International School on Aperiodic Crystals

Examples of incommensurately modulated structures and composites studied using transmission electron microscopy

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Purpose of this lecture

At the end of this lecture you should be able to:

- Understand the TEM paragraph in papers about IMS and CS
- Be able to make solid comments about conclusions claimed from TEM by different sources (collaborators, papers,…) by knowing some possible pitfalls
- Decide whether it would be useful to do TEM on your own IMS or CS
- Make basic interpretations of TEM data on your own materials by yourself

Outline of the lecture

The three most frequently used techniques in case of IMS/CS:

- Electron diffraction
- HAADF-STEM
- HRTEM

ED: the main differences with XRD

- Shorter wavelength, almost flat sections through reciprocal space
- A nanometer size particle is enough
- Multiple diffraction
- Can be combined with direct imaging and compositional analysis

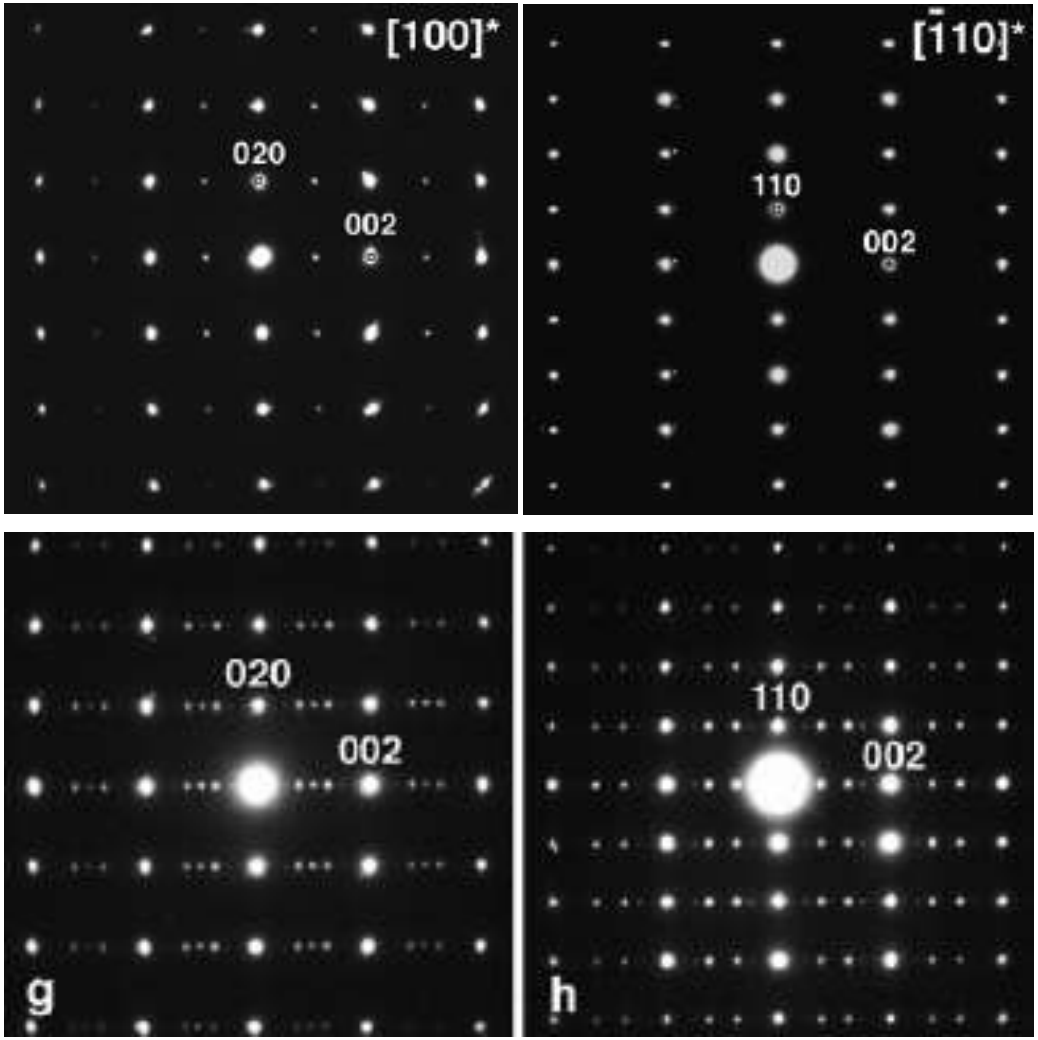
Appearance very much like single crystal XR patterns

Incommensurately modulated structure example

Related commensurate structure

Sb_2MnO_4

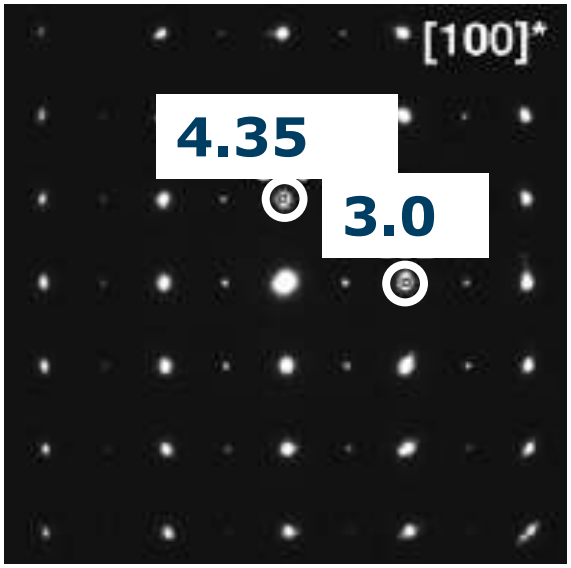
$Sb_{1.155}Pb_{1.216}Mn_{0.628}O_4$

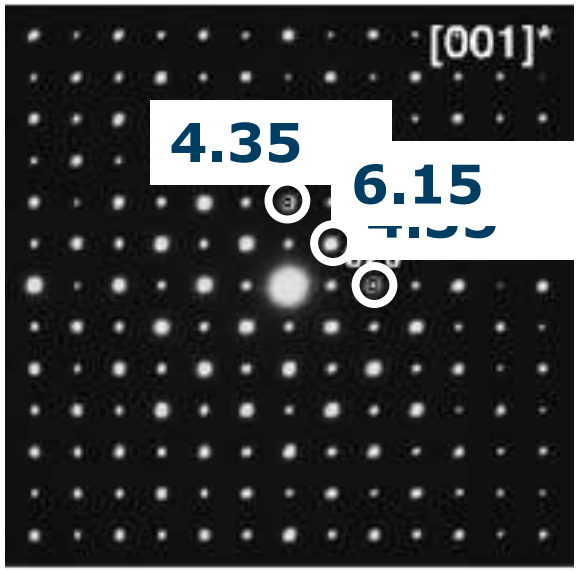


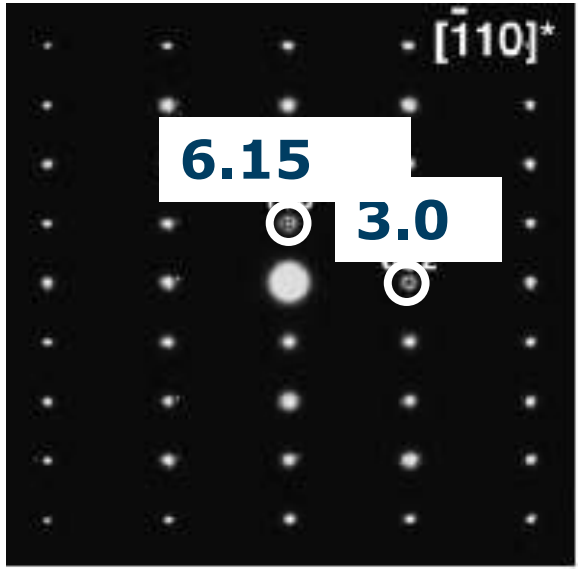
Abakumov et al., Chemistry of Materials, 17, 5, 2005, 1123-1134

IMS: indexing the subcell reflections

- Related commensurate structure Sb_2MnO_4
- $P4_2/mbc$; a=b=8.7 Å, c= 6.0 Å
- Measure *R*, calculate *d* with *R.d*=C (know instrument constant)
- Index each reflection according to list of d-values for each reflection (cf. XRD)



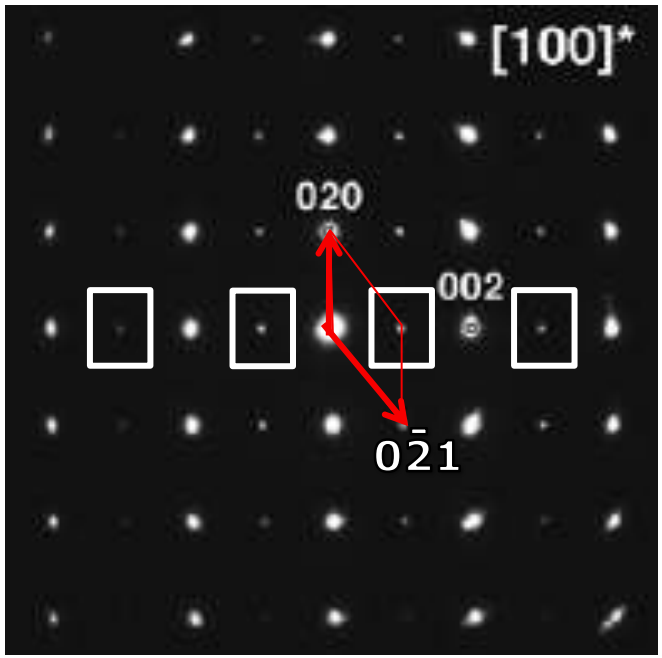


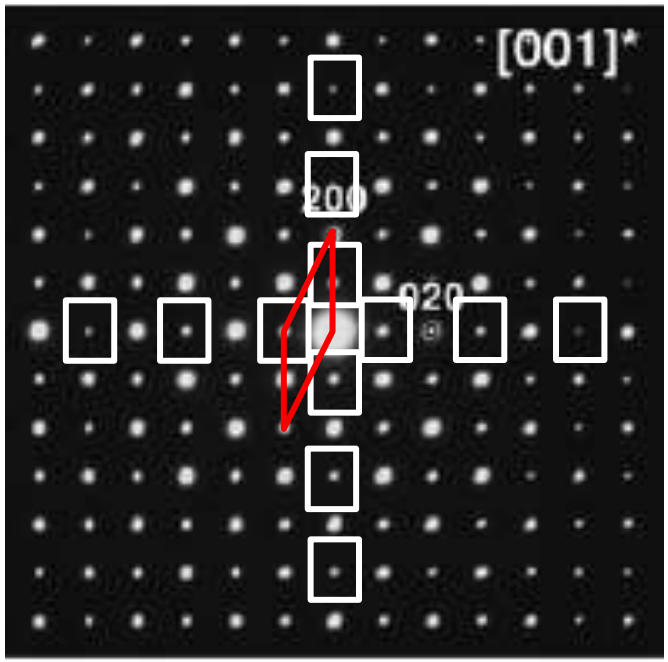


All distances in Å

Dangers of double diffraction!

- $P4_2/mbc$
- Reflection conditions: 0kl: k=2n; hhl: l=2n; 00l: l=2n; h00: h=2n
- In contradiction: 001,003,…,100,300,…,010, 030, … all caused by double diffraction



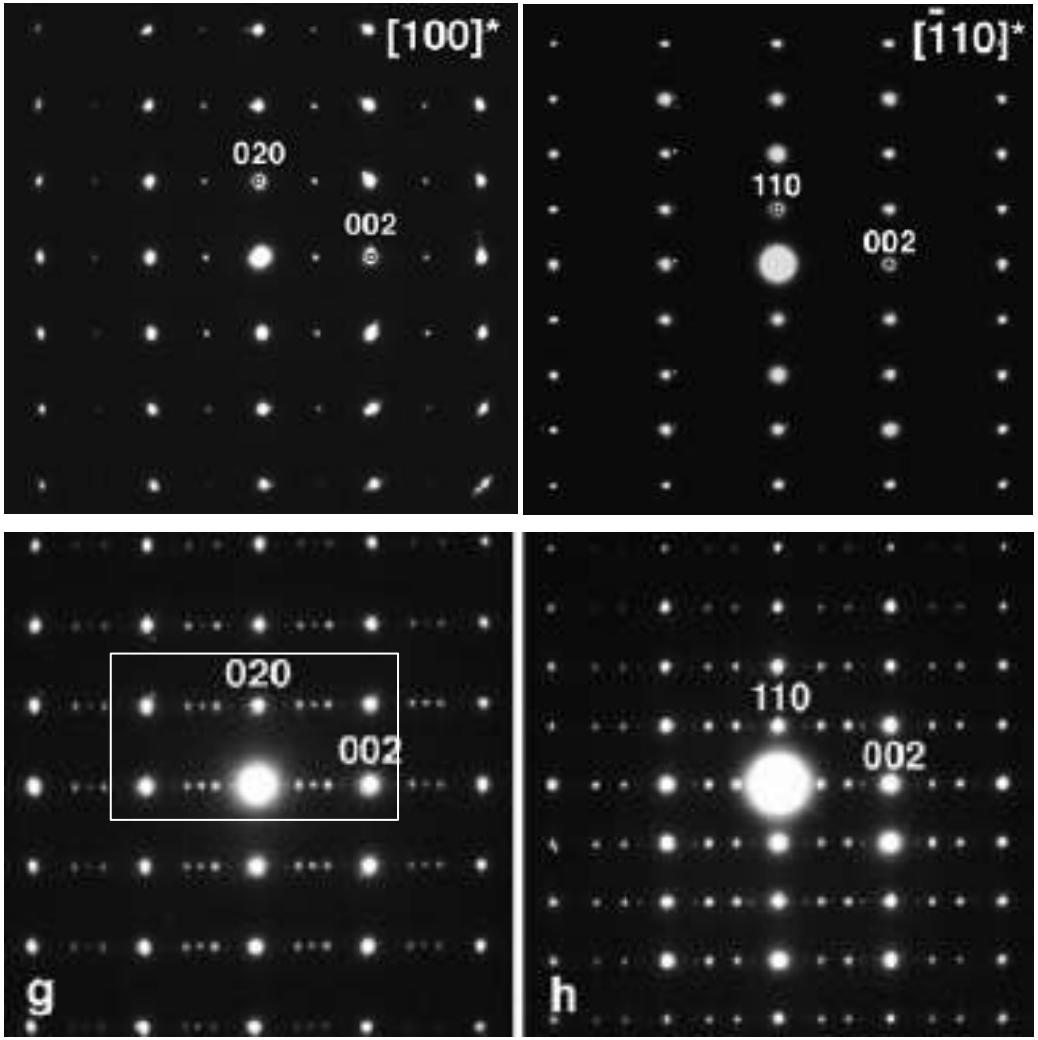


- Tilt around the row: forbidden reflections will disappear

Subcell vs. IMS

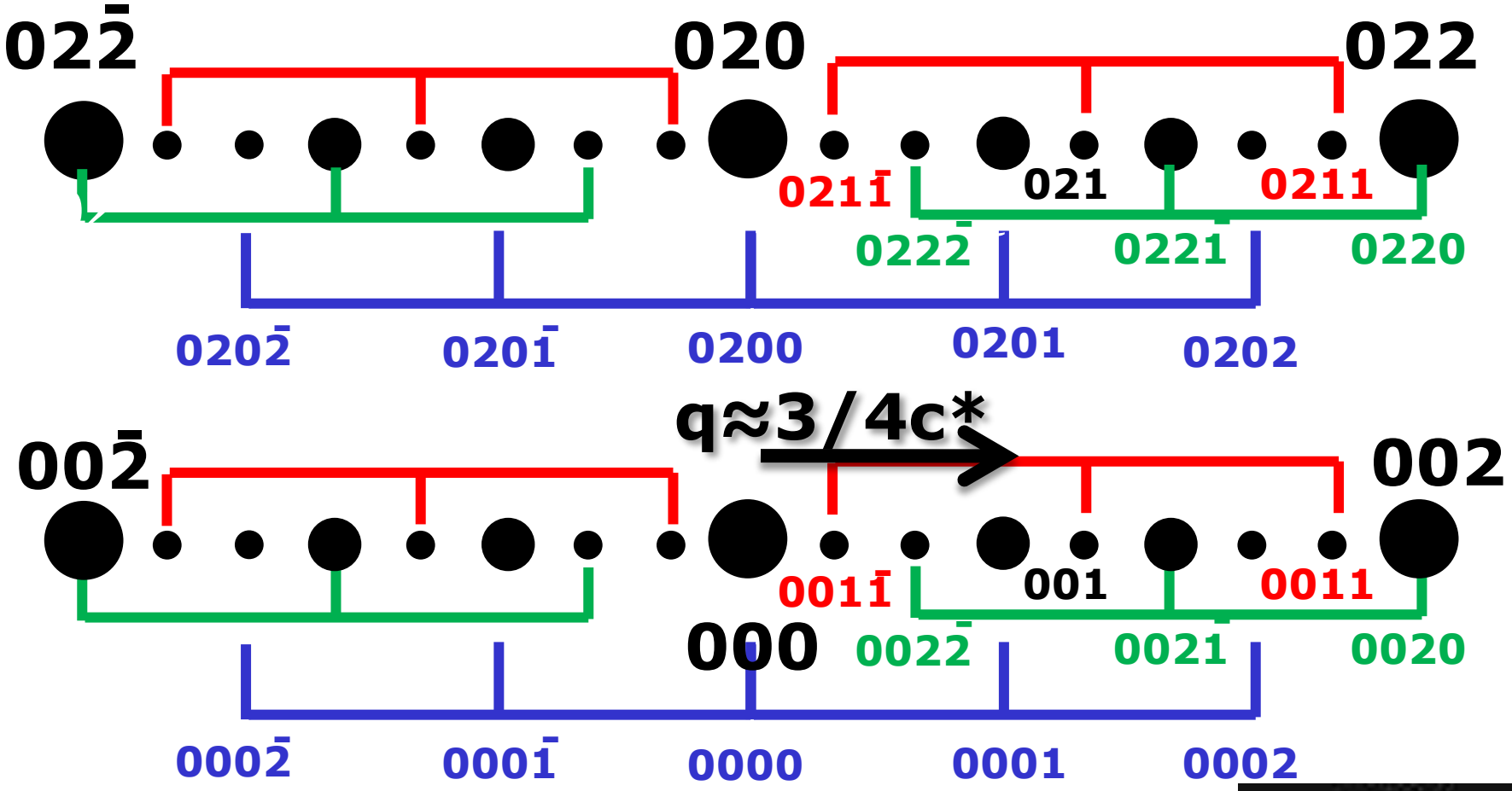
Sb_2MnO_4

$Sb_{1.155}Pb_{1.216}Mn_{0.628}O_4$



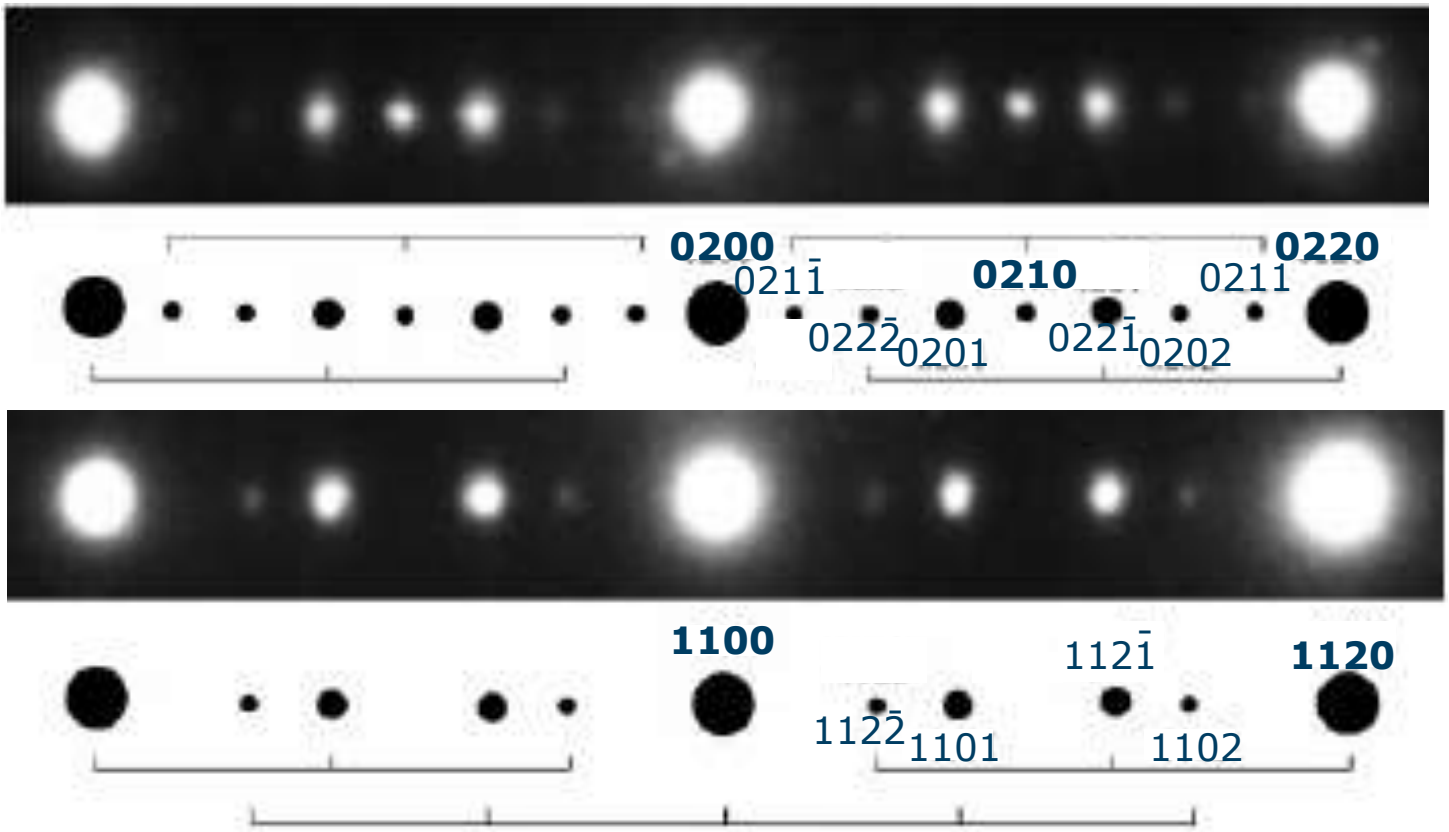
Abakumov et al., Chemistry of Materials, 17, 5, 2005, 1123-1134

Indexing the IMS



$Sb_{1.155}Pb_{1.216}Mn_{0.628}O_4$

Reflection conditions for m

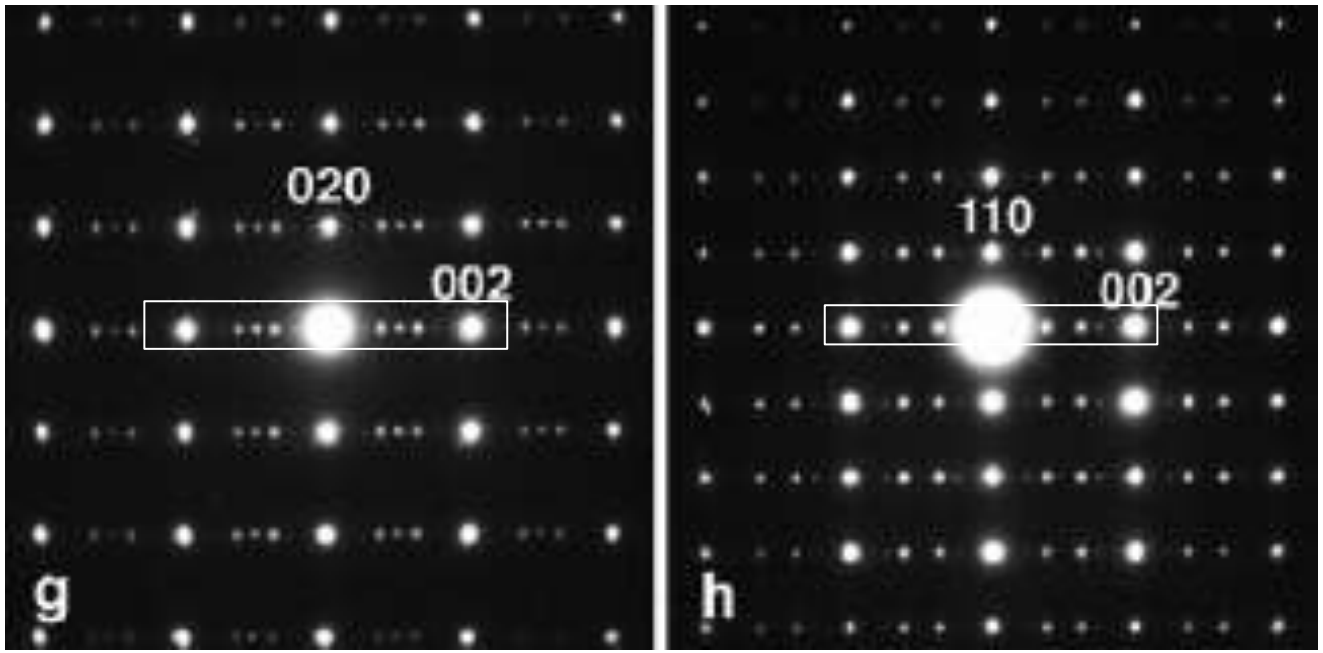


q≈3/4c*

For thís material: no special conditions for m: if subcell reflection is seen, also hklm with m=1 and m=2 is seen.

$Sb_{1.155}Pb_{1.216}Mn_{0.628}O_4$

Reflection conditions

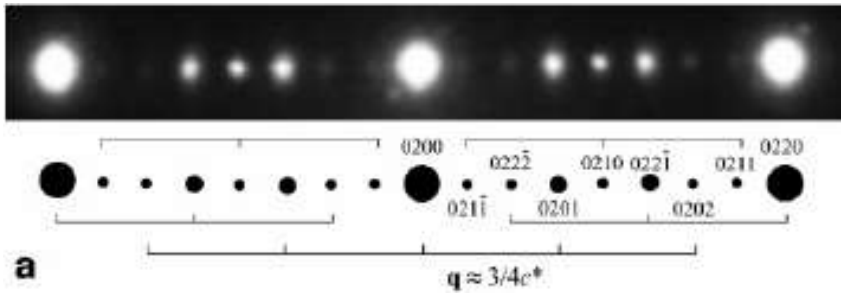


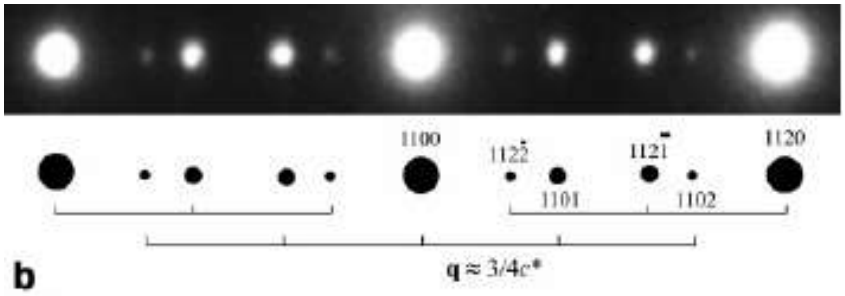
$$\left\{ \begin{array}{c} P4_2/mbc \\ 0kl:\ k=2n \\ hhl:\ l=2n \end{array} \right\}$$

0klm: k=2n

hhlm: l=2n

$P4_2/mbc(00\gamma)$



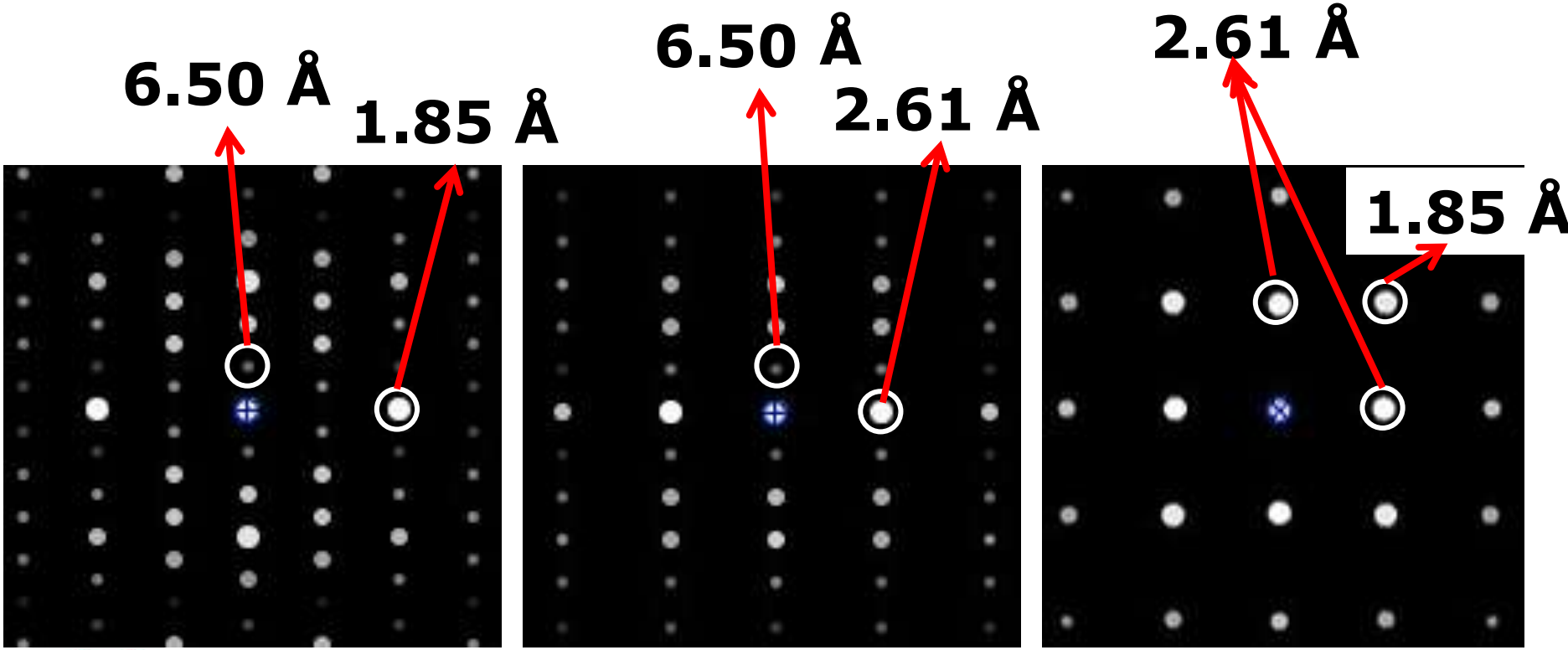


$Sb_{1.155}Pb_{1.216}Mn_{0.628}O_4$

Exercise 1-1: IMS: index the non-modulated phase

- Index the commensurate structure $LaSrCuO_4$, this will help you with indexing the next, incommensurate one.

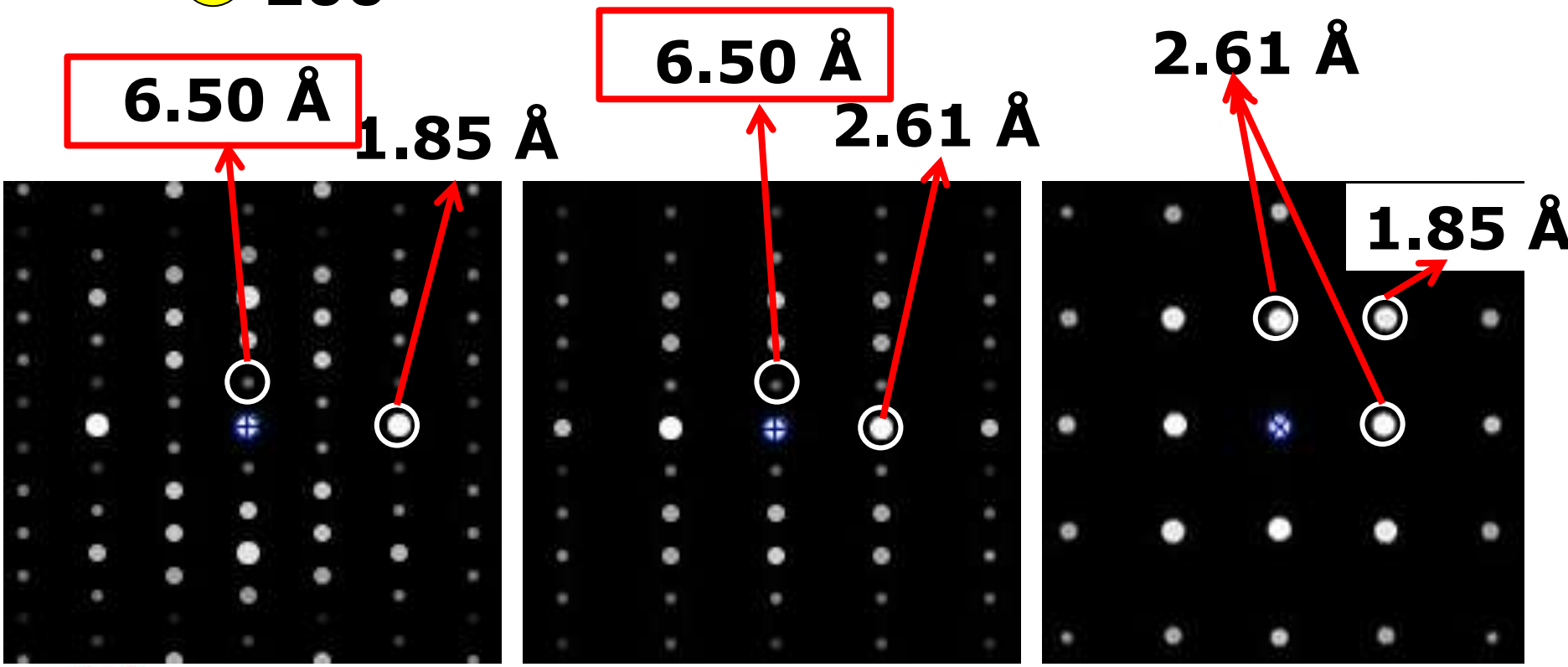
Given data:
cell parameters of $LaSrCuO_4$: a=b=3.7 Å, c=13 Å.



(Simulated ED patterns)

Given data:
cell parameters of $LaSrCuO_4$: a=b=3.7 Å, c=13 Å.

001
002
200



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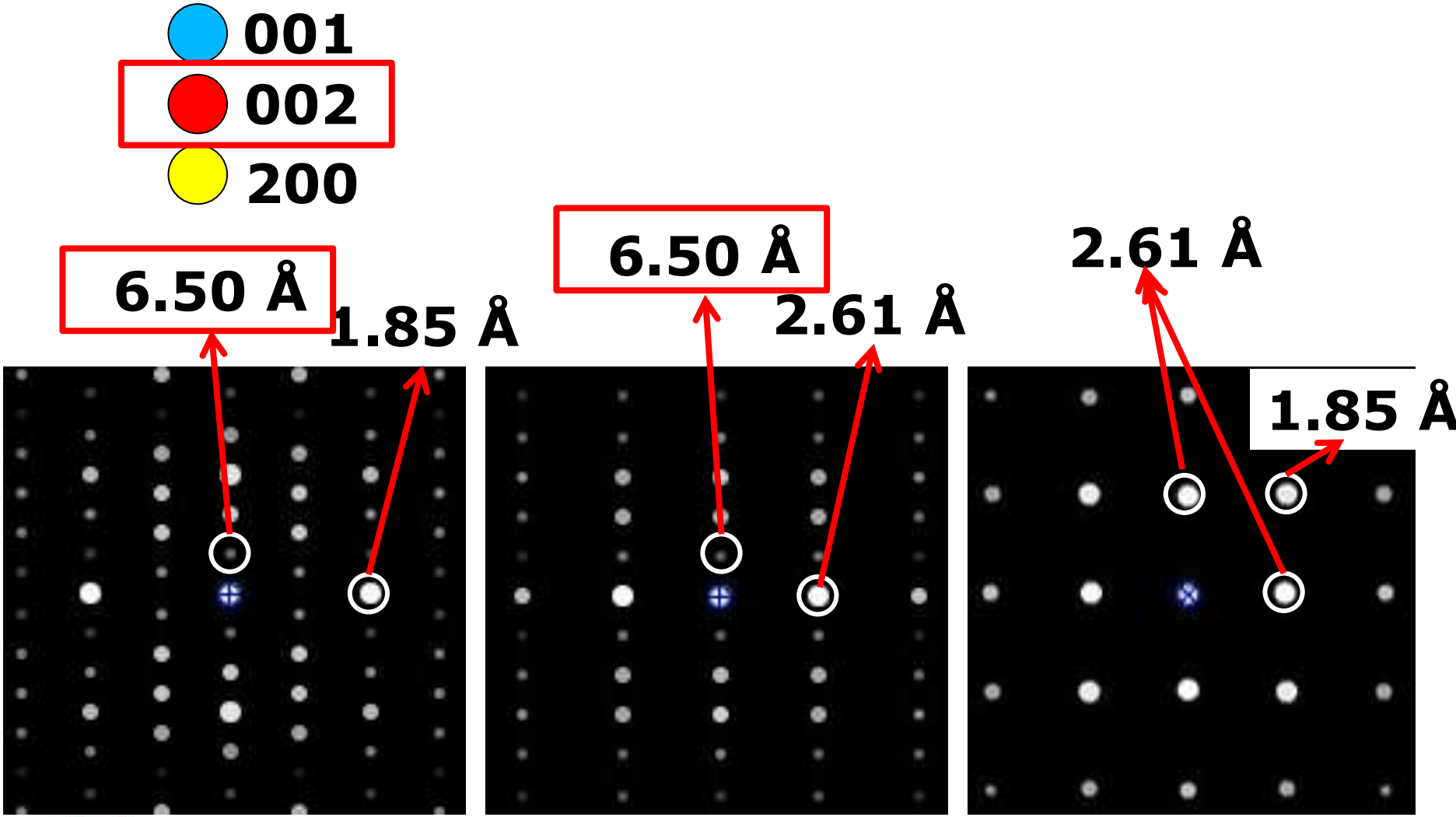
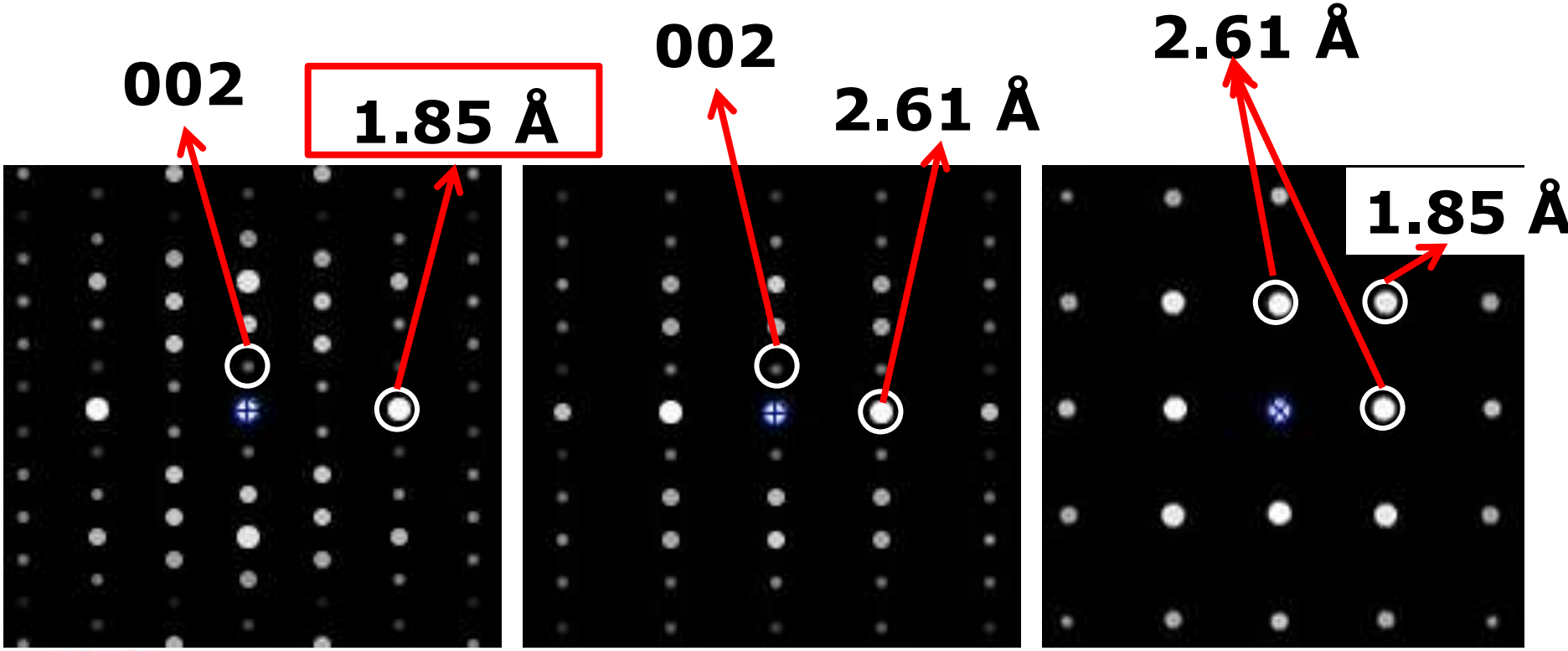


(Simulated ED patterns)

Given data:
cell parameters of $LaSrCuO_4$: a=b=3.7 Å, c=13 Å.

010
020
110



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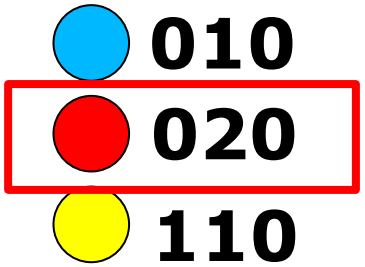

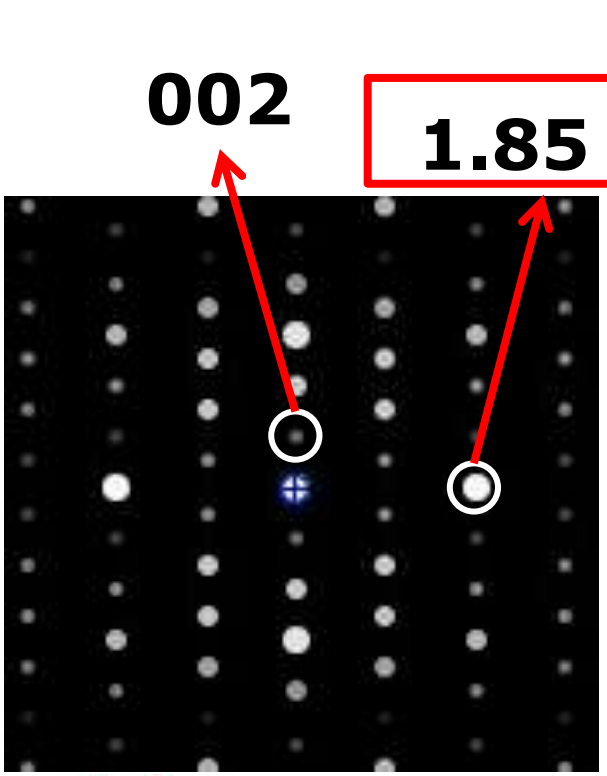

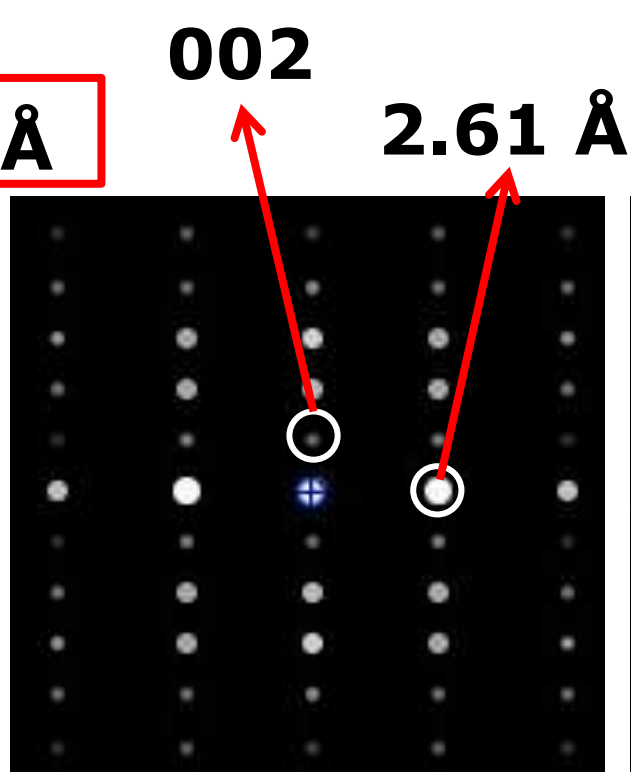

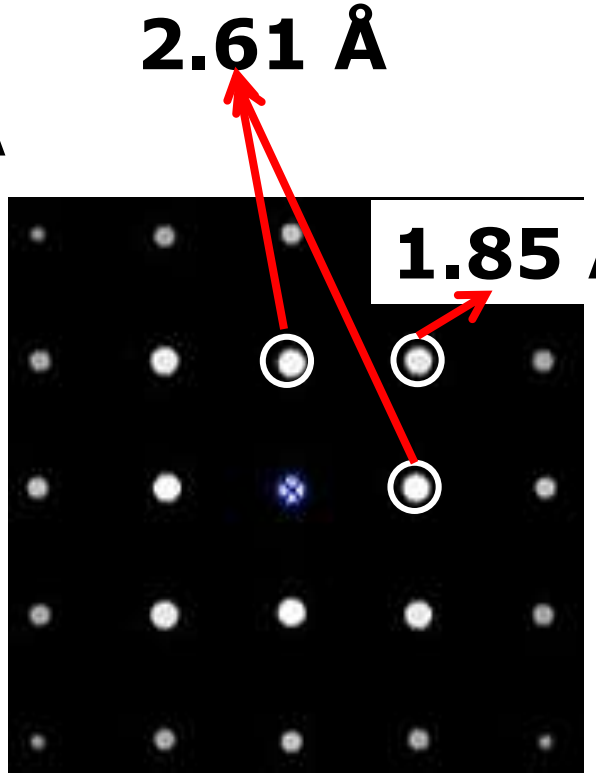

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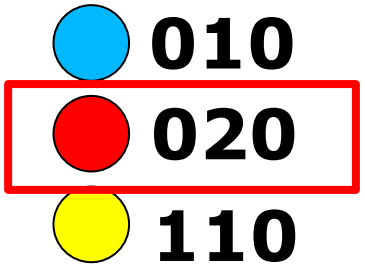

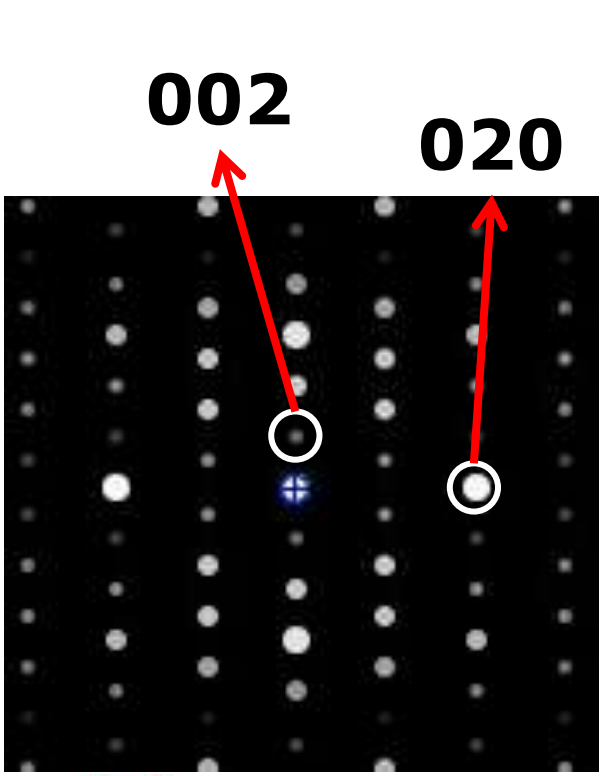

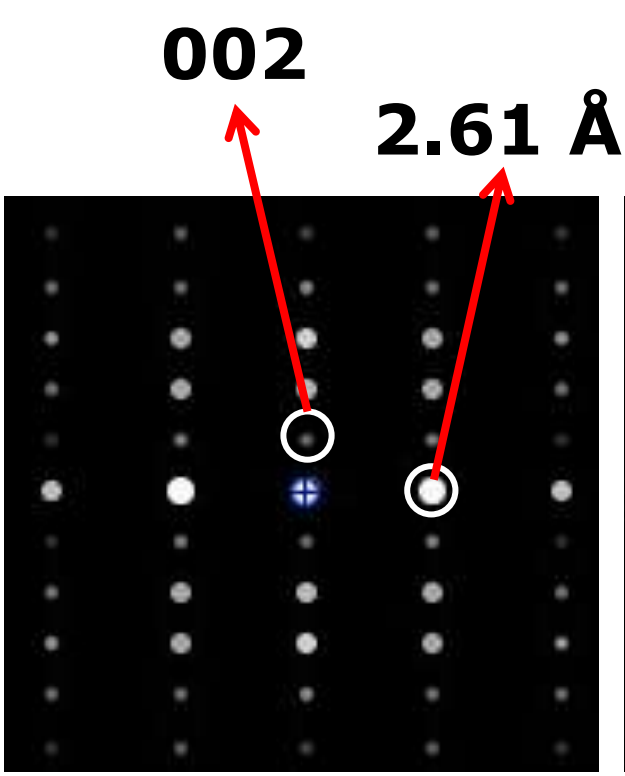

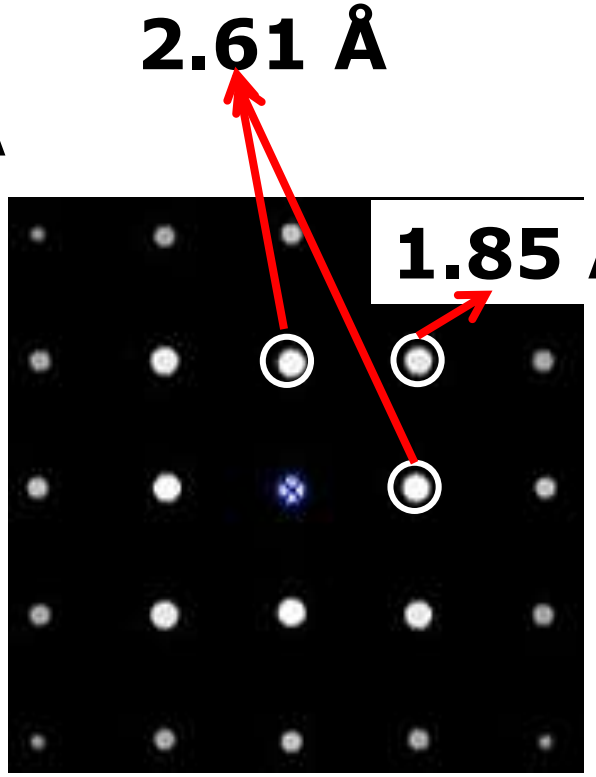

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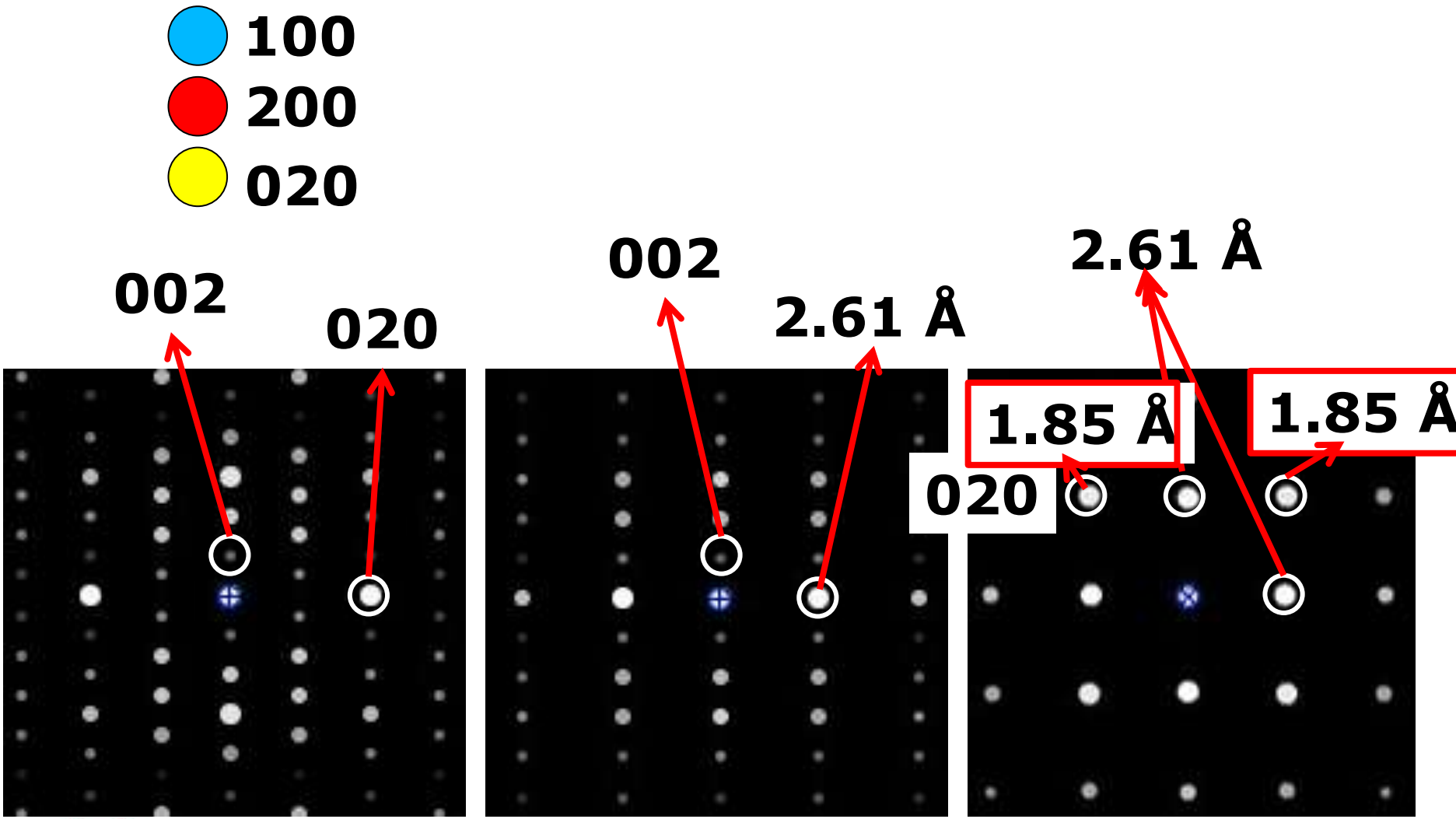

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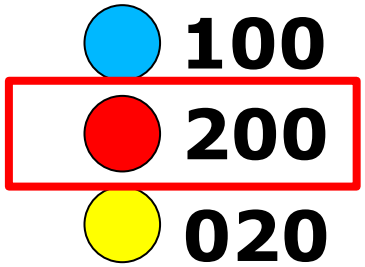
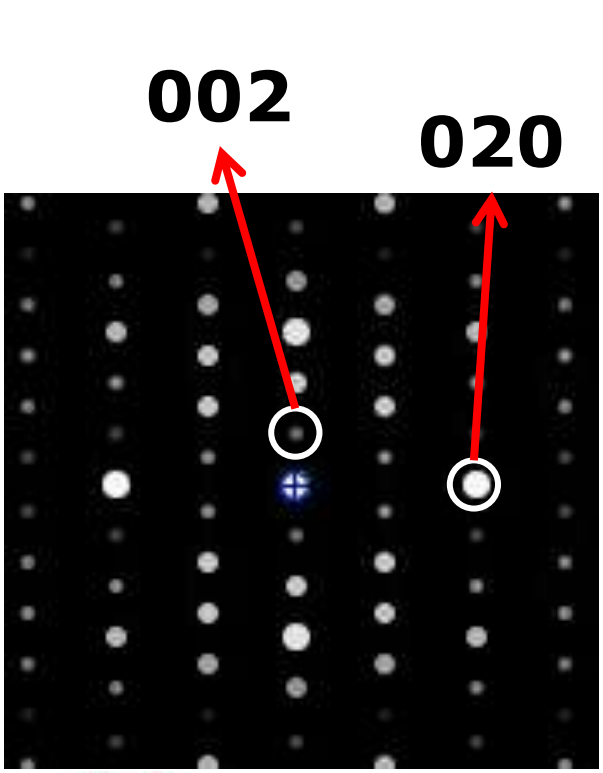
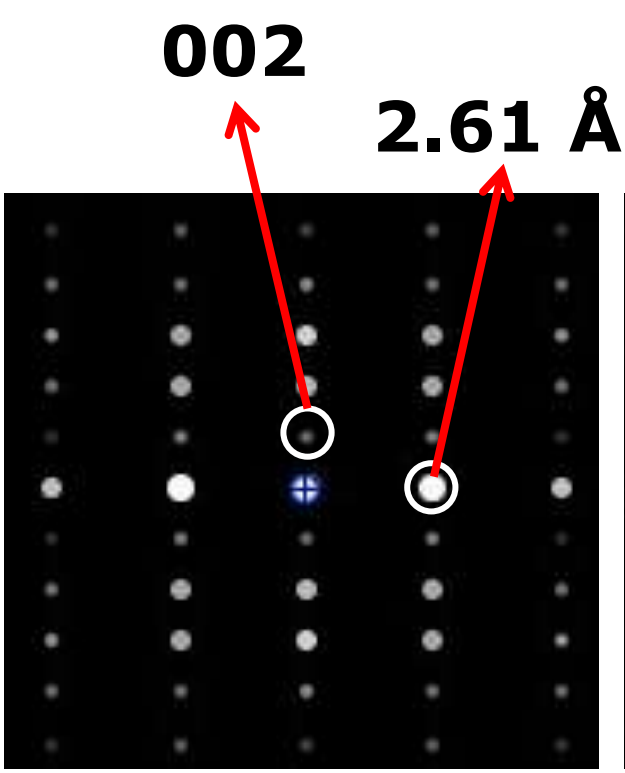
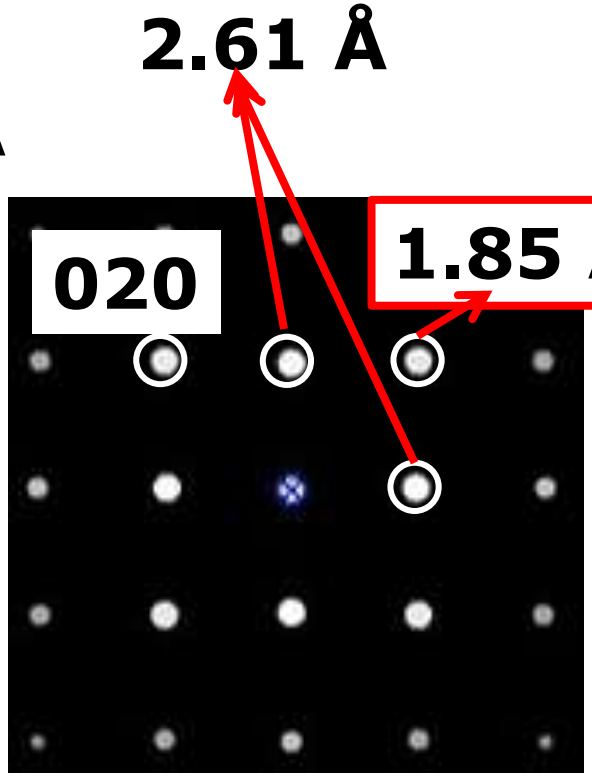




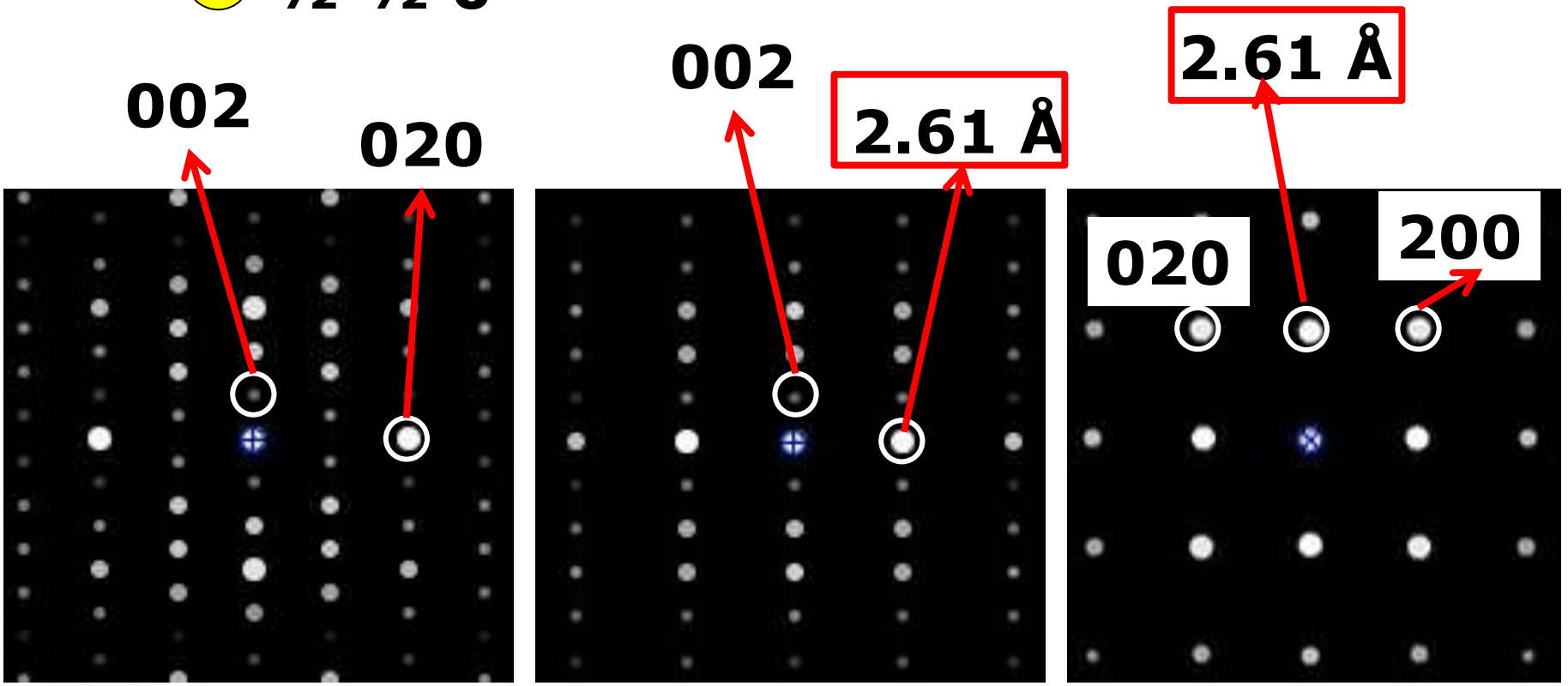




(Simulated ED patterns)

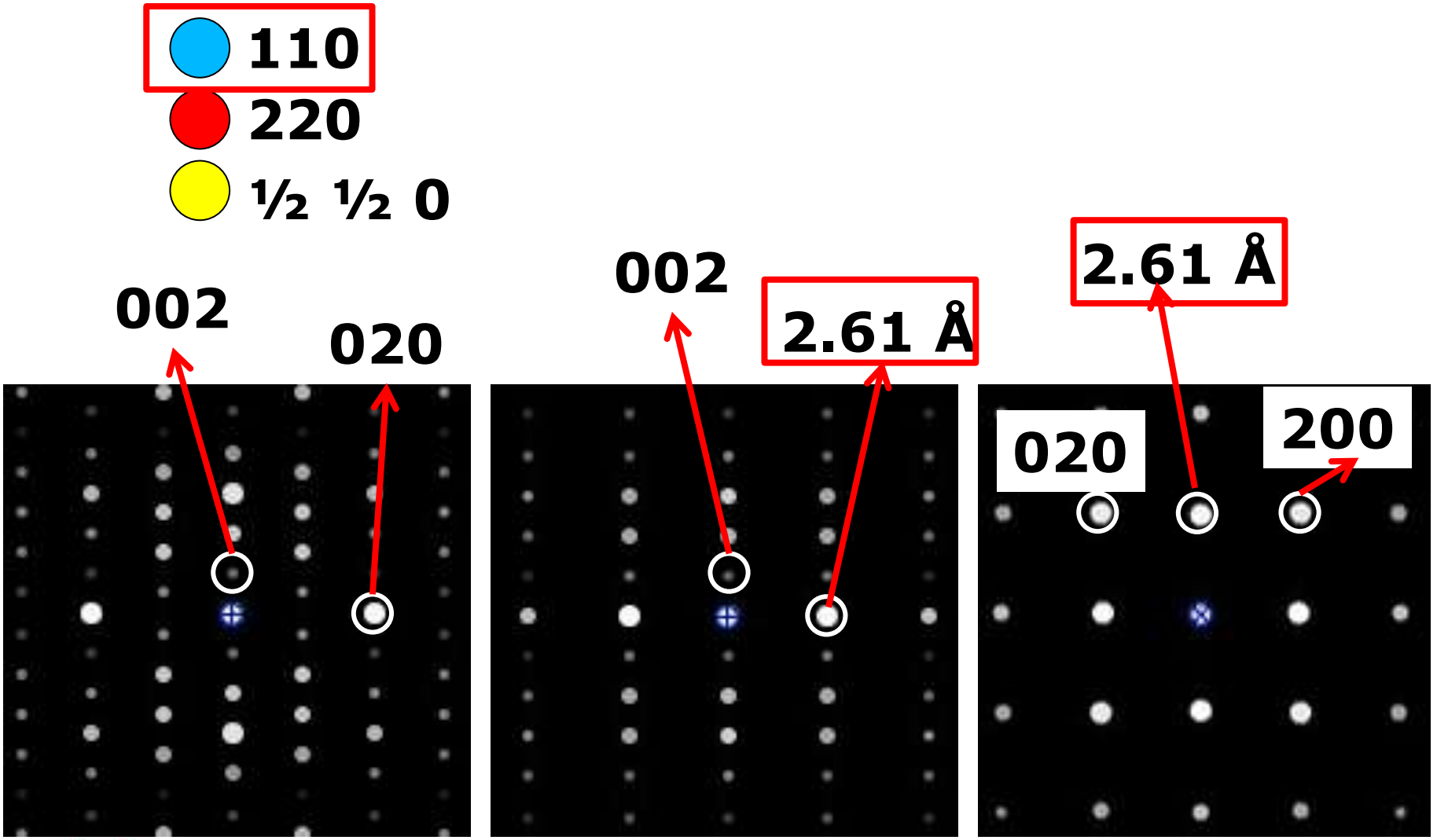
Given data:
cell parameters of $LaSrCuO_4$: a=b=3.7 Å, c=13 Å.

110
220
½ ½ 0



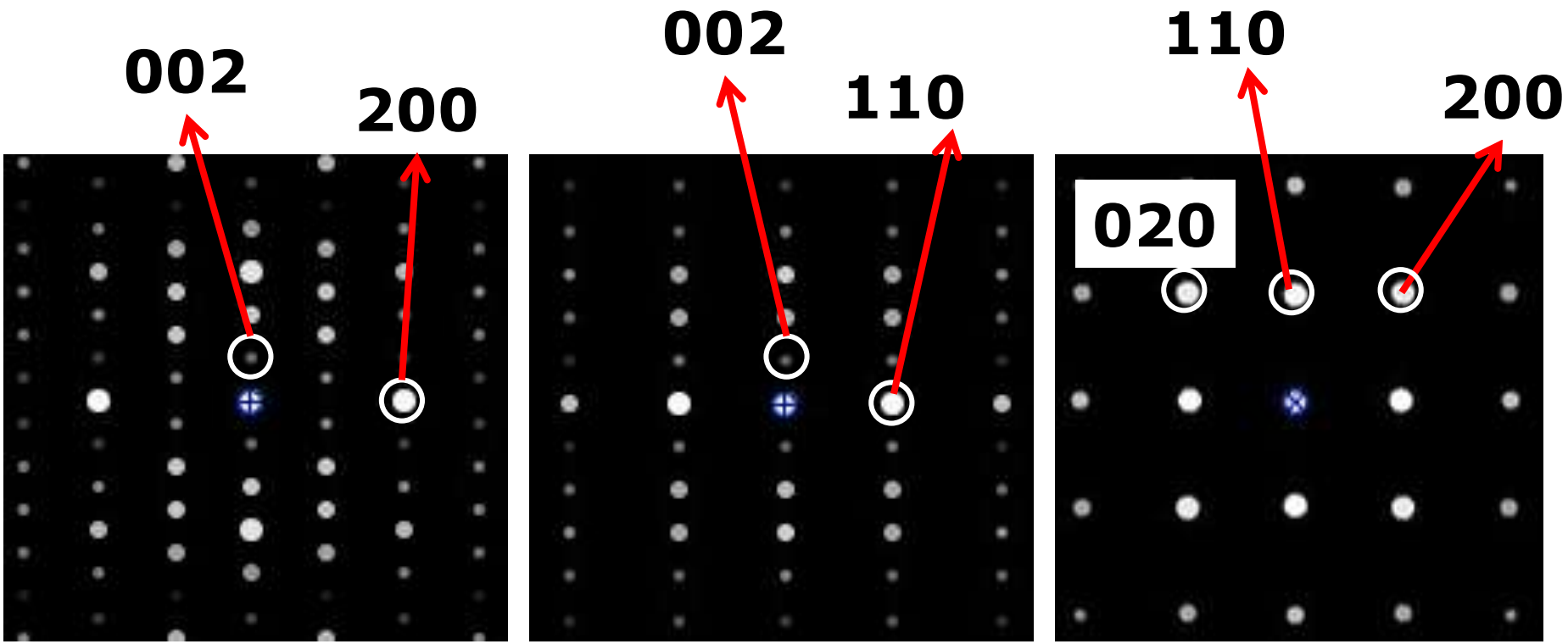
(Simulated ED patterns)

Given data:
cell parameters of $LaSrCuO_4$: a=b=3.7 Å, c=13 Å.

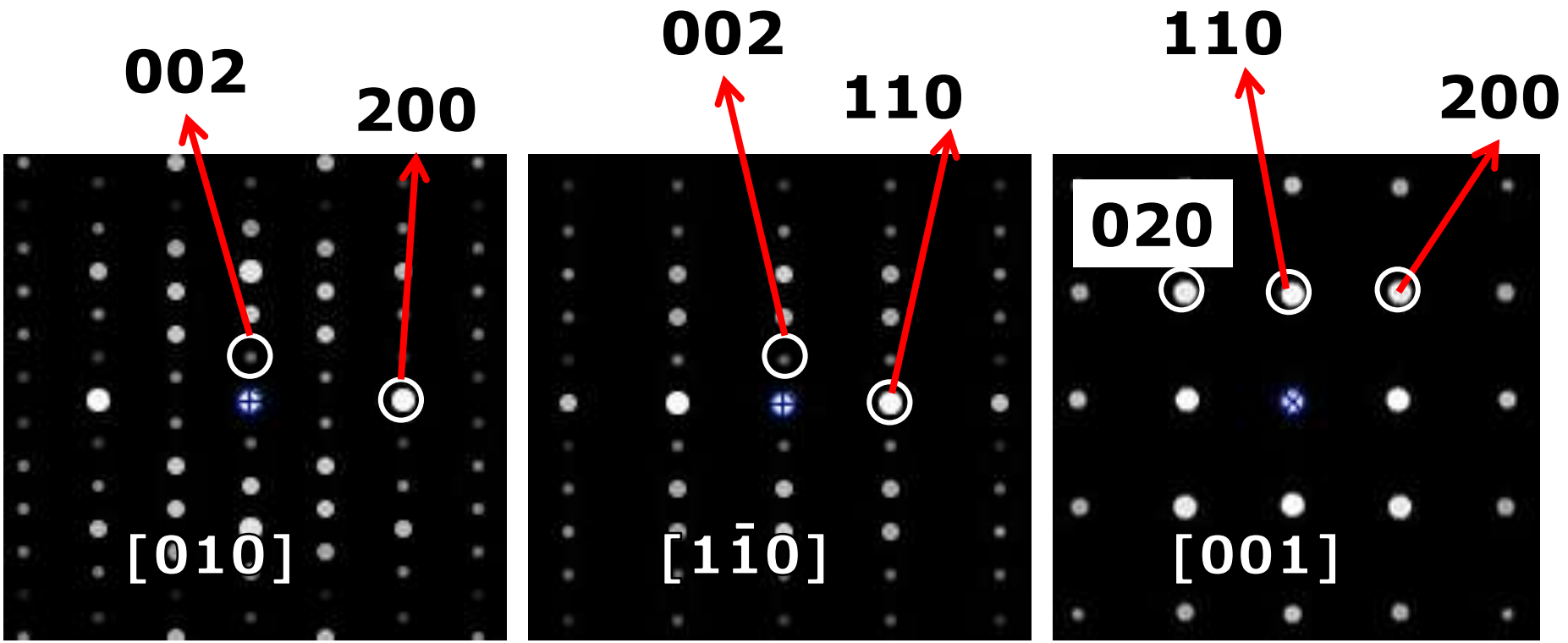


(Simulated ED patterns)

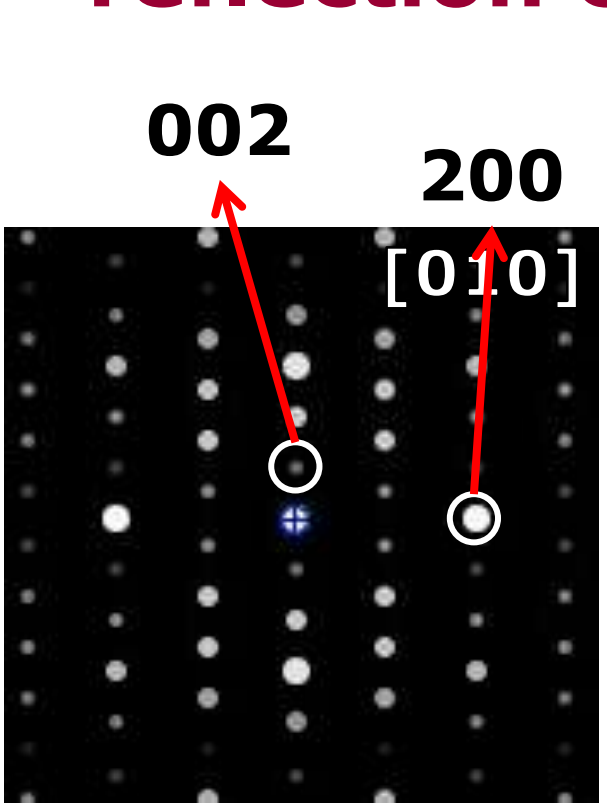
Indexed solution

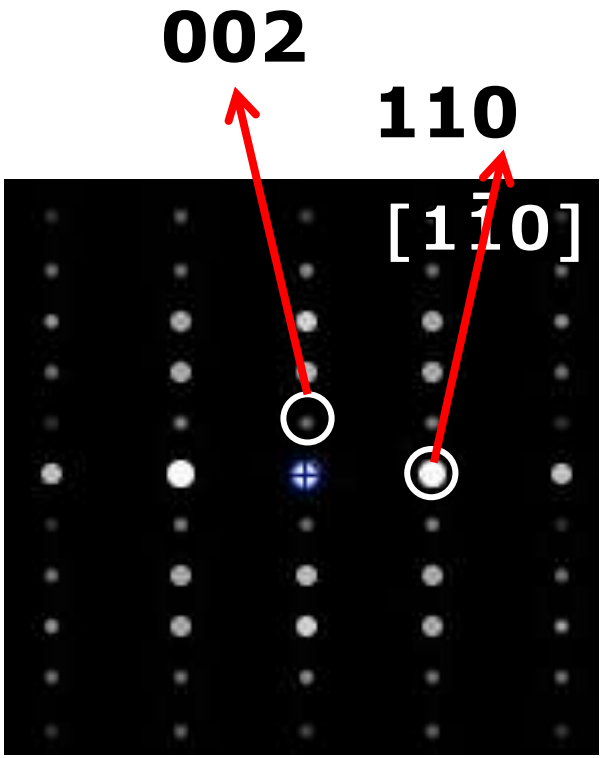


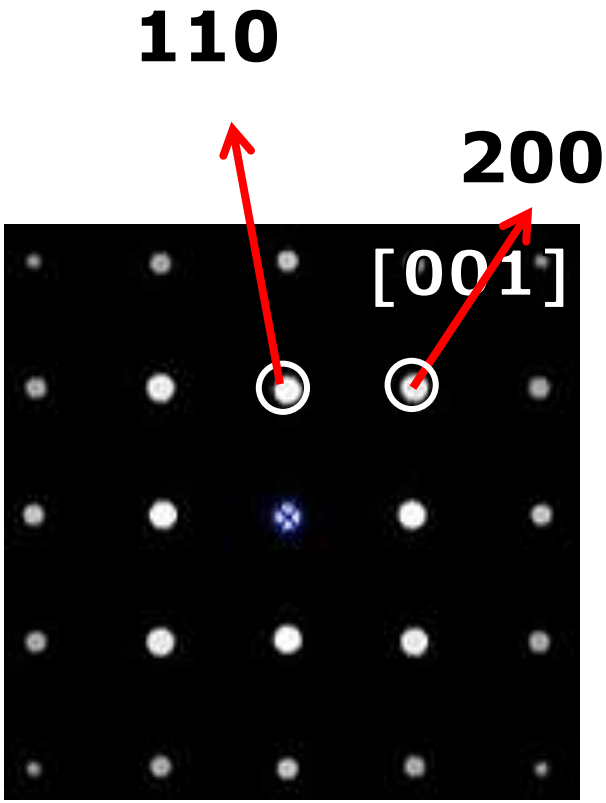
Zone indices



Exercise 1-2: IMS: determine the reflection condition h0l





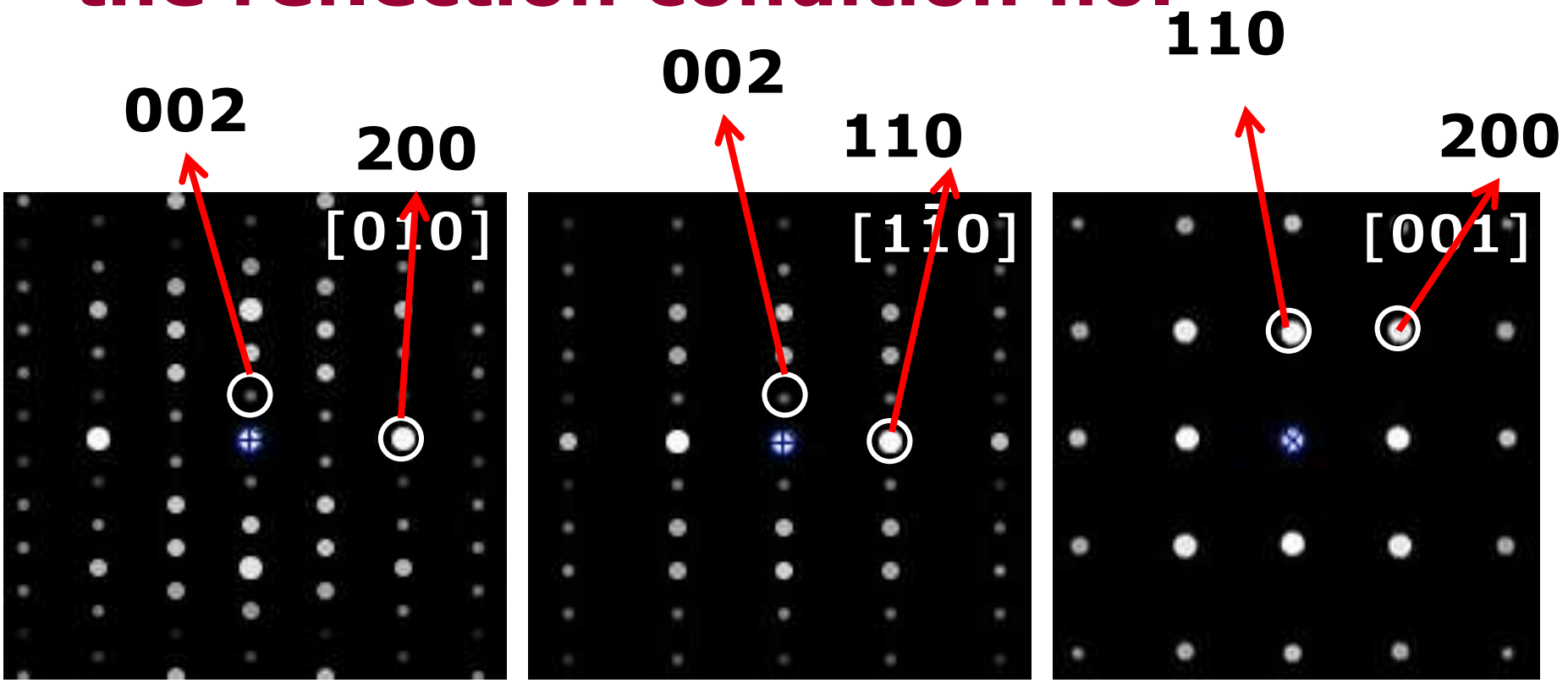


h0l: **h+l=2n**

h = 2n

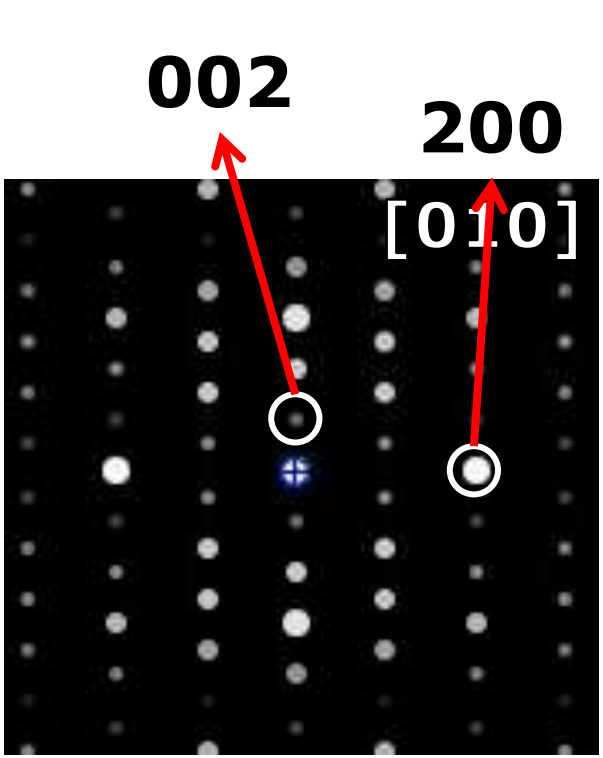
l = 2n

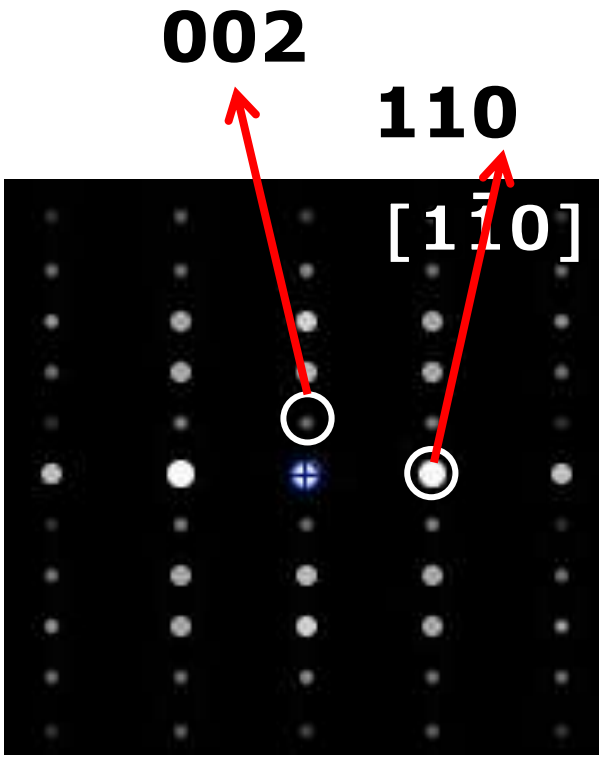
Exercise 1-2: IMS: determine the reflection condition h0l

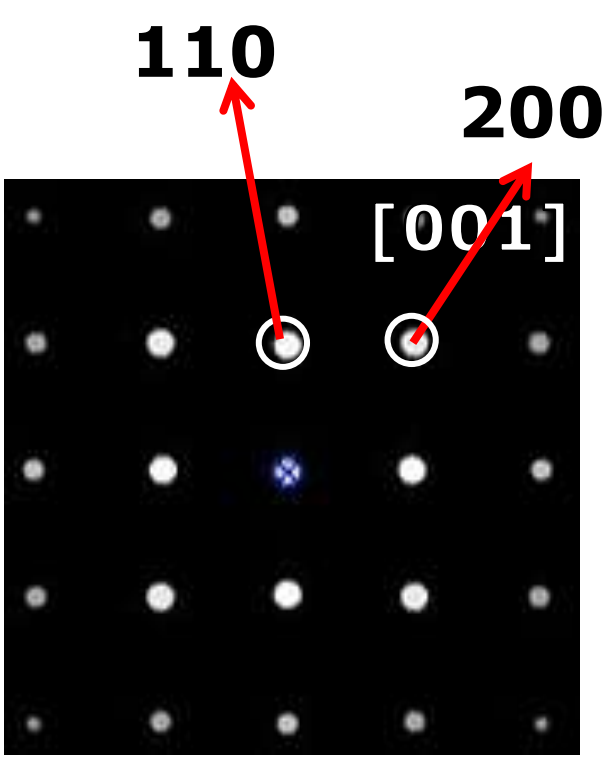


h0l: h+l=2n

Exercise 1-2: IMS: determine the reflection condition hhl







h0l: h+l=2n

hhl: h+l=2n

h = 2n

l = 2n

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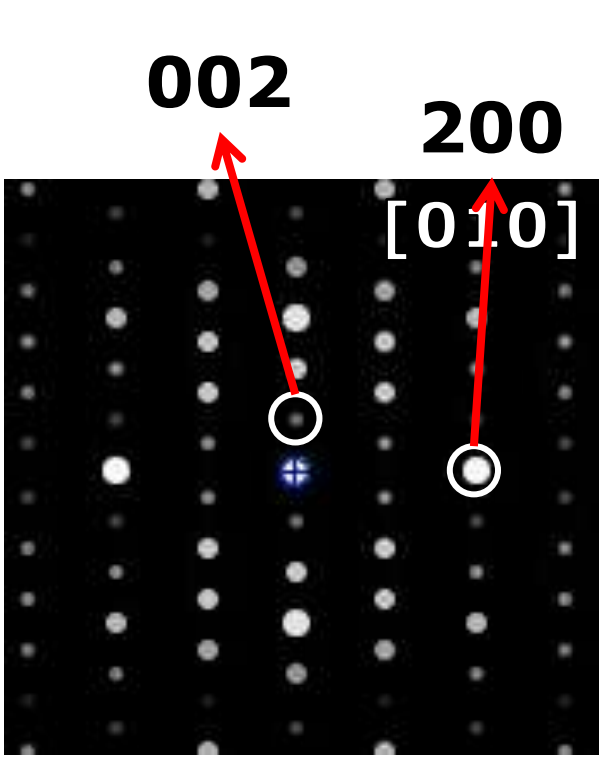
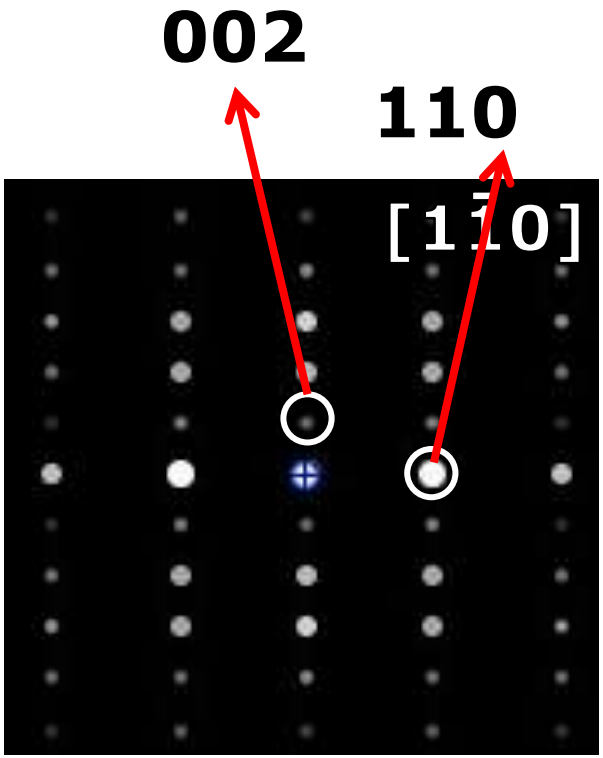
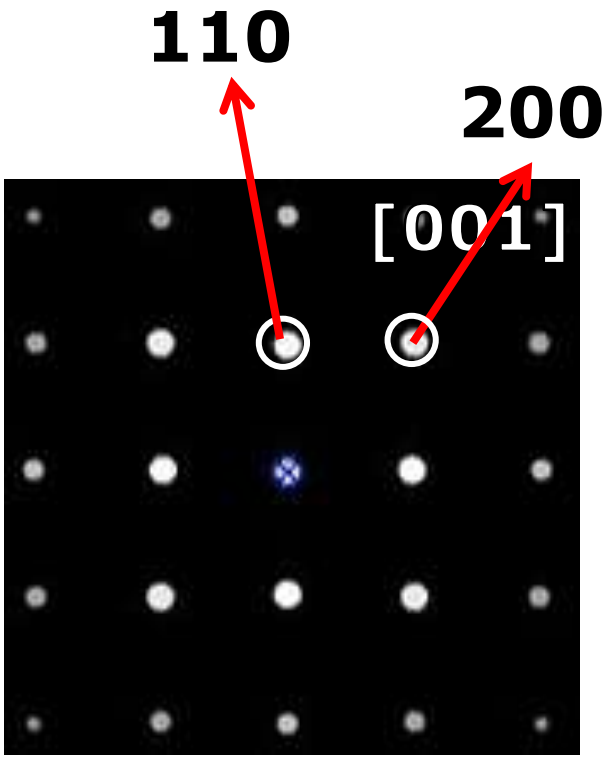
Exercise 1-2: IMS: determine the reflection condition hhl





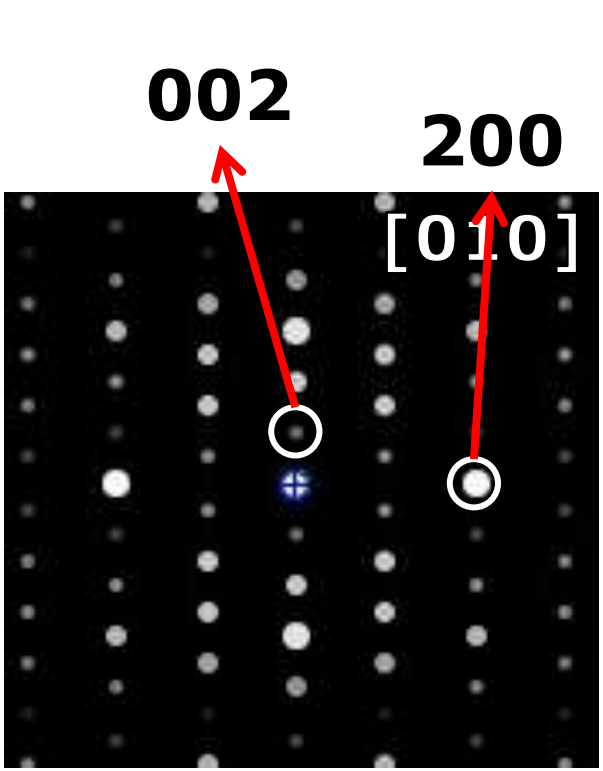


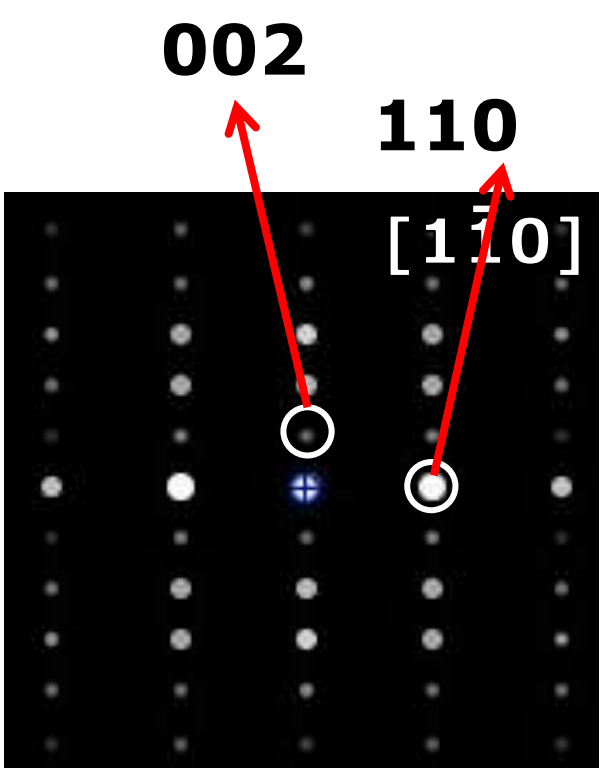
h0l: h+l=2n

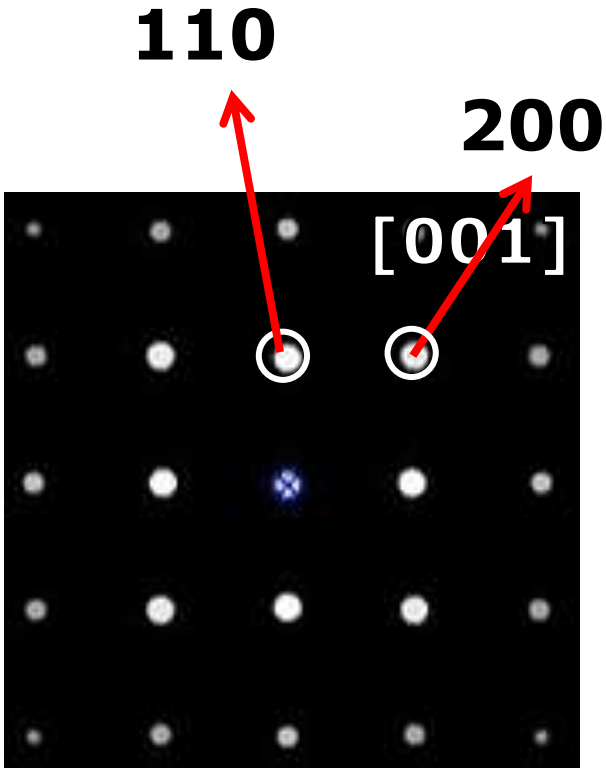
hhl:

l = 2n

Exercise 1-2: IMS: determine the reflection condition hk0







h0l: h+l=2n

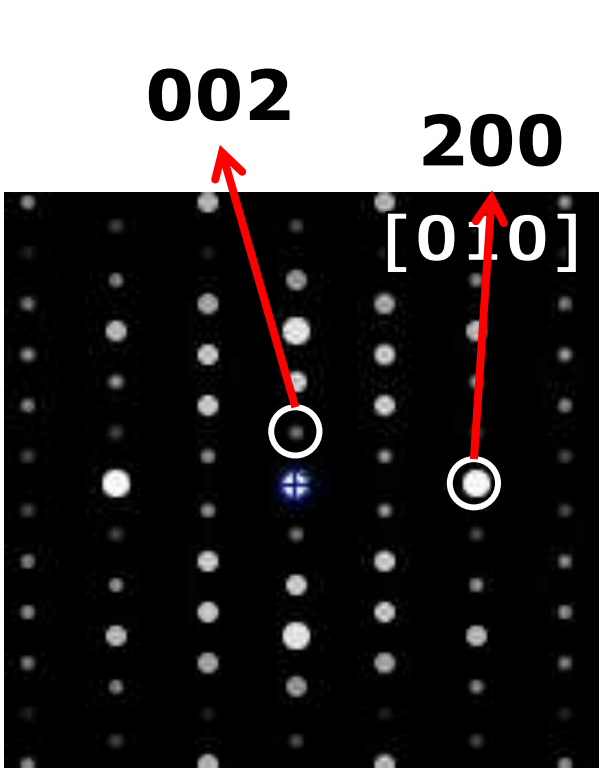
hhl: l = 2n

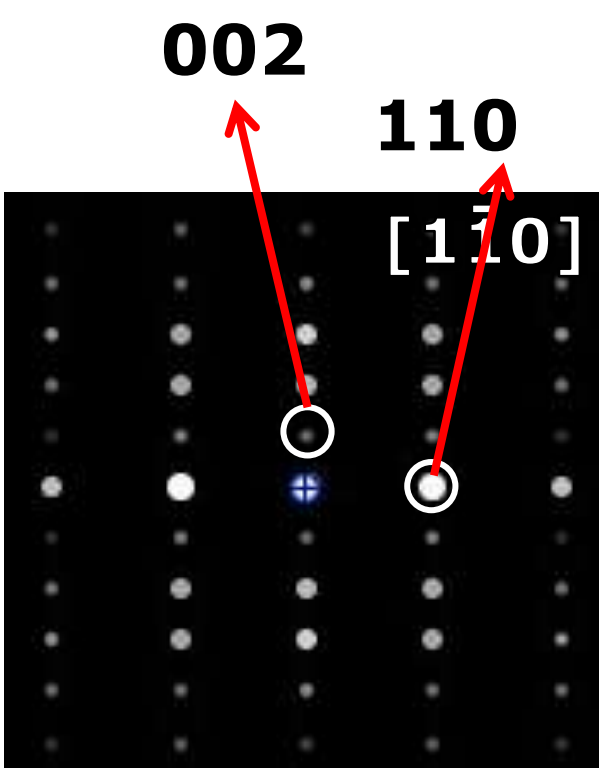
hk0: h+k=2n

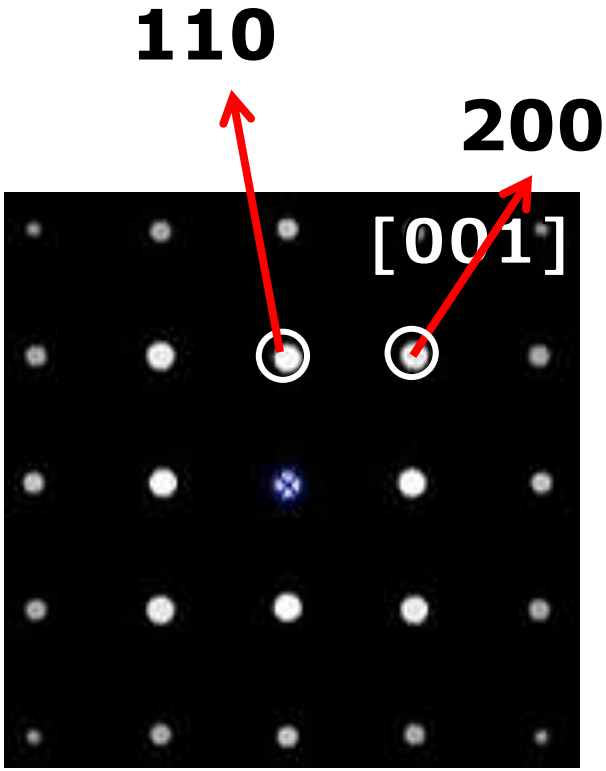
h = 2n

k = 2n

Exercise 1-2: IMS: determine the reflection condition hk0

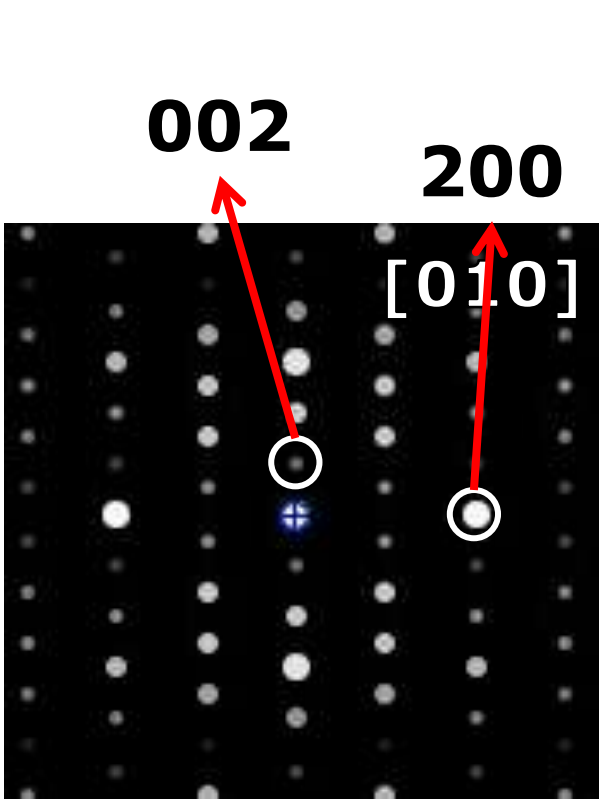


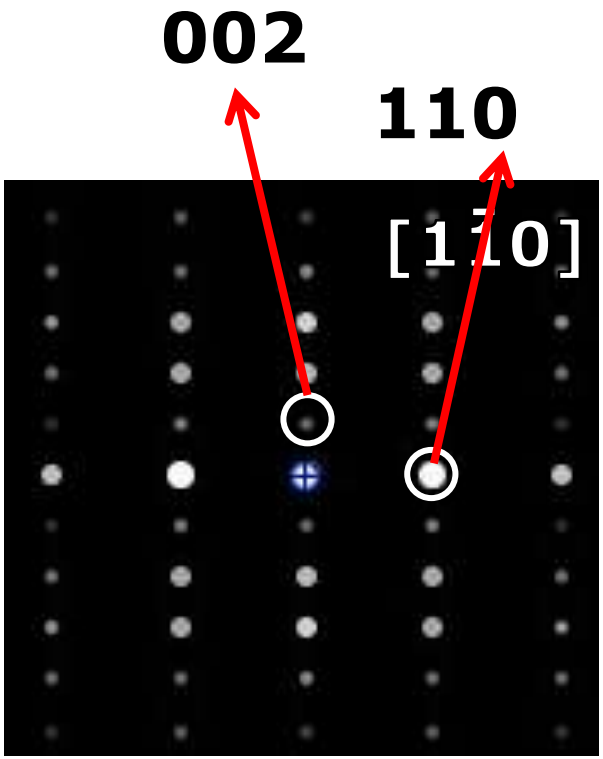


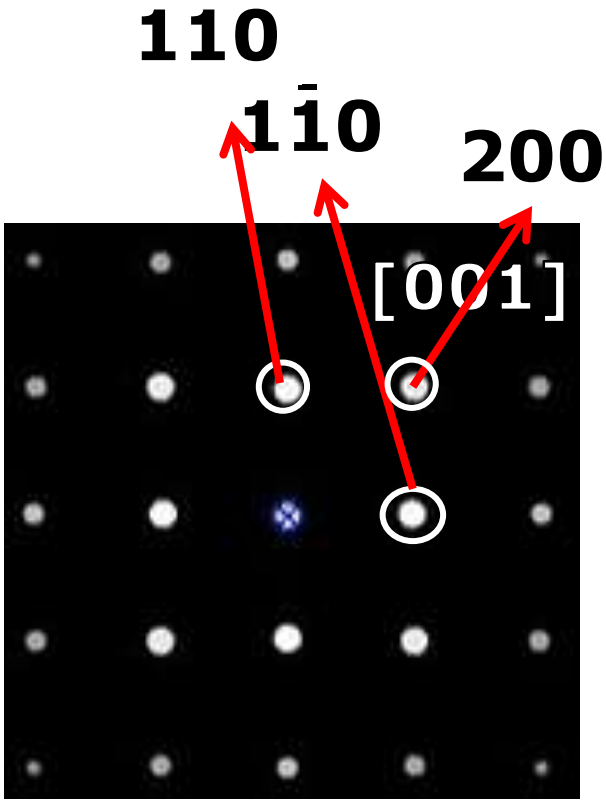


h0l: h+l=2n **hhl: l = 2n** **hk0: h+k=2n**

Solved reflection conditions







h0l:h+l=2n **hhl:l=2n** **hk0:h+k=2n**

Also (from rest of the zones) hkl: h+k+l=2n.

Determine space group

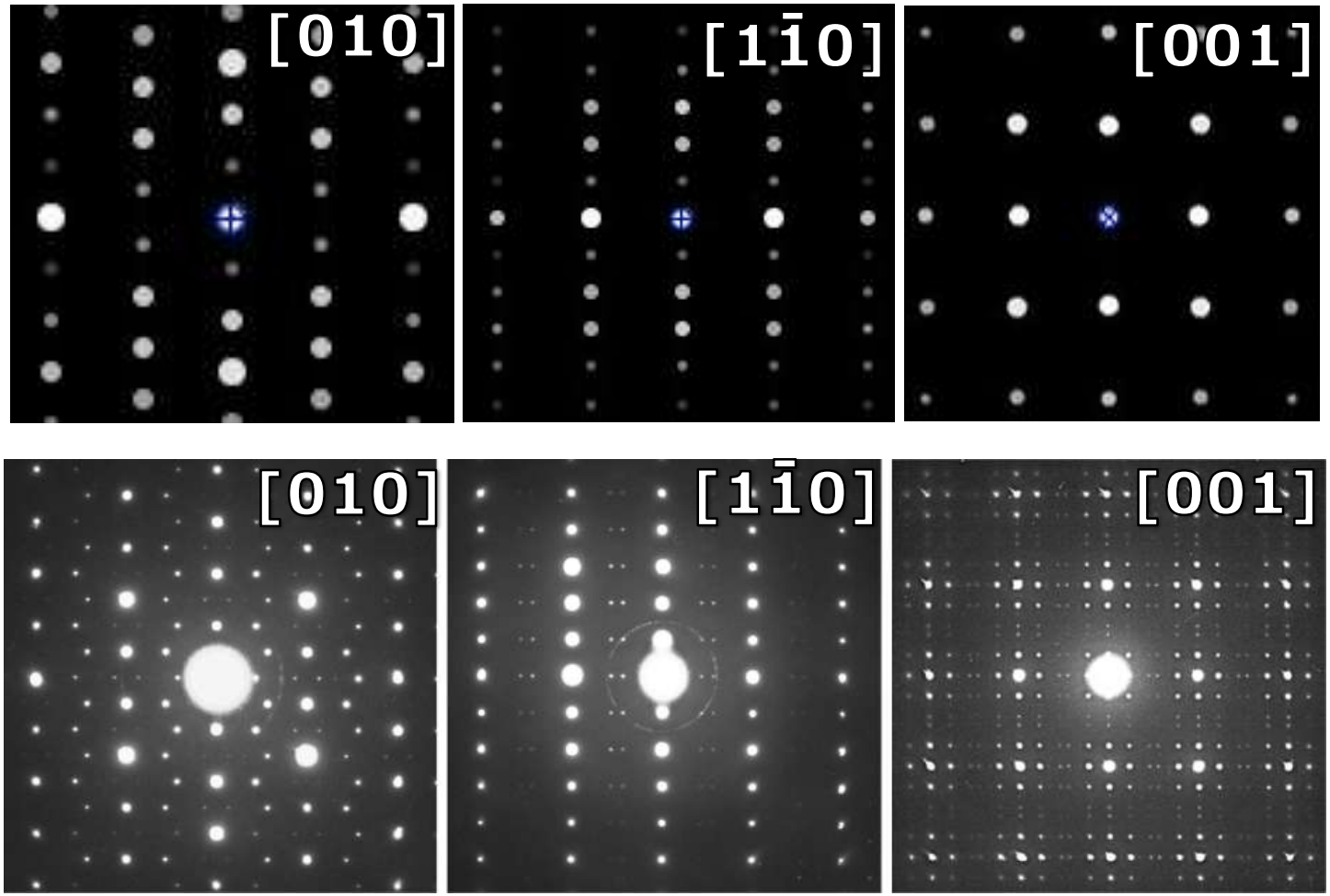
TETRAGONAL, Laue classes $4/m$ and $4/mmm$ (*cont.*)

Reflection conditions							Extinction symbol	Laue class						
								$4/m$			$4/mmm$ ($4/m\,2/m\,2/m$)			
							Point group							
hkl	$hk0$	$0kl$	hhl	$00l$	$0k0$	$hh0$		4	$\bar{4}$	$4/m$	422	4*mm*	$\bar{4}2m$ $\bar{4}m2$	$4/mmm$
	$h+k$	k			k		$Pnb-$							*P*4/*nbm* (125)
	$h+k$	k	l	l	k		$Pnbc$							*P*4$_2$/*nbc* (133)
	$h+k$	l		l	k		$Pnc-$							*P*4$_2$/*ncm* (138)
	$h+k$	l	l	l	k		$Pncc$							*P*4/*ncc* (130)
	$h+k$	$k+l$		l	k		$Pnn-$							*P*4$_2$/*nnm* (134)
	$h+k$	$k+l$	l	l	k		$Pnnc$							*P*4/*nnc* (126)
$h+k+l$	$h+k$	$k+l$	l	l	k		$I---$	*I*4 (79)	*I*$\bar{4}$ (82)	*I*4/*m* (87)	*I*422 (97)	*I*4*mm* (107)	*I*$\bar{4}2m$ (121)	*I*4/*mmm* (139)
													I$\bar{4}m2$ (119)	
$h+k+l$	$h+k$	$k+l$	l	$l=4n$	k		$I4_1---$	*I*4$_1$ (80)			*I*4$_1$22 (98)			
$h+k+l$	$h+k$	$k+l$	$\frac{1}{4}$	$l=4n$	k	h	$I---d$					*I*4$_1$*md* (109)	*I*$\bar{4}2d$ (122)	
$h+k+l$	$h+k$	k, l	l	l	k		$I-c-$					*I*4*cm* (108)	*I*$\bar{4}c2$ (120)	*I*4/*mcm* (140)
$h+k+l$	$h+k$	k, l	$\frac{1}{4}$	$l=4n$	k	h	$I-cd$					*I*4$_1$*cd* (110)		
$h+k+l$	h, k	$k+l$	l	$l=4n$	k		$I4_1/a--$			*I*4$_1$/*a* (88)				
$h+k+l$	h, k	$k+l$	$\frac{1}{4}$	$l=4n$	k	h	$Ia-d$							*I*4$_1$/*amd* (141)

$h+k+l$	$h+k$	$k+l$	l	l	k		$I---$	*I*4/*mmm* (139)

- International Tables: I---
- Most symmetrical I4/mmm

Incommensurate vs. basic cell

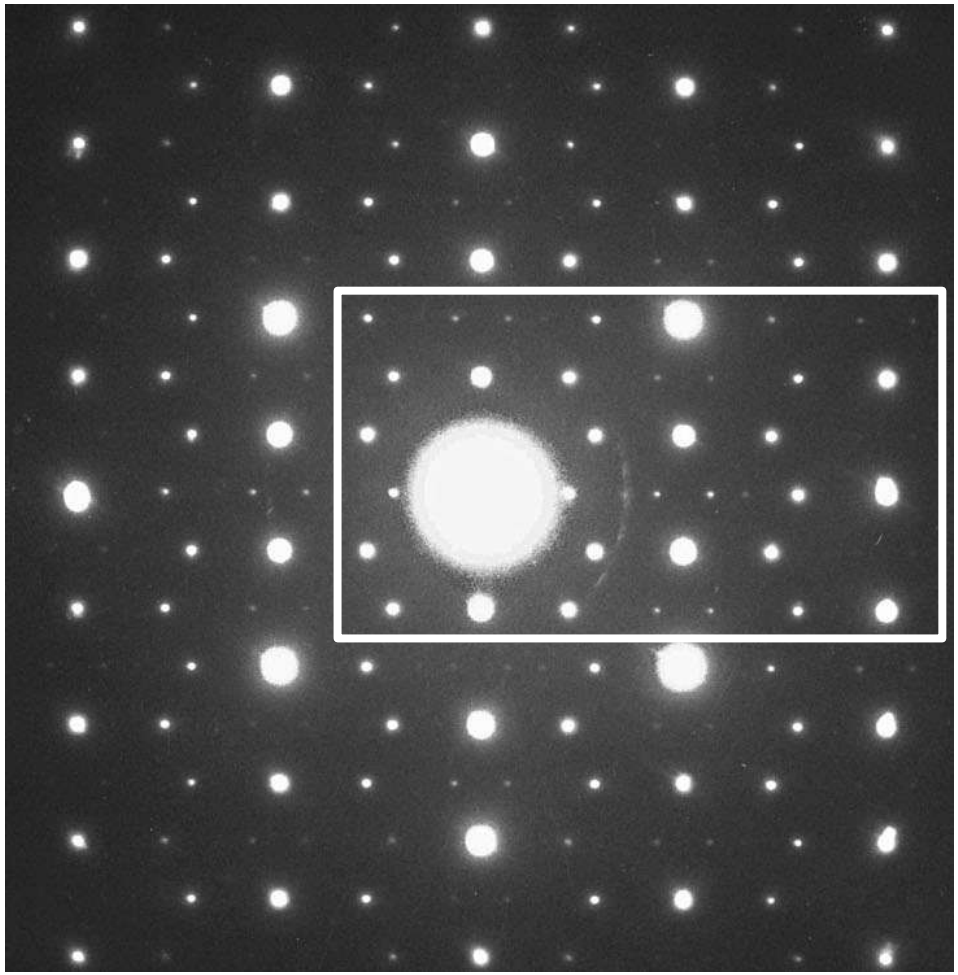


Hadermann et al., Journal of Materials Chemistry, 17, 22, 2007, 2344-2350

$LaSrCuO_{3.52}$

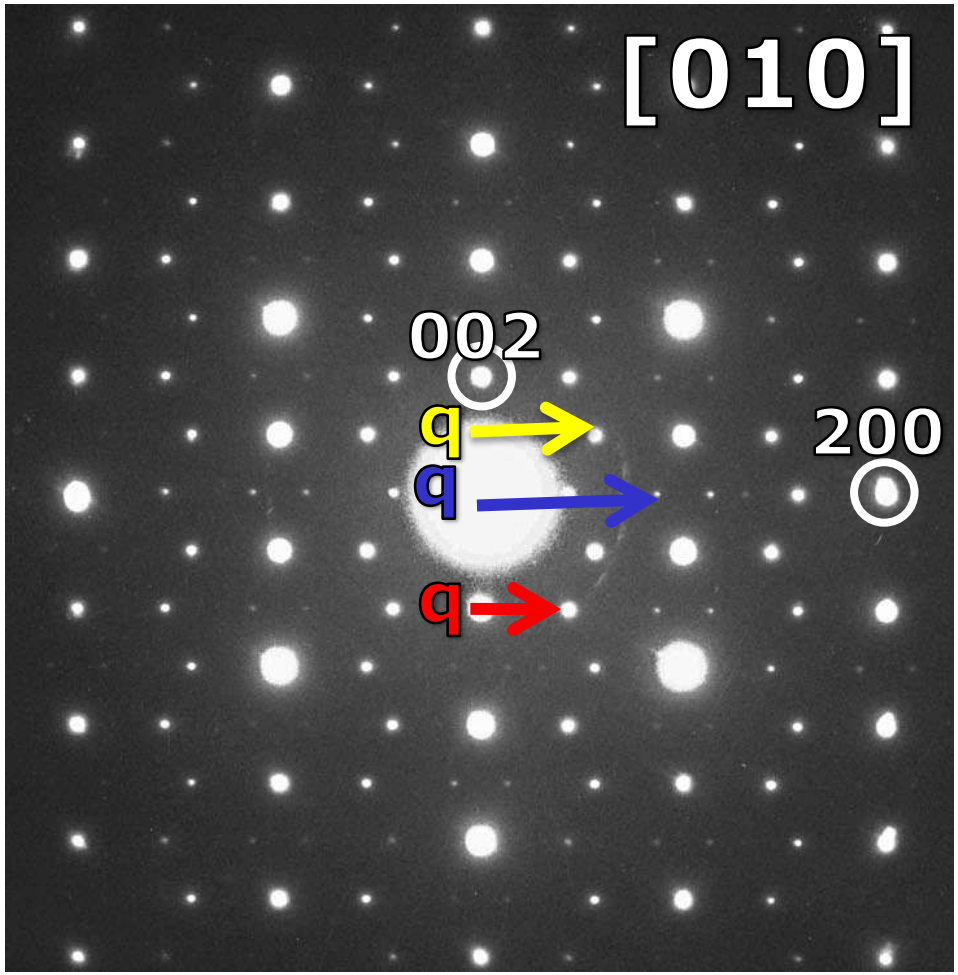
Exercise 1-3: index the IMS

Identify and index the subcell reflections.



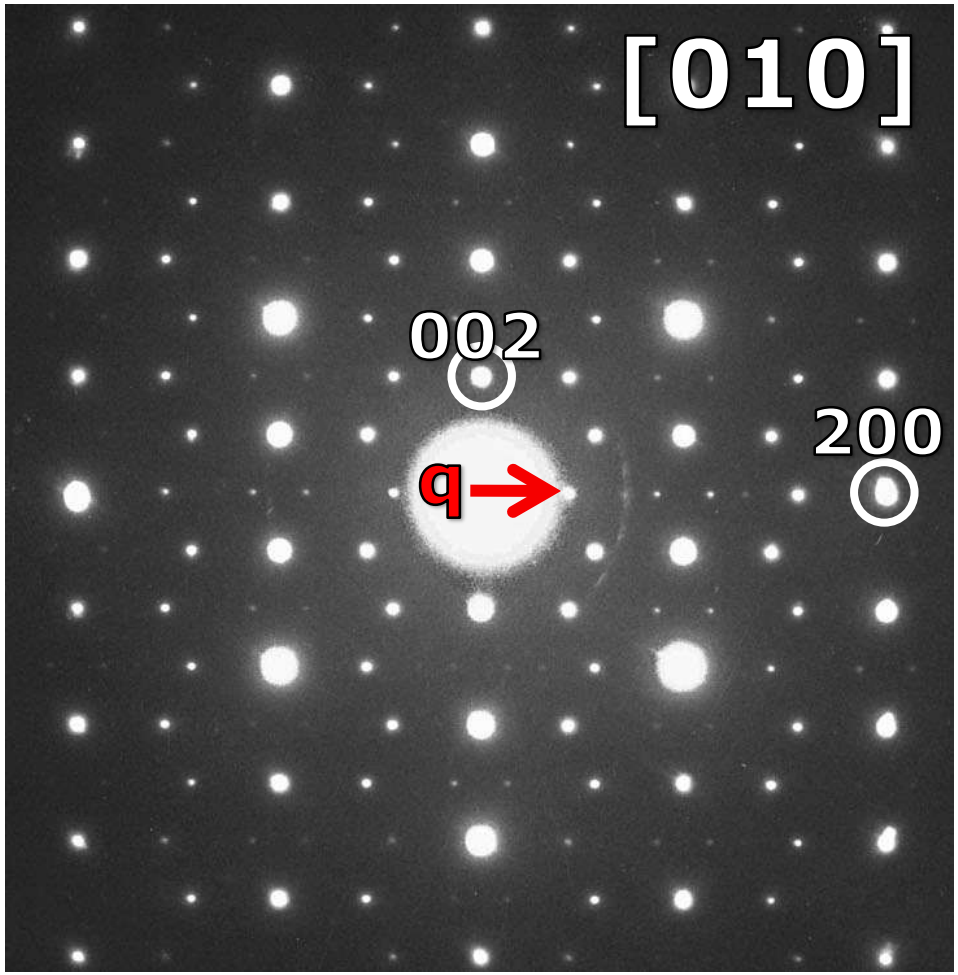
$LaSrCuO_{3.52}$

Propose a modulation vector.



$LaSrCuO_{3.52}$

- $q=\alpha a^*$
- $\alpha<0.5$



$LaSrCuO_{3.52}$

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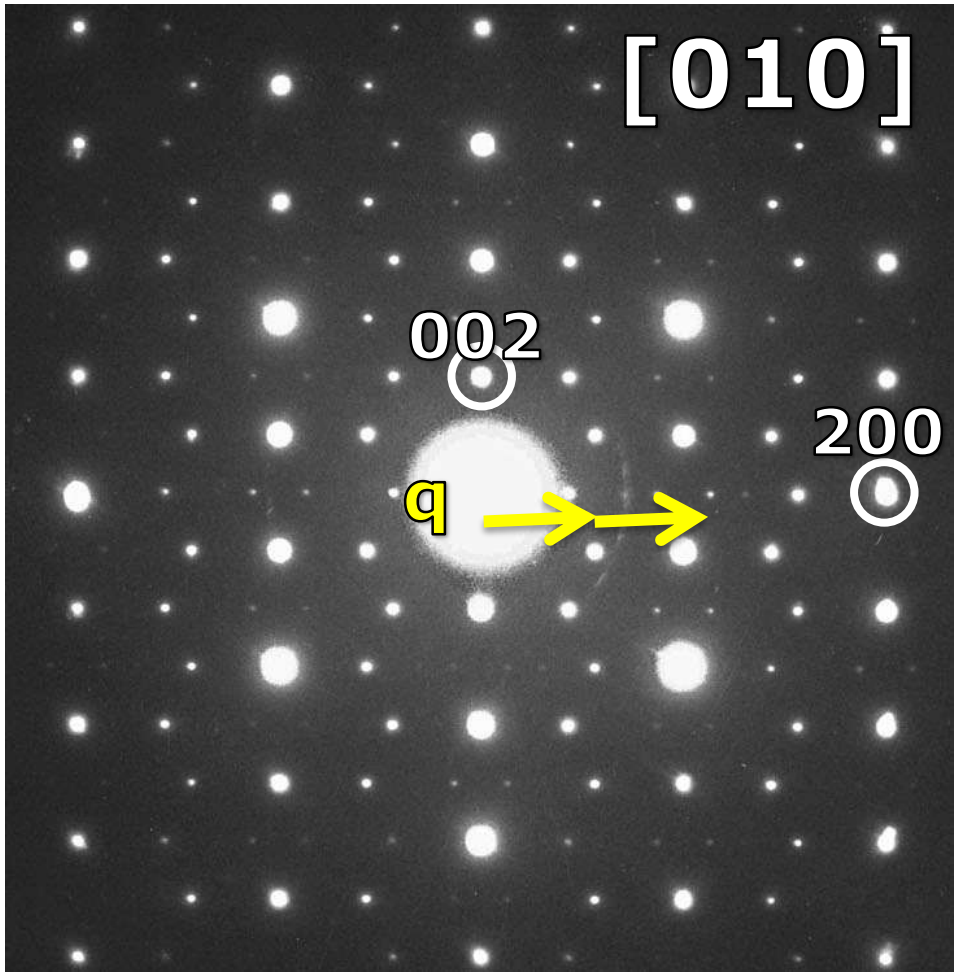
- $q=\alpha a^*$
- $\alpha<0.5$



$LaSrCuO_{3.52}$

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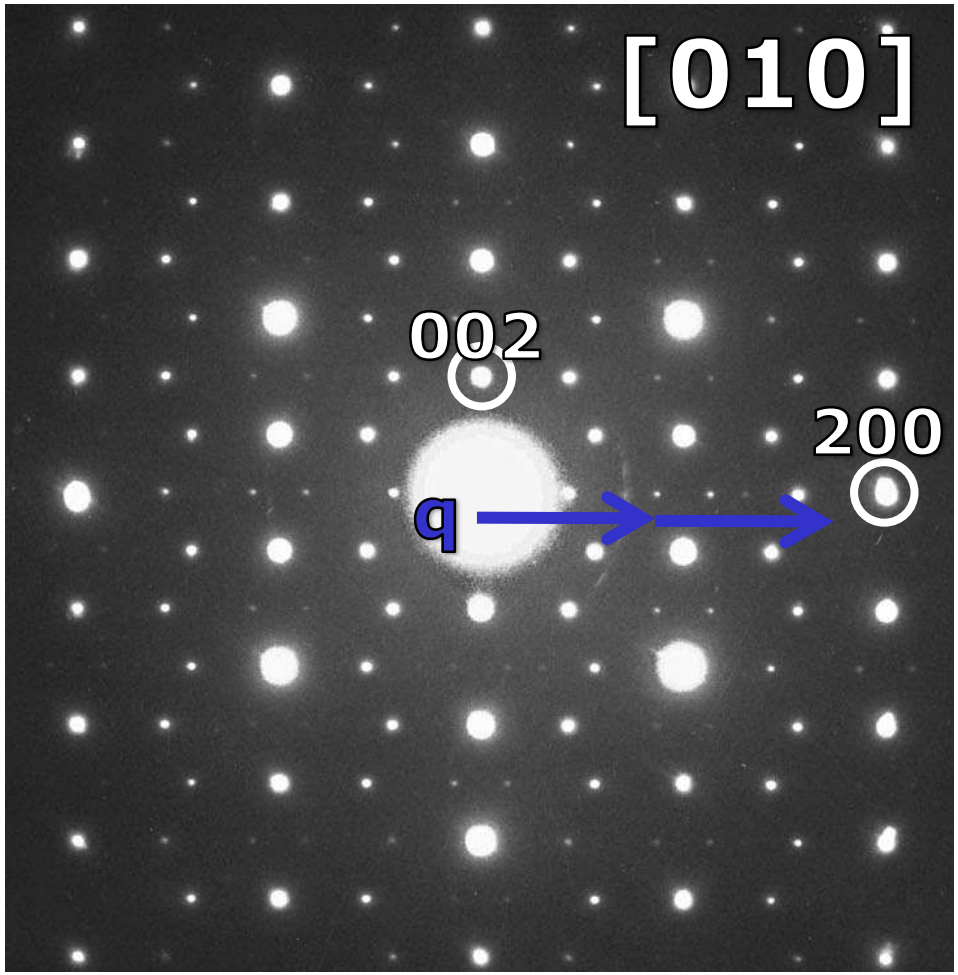
- $q=\alpha a^*$
- $\alpha<0.5$



$LaSrCuO_{3.52}$

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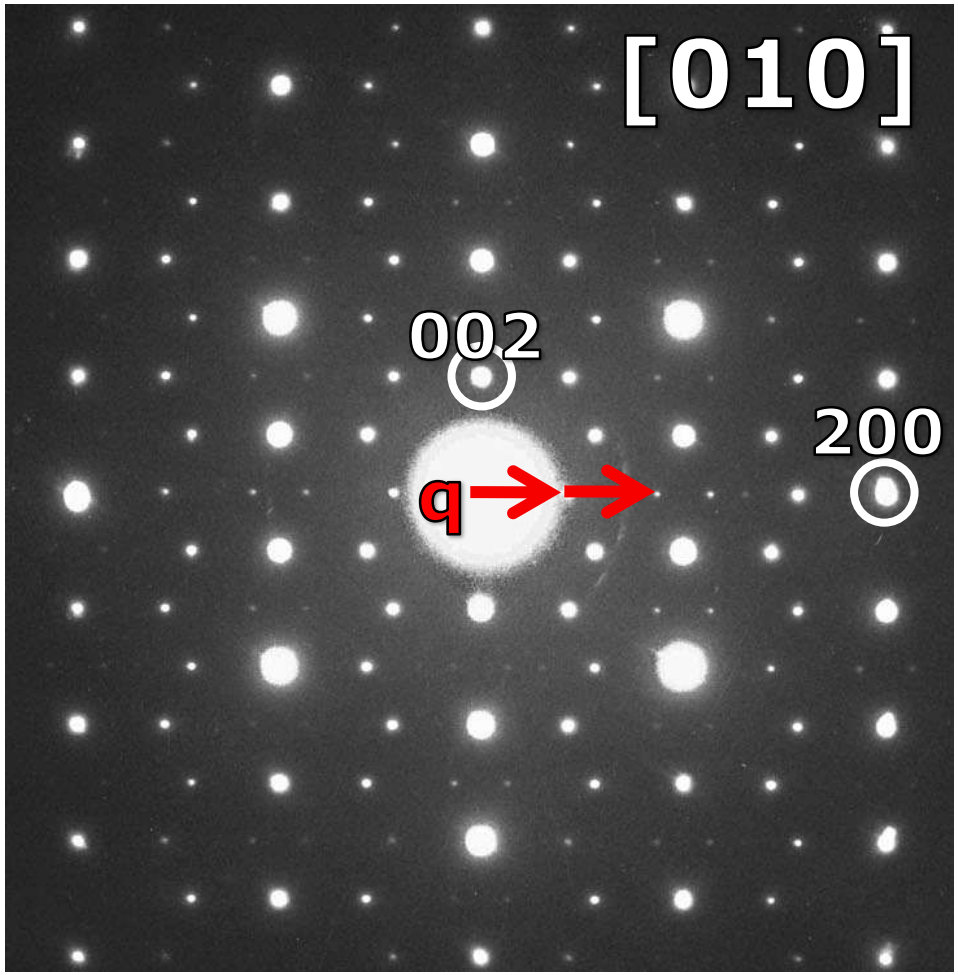
Possible solution

- $q=\alpha a^*$
- $\alpha<0.5$



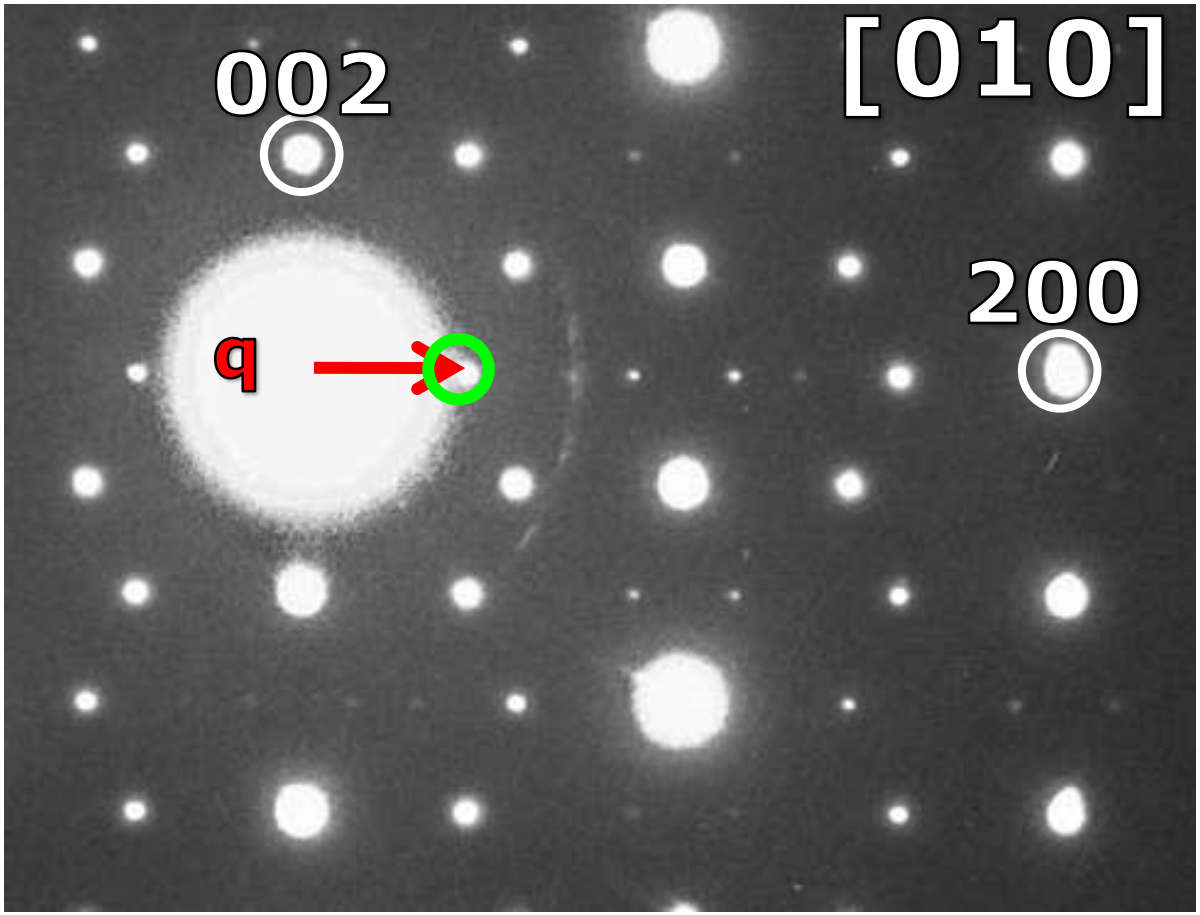
$LaSrCuO_{3.52}$

Index the satellite indicated in green

001

0001

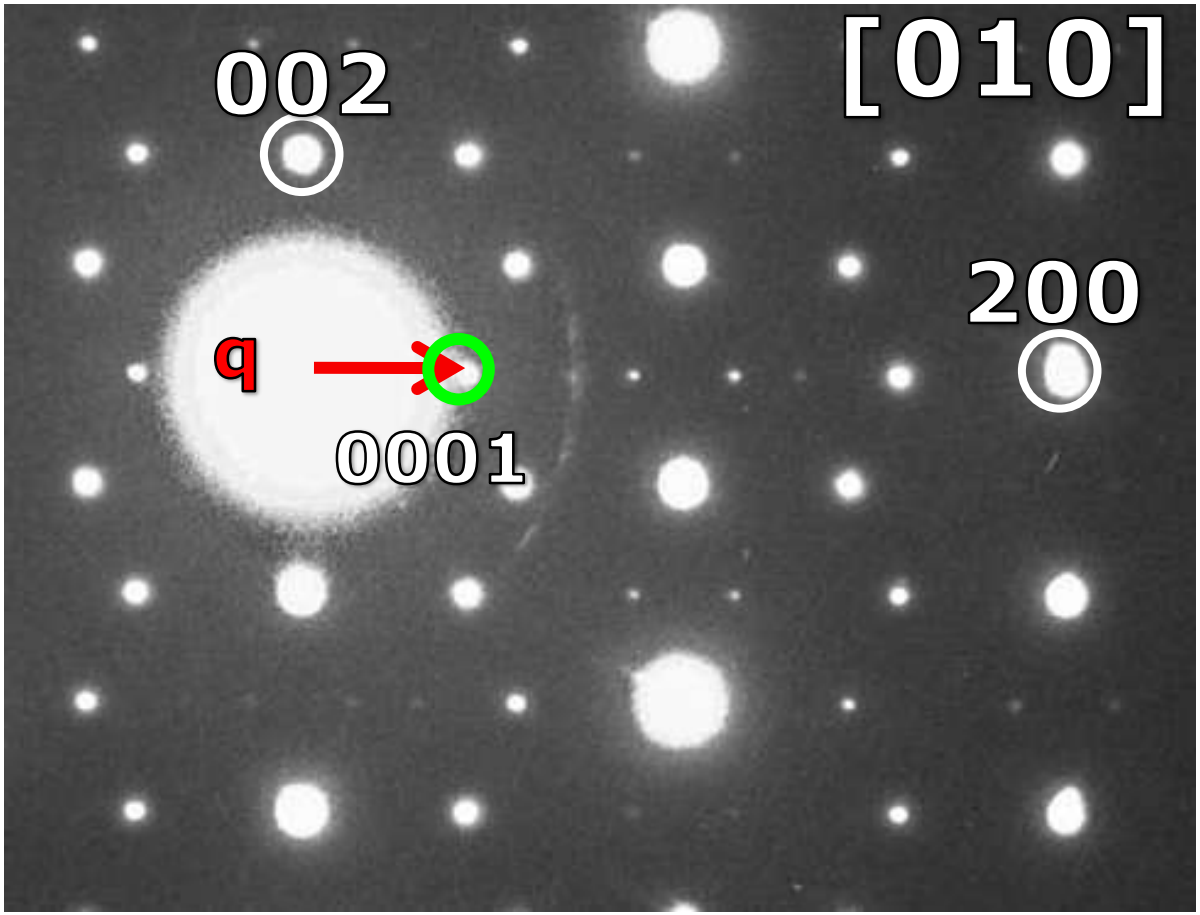
100



$LaSrCuO_{3.52}$

Index the satellite indicated in green

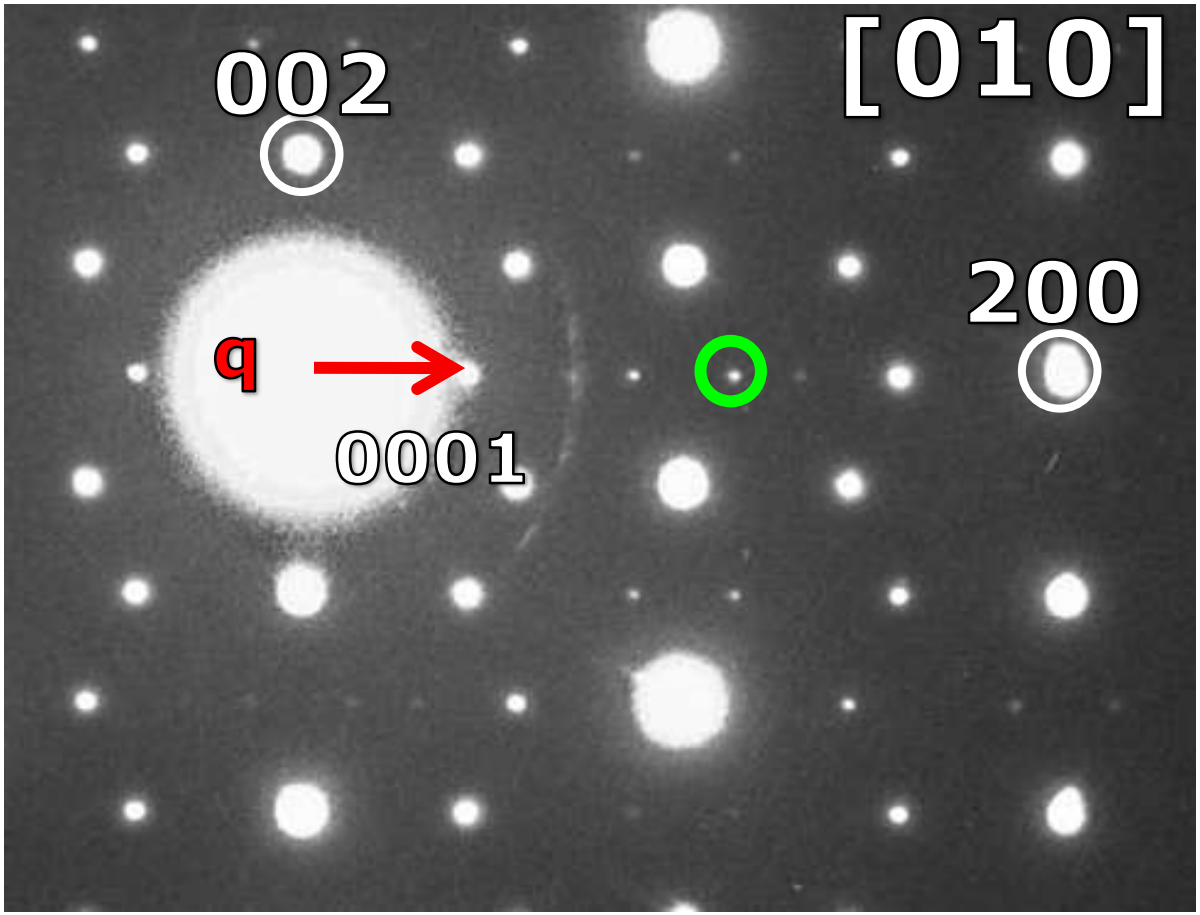
0001



$LaSrCuO_{3.52}$

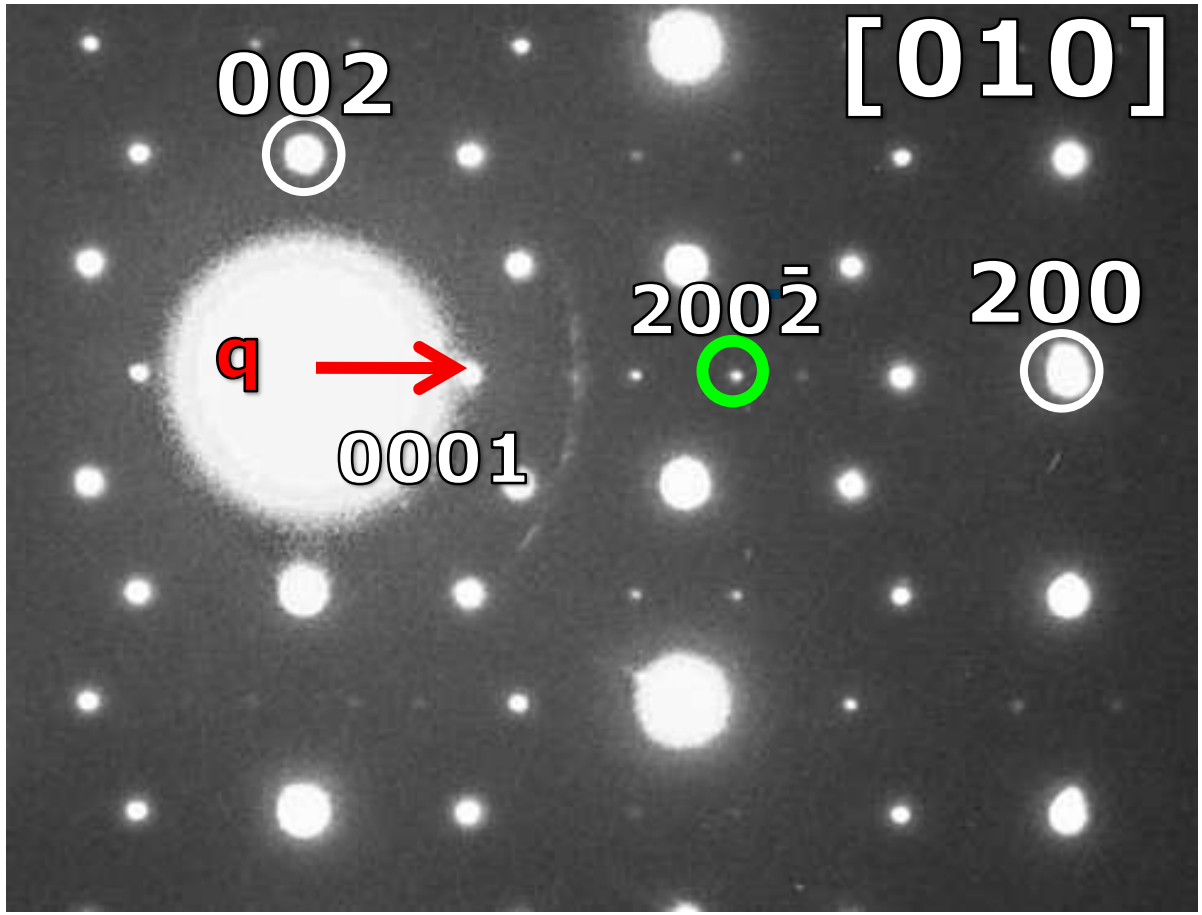
Index the next indicated satellite

- 0002
- $200\bar{1}$
- $200\bar{2}$



$LaSrCuO_{3.52}$

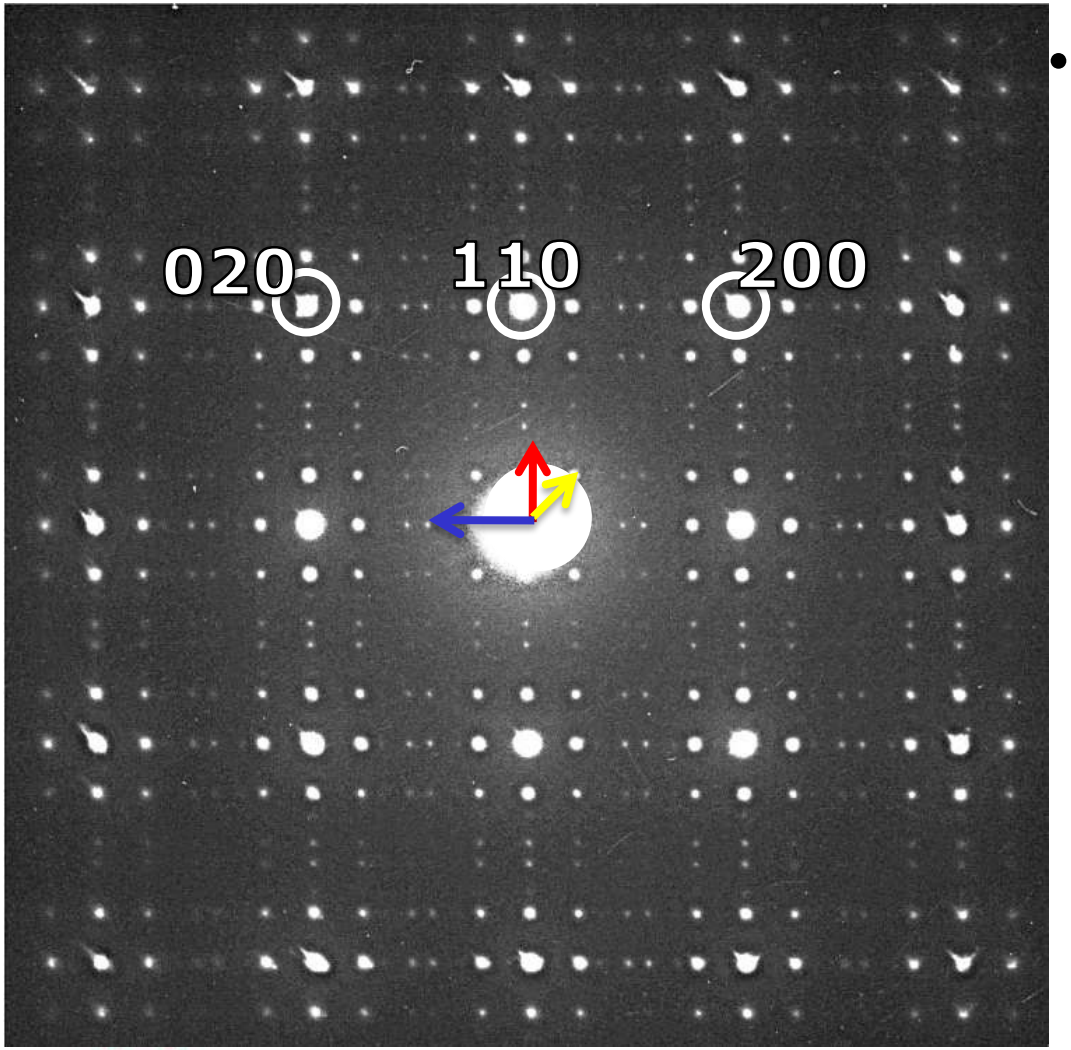
Index the next indicated satellite



● 200$\bar{2}$

$LaSrCuO_{3.52}$

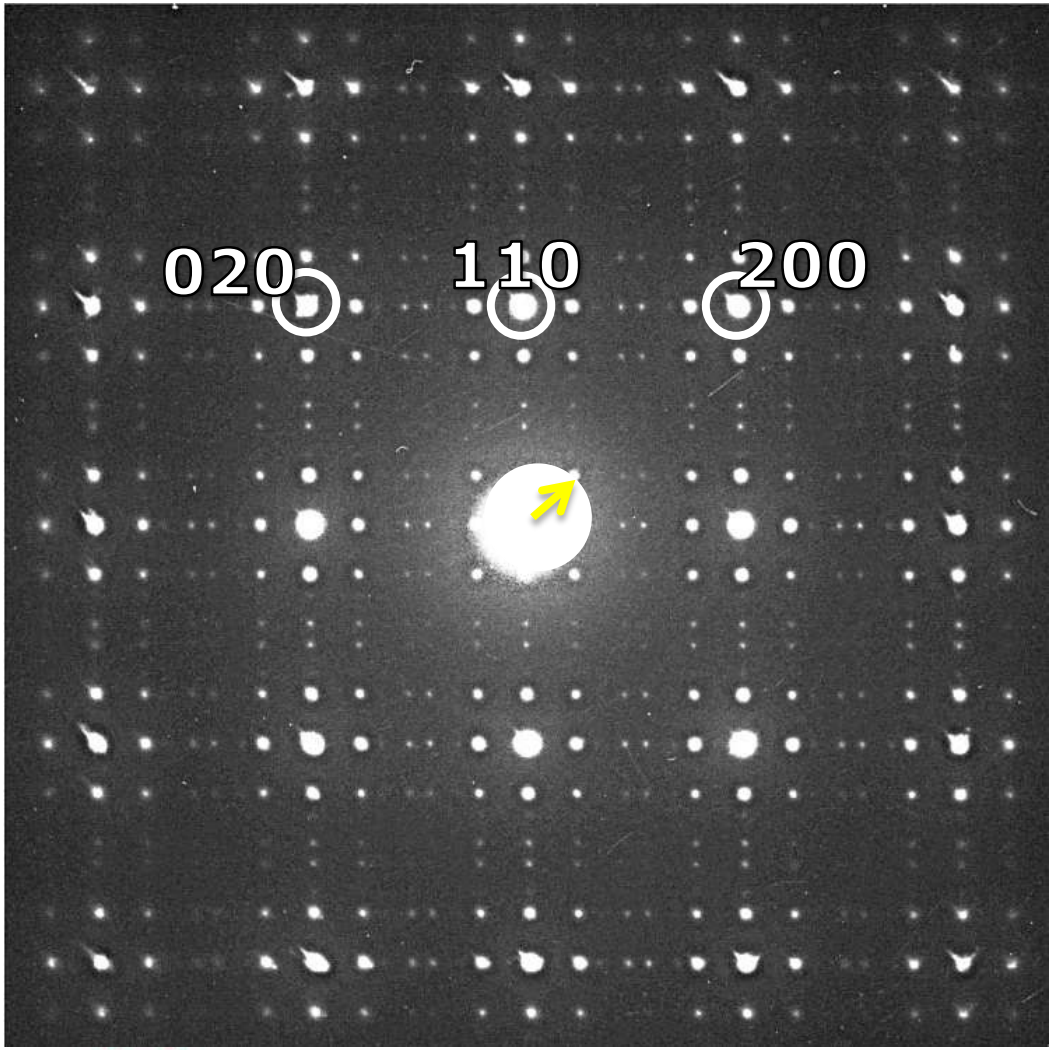
Exercise 1-4: IMS with more complete data



- Which of the indicated vectors corresponds to the modulation vector chosen on the previous slides?

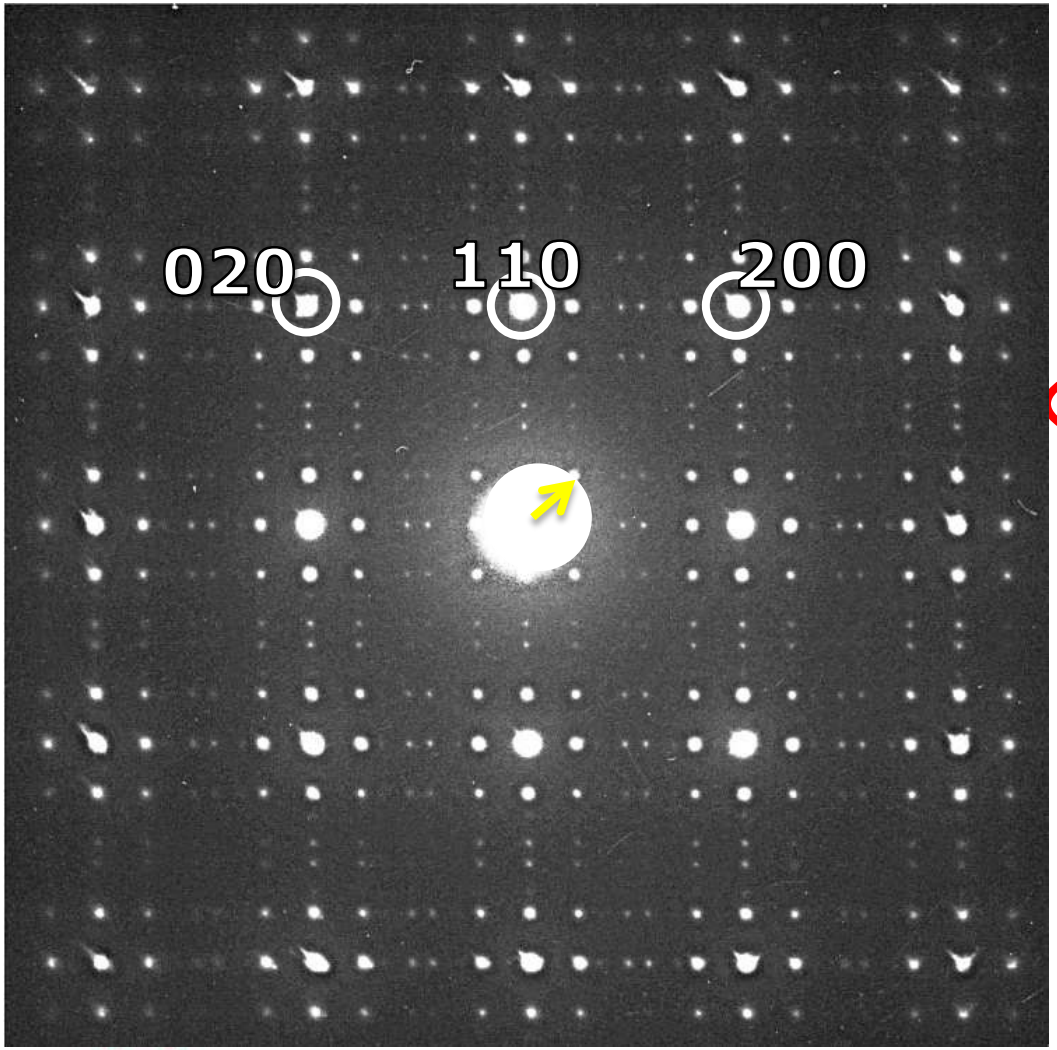
$LaSrCuO_{3.52}$

Exercise 1-4: IMS with more complete data



- Which of the indicated vectors corresponds to the modulation vector chosen on the previous slides?

$LaSrCuO_{3.52}$



Is the proposed vector still valid?

yes

no

$LaSrCuO_{3.52}$

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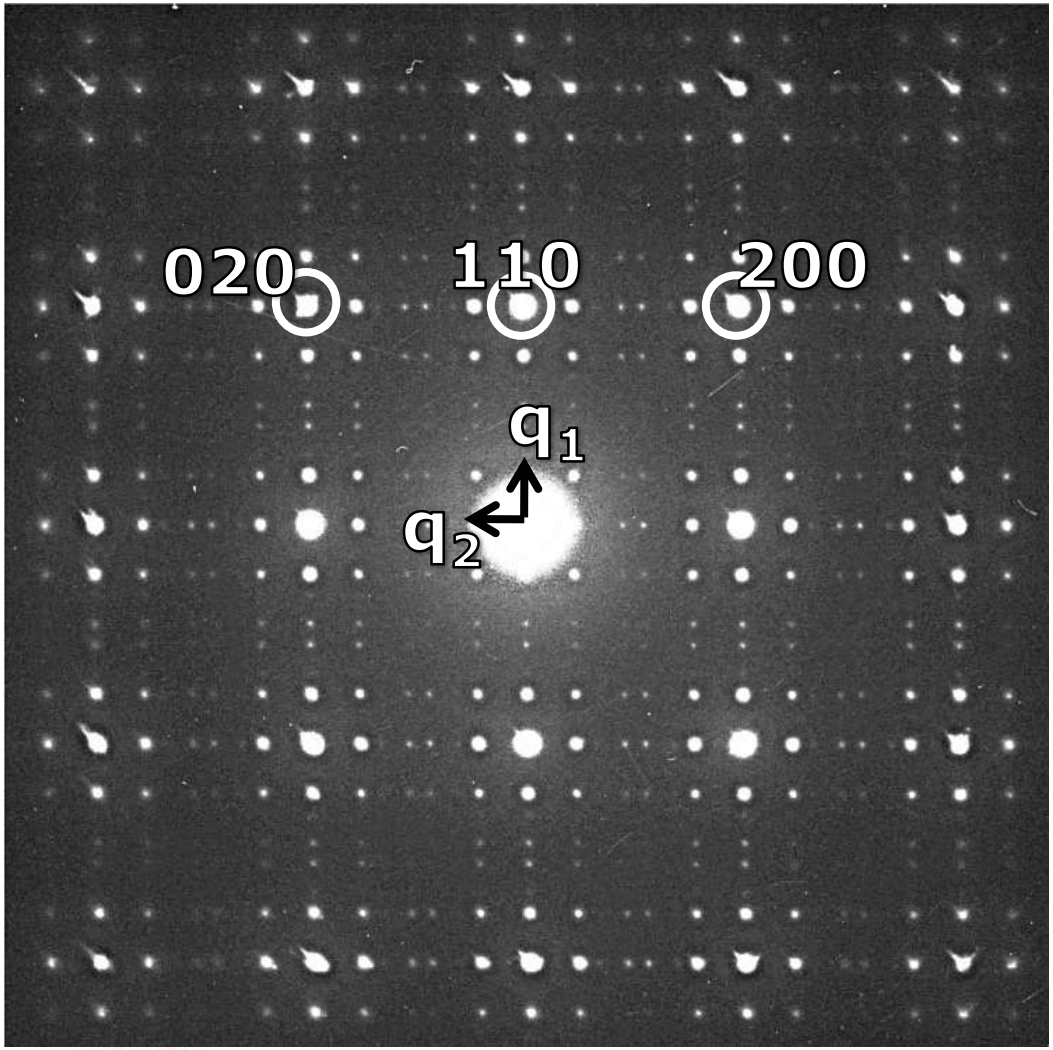


Indicate the correct modulation vector(s) on the central white area.

You need

- q_1
- q_2
- q_1 ànd q_2

$q_1 = \alpha a^* + \beta b^*$

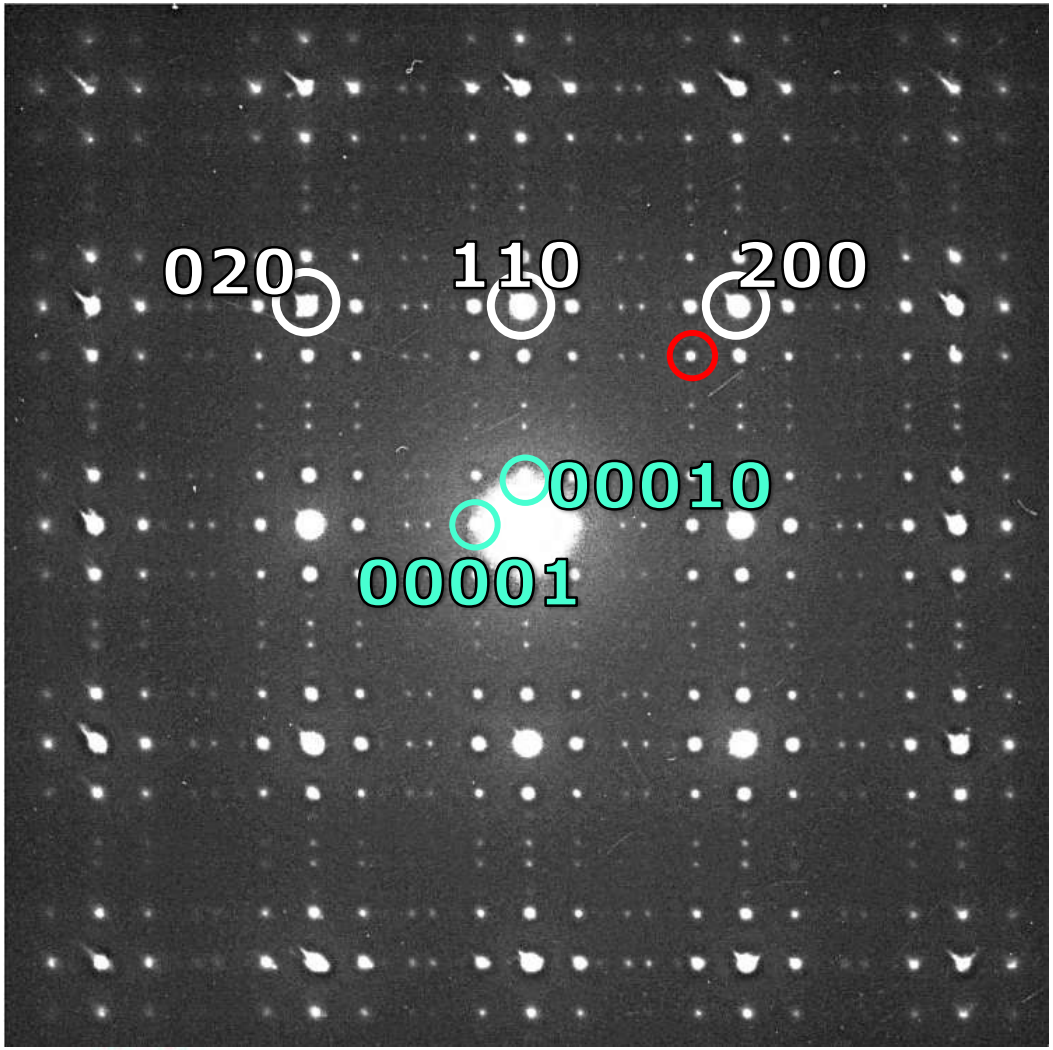
$q_2 = -\alpha a^* + \beta b^*$

$\alpha = \beta < 0.25$

hklmn

$LaSrCuO_{3.52}$

Index the reflection indicated in red



- 20011
- 200$\bar{1}$1
- 2001$\bar{1}$

$LaSrCuO_{3.52}$

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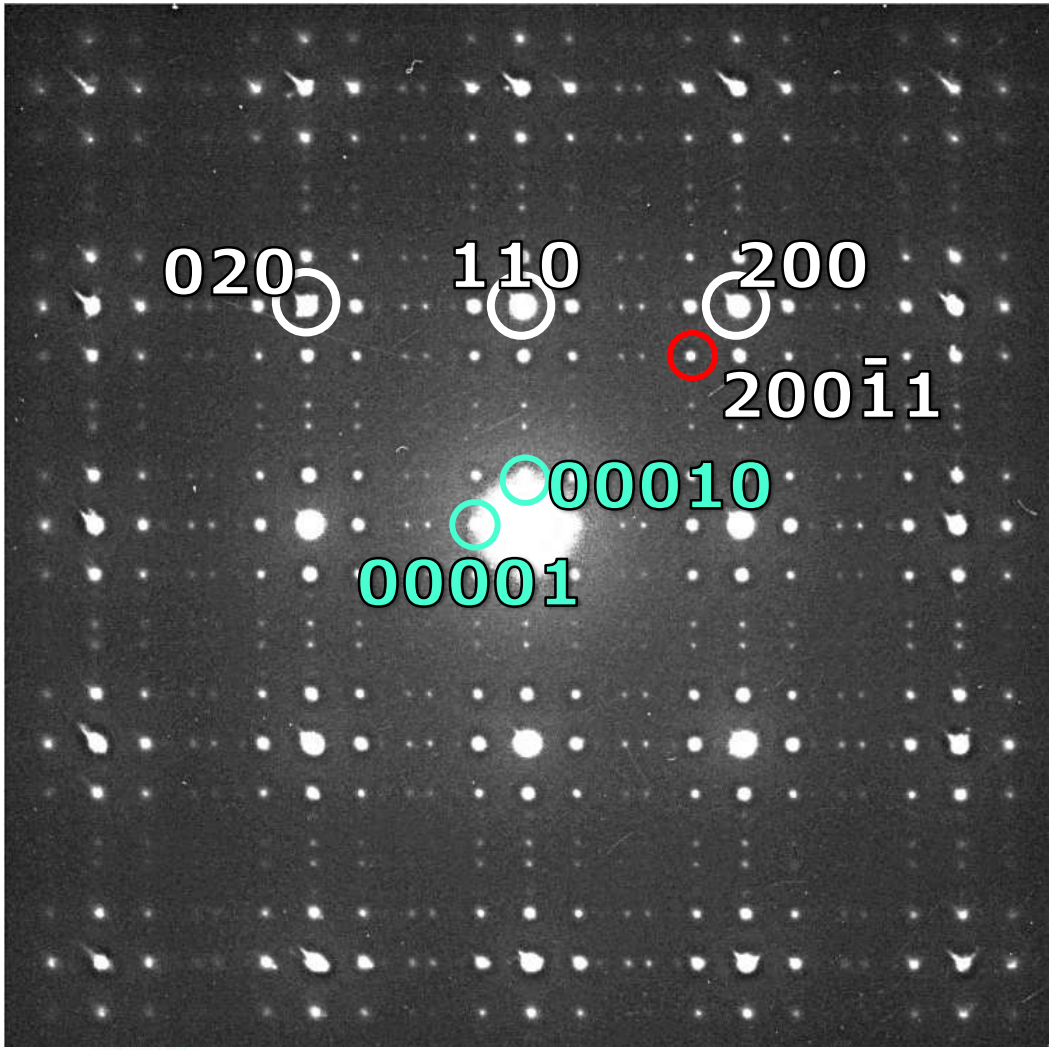
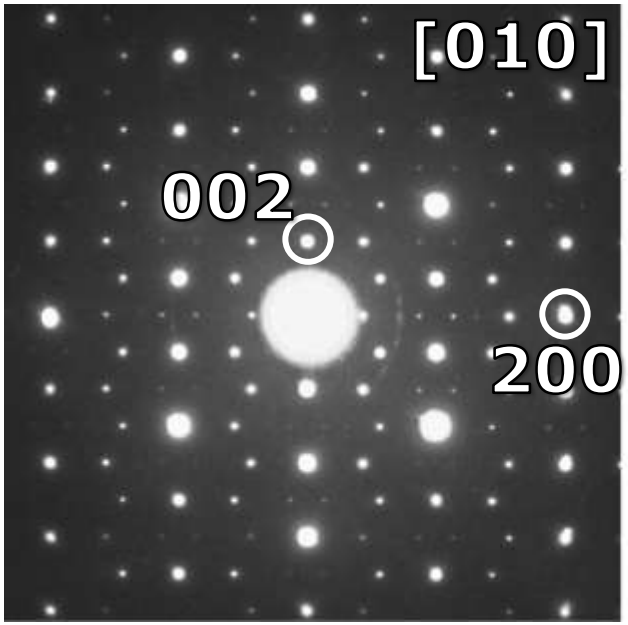
Index the reflection indicated in red

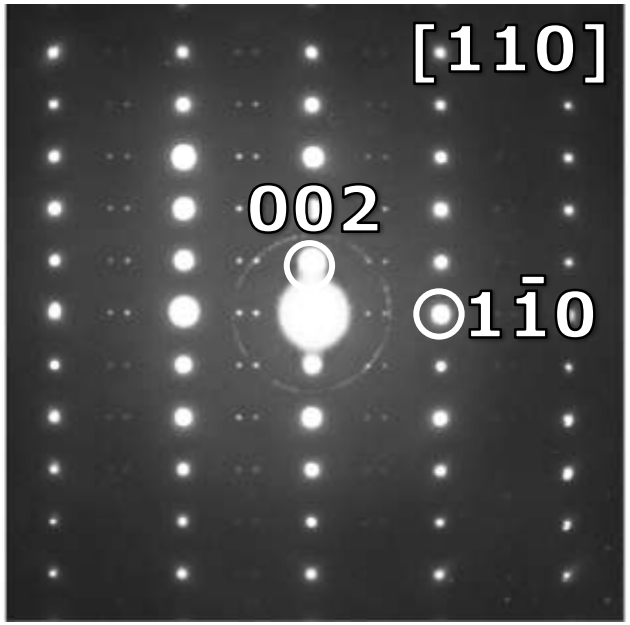


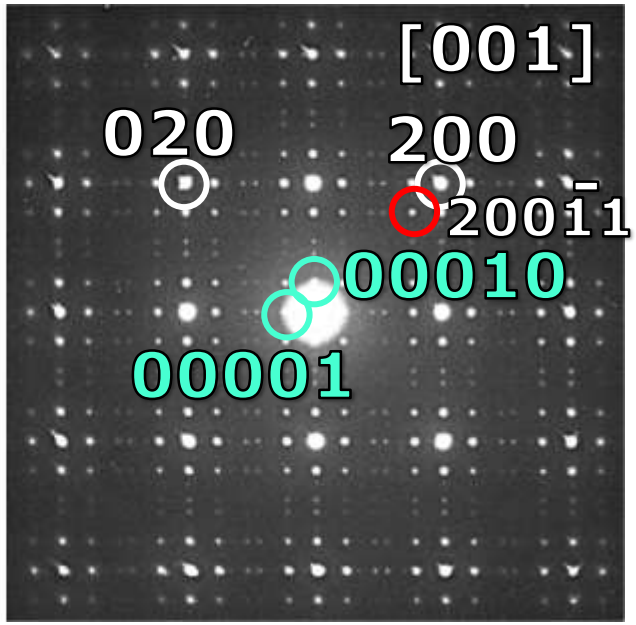
● 200$\bar{1}$1

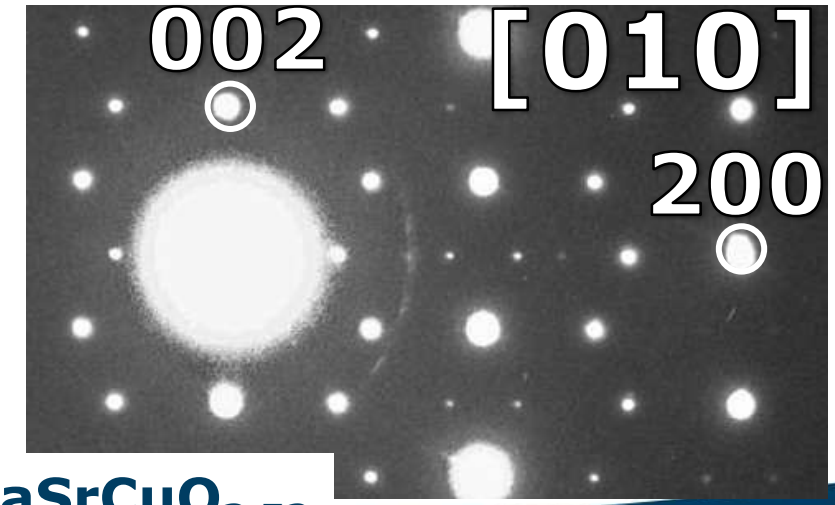
$LaSrCuO_{3.52}$

Index the others patterns consistently with this new choice.

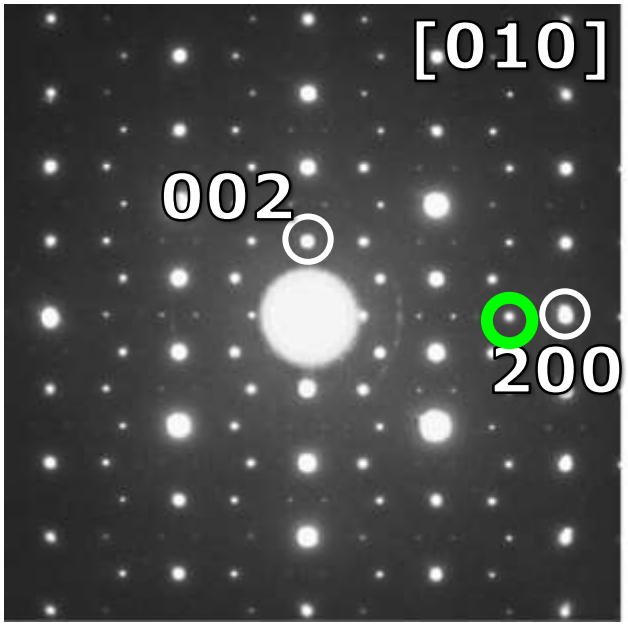


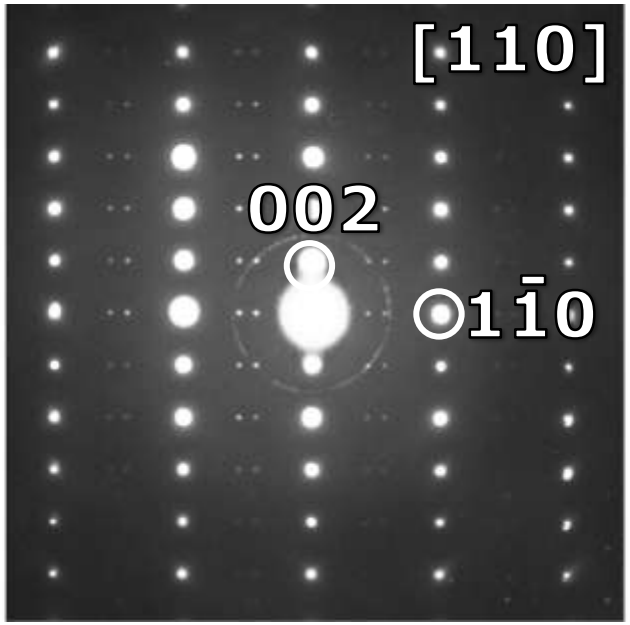


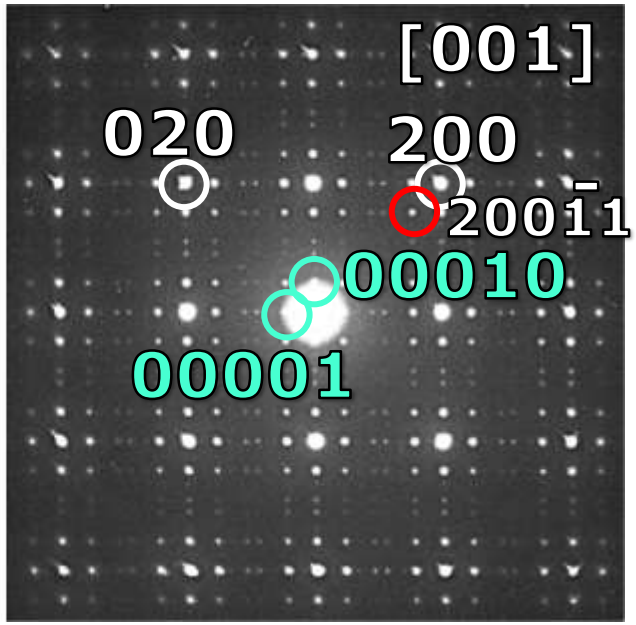


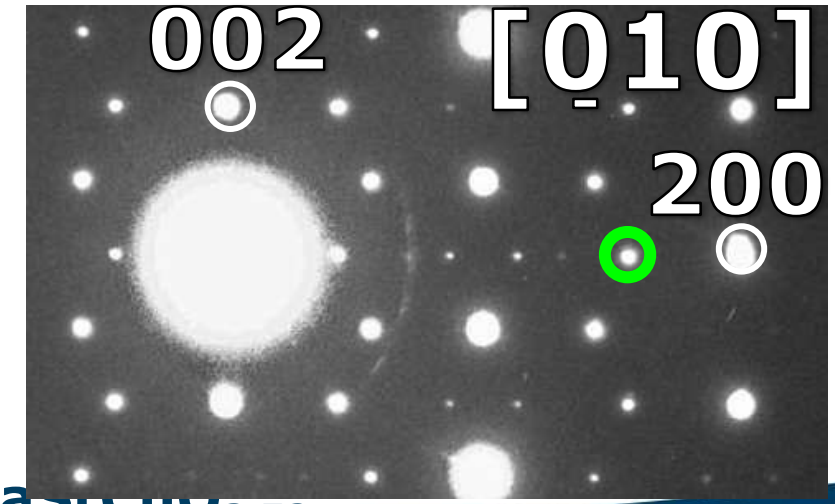


Index the reflection indicated in green







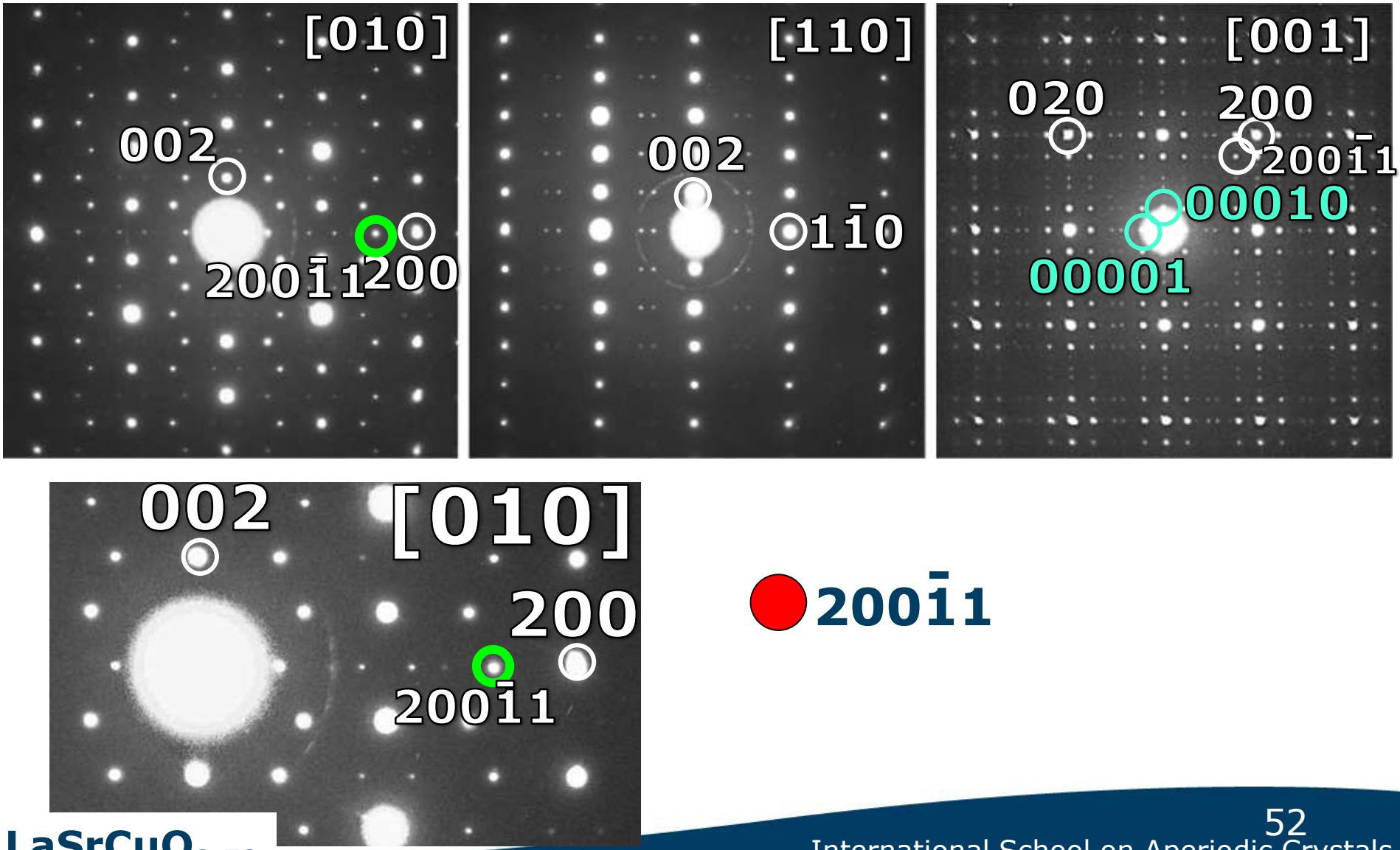


20011

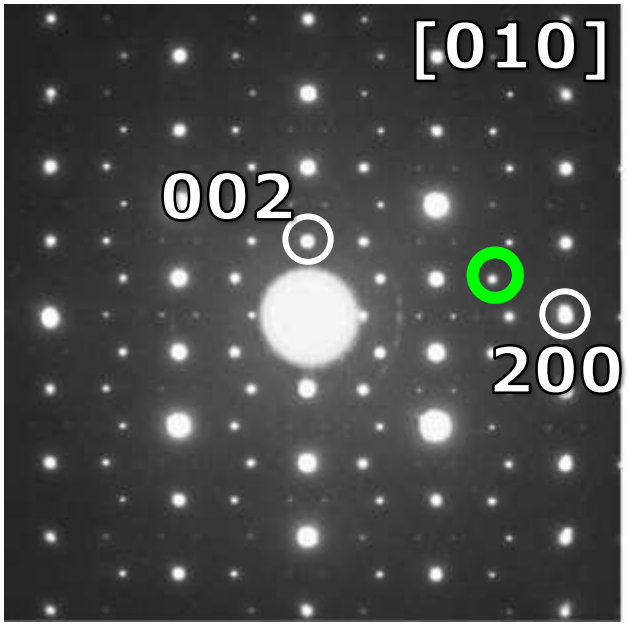
20$\bar{1}$1

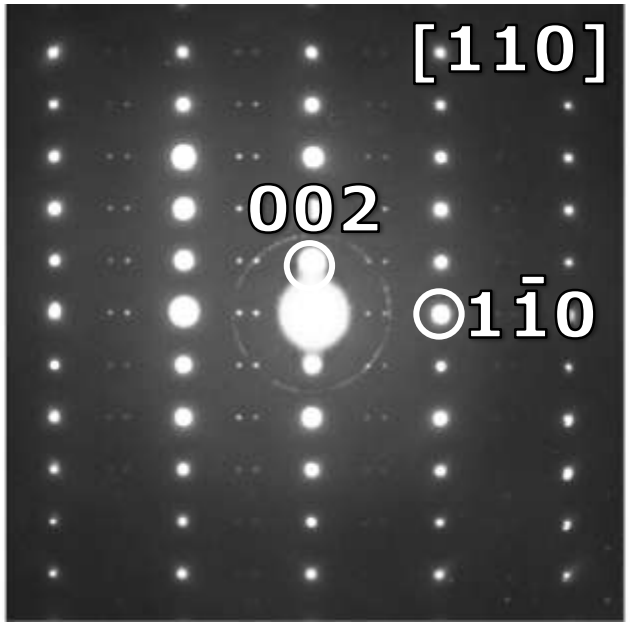
200$\bar{1}$

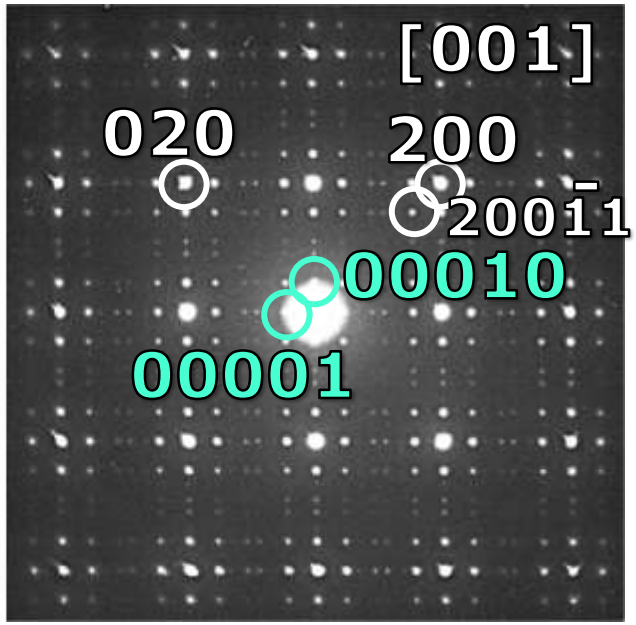
Index the reflection indicated in green

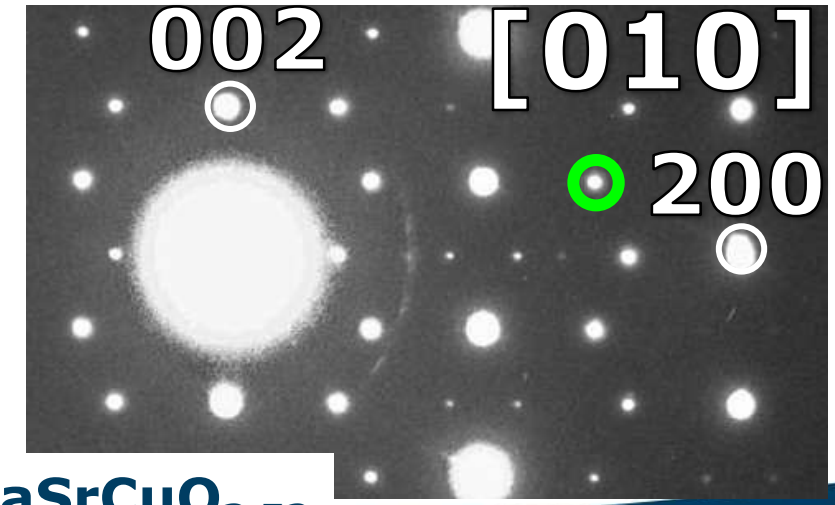


Index the reflection indicated in green







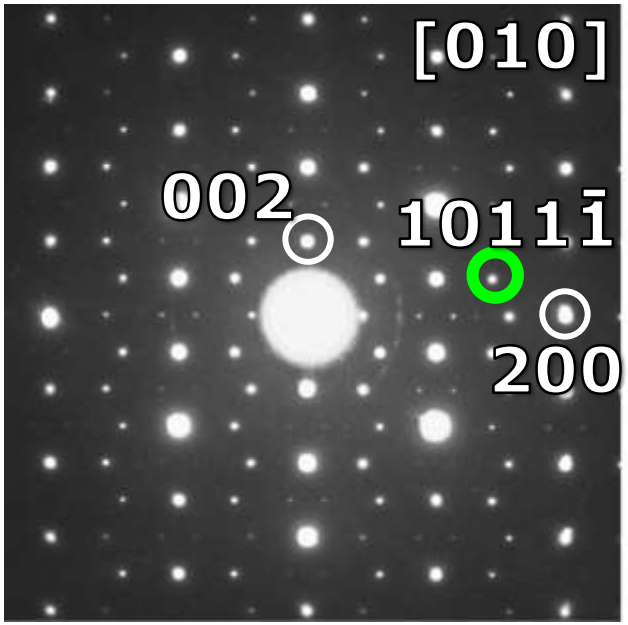


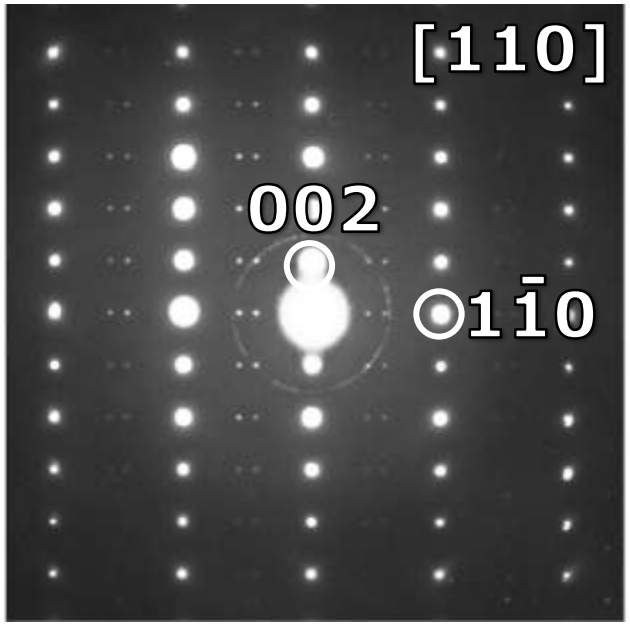
10110

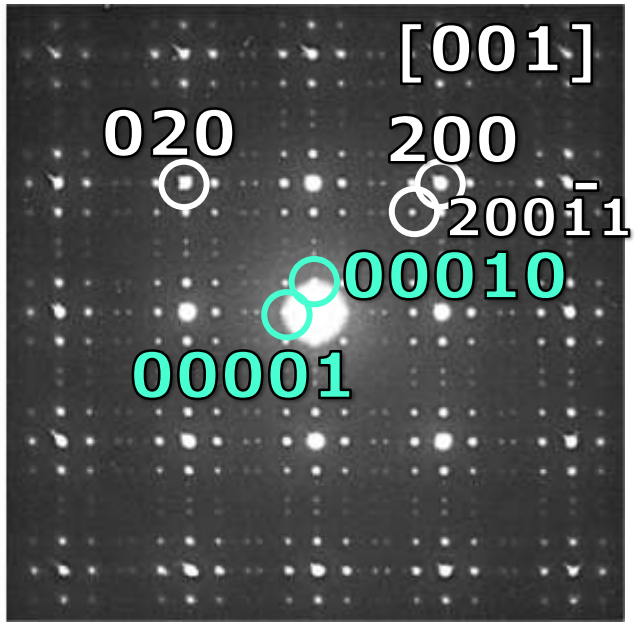
10111

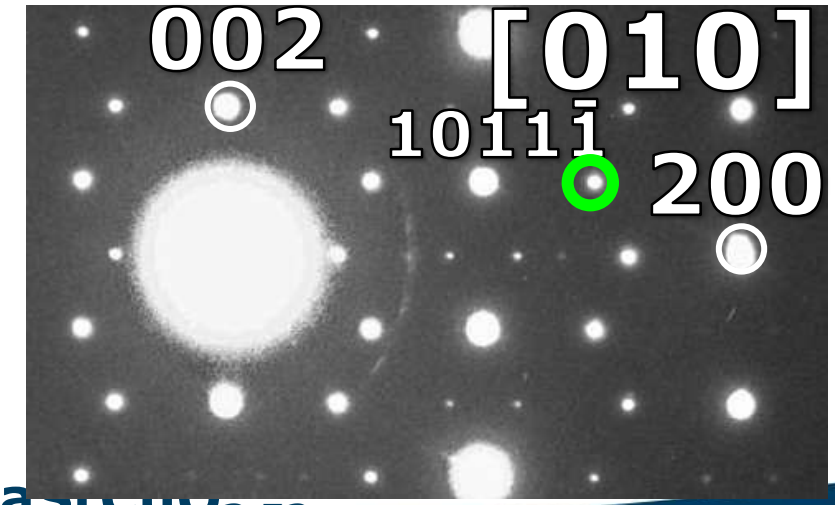
10$\bar{1}$11$\bar{1}$

Index the reflection indicated in green



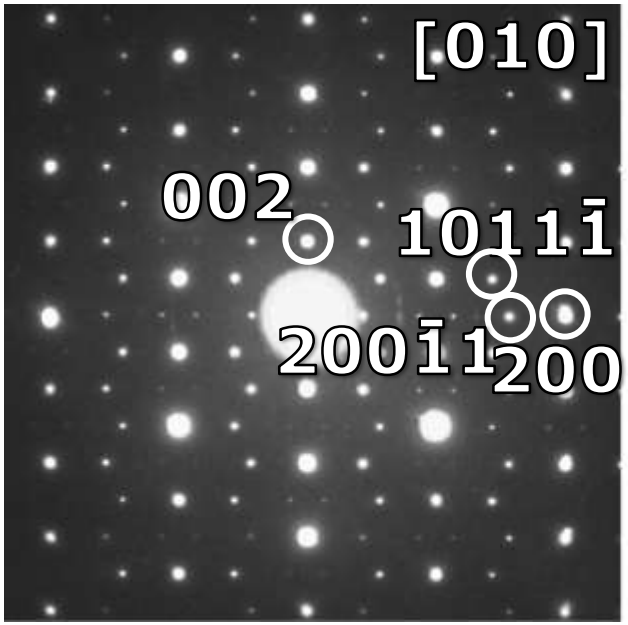


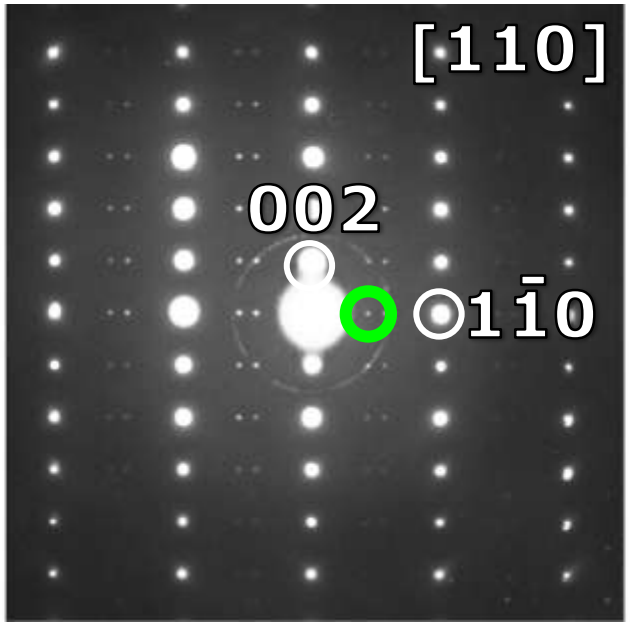


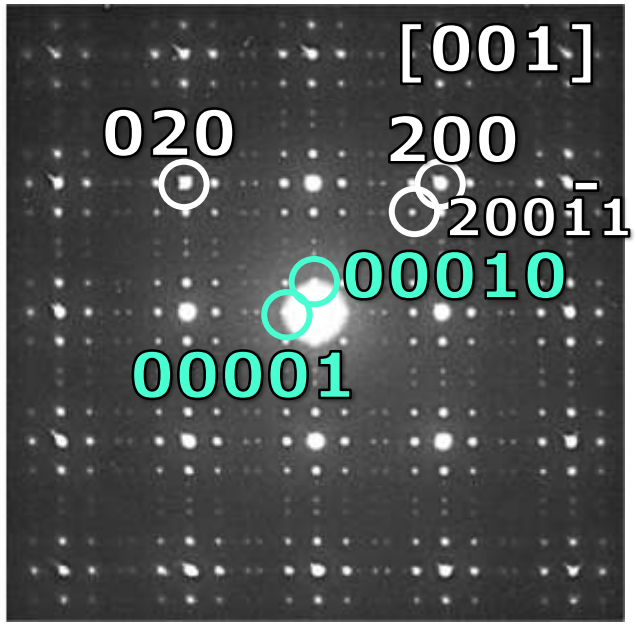


10$\bar{1}$1$\bar{1}$

Index the reflection indicated in green





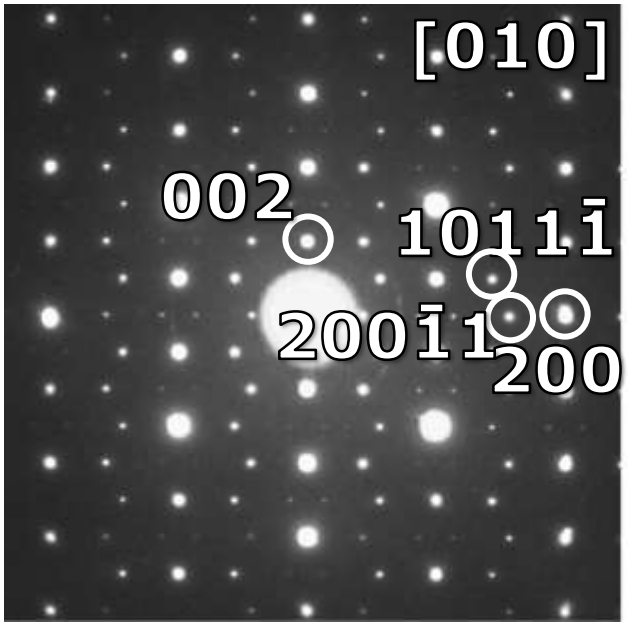


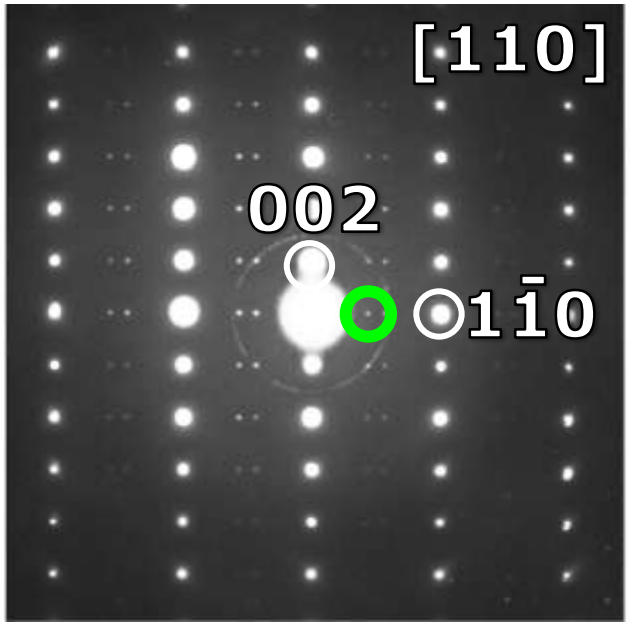
00002

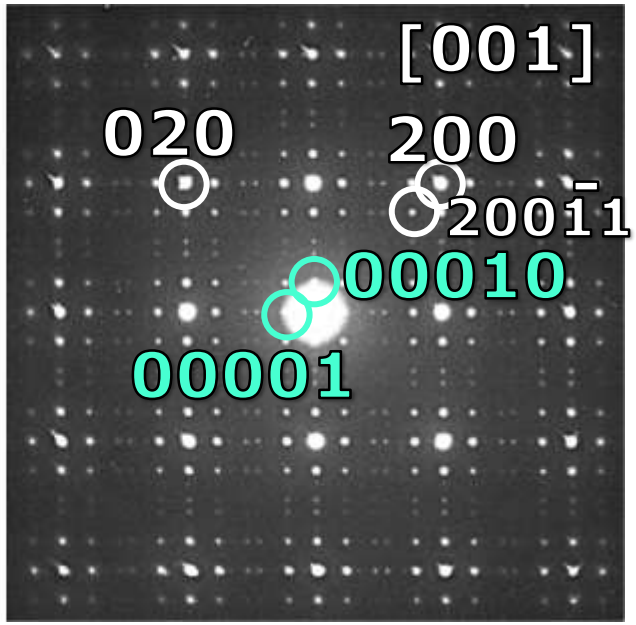
0000$\bar{2}$

0000$\bar{1}$

Index the reflection indicated in green

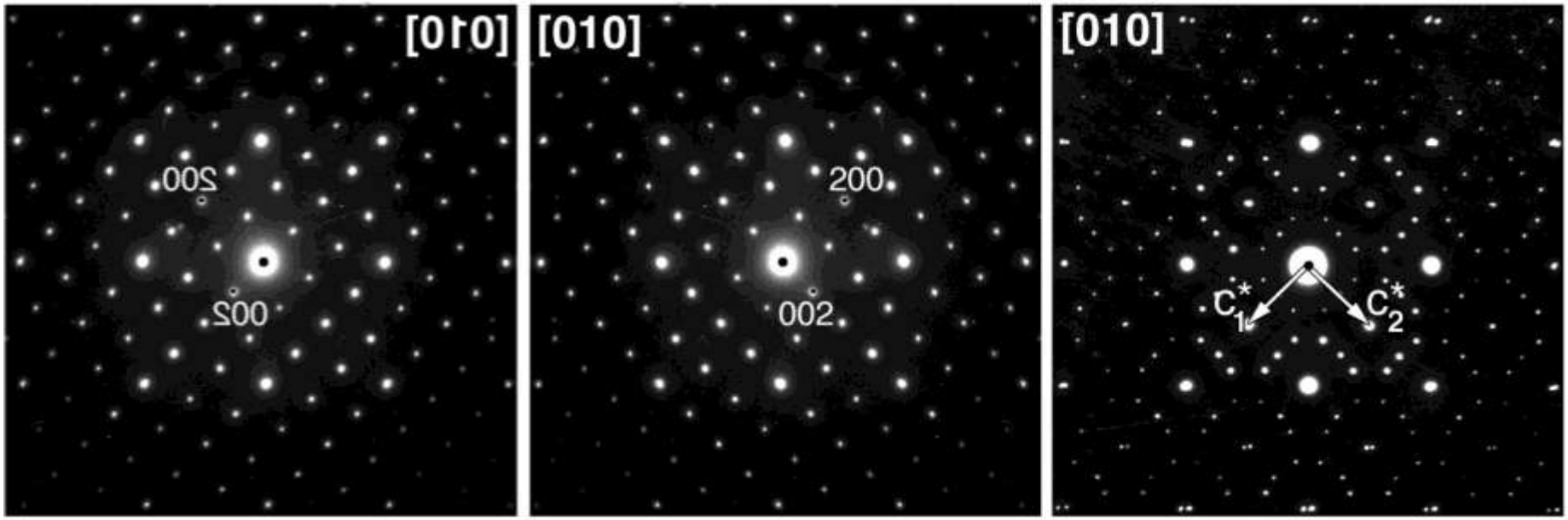






00002̄

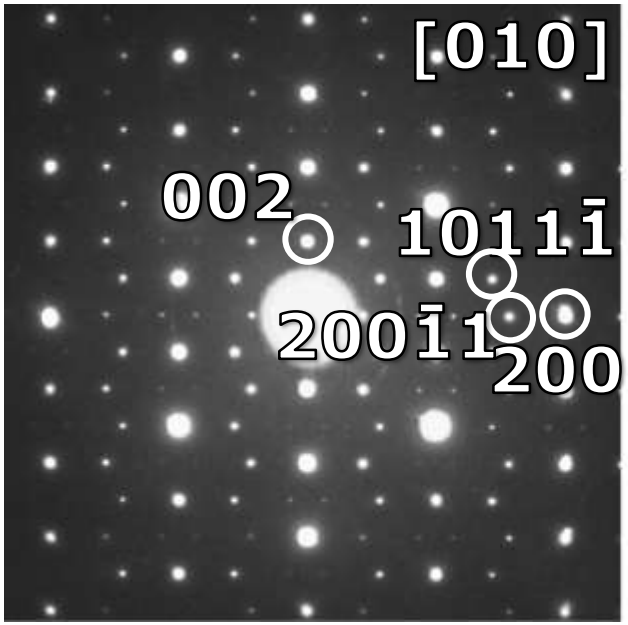
Look out for twinning!

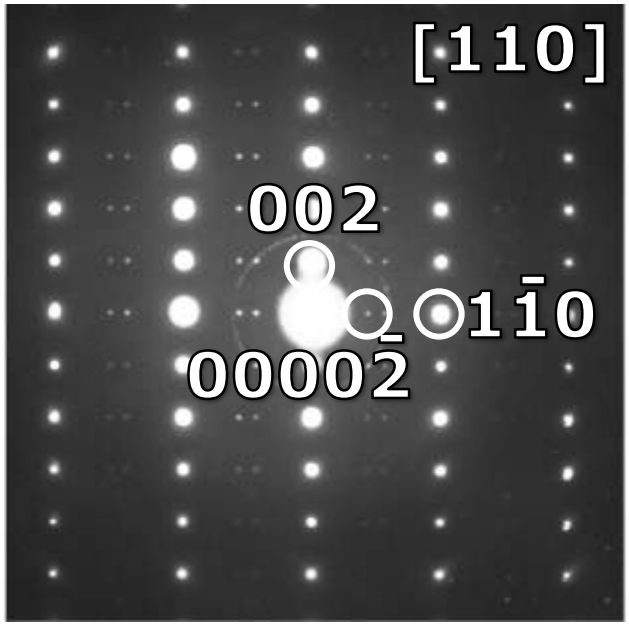


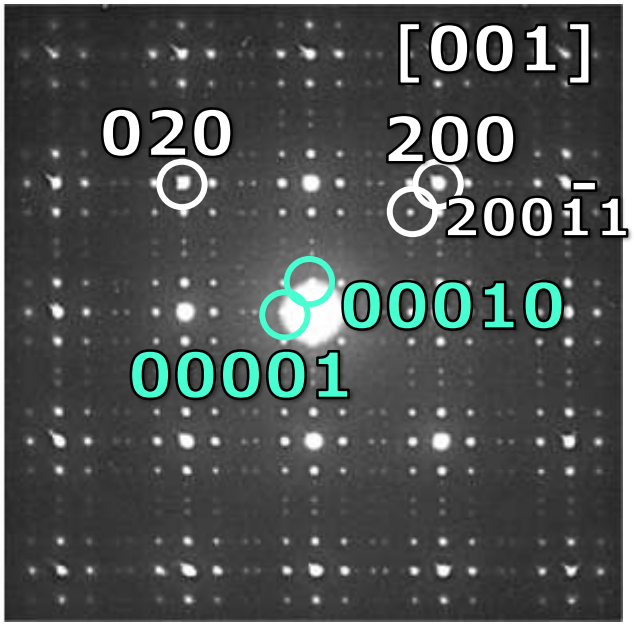
$Y_{0.8}Sr_{2.2}Mn_2GaO_{8-\delta}$

Gillie et al., Journal of Physics and Chemistry of Solids, 65, 1 (2004) 87-93

Exercise 1-5: twinning?



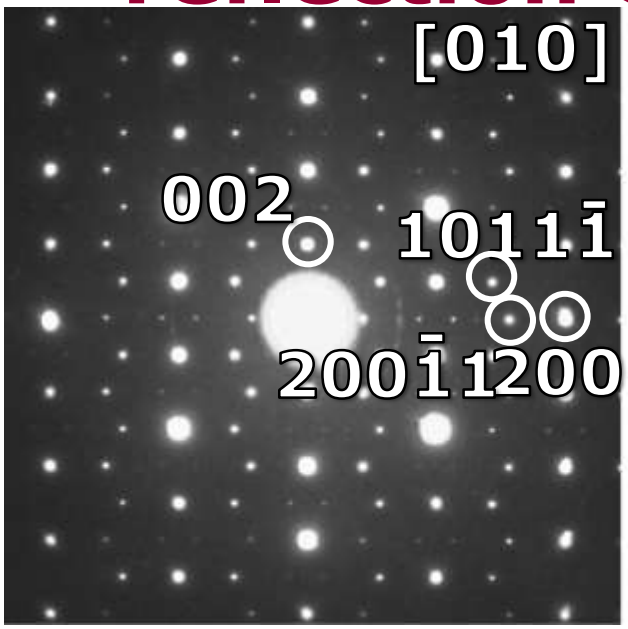


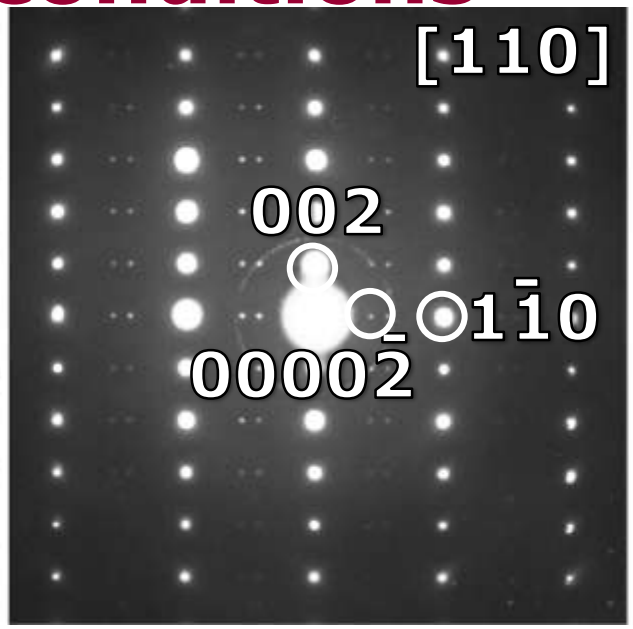


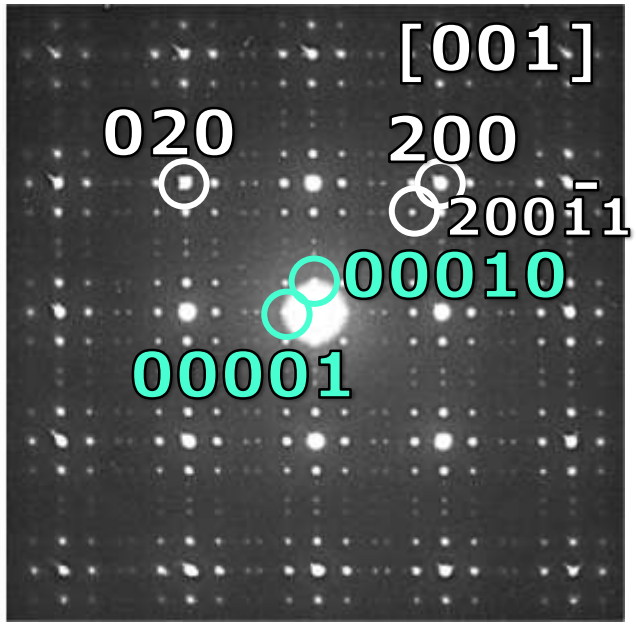
Could it be twinning and thus sufficient to use only one q-vector?

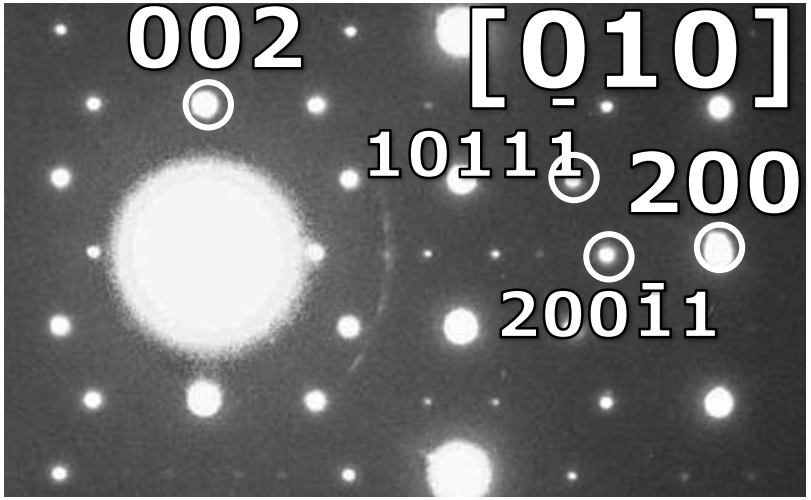
- yes
- no

Exercise 1-6: derive the reflection conditions







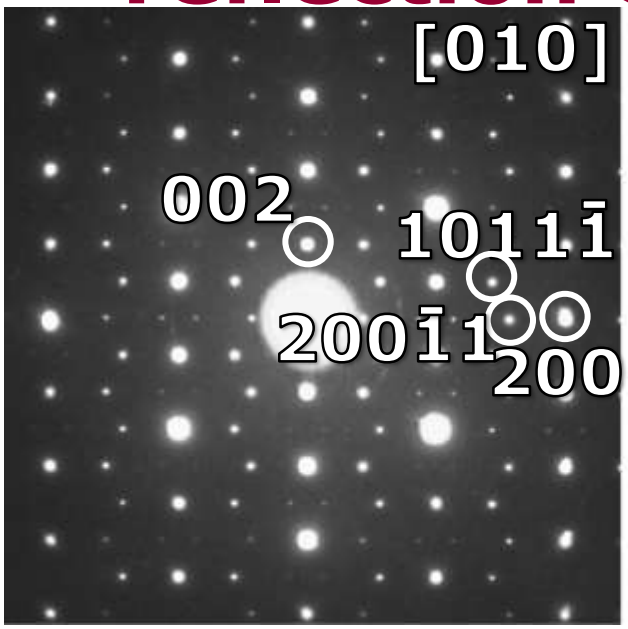


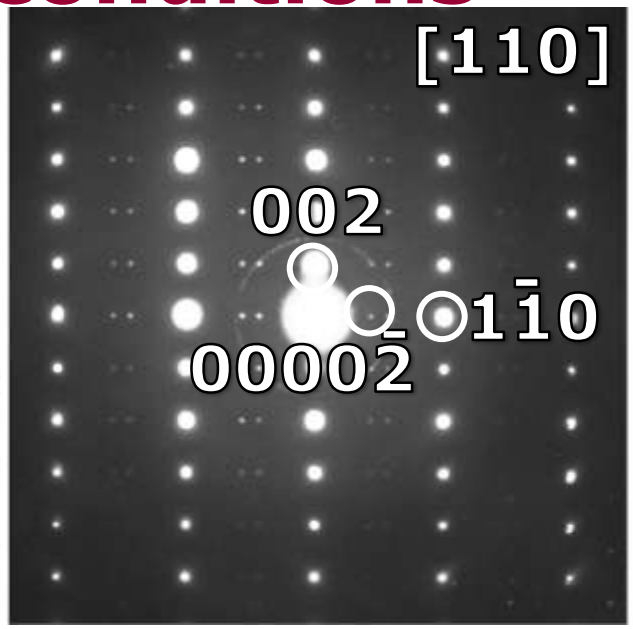
hkl:h+k+l=2n
hhl:l=2n

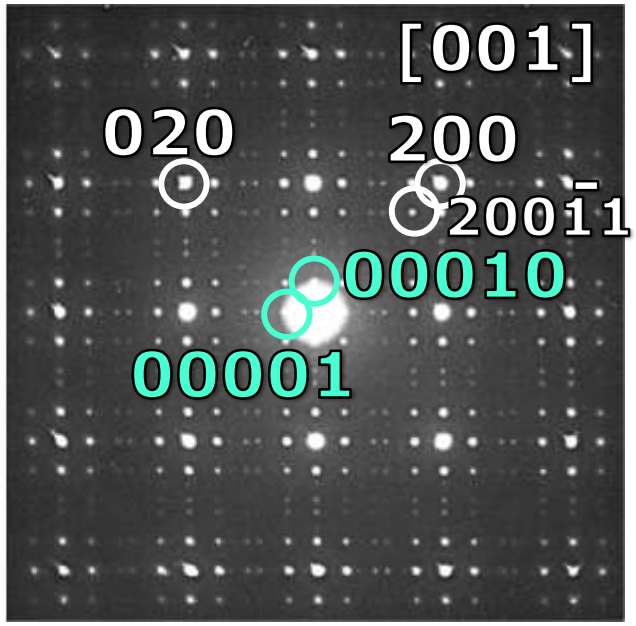
hklmn:

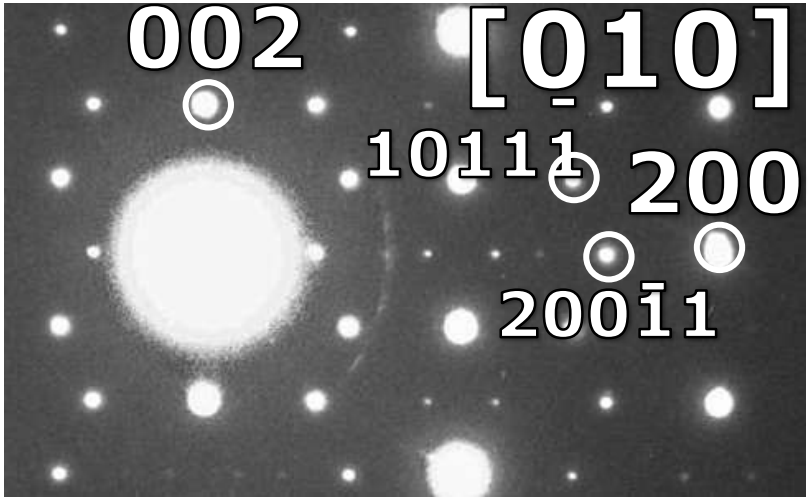
- h+k+l+m+n=2i
- h+k+l=2i
- m+n=2i

Exercise 1-6: derive the reflection conditions







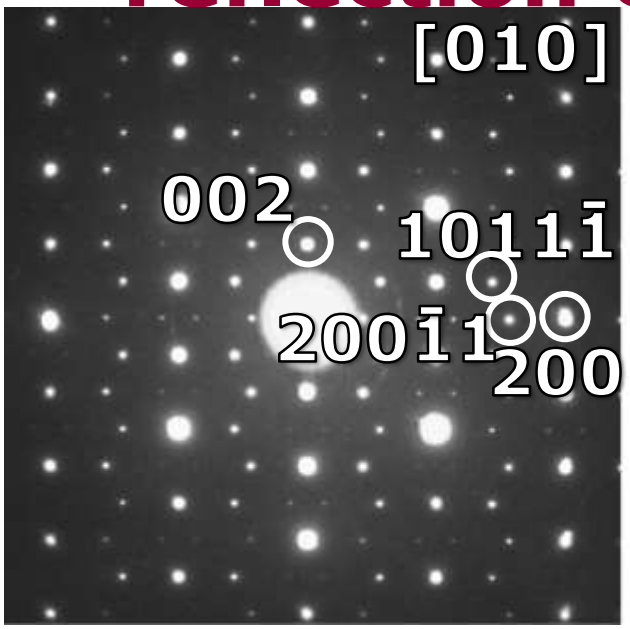


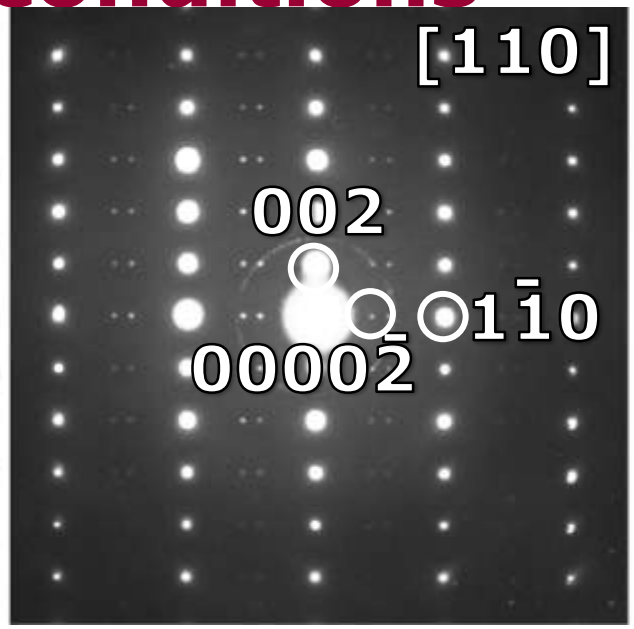
hkl:h+k+l=2n
hhl:l=2n

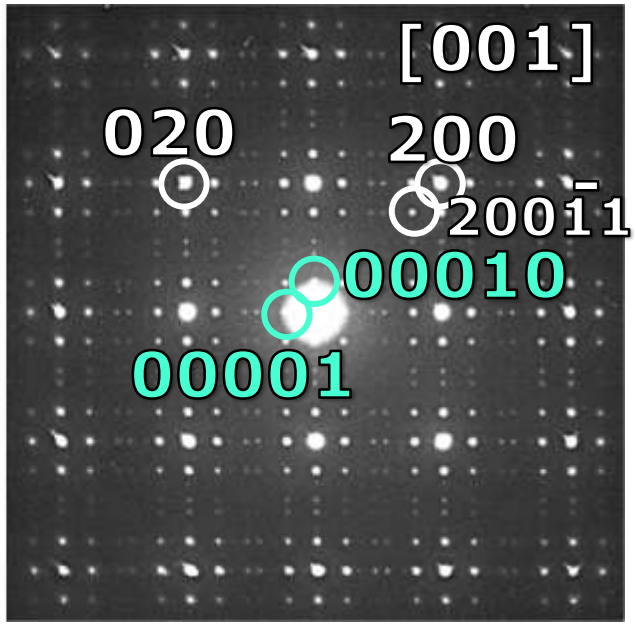
hklmn:

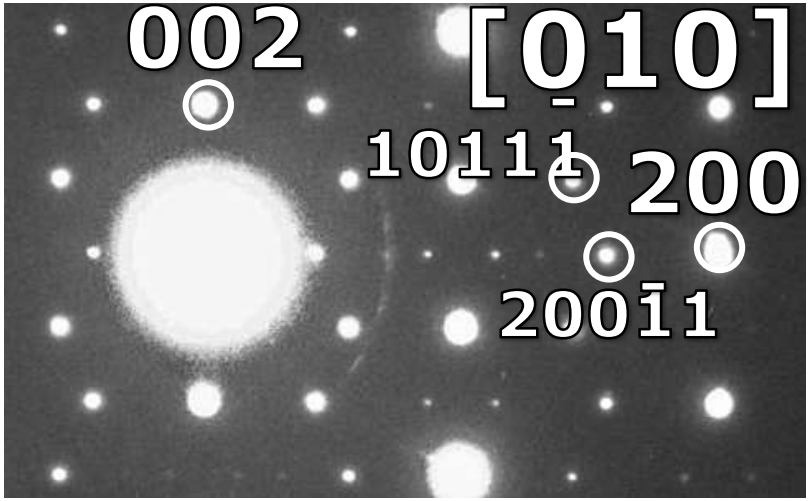
h+k+l=2i

Exercise 1-6: derive the reflection conditions









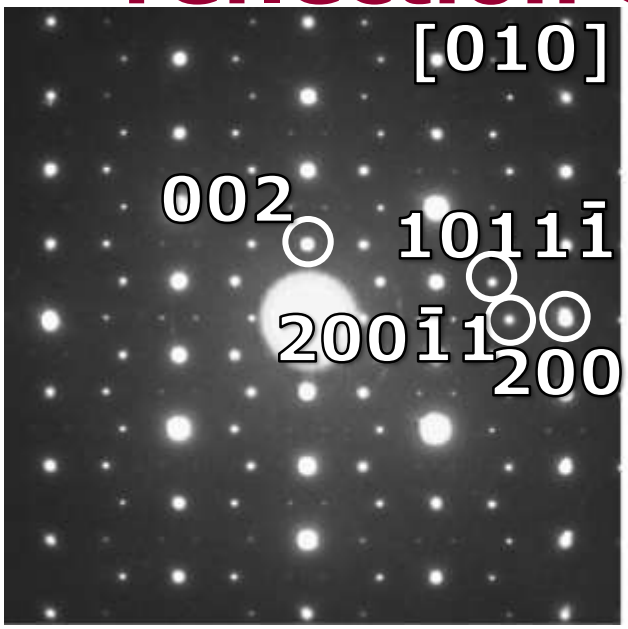
hkl:h+k+l=2n

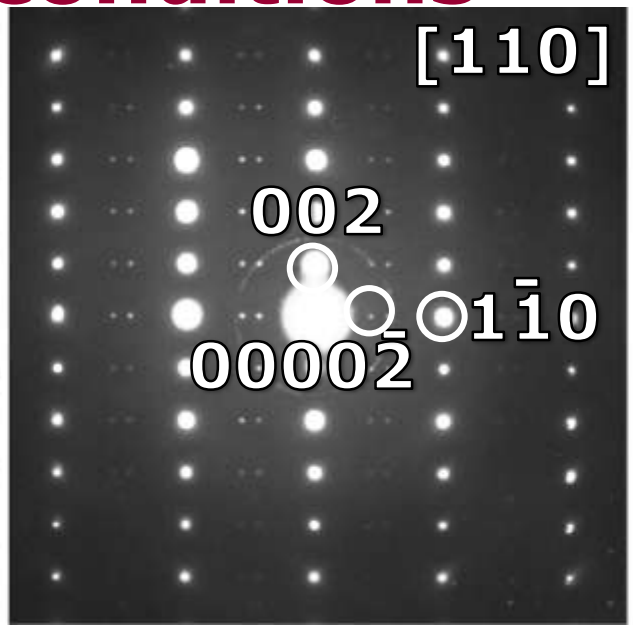
hhl:l=2n

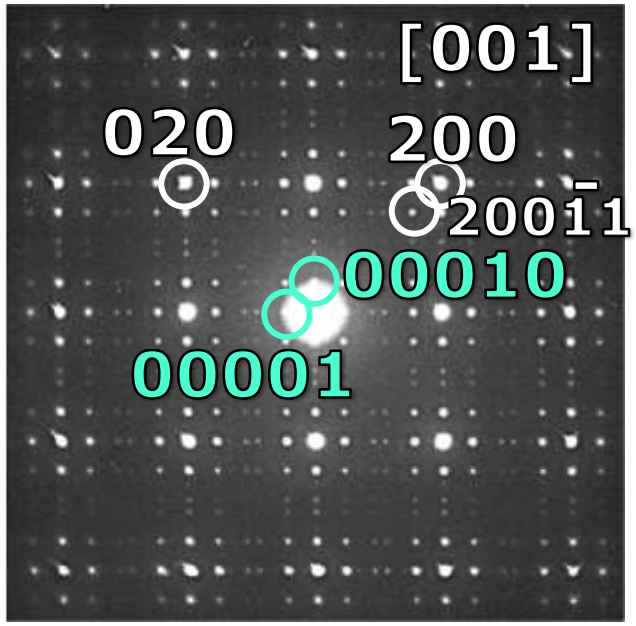
hhlm0:

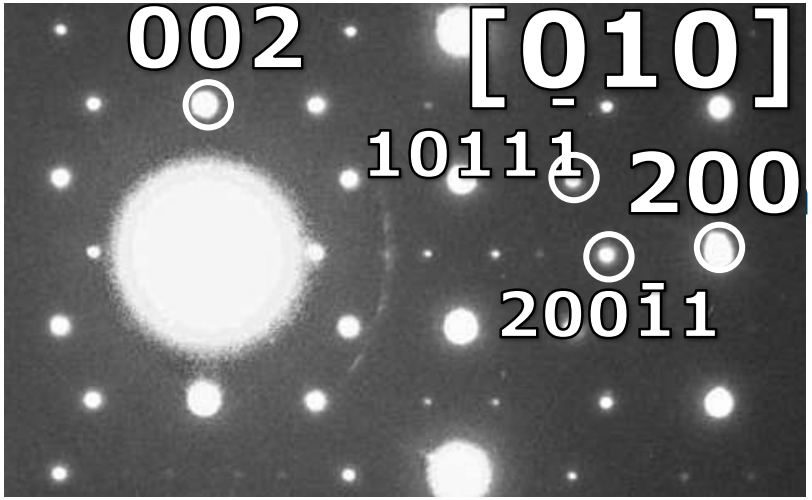
- l=2i
- h=2i
- l,m=2i

Exercise 1-6: derive the reflection conditions









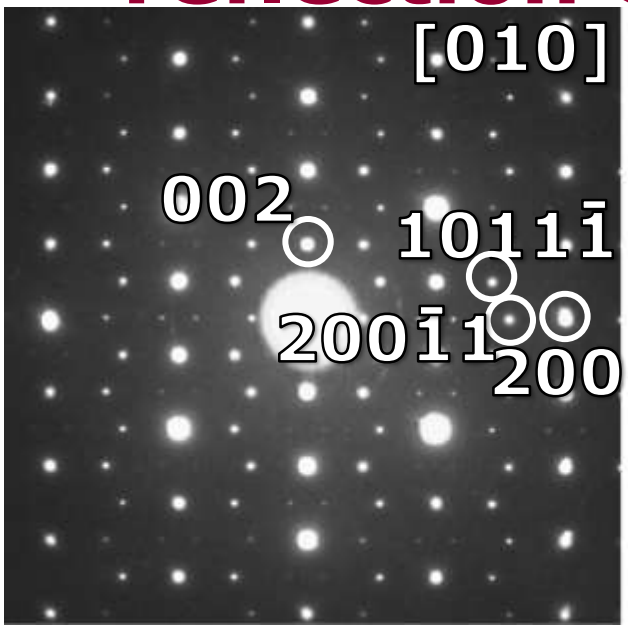
hkl:h+k+l=2n
hhl:l=2n

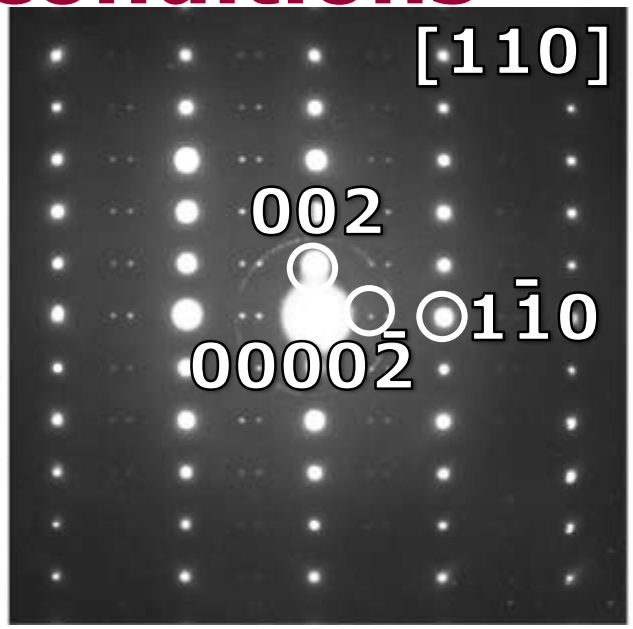
hlm0:

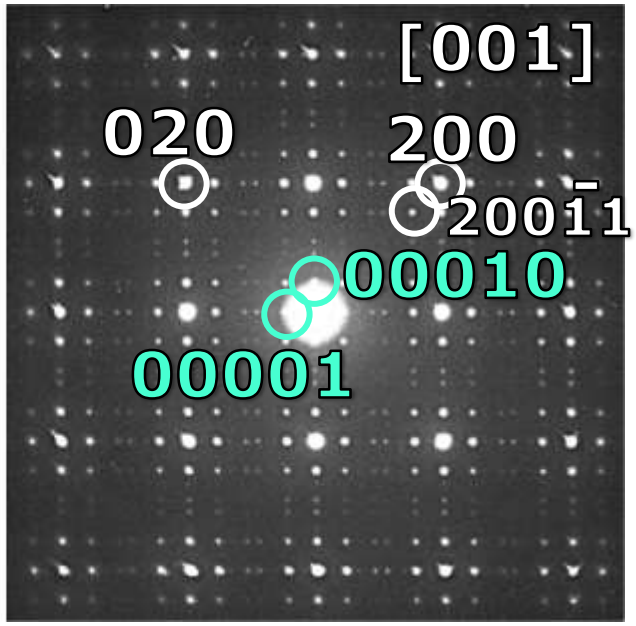
l,m=2i

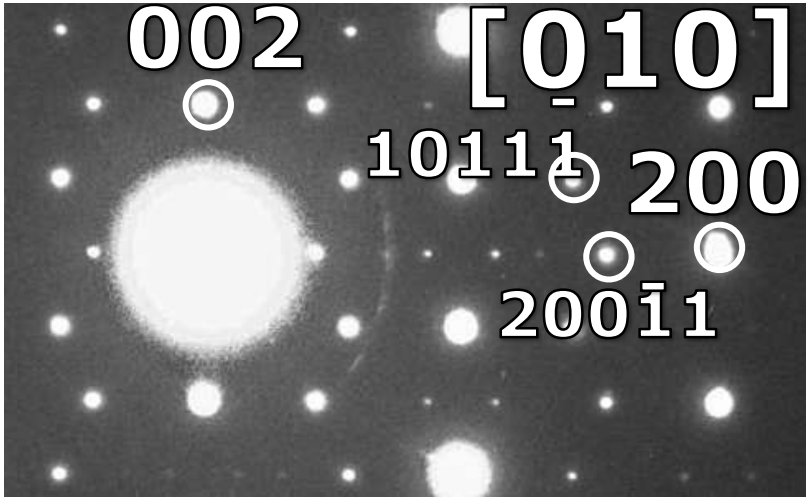
but hhlm0:m=2i is sufficient

Exercise 1-6: derive the reflection conditions





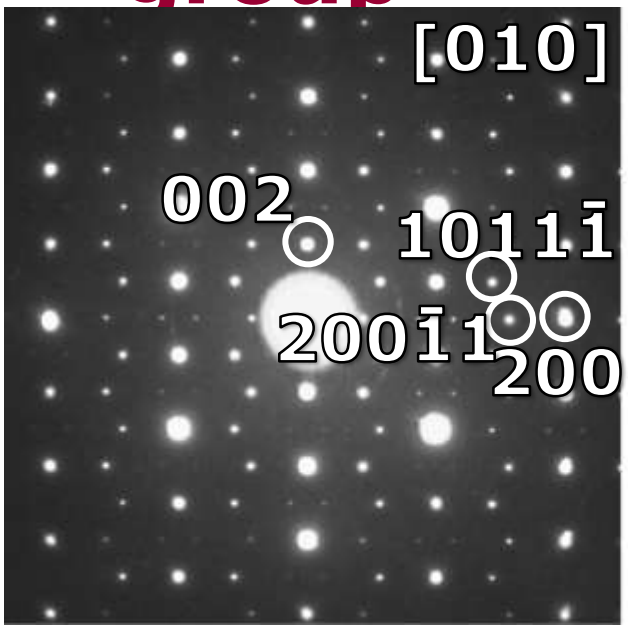


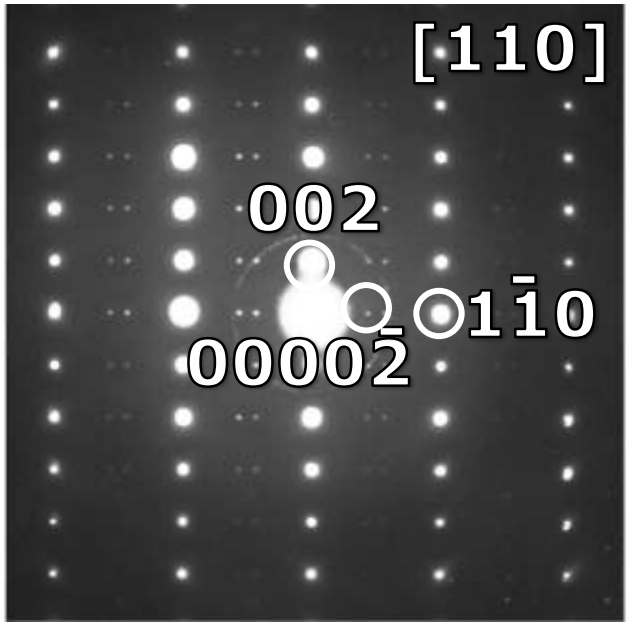


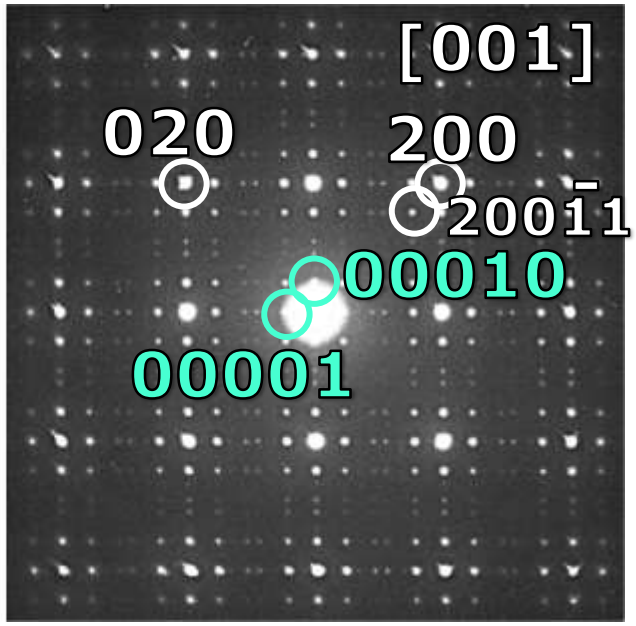
$$\left\{\begin{array}{c} \mathbf{hkl{:}h+k+l=2n} \\ \mathbf{hhl{:}l=2n} \end{array}\right\}$$

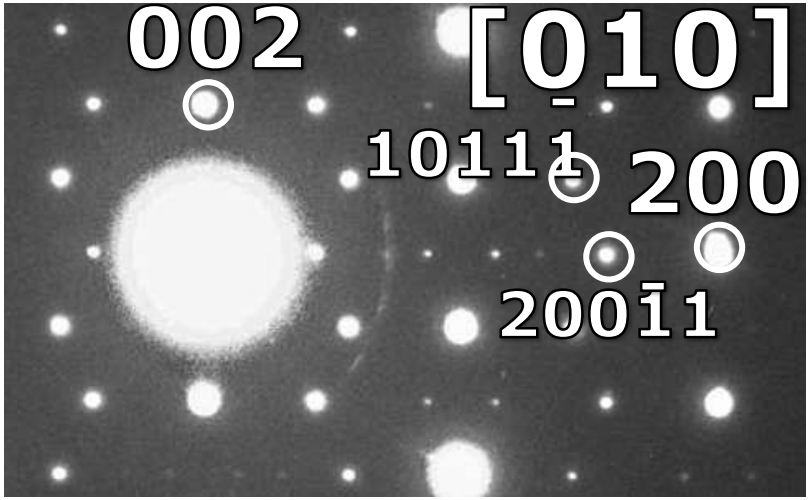
- hklmn:h+k+l=2i
- hhlm0:m=2i
  (-hhl0n: n=2i)

Determining the superspace group









- Online tables Yamamoto (Acta Cryst.A 1996, A52, 509)
- I4/mmm(α α0, -αα0)00mg

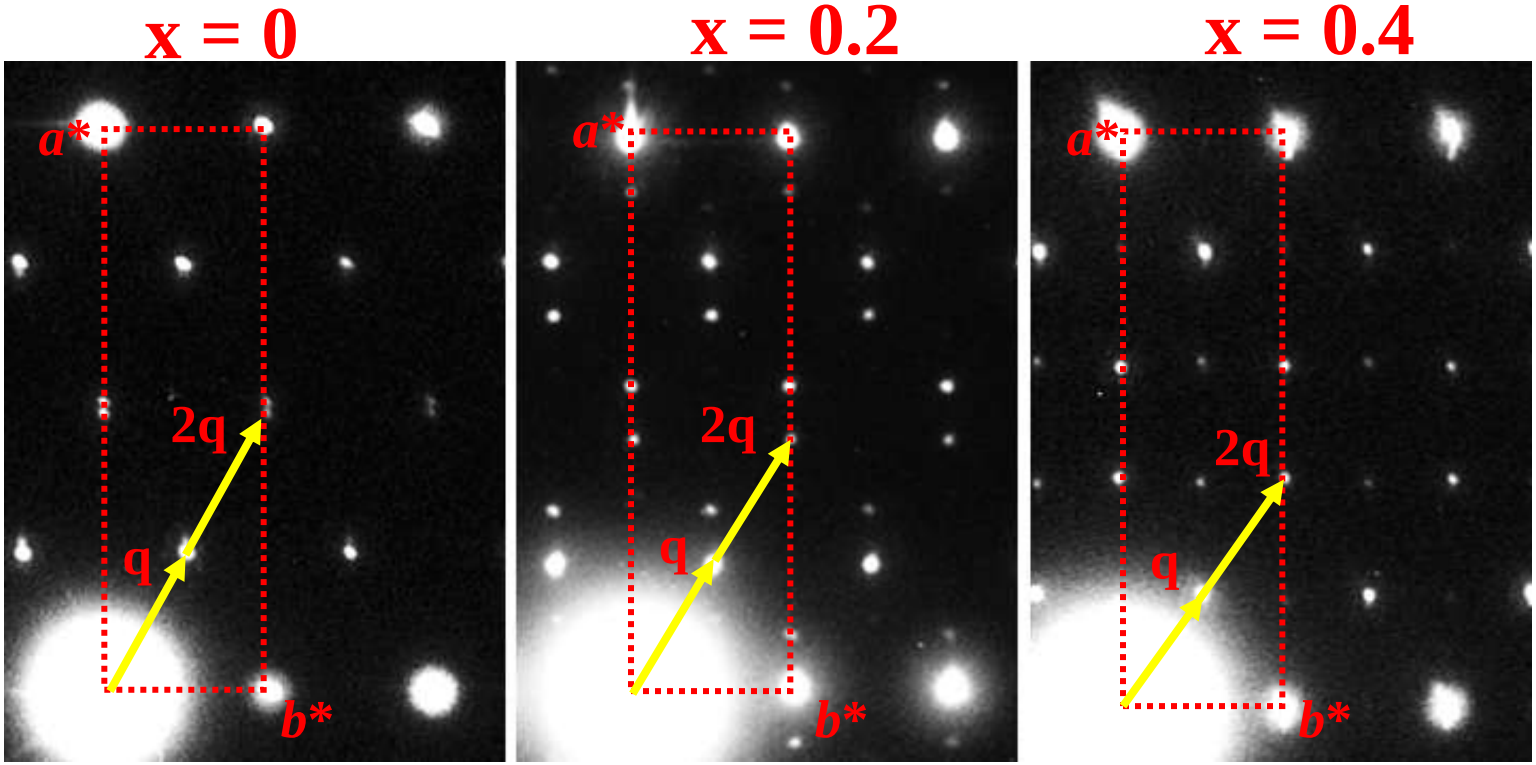
Use of doing ED

- Deriving approximate cell parameters, modulation vector and superspace group
- Not useful for: precise parameters, precise modulation vector
- Excellent if multiphase sample or satellites very weak in XRD/ND

- Be aware of:
  - Twinning
  - Multiple diffraction (for forbidden refls., for using intensities,…)
  - The possibility of missing important sections of reciprocal space

Relation composition – modulation vector

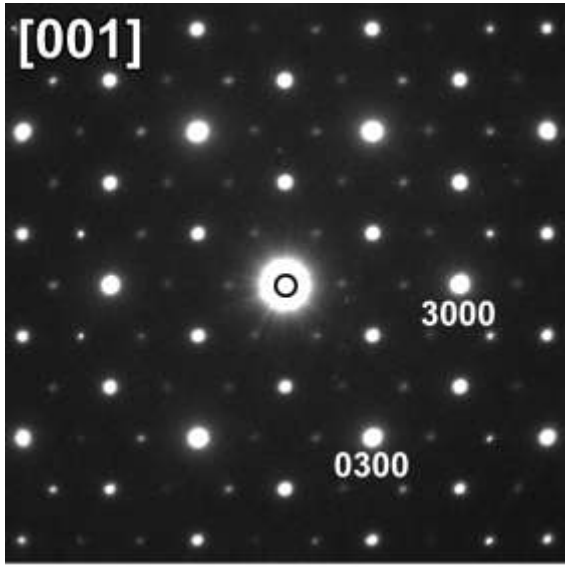
- Most TEM have EDX available for composition determination
- Determination of direct links between composition and modulation vector, also in multiphased samples

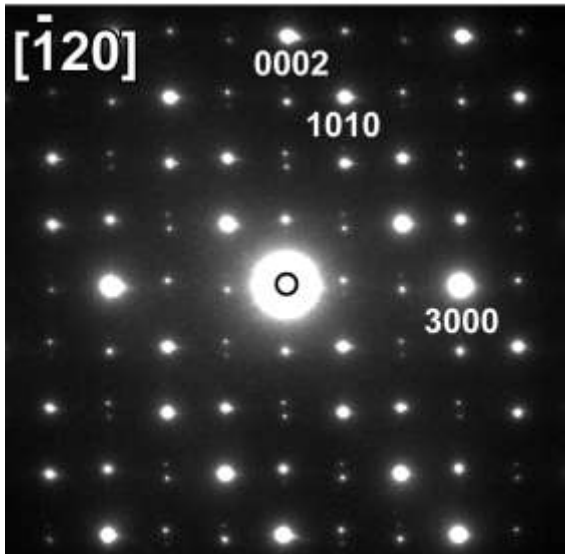


$Ba_4In_{6-x}Mg_xO_{13-x/2}$

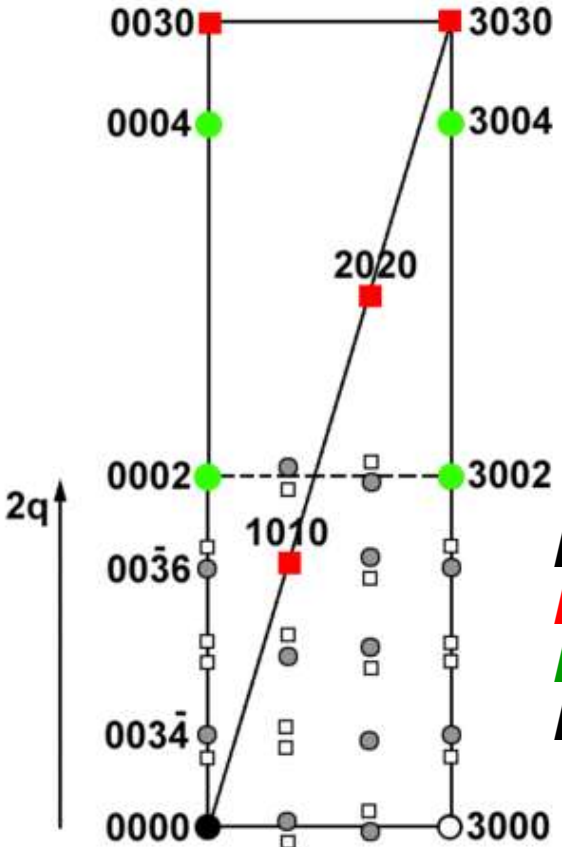
(Abakumov et al., Chem. Mater. 20 (13), pp. 4457-4467)

ED of a composite structure (CS)





$a_1 = a_2$, $b_1 = b_2$, $c_1 \neq c_2$, $q = \gamma c_1^* = c_2^*$



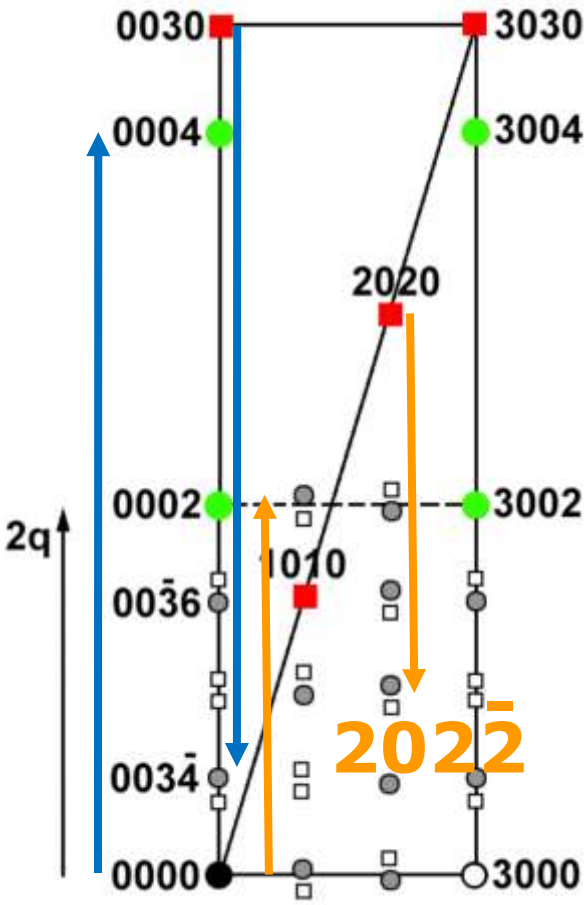
***hk*00 average cell**
***hkl*0 first subsystem**
***hk*0*m* second subsystem**
***hklm* satellites**

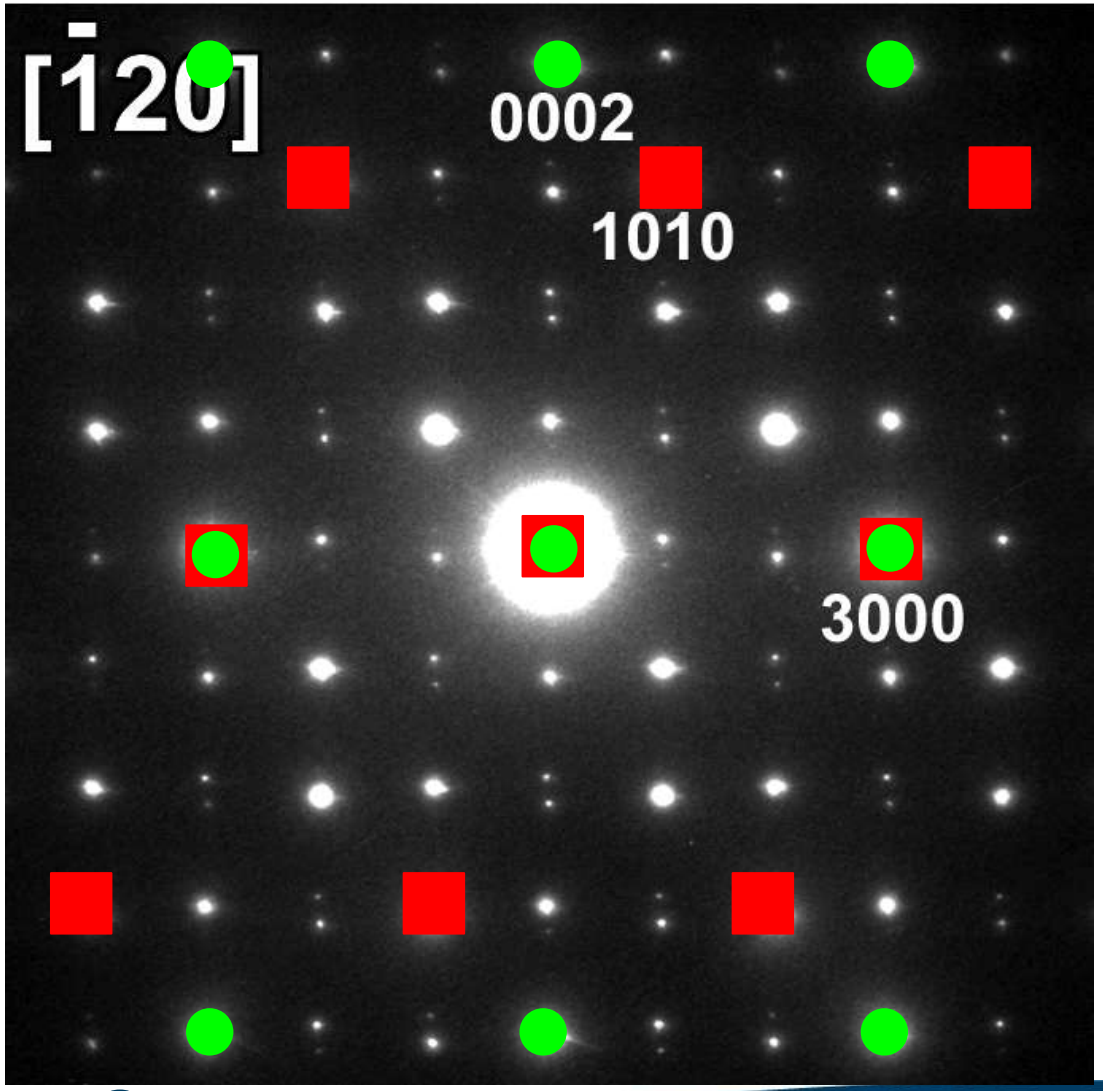
$A_{1+x}A'_xB_{1-x}O_3$

first subsystem $[(B, A')O_3]_\infty$
second subsystem $[A]_\infty$

$Sr_{1.3}Co_{0.8}Mn_{0.2}O_3$ Mandal et al., Chem. Mater., 19, 25 (2007) 6158

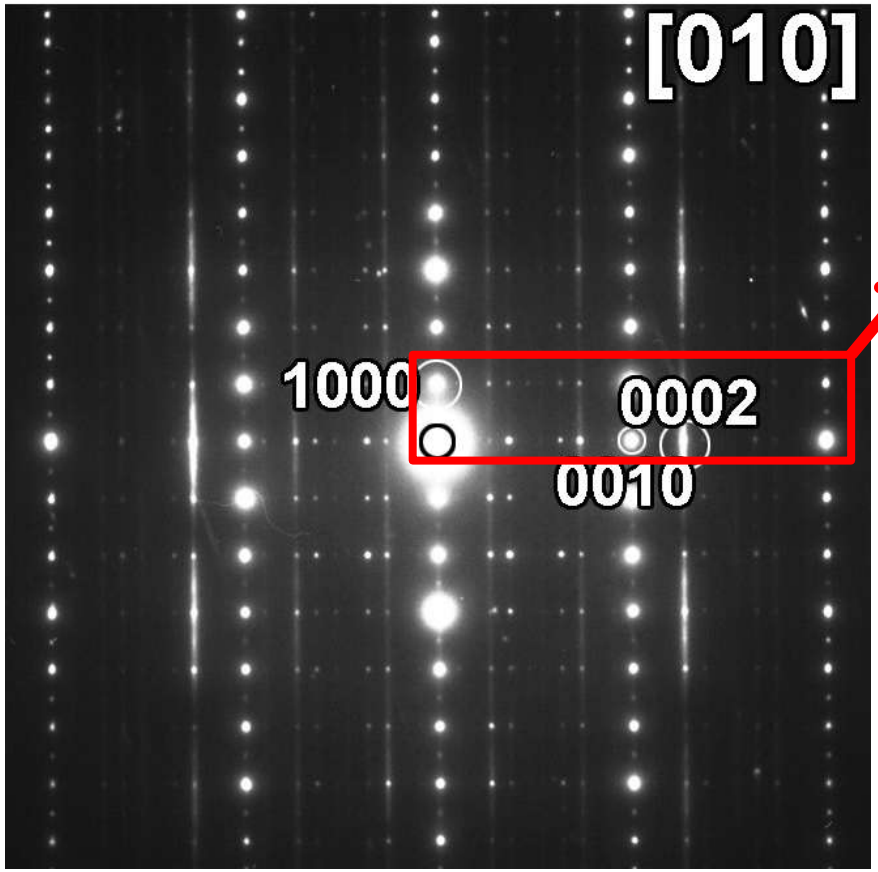
ED of a composite structure (CS)

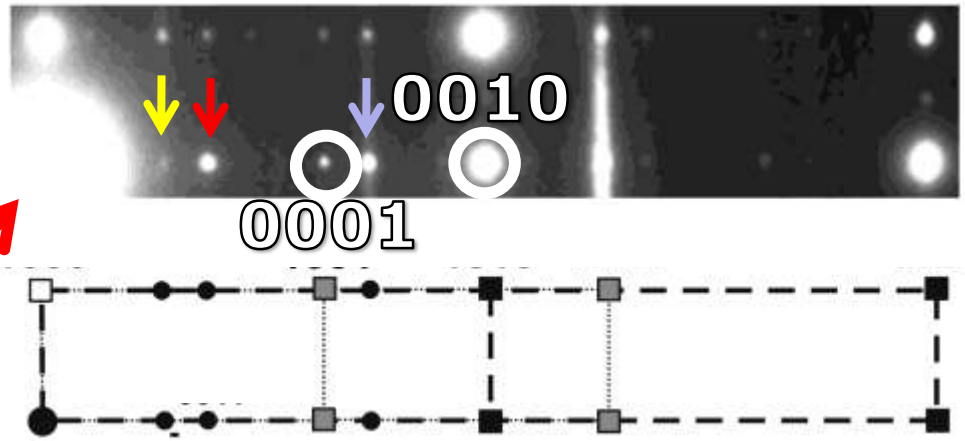




$Sr_{1.3}Co_{0.8}Mn_{0.2}O_3$

Exercise 2: composite structure: index the pattern



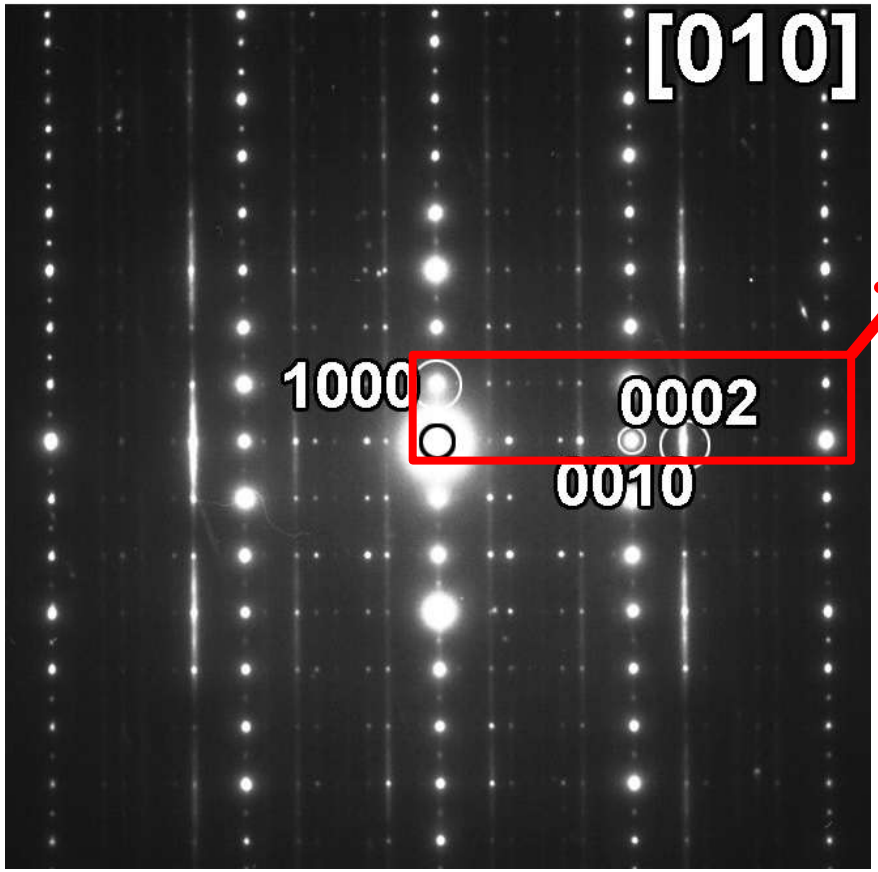


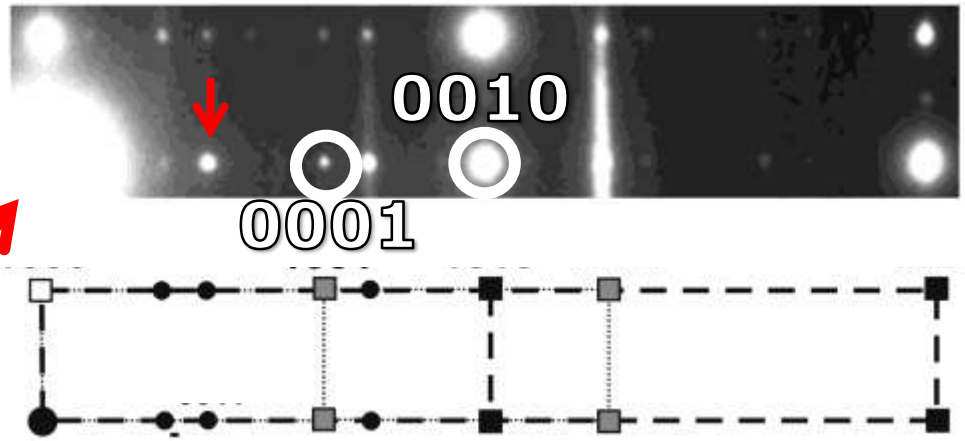
Which reflection is $00\bar{1}1$?

$[SrF_{0.82}(OH)_{0.18}]_{2.5}[Mn_6O_{12}]$

Abakumov et al., Chem.Mater. 19, 5 (2007) 1181-1189

Exercise 2: composite structure: index the pattern

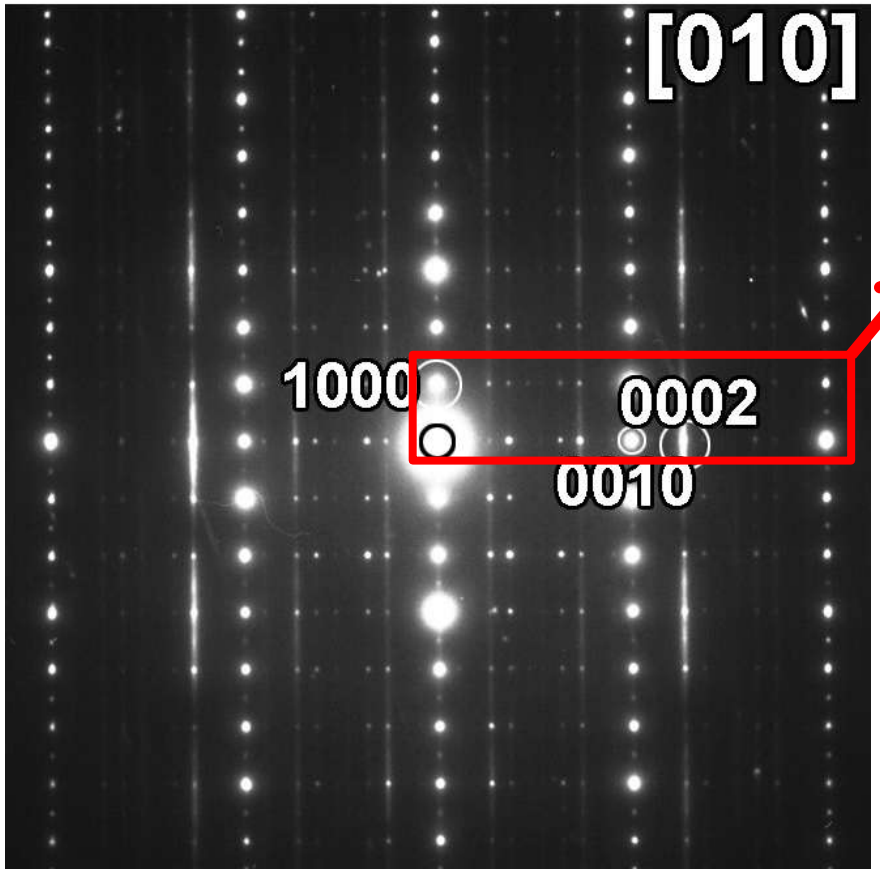


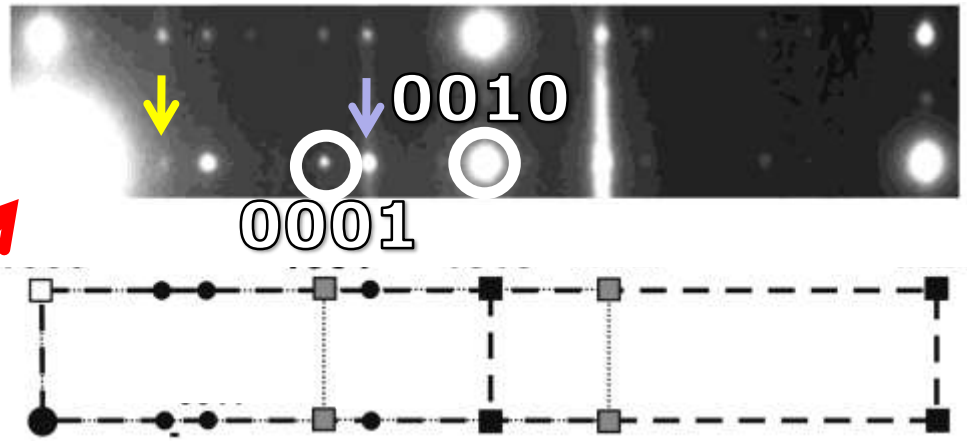


Which reflection is $00\bar{1}1$?

$$[SrF_{0.82}(OH)_{0.18}]_{2.5}[Mn_6O_{12}]$$

Exercise 2: composite structure: index the pattern

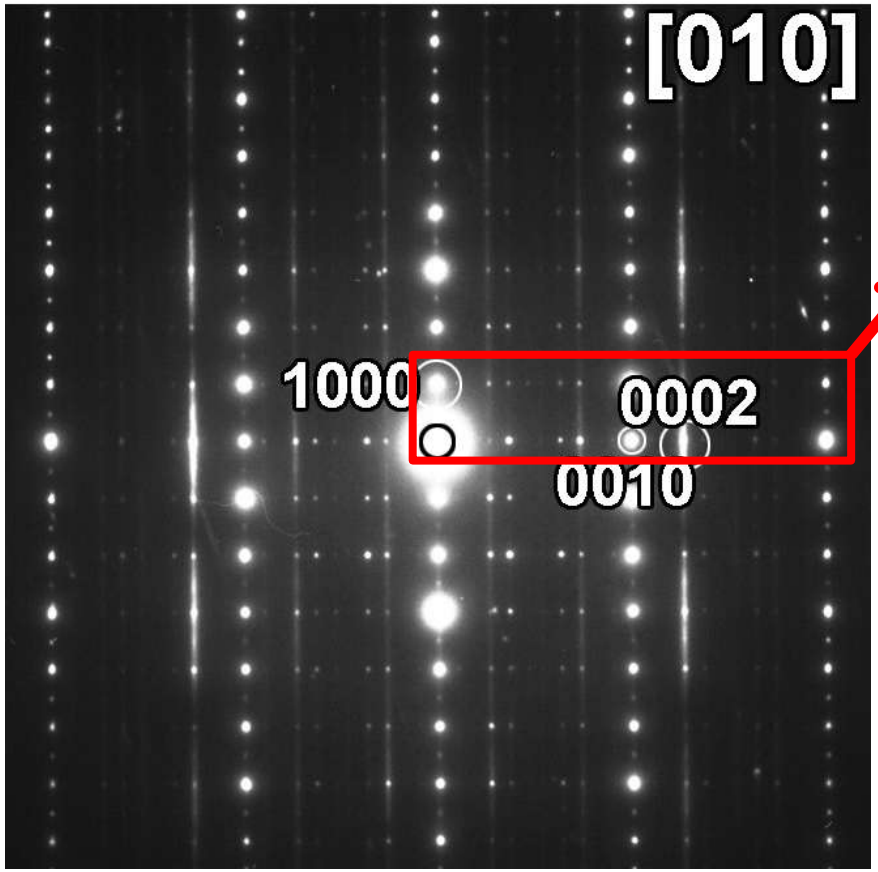


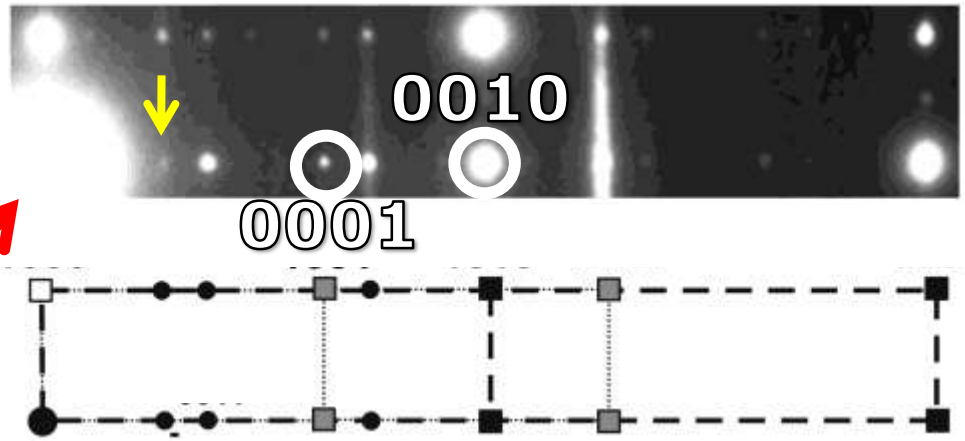


Which reflection is $00\bar{1}2$?

$$[SrF_{0.82}(OH)_{0.18}]_{2.5}[Mn_6O_{12}]$$

Exercise 2: composite structure: index the pattern

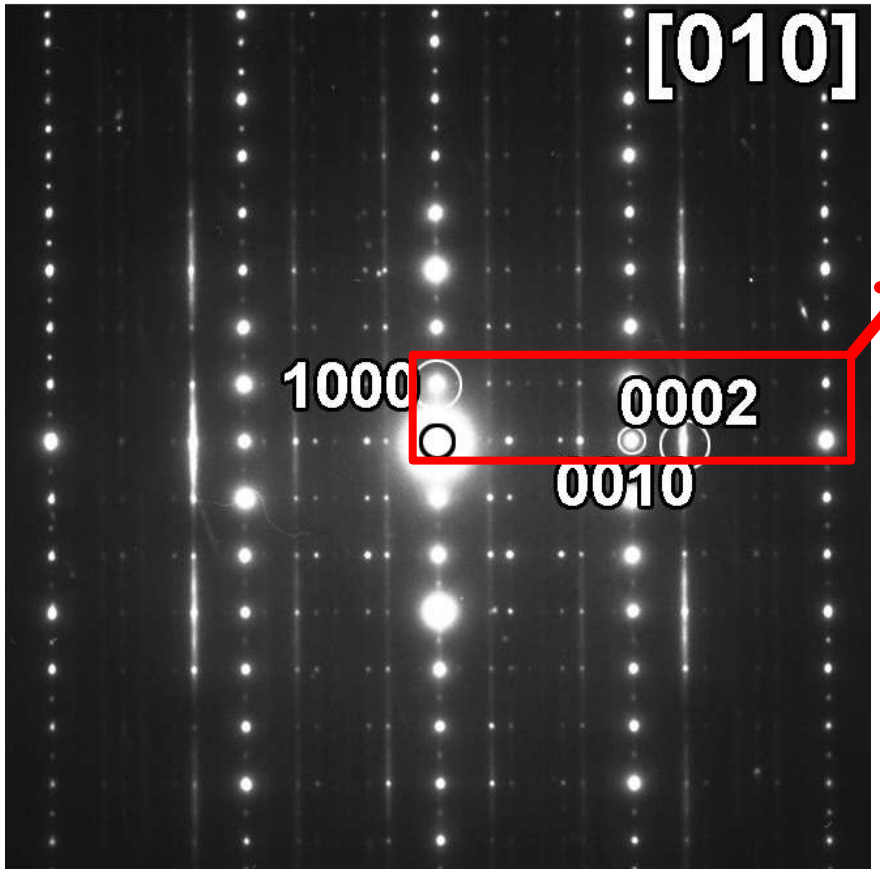


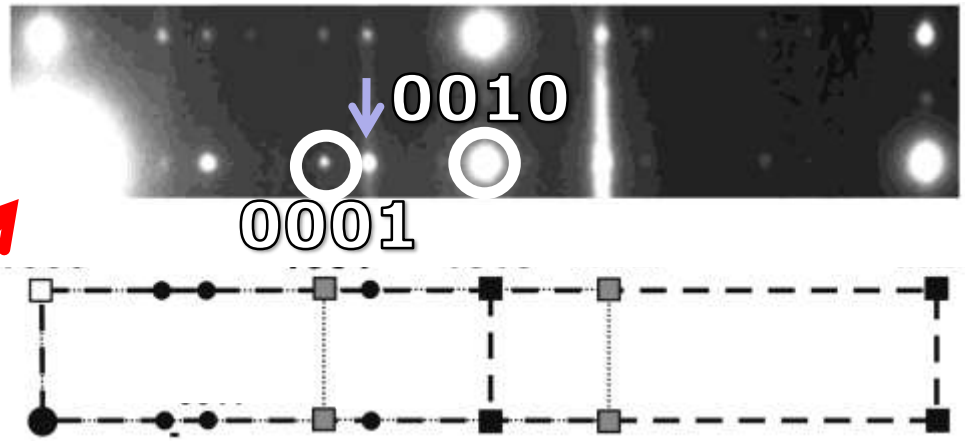


Which reflection is $00\bar{1}2$?

$$[SrF_{0.82}(OH)_{0.18}]_{2.5}[Mn_6O_{12}]$$

Exercise 2: composite structure: index the pattern





Which reflection does the blue arrow point at?

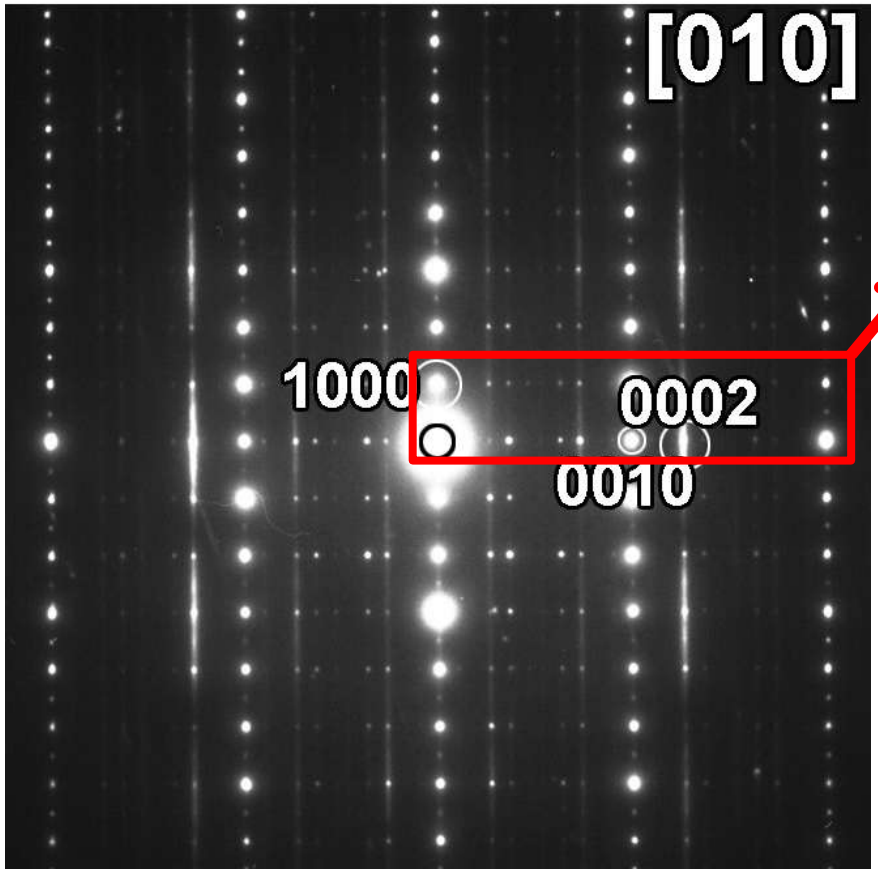
$00\bar{2}2$ ●

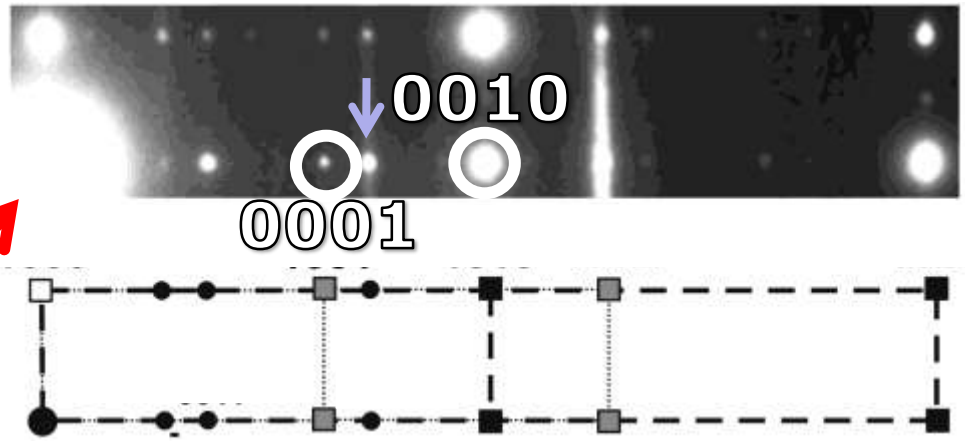
$00\bar{2}1$ ●

$001\bar{2}$ ●

$[SrF_{0.82}(OH)_{0.18}]_{2.5}[Mn_6O_{12}]$

Exercise 2: composite structure: index the pattern



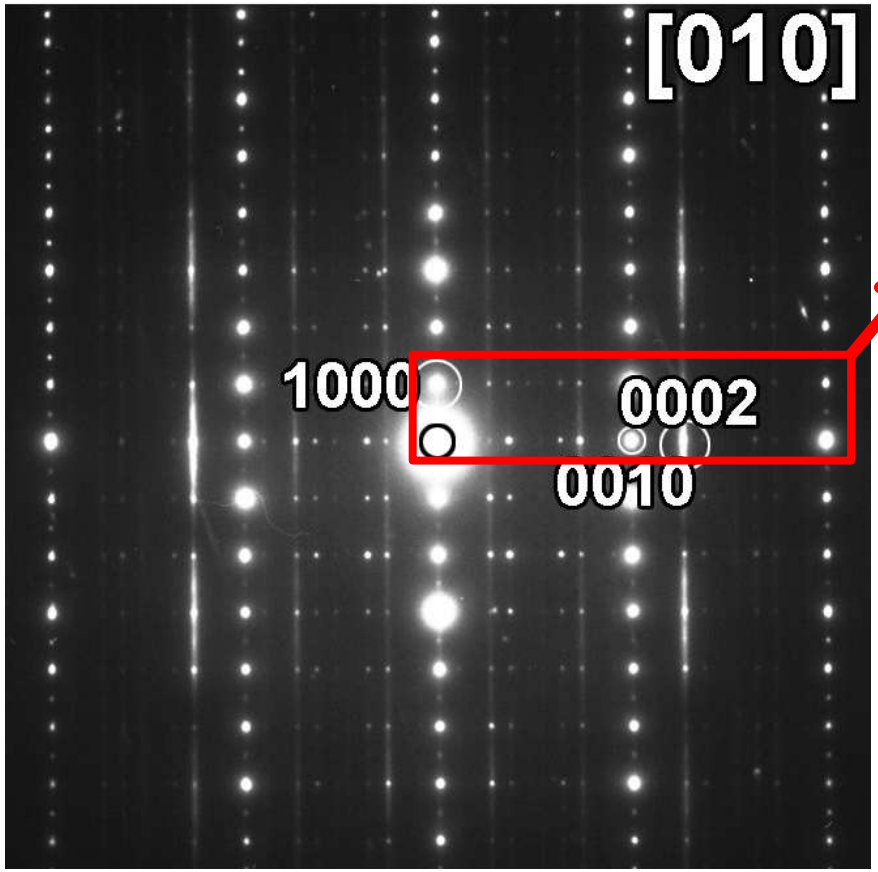


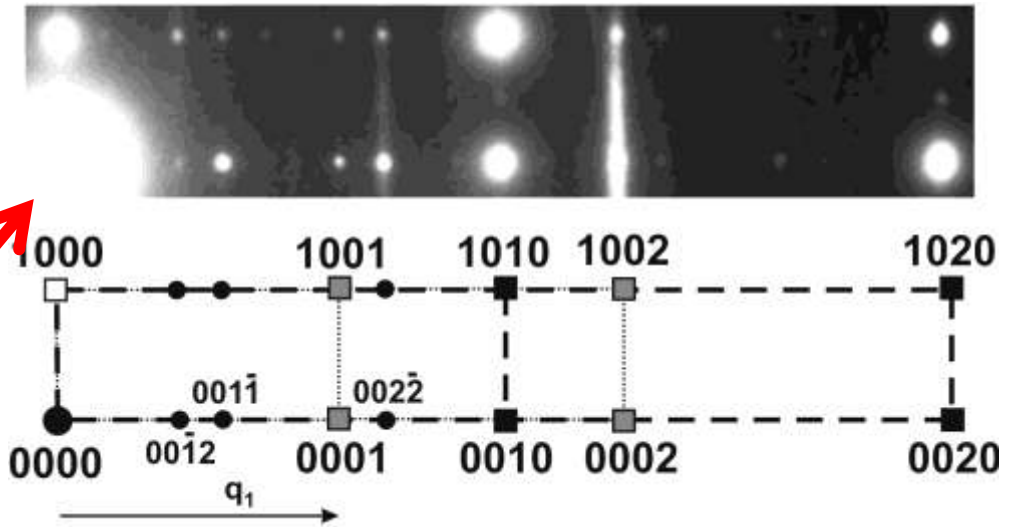
Which reflection does the blue arrow point at?

$00\bar{2}2$

$$[SrF_{0.82}(OH)_{0.18}]_{2.5}[Mn_6O_{12}]$$

Exercise 2: composite structure: index the pattern - solution



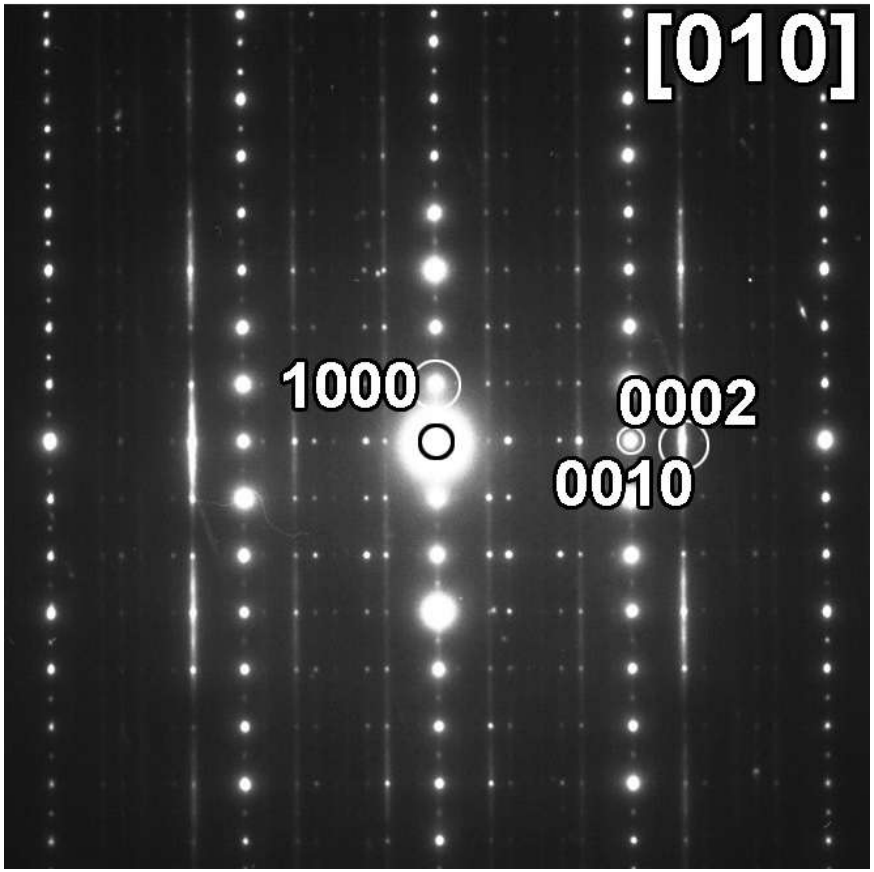


$[SrF_{0.82}(OH)_{0.18}]_{2.5}[Mn_6O_{12}]$

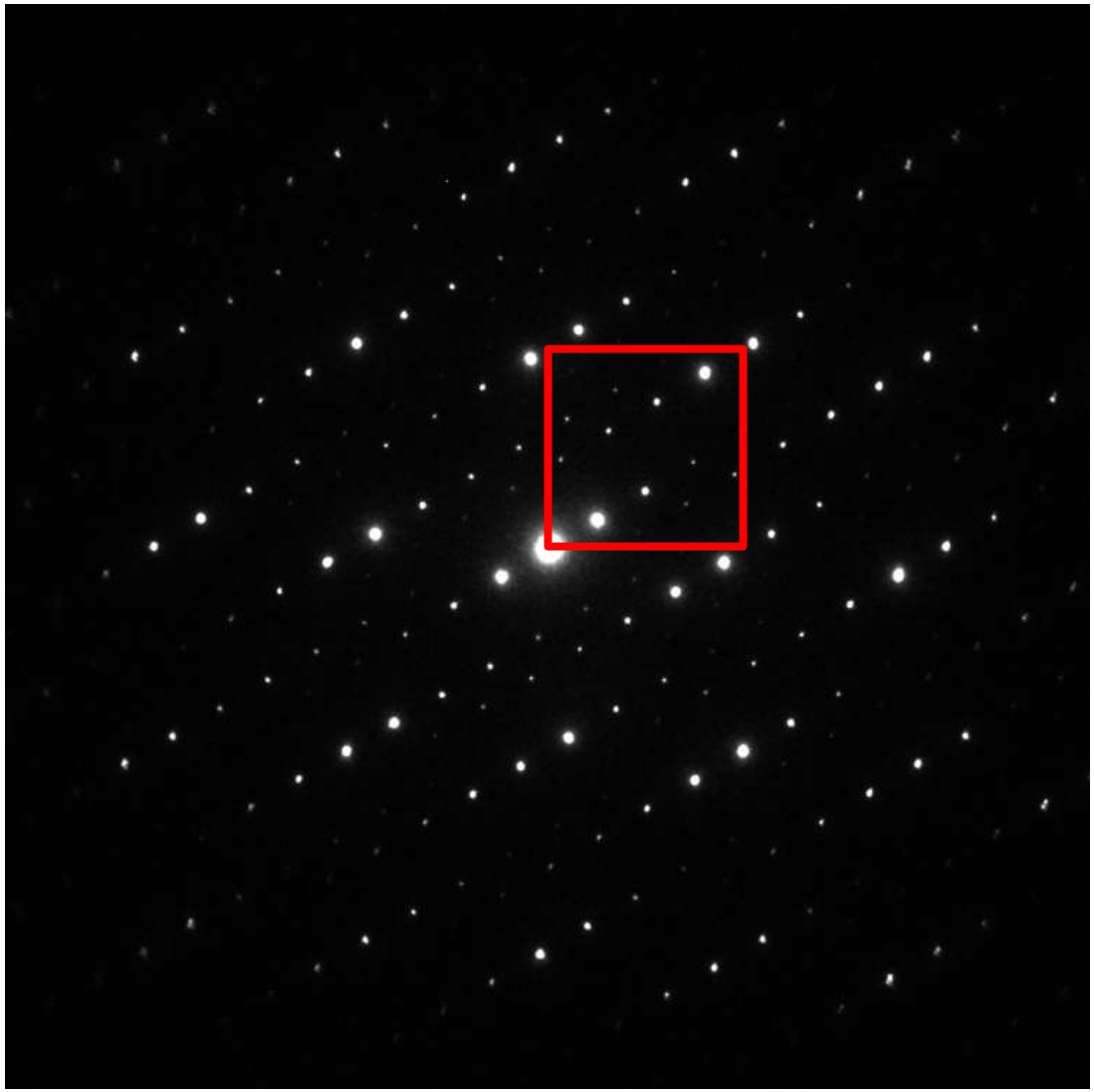
Streaks

- order in the plane, disorder between these planes: streak on ED pattern

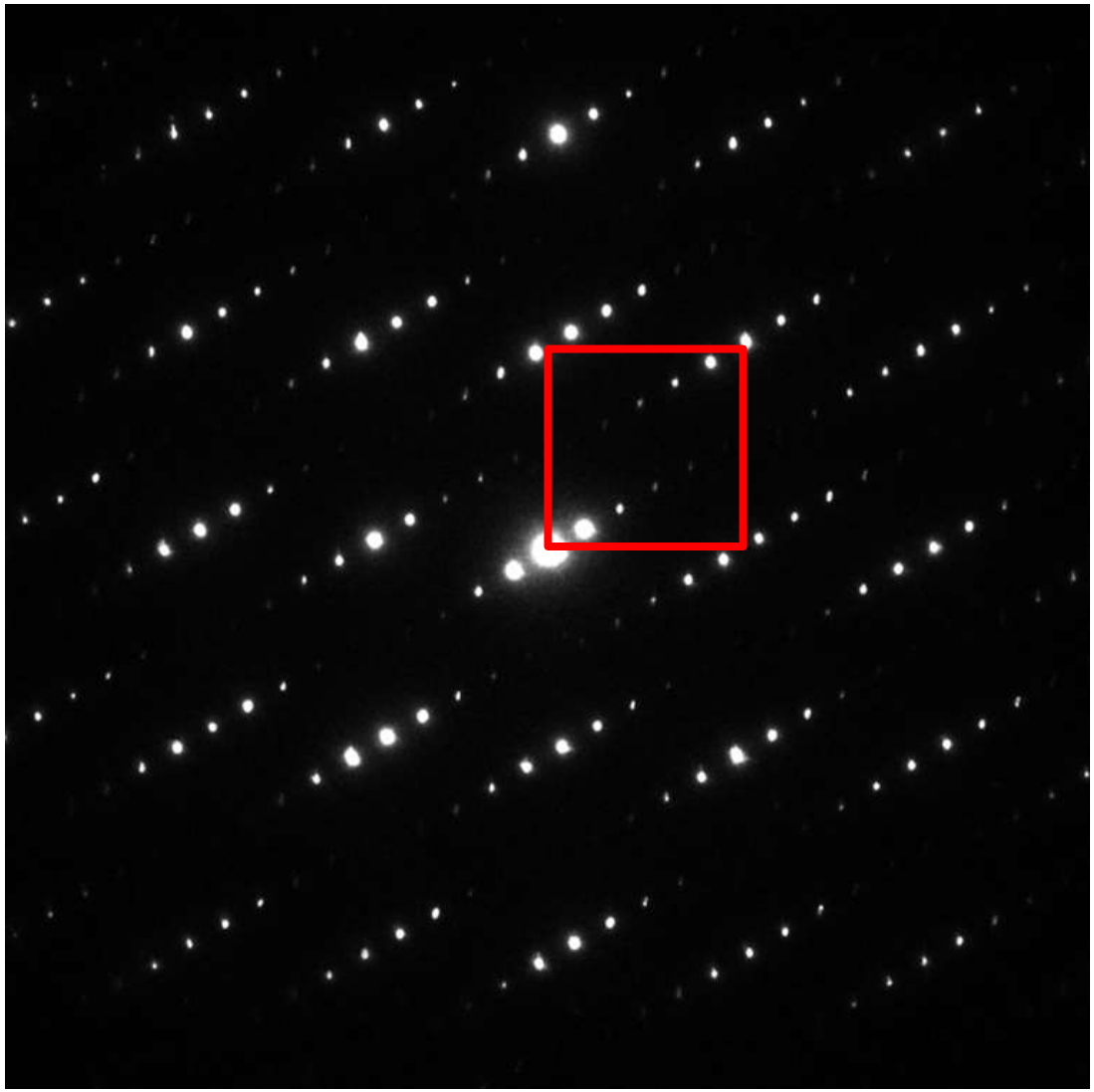
- disorder in two directions: diffuse intensity plane: streak or background intensity depending on the intersection



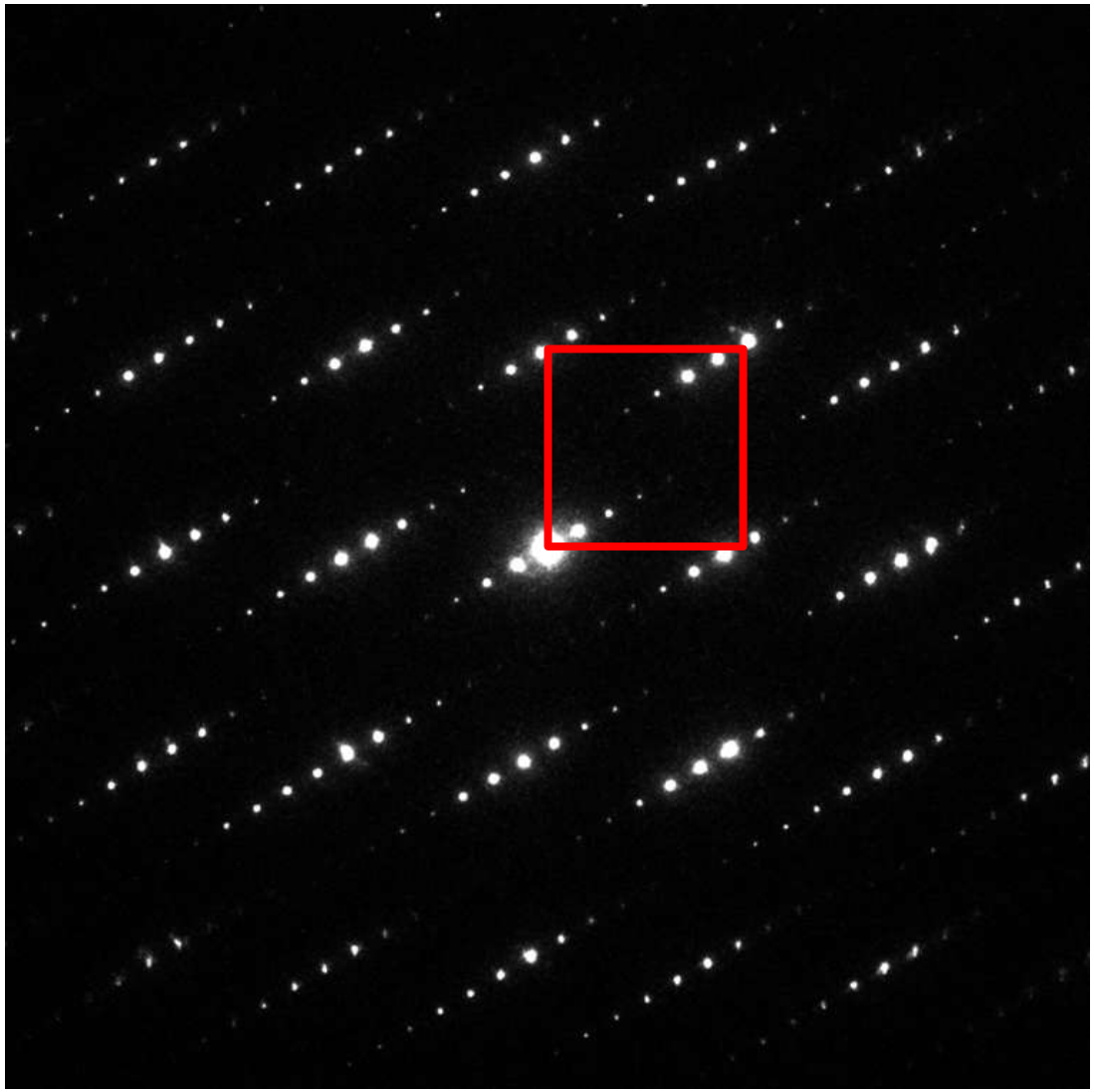
$Pb_{1-x}Bi_xFeO_{2.5+x/2}$ (Pb:Bi=7:0.5)



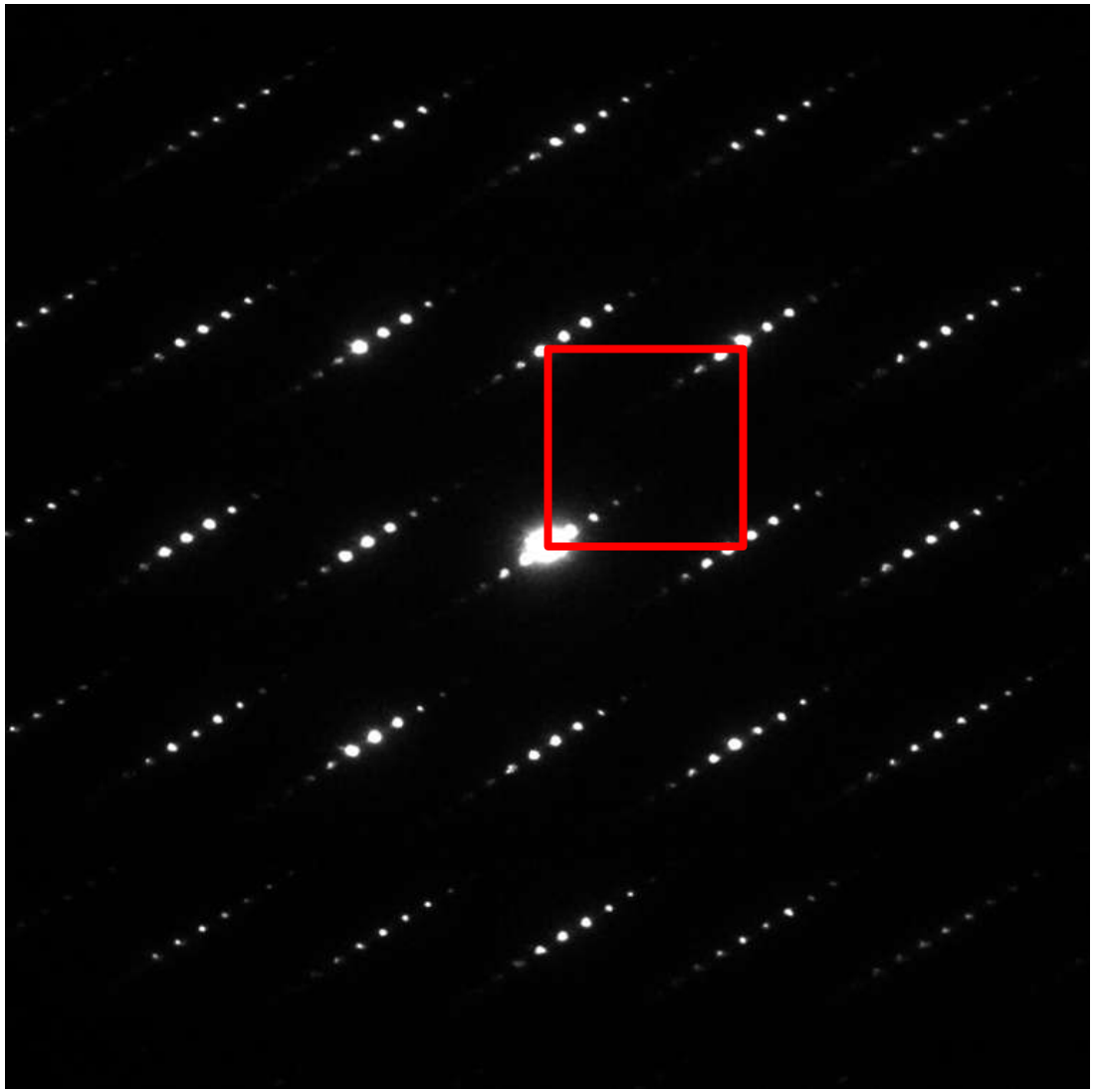
$Pb_{1-x}Bi_xFeO_{2.5+x/2}$(Pb:Bi=7:3)



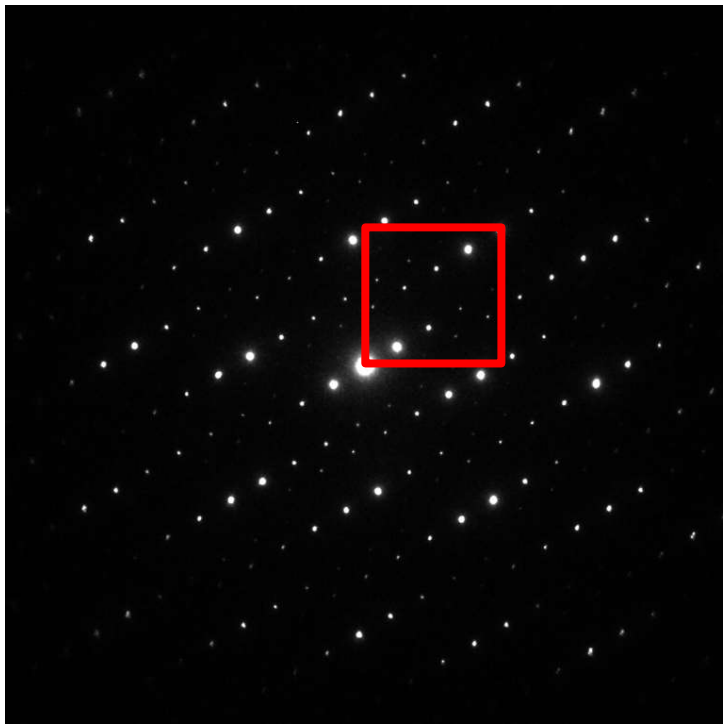
$Pb_{1-x}Bi_xFeO_{2.5+x/2}$ (Pb:Bi=7:5)

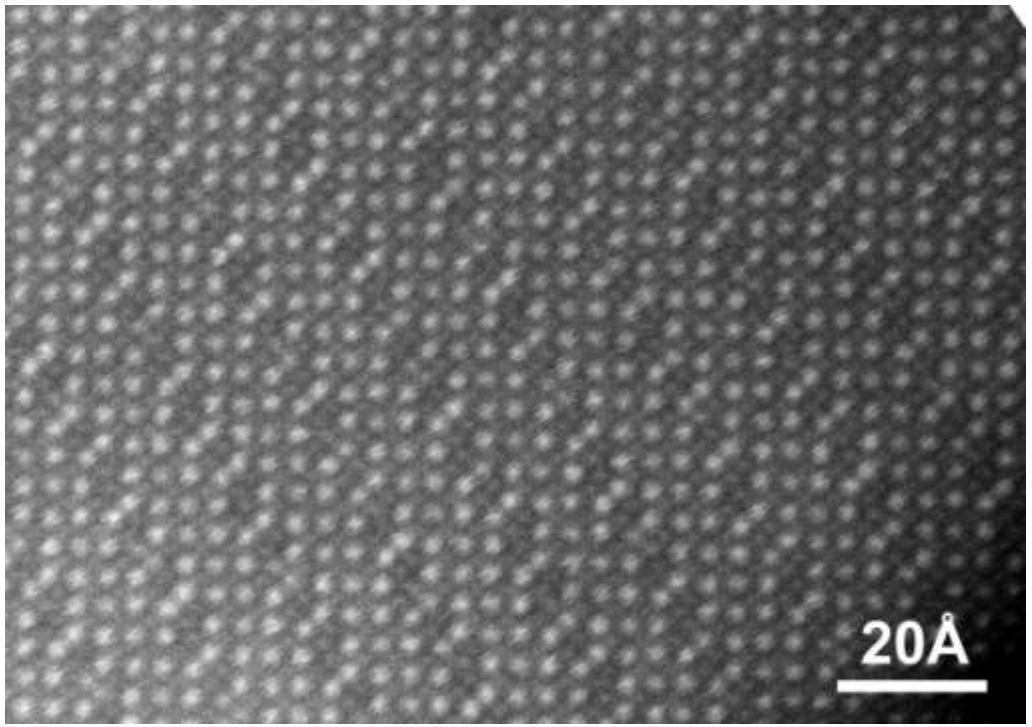


$Pb_{1-x}Bi_xFeO_{2.5+x/2}$ (Pb:Bi=7:8)



$Pb_{1-x}Bi_xFeO_{2.5+x/2}$ (Pb:Bi=7:0.5)





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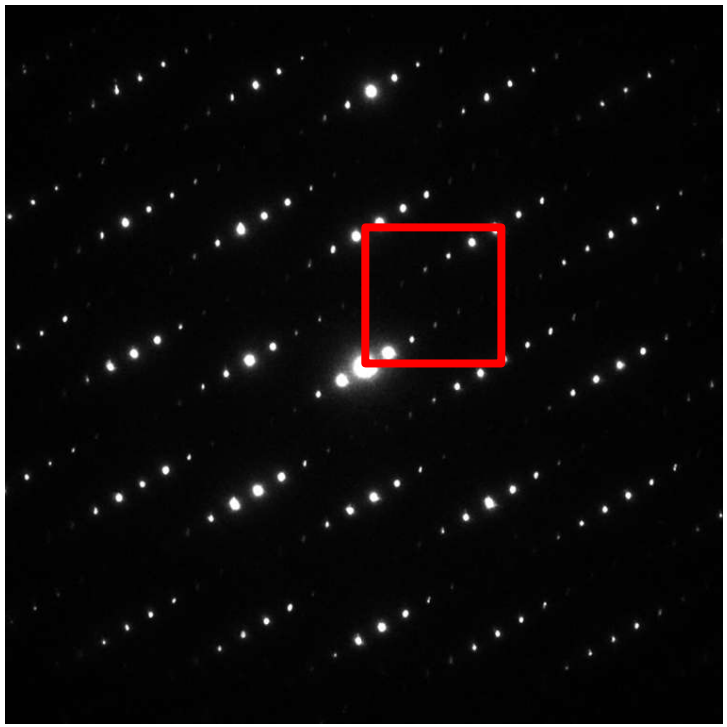
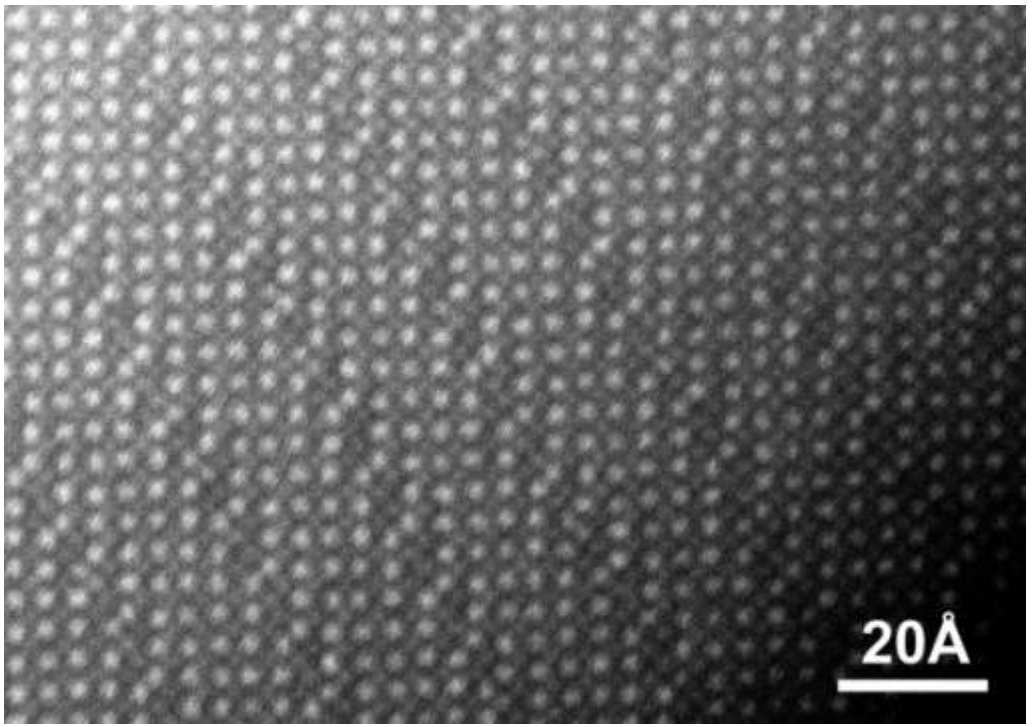
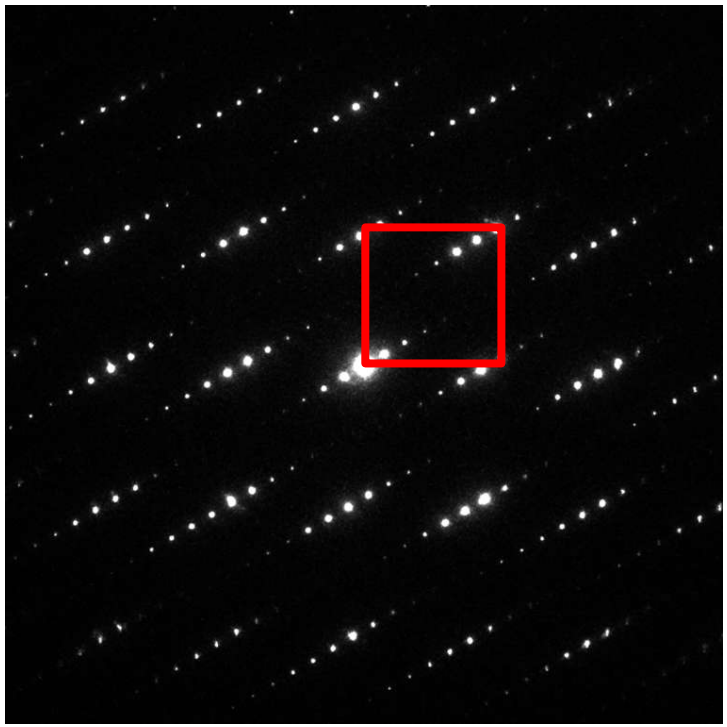
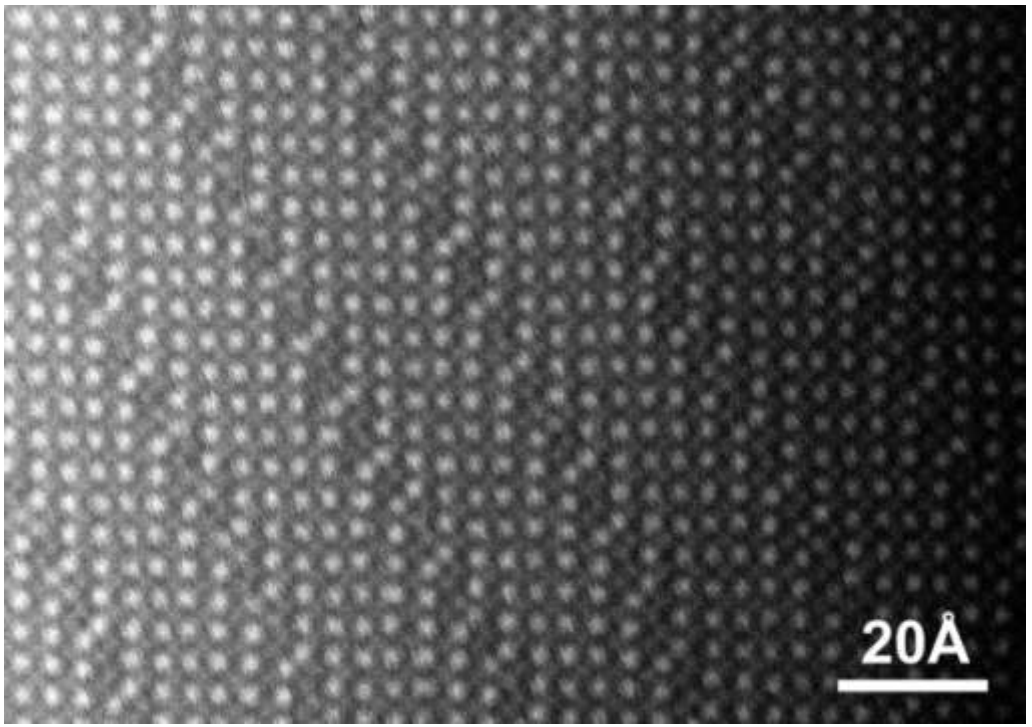
$Pb_{1-x}Bi_xFeO_{2.5+x/2}$(Pb:Bi=7:3)



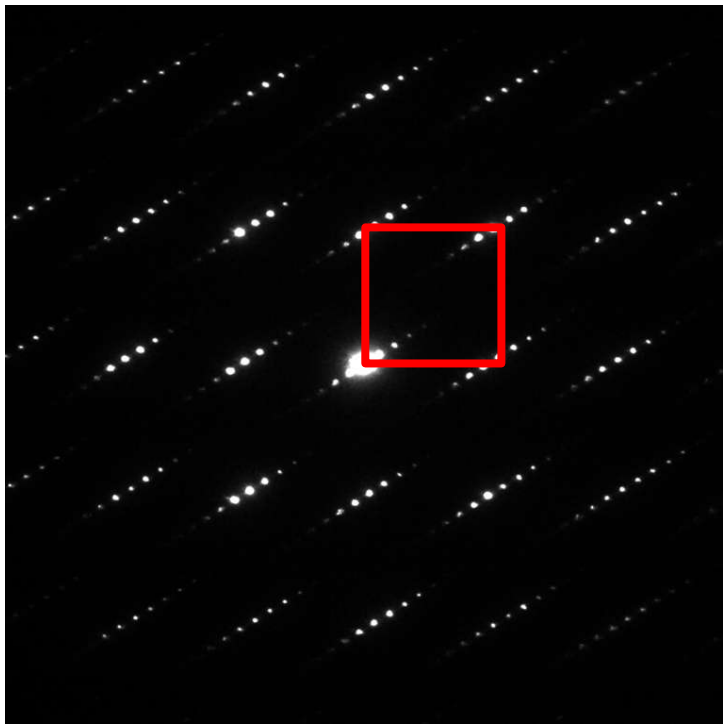


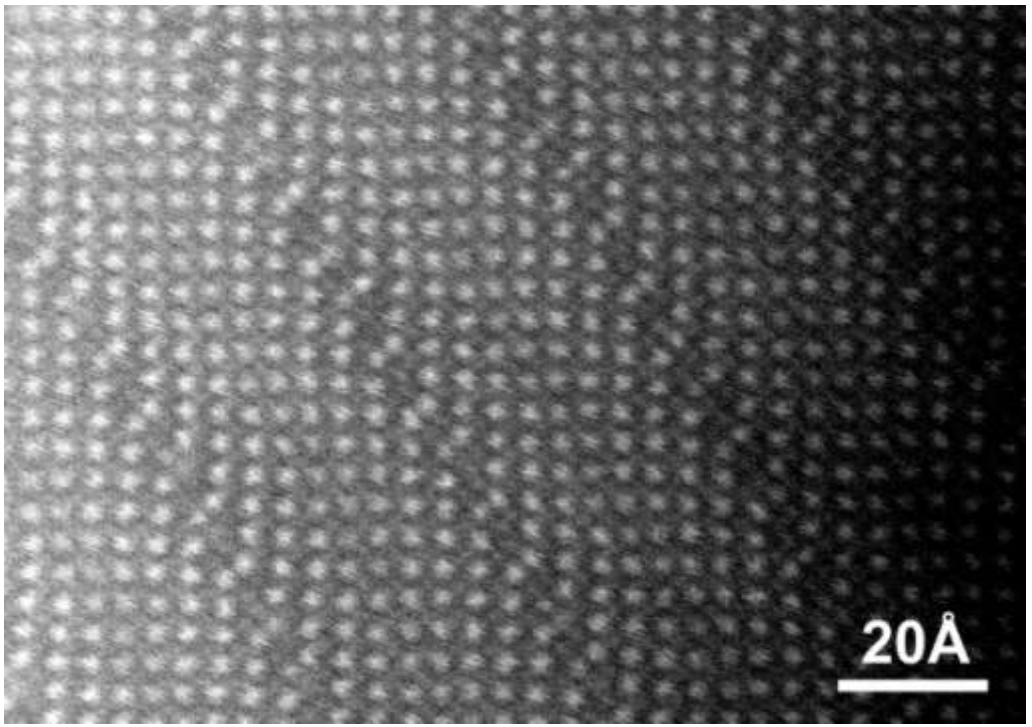
$Pb_{1-x}Bi_xFeO_{2.5+x/2}$ (Pb:Bi=7:5)





$Pb_{1-x}Bi_xFeO_{2.5+x/2}$ (Pb:Bi=7:8)





HRTEM and HAADFSTEM-images

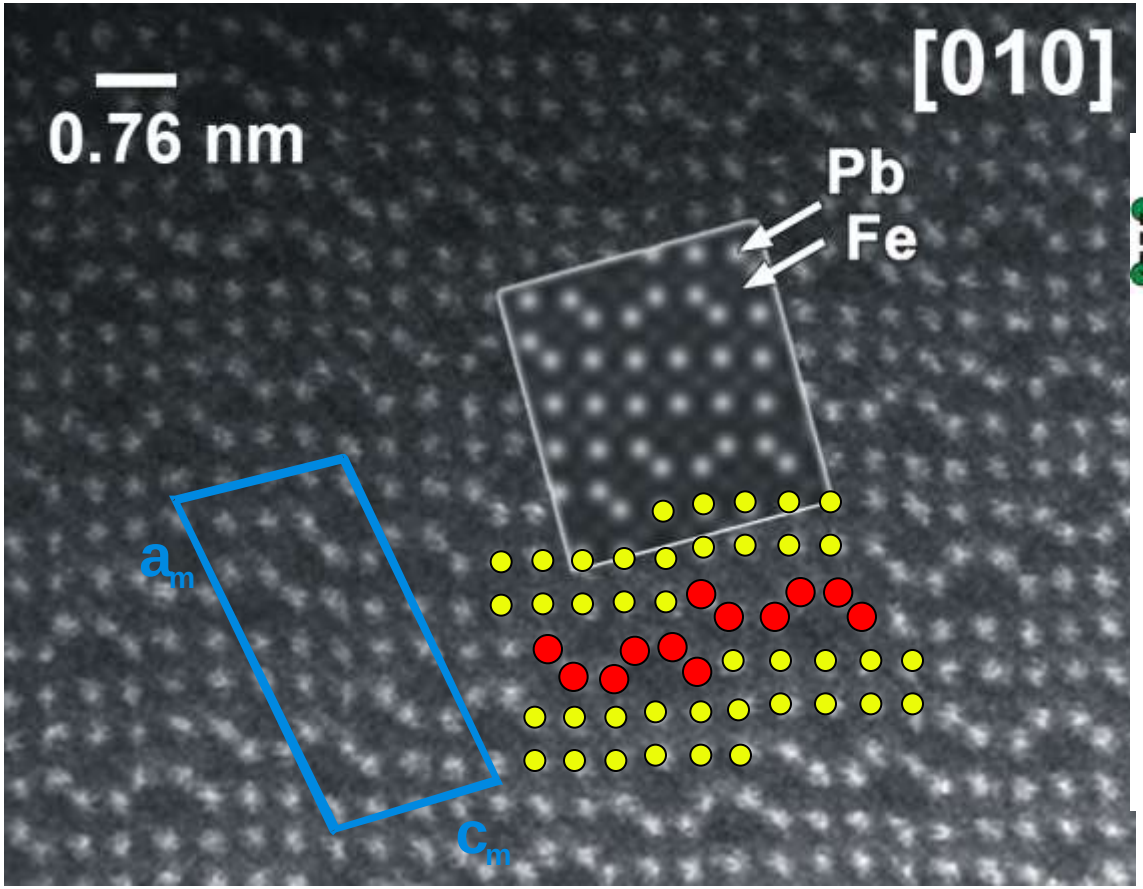
HAADF-STEM

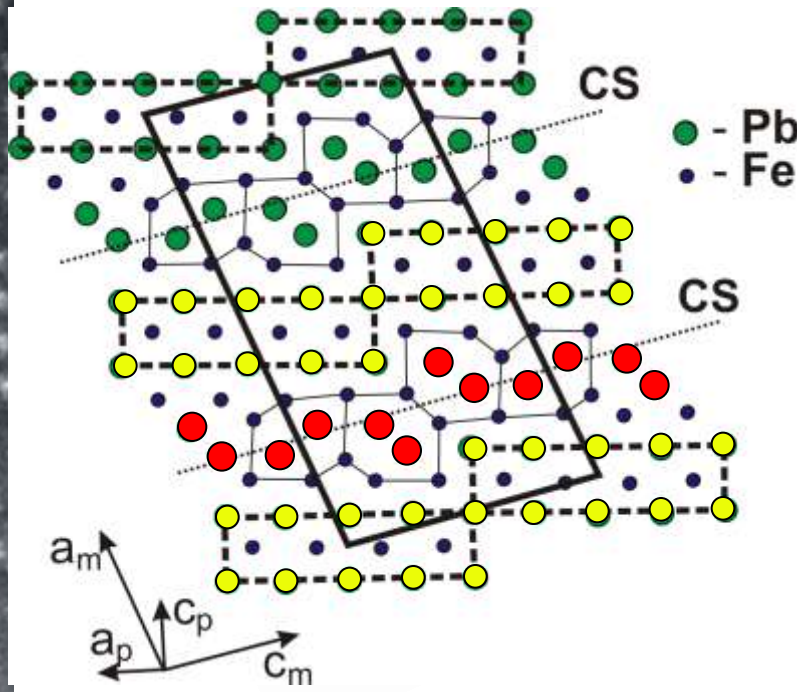
- contrast related to Z^n
- direct information about the heavy atom positions
- brighter with thickness also
- correct orientation very important!
- scanned image: positions imprecise

HRTEM

- complicated phase transfer function
- no direct interpretation possible
- contrast changes with thickness and defocus
- correct orientation very important!
- one-shot image: position of the contrast objects reliable

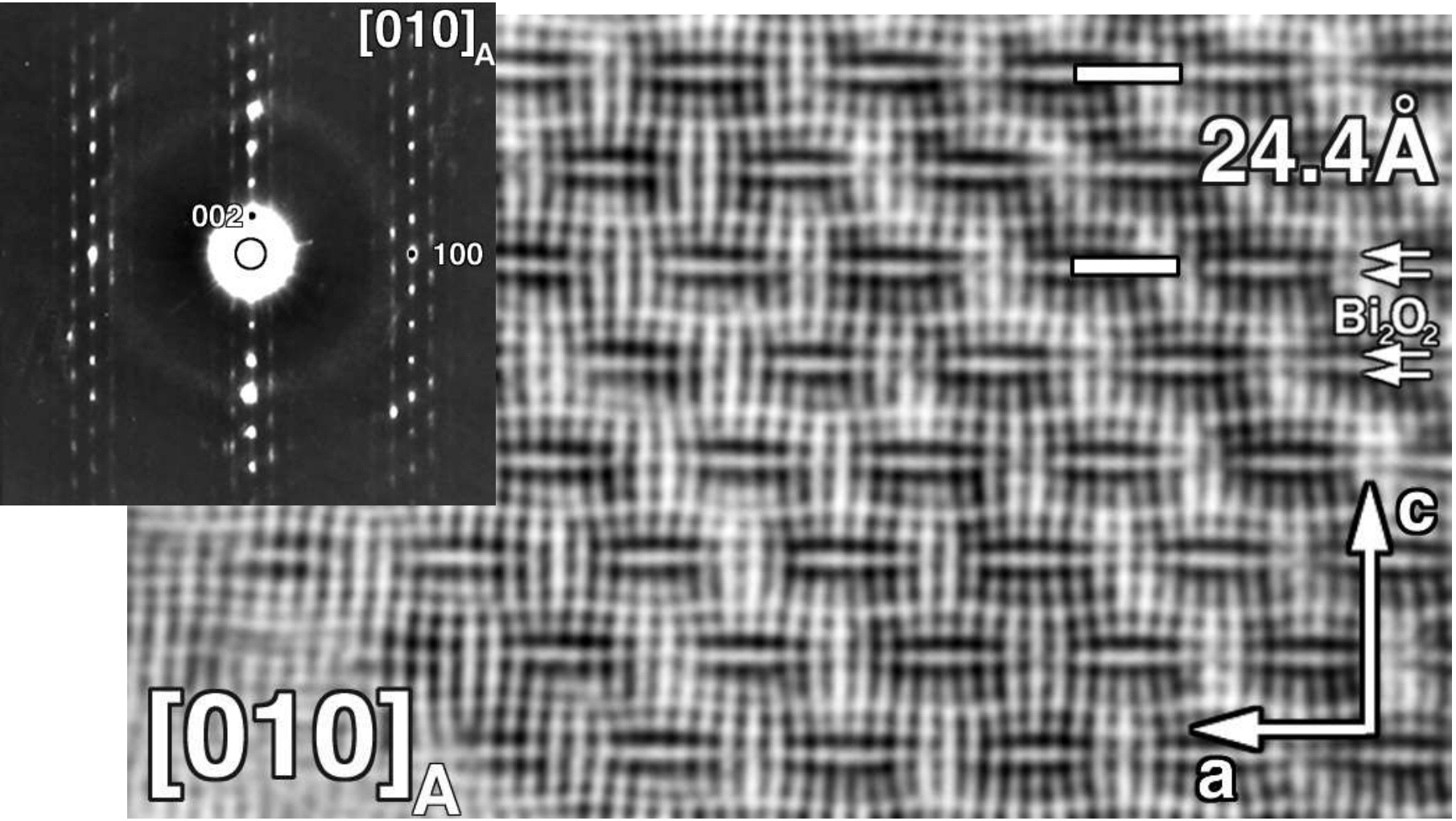
Heavy atoms from HAADF-STEM





"$Pb_2Fe_2O_5$" Abakumov et al., Ang.Chemie-Int.Ed., 45, 40 (2006) 6697-6700

High resolution transmission electron microscopy (HREM)



$Bi_2Sr_{1.2}La_{0.8}CuO_{6.46-x}F_{2x}$ Hadermann et al., JSSC, 156, 2 (2001) 455-451

Relation structure – image in HRTEM

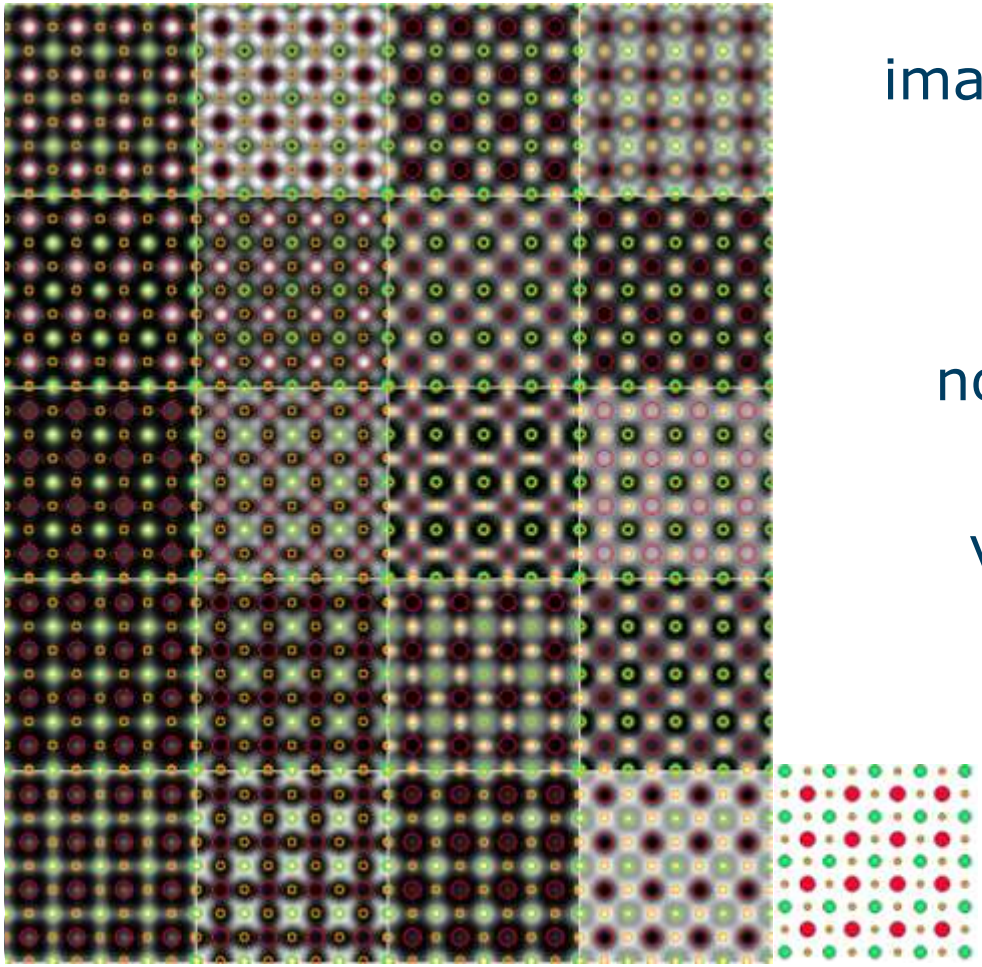
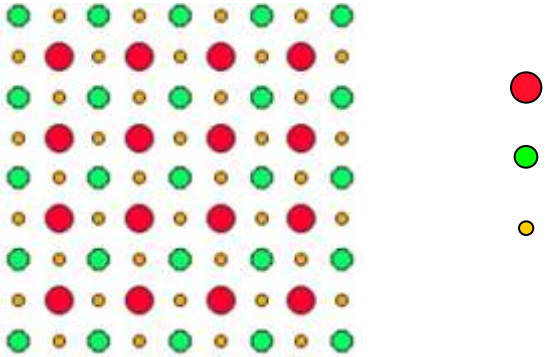


image influenced by contrast transfer function of the microsope

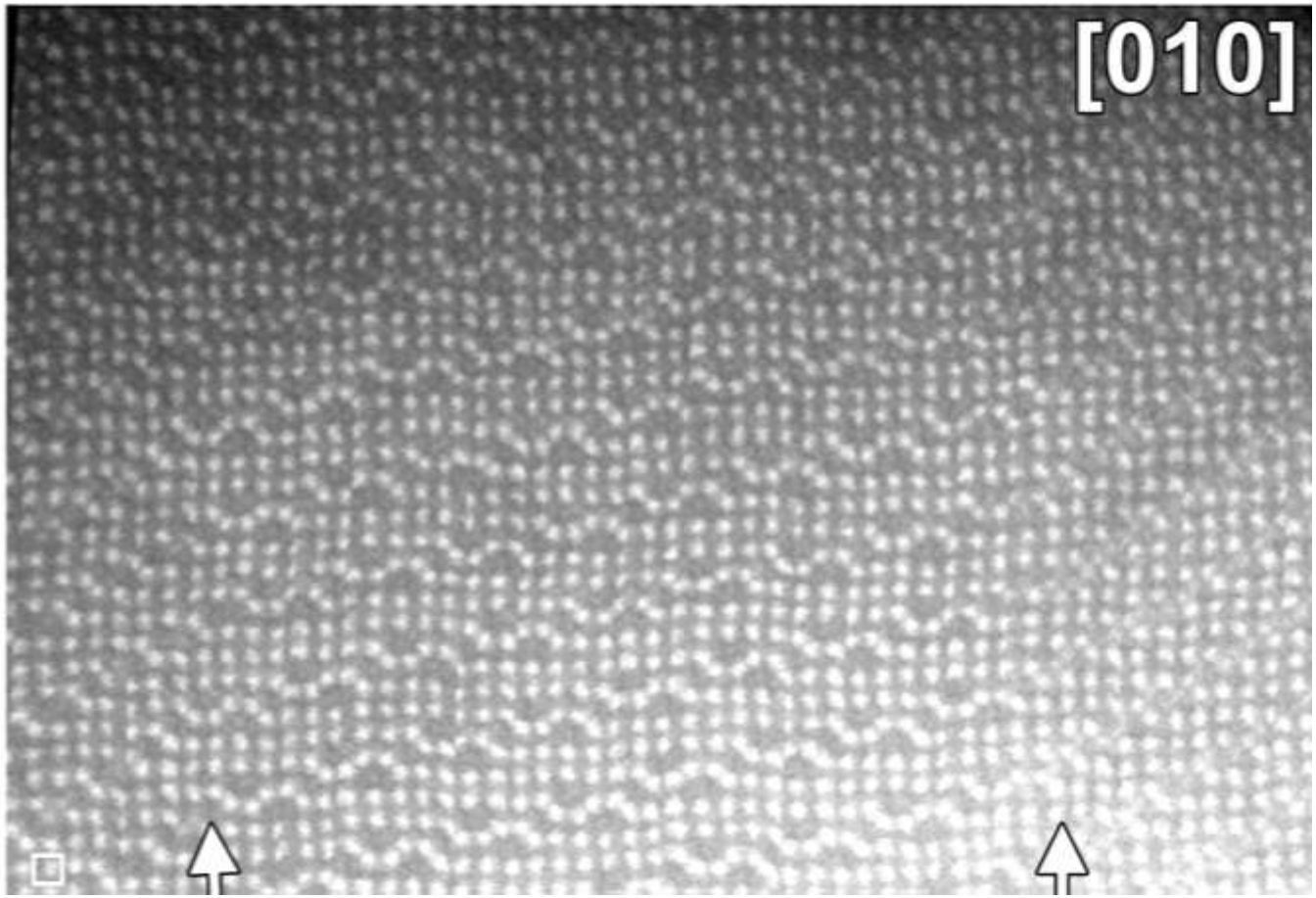
no direct correspondence

visual comparison with simulations needed



simple perovskite

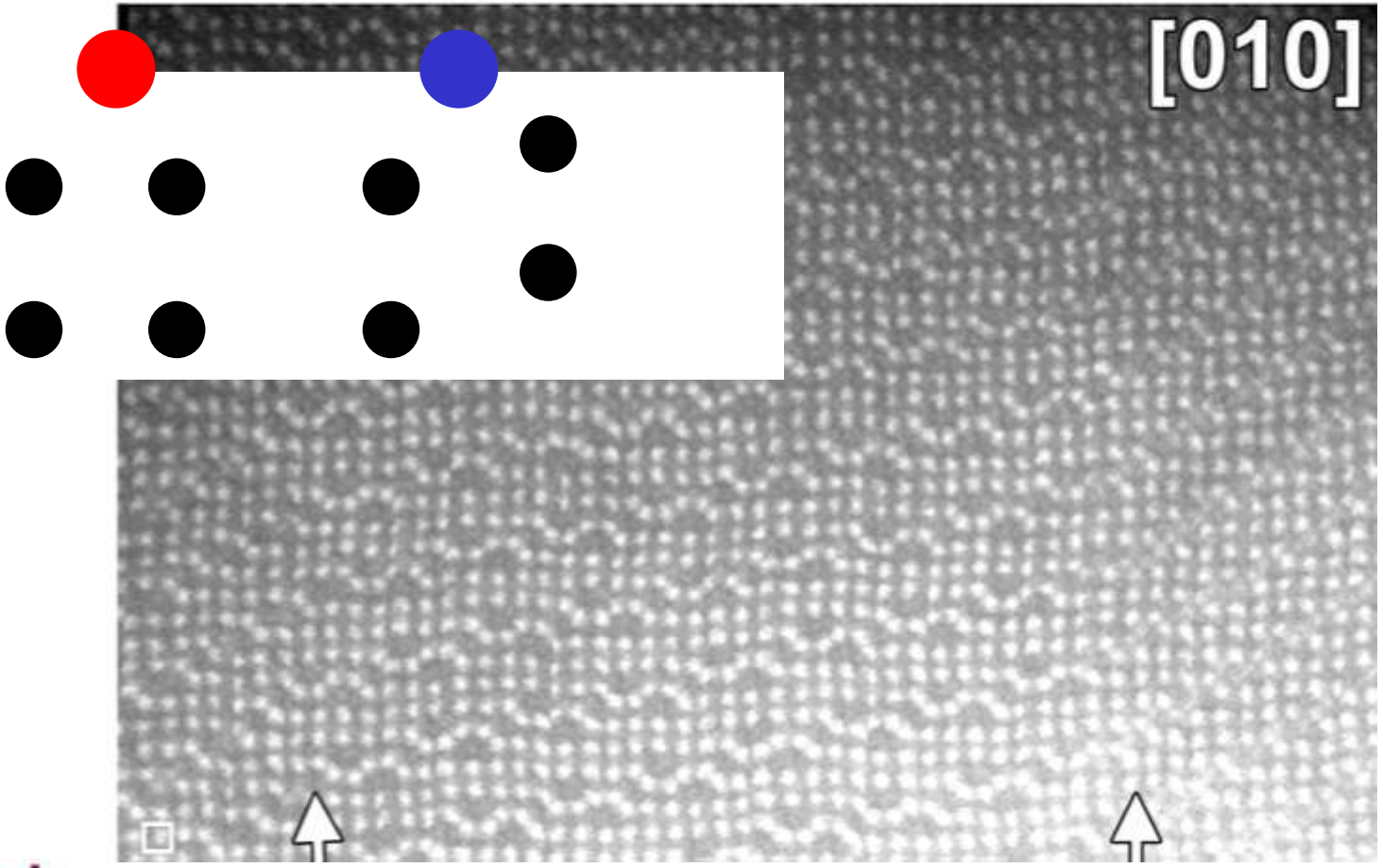
Exercise 3: predict what the ED pattern will roughly look like



Hadermann et al., Solid State Sciences, 10; 4 (2008) 382-389

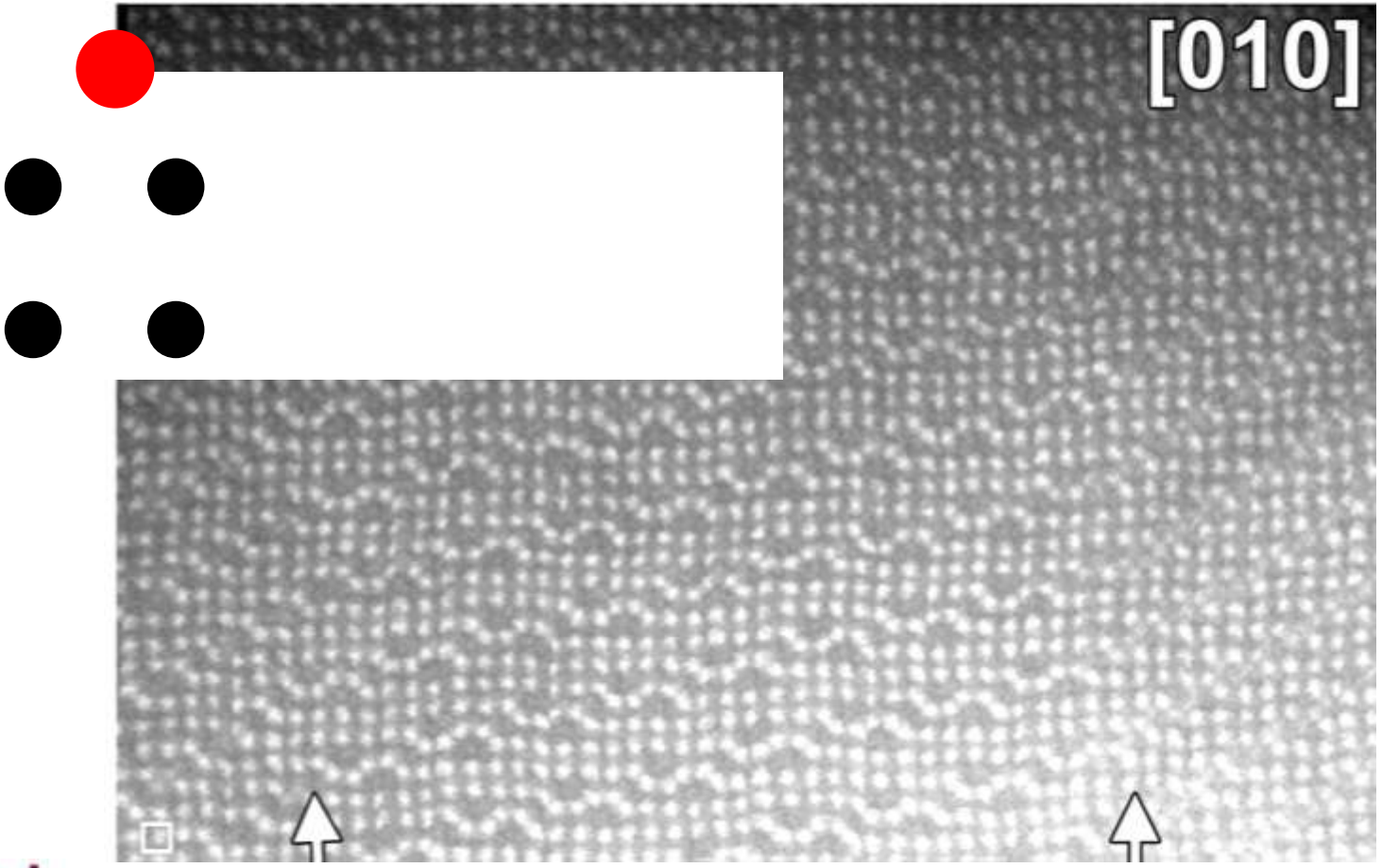
Exercise 3: predict what the ED pattern will roughly look like

What will be the subcell reflections?

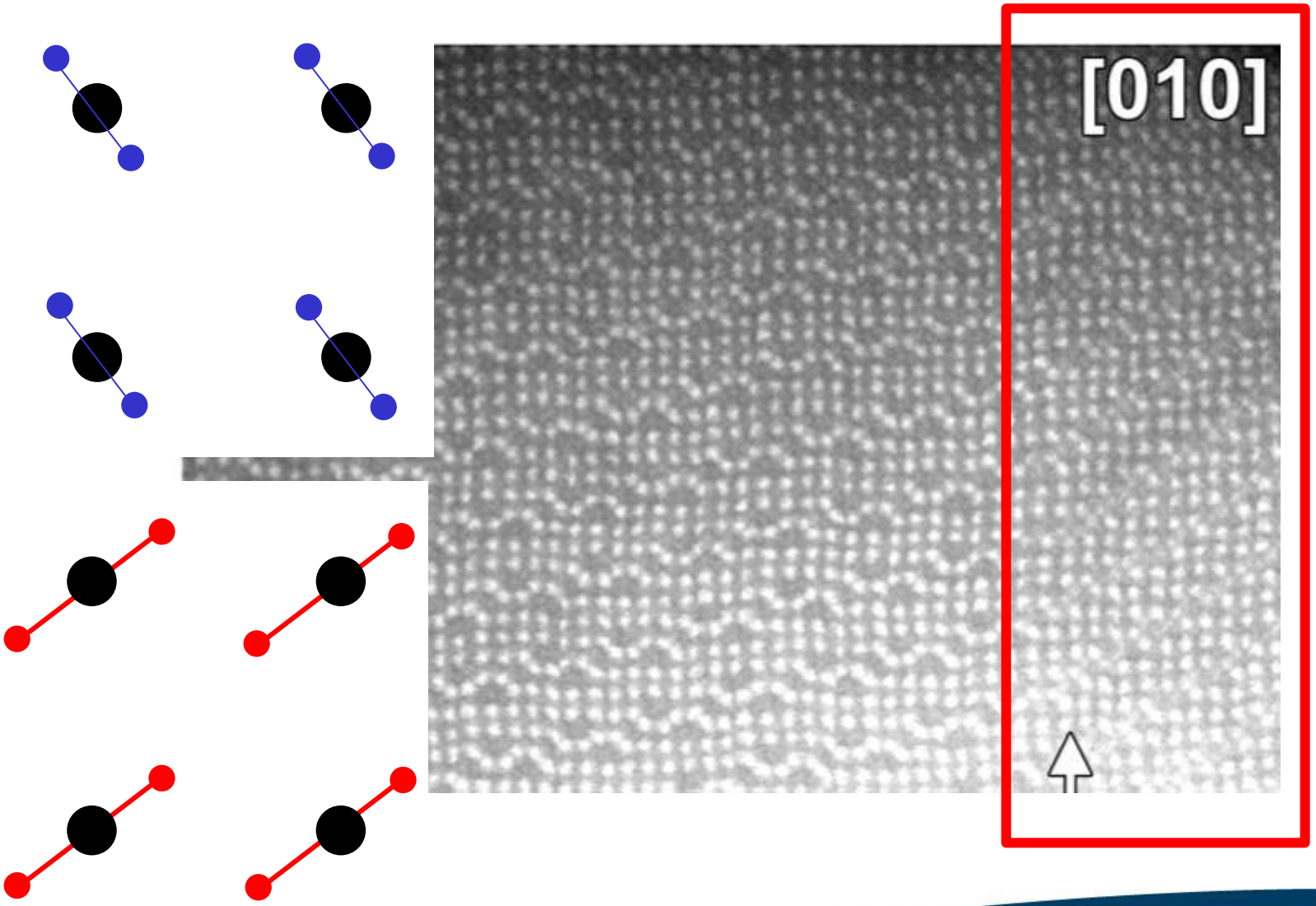


Exercise 3: predict what the ED pattern will roughly look like

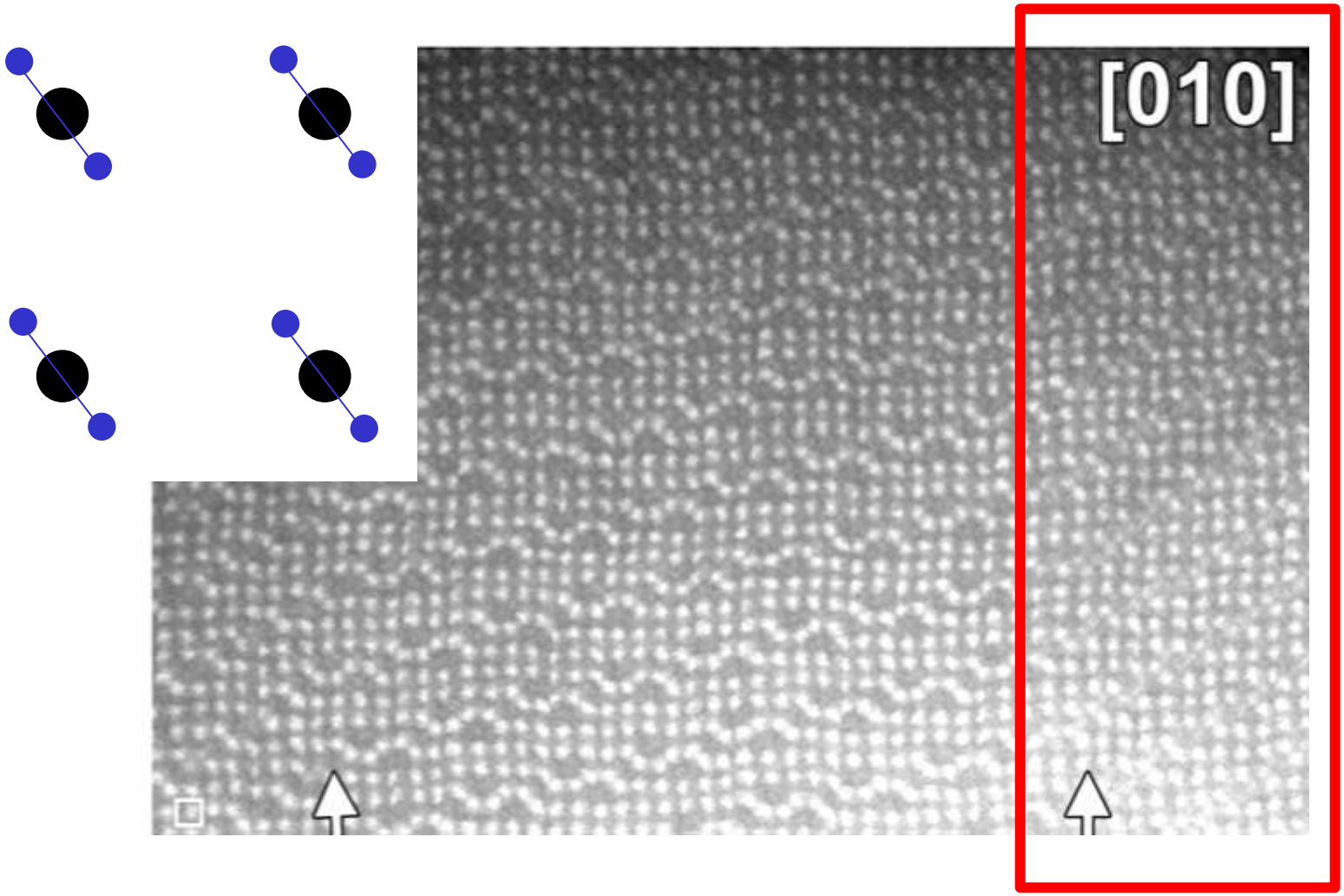
What will be the subcell reflections?



Exercise 3: predict what the ED pattern will roughly look like



Exercise 3: predict what the ED pattern will roughly look like



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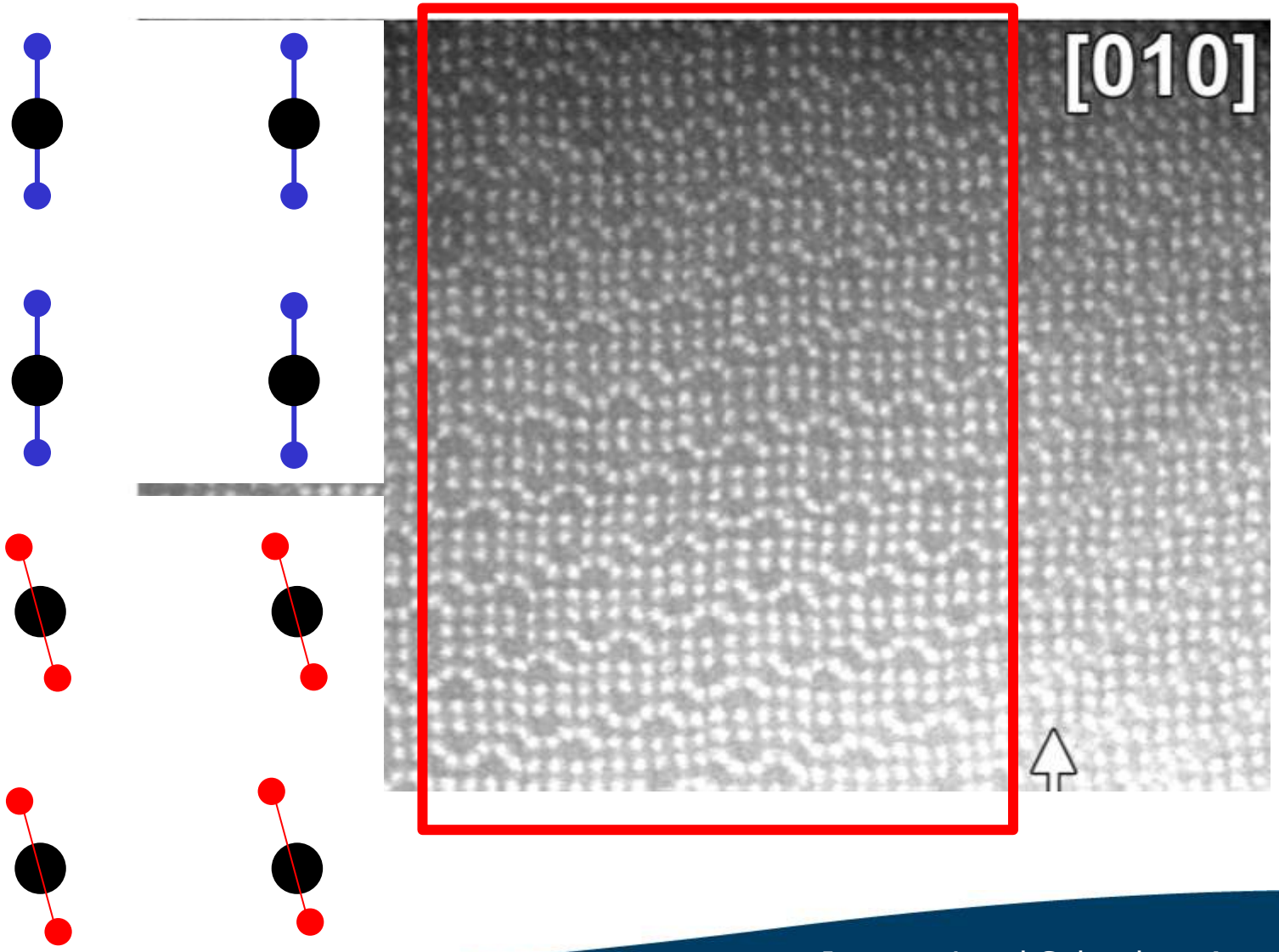
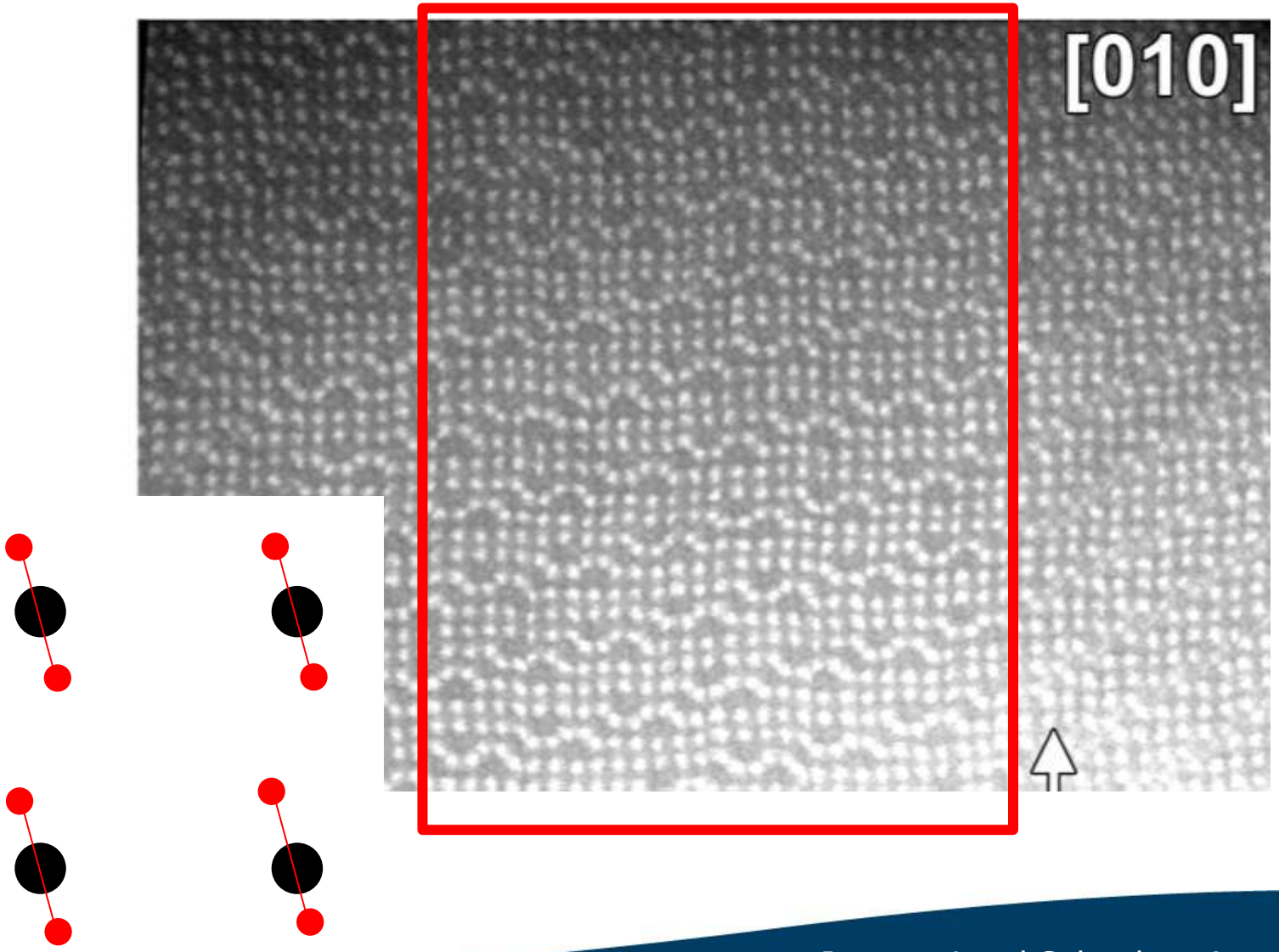
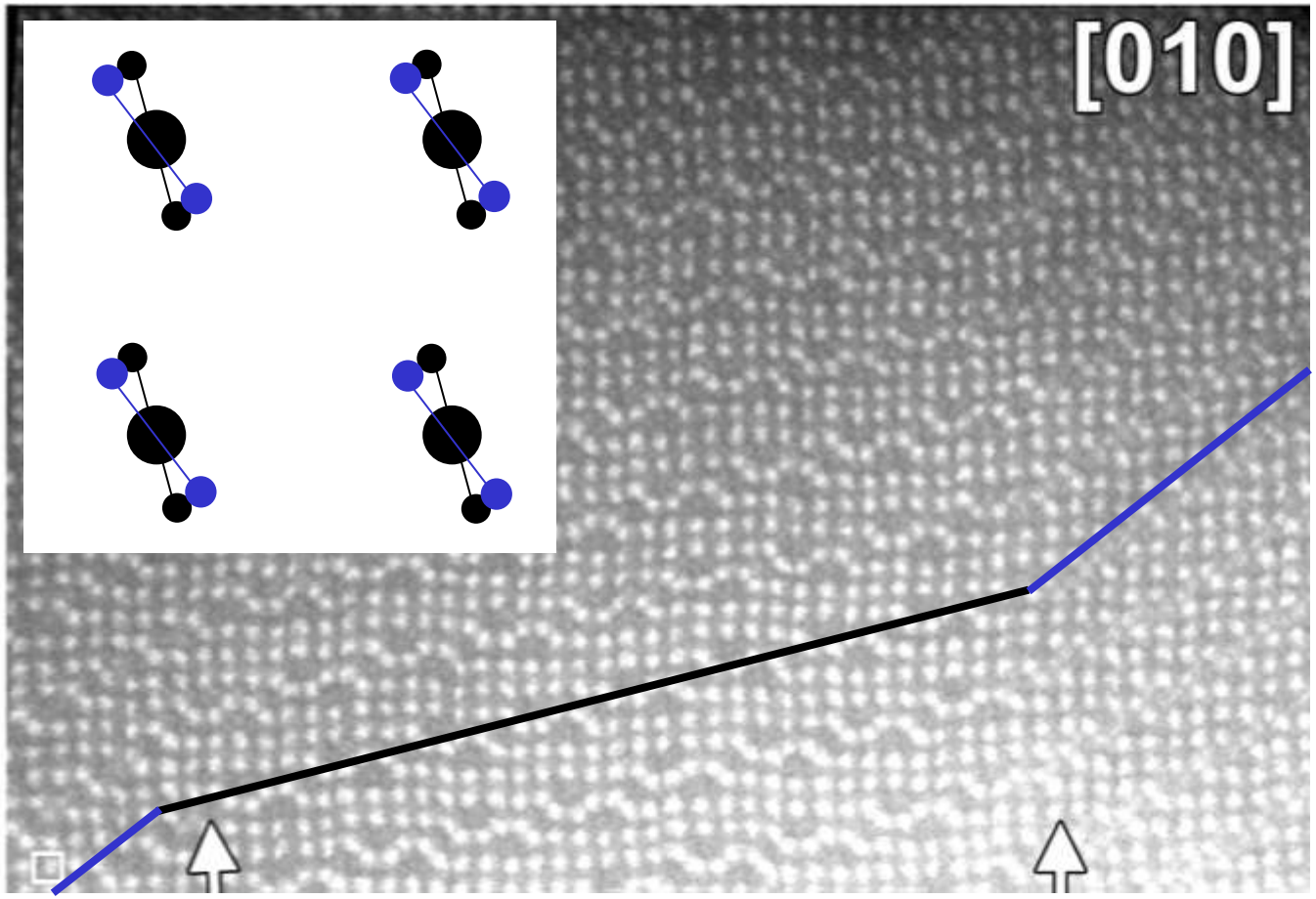
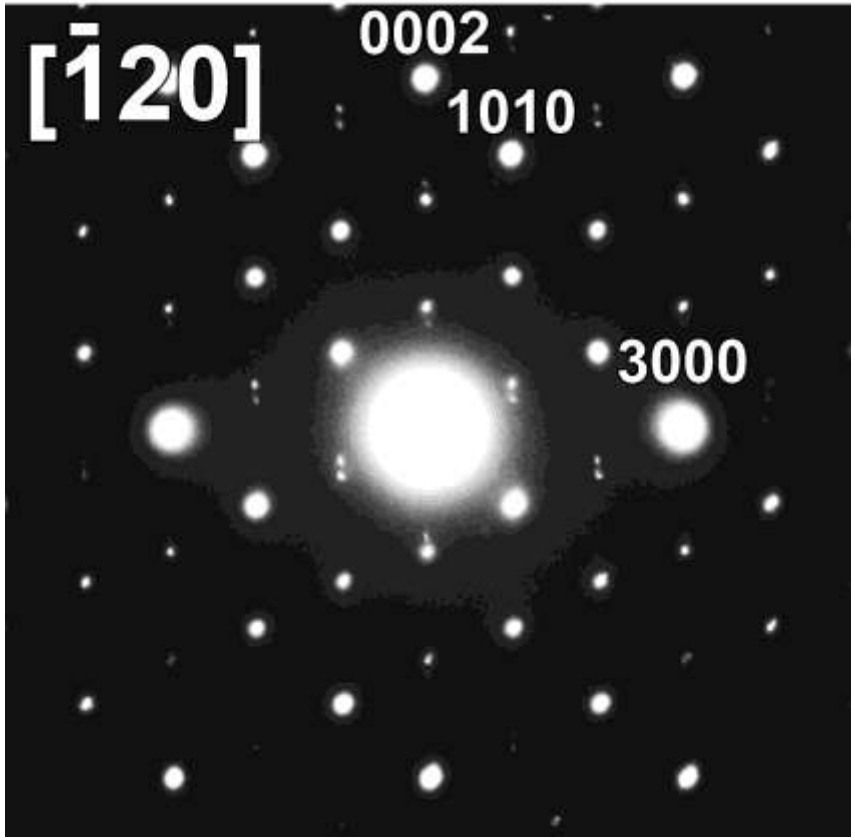


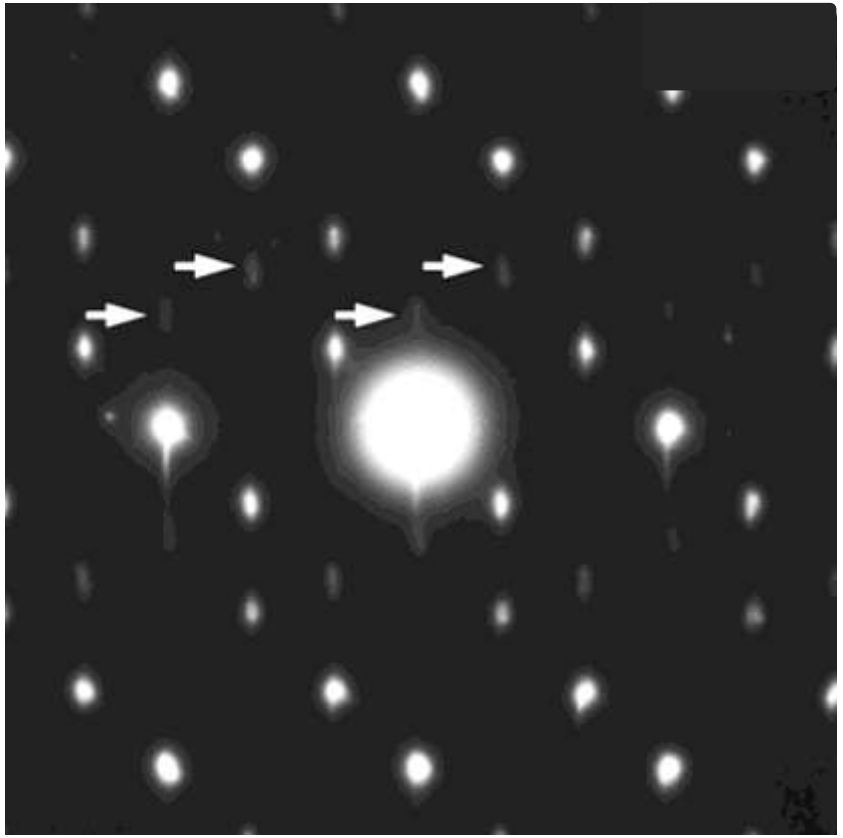
Exercise 3: predict what the ED pattern will roughly look like




[010]

Domains with varying q





$Sr_{1.3}Co_{0.8}Mn_{0.2}O_3$

Mandal et al., Chem. Mater., 19, 25 (2007) 6158

Comments to the applicability of conclusions from TEM

- If the satellites cannot be seen on the XRPD-NPD patterns it is no use to try to refine the structure using the ED cell.

- Precision of parameters determined from ED is not high. ED is good for determining parameters (cell parameters and direction and length of q) qualitatively.

- Good for determining symmetry.

- Can give direct space information and compositional information also.

Purpose of this lecture

At the end of this lecture you should be able to:

- Understand the TEM paragraph in papers about IMS and CS
- Be able to make solid comments about conclusions claimed from TEM by different sources (collaborators, papers,…) by knowing some possible pitfalls
- Decide whether it would be useful to do TEM on your own IMS or CS
- Make basic interpretations of TEM data on your own materials by yourself