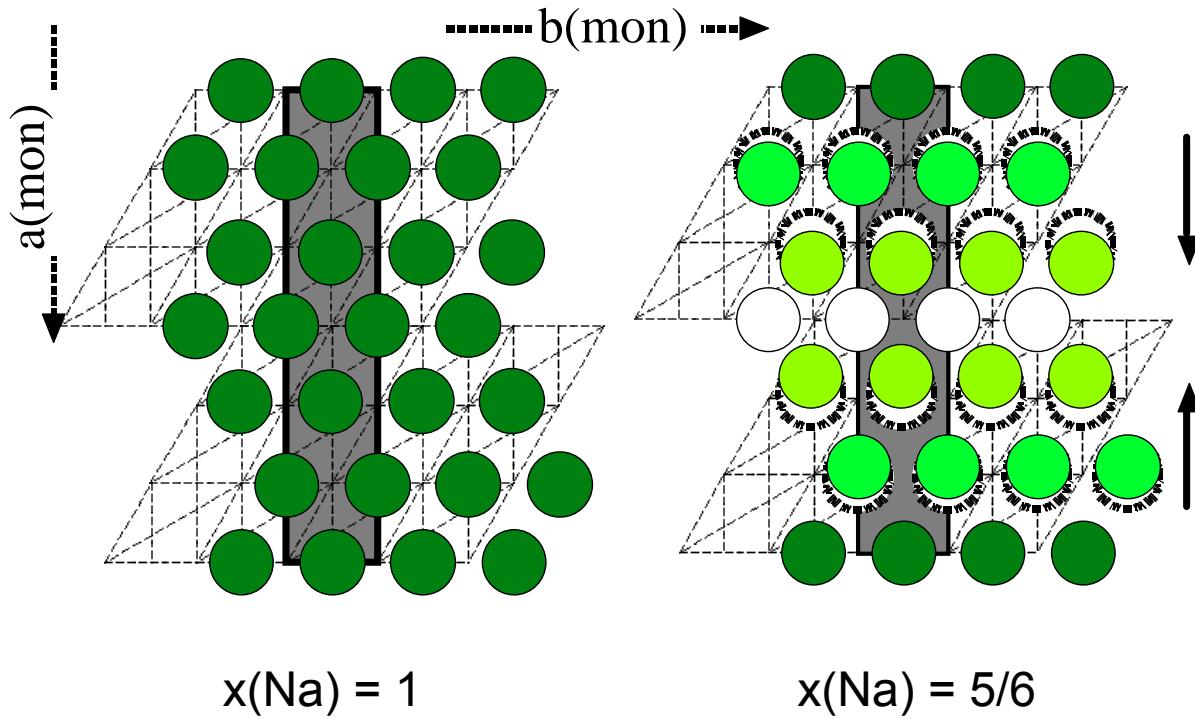


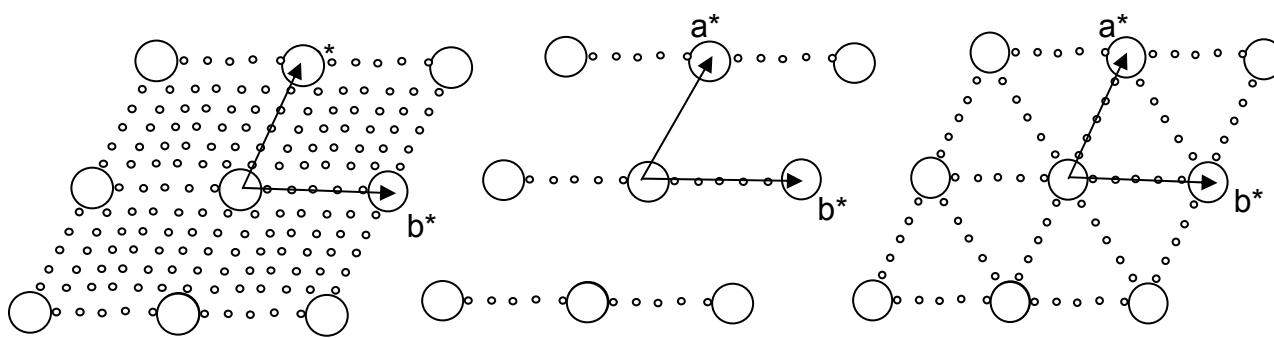
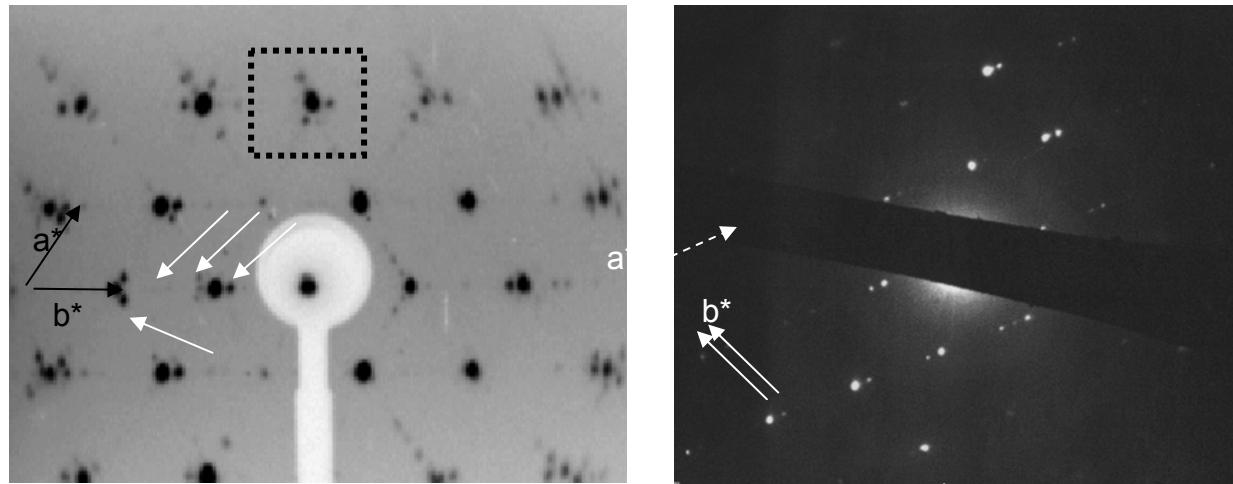
# SYSTEME ‘RHOMBOEDRIQUE’ Na( $5/6 \pm \delta$ )-Co-O<sub>2</sub> distorsion monoclinique du réseau cobalt

$a = 4.8990(2)\text{\AA}$ ,  $b = 2.8725(1)\text{\AA}$     $c = 5.7885(3)\text{\AA}$     $\beta = 111.866(2)^\circ$   
 $2.828\text{\AA}$                      $2.873\text{\AA}$                      $106.50^\circ$   
 $q(a^*) = .2910(2)$ ,                     $q(c^*) = -.2078(3)$   
 Monoclinic S. G. : C 1 2/1 1

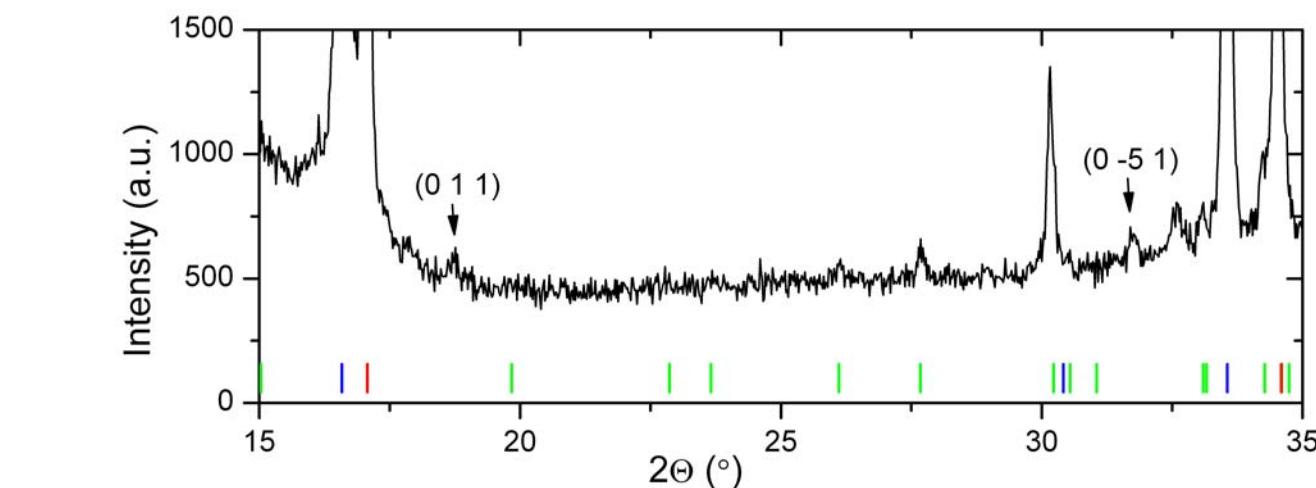


# domaine monoclinique $x(\text{Na}) = 5/6 \pm \delta$



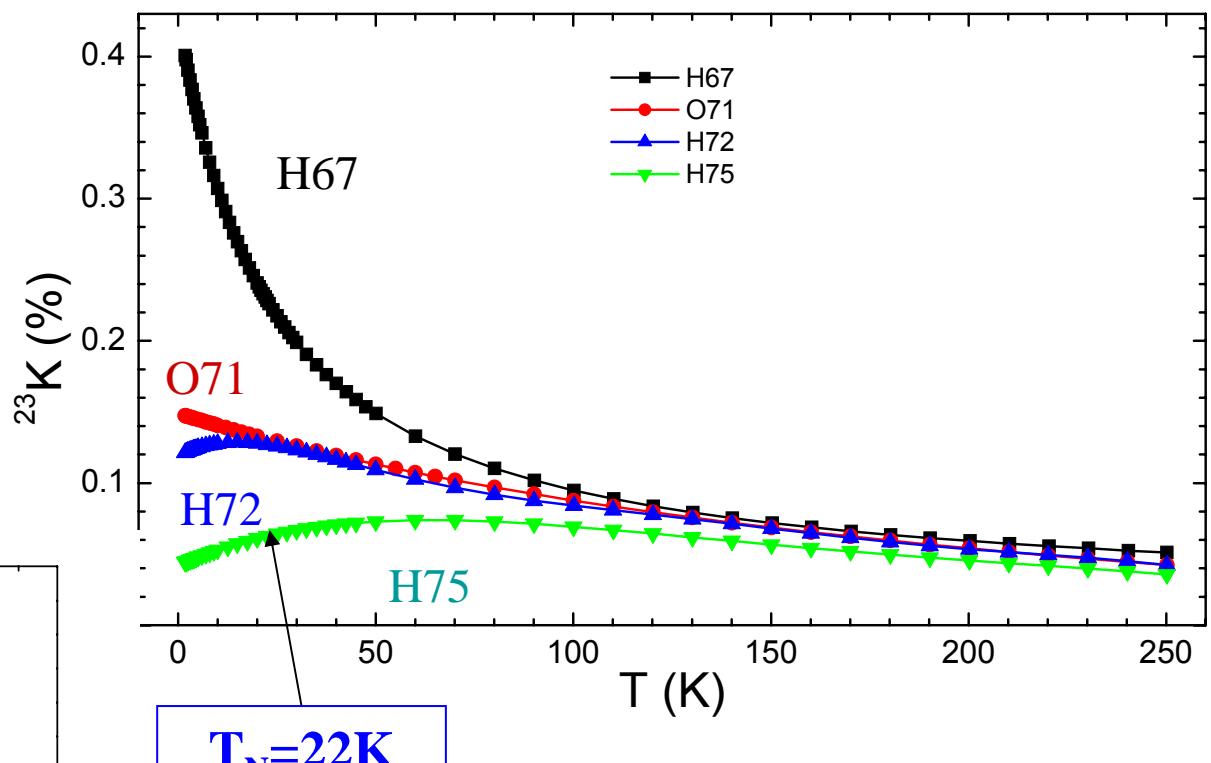
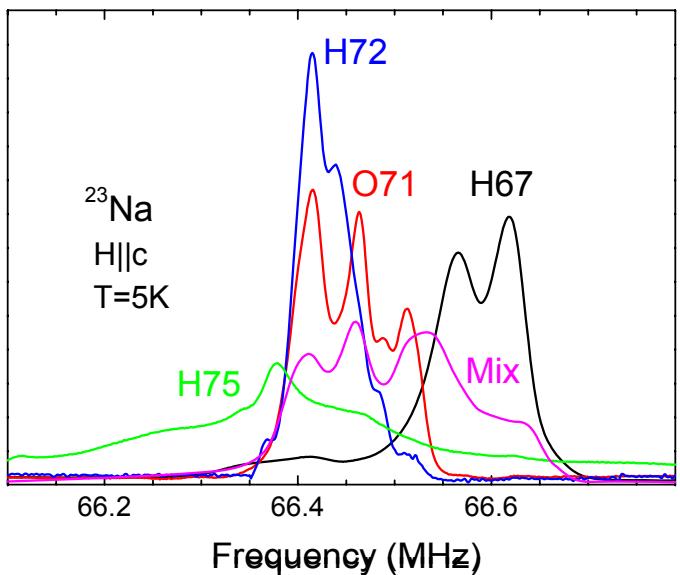
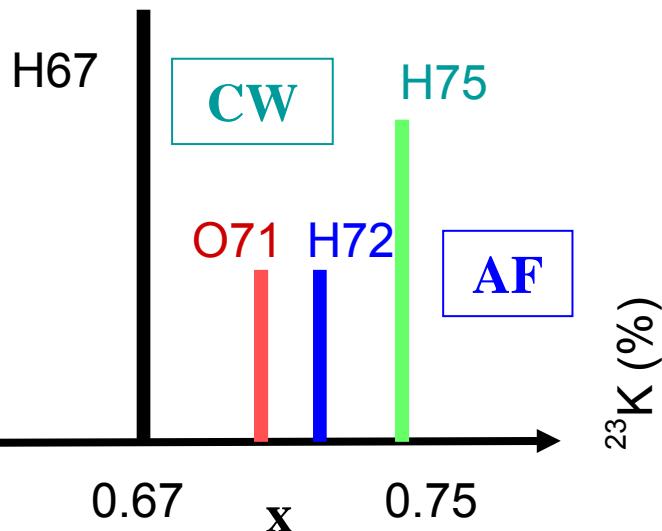


P. Foury  
monocrystal

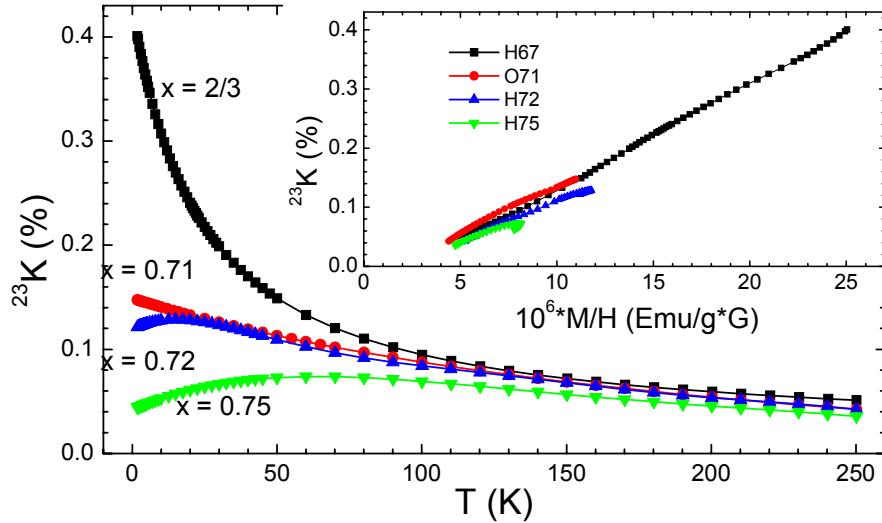


# Various phases for $0.67 < x \leq 0.75$

*H. Alloul , I. Mukhamedshin et al , EPL 2008*

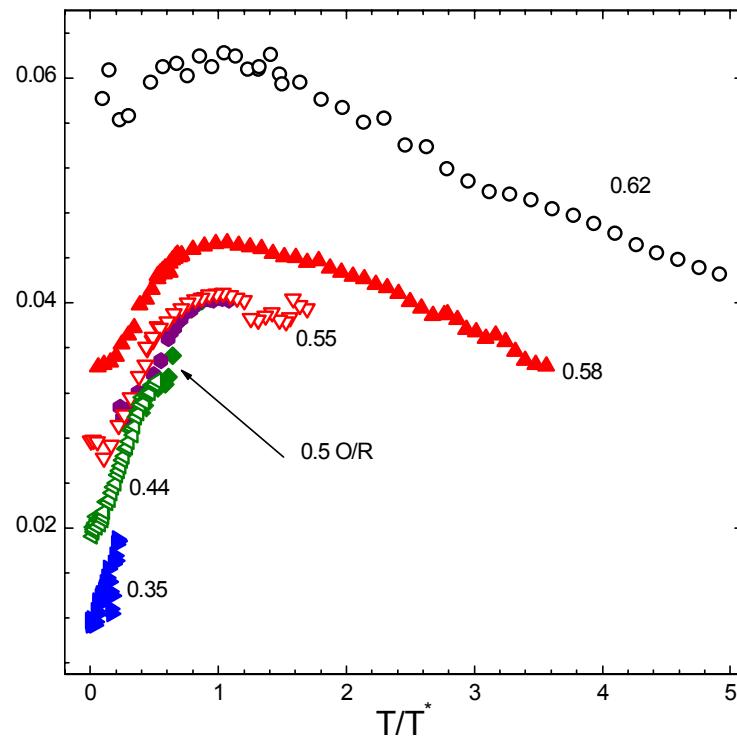
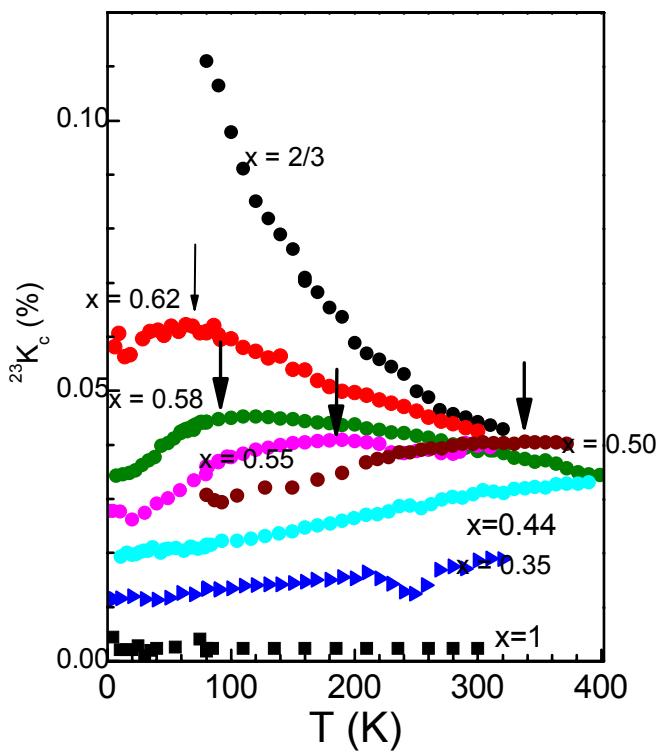


Distinct well ordered phases  
Similar susceptibility above 100K  
Large differences below 100K



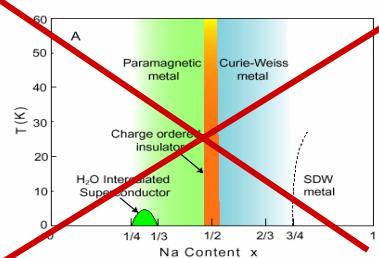
SPECIAL POSITION OF  $x(\text{Na}) = 2/3$   
A pronounced maximum  
in the susceptibility phase diagram

from Irek Mukhamedshin et al.

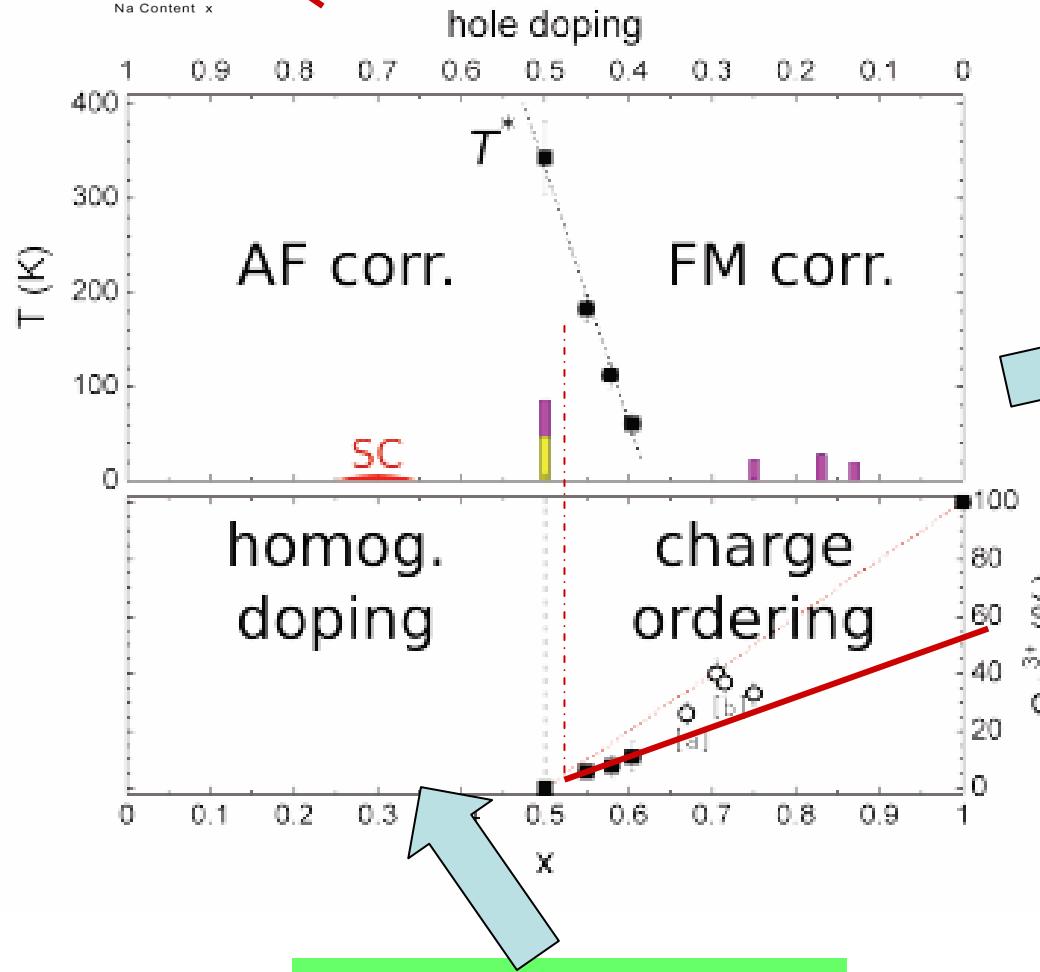


from Guillaume Lang, et al, PRB, 2008

# Phase diagram of $\text{Na}_x\text{CoO}_2$



Magnetic correlations for all  $x$



No Na atomic ordering  
identical Co sites

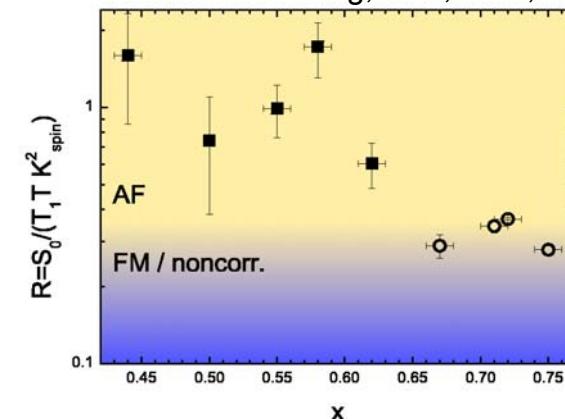
For  $x > 0.5$   
Appearance of non magnetic  $\text{Co}^{3+}$   
and magnetic  $\text{Co}^{(3+\delta)+}$

Na atomic ordering



Co Charge ordering

from Guillaume Lang, et al, PRB, 2008



the dimensionality of the dominant AF couplings is smaller than or equal to 2

