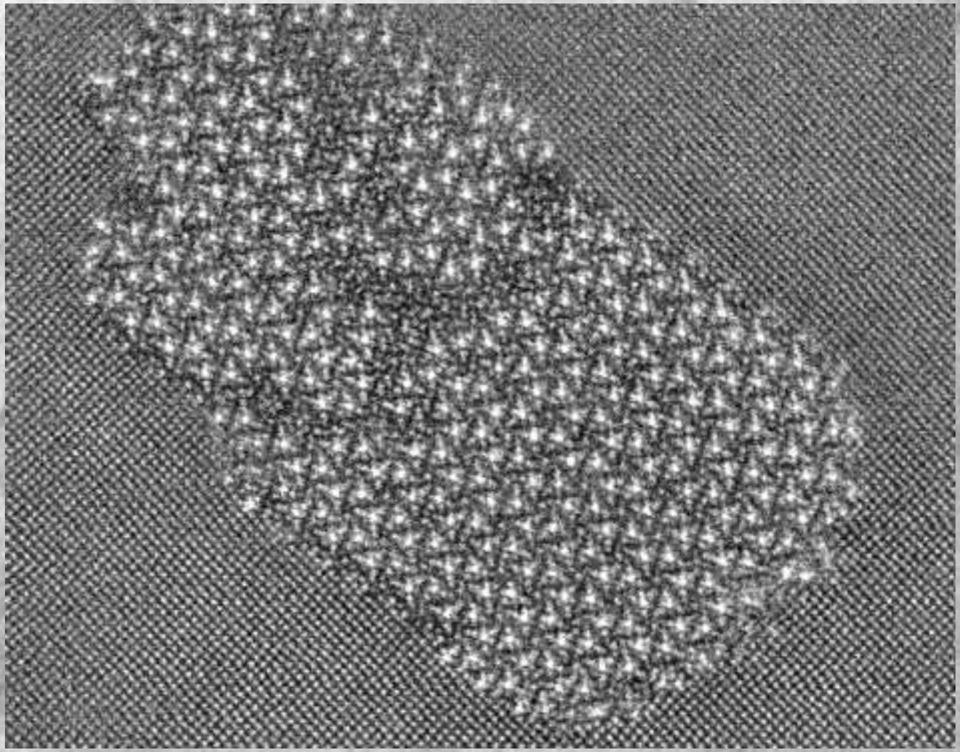
Précipitation métastable dans les alliages Al 6XXX : apports de l'imagerie en *STEM HAADF* à l'échelle atomique



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OUTLINE

STEM-HAADF imaging in a Transmission Electron Microscope

Transmission Electron Microscopy (High Resolution TEM) / vs.
Scanning TEM (STEM-*HAADF*: *High Angle Annular Dark Field*)
C_s correction in TEM

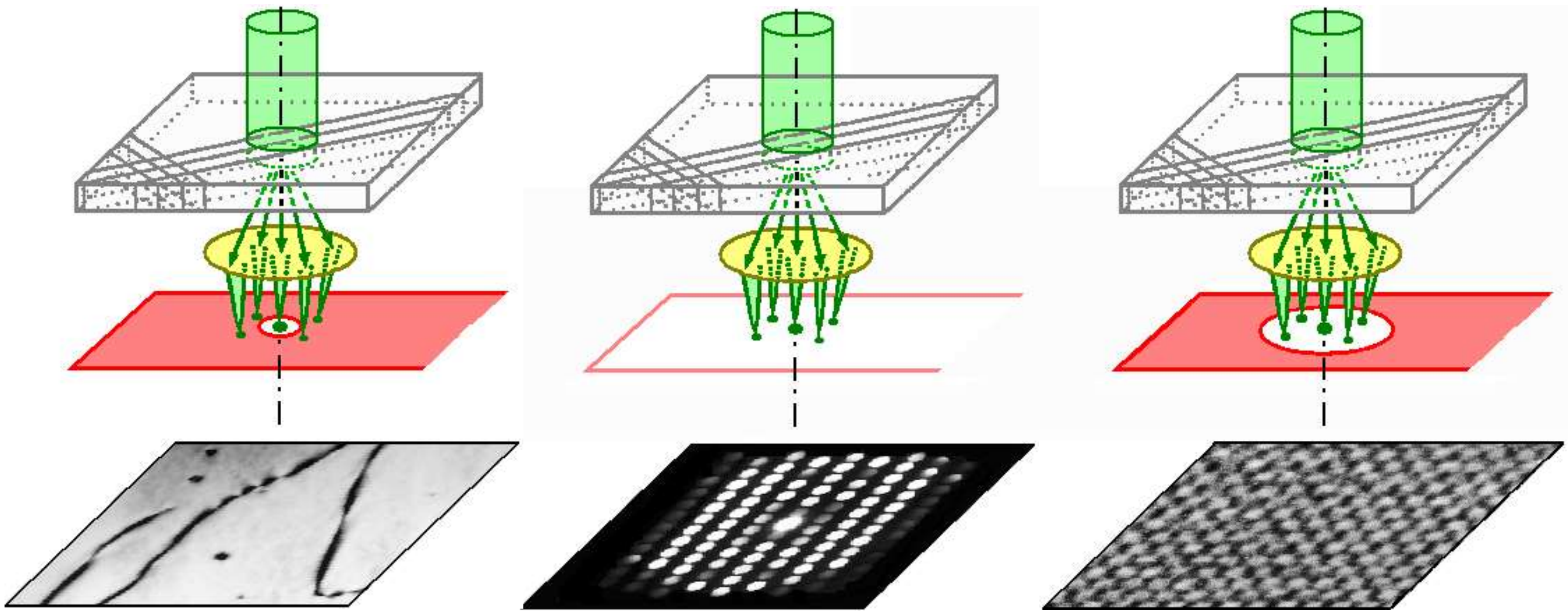
STEM-HAADF study of precipitates in an Al 6061 alloy

Context: precipitation in Al 6XXX alloys
Results 6061 alloy Al-Mg,Si,Cu: **treatments @ 200°C and 300°C**
(transformation QC → Q')

Summary

High Resolution Electron Microscopy

Conventional TEM | *Electron Diffraction* | *High Resolution TEM*

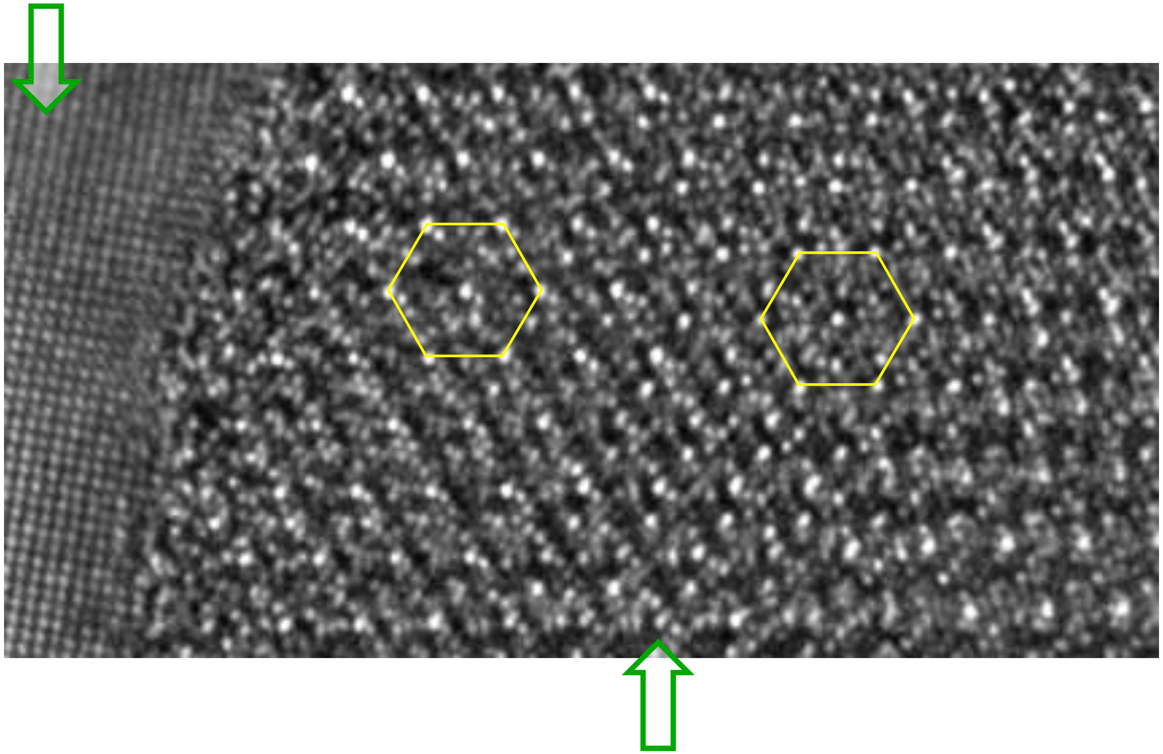


ABERRATIONs + partial coherence → blurring of lattice fringes
LOSS of RESOLUTION

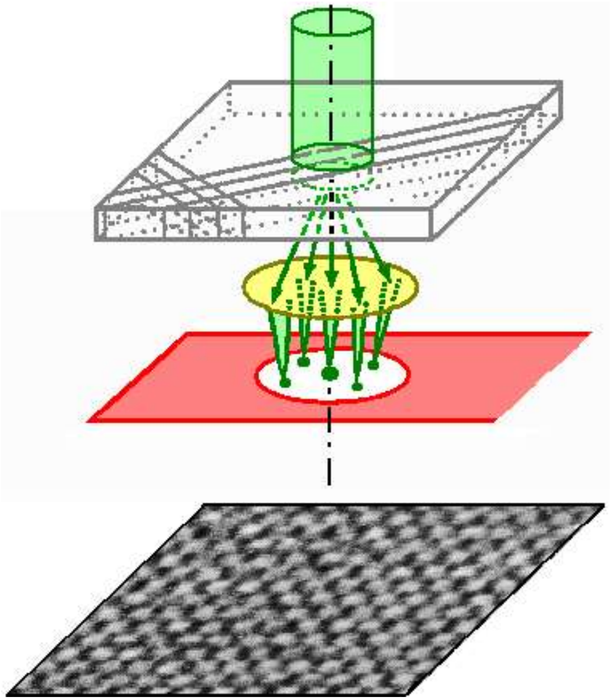
INTERFERENCES + dynamical scattering → phase shifts
POSITIONING of ATOMIC COLUMNS?

High Resolution Electron Microscopy

Al [001], f.c.c. $Fm\bar{3}m$: **a = 0.405 nm**



High Resolution TEM

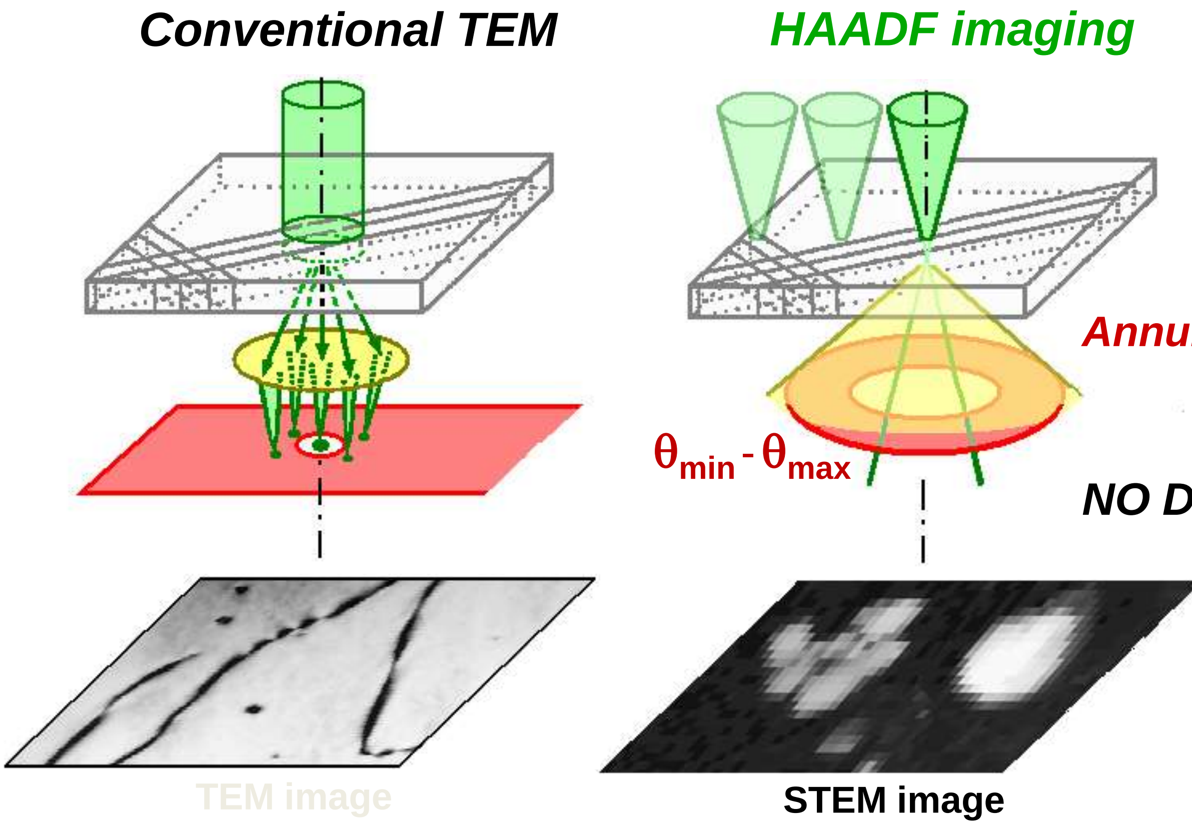


Q *(or λ)* **$Al_4Mg_8Si_7Cu_2$** [0001],

hexagonal P6: **a = 1.039 nm, c = 0.402 nm**

High Angle Annular Dark Field

***S**canning **T**ransmission **E**lectron **M**icroscopy*
***H**igh **A**ngle **A**nnular **D**ark **F**ield*



Annular detector → collection of INCOHERENT electrons scattered at high angle

NO DYNAMICAL SCATTERING

$$I_{HAADF}(q) \propto Z^2$$

or $I_{HAADF} \propto Z^{\alpha}$ with $\alpha \approx$ **1.6 – 2**

(collection angles θ_{min} - θ_{max})

[D.E. JESSON, S. PENNYCOOK, *Proc. Roy. Soc. London*, **A449**, (1995), 273-293]

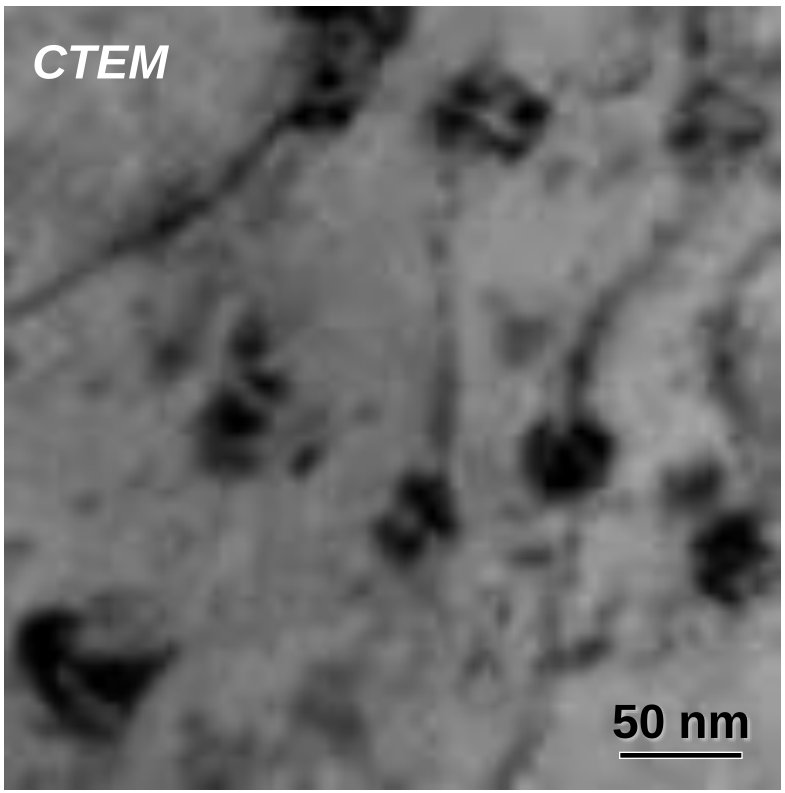
Illustration: Conventional TEM vs. STEM-HAADF

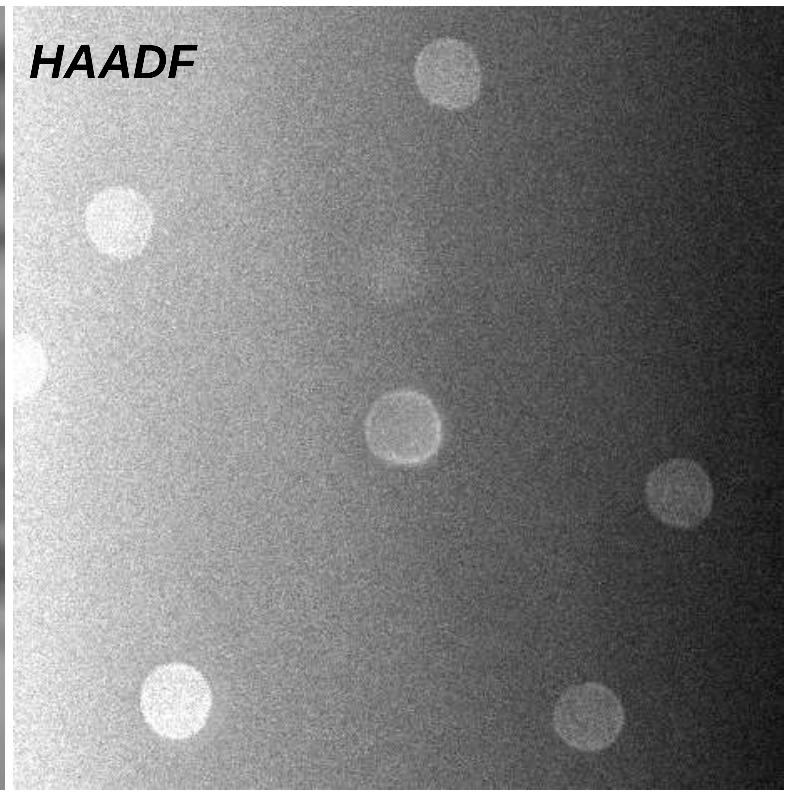
JEOL 2010F *200 kV*

$Al_3(Zr,Sc)$ $L1_2$ precipitates in Al

[T. EPICIER, *Adv. Eng. Mater.* **8**, (2006), 12,

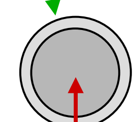
E. CLOUET (T. EPICIER, W. LEFEBVRE) et al., *Nature Materials* **5**, (2006), 482-488]





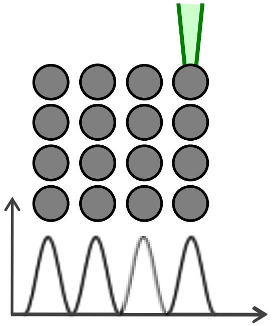
$I_{HAADF}(q) \propto Z^2$

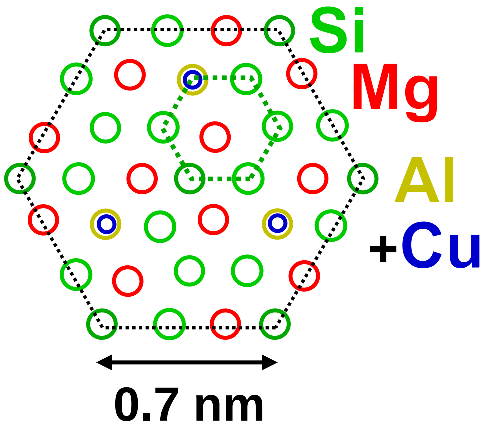
Zr-rich SHELL (Z_{Zr} = 40)



Sc-rich CORE (Z_{Sc} = 21)

STEM-HAADF at the ATOMIC LEVEL





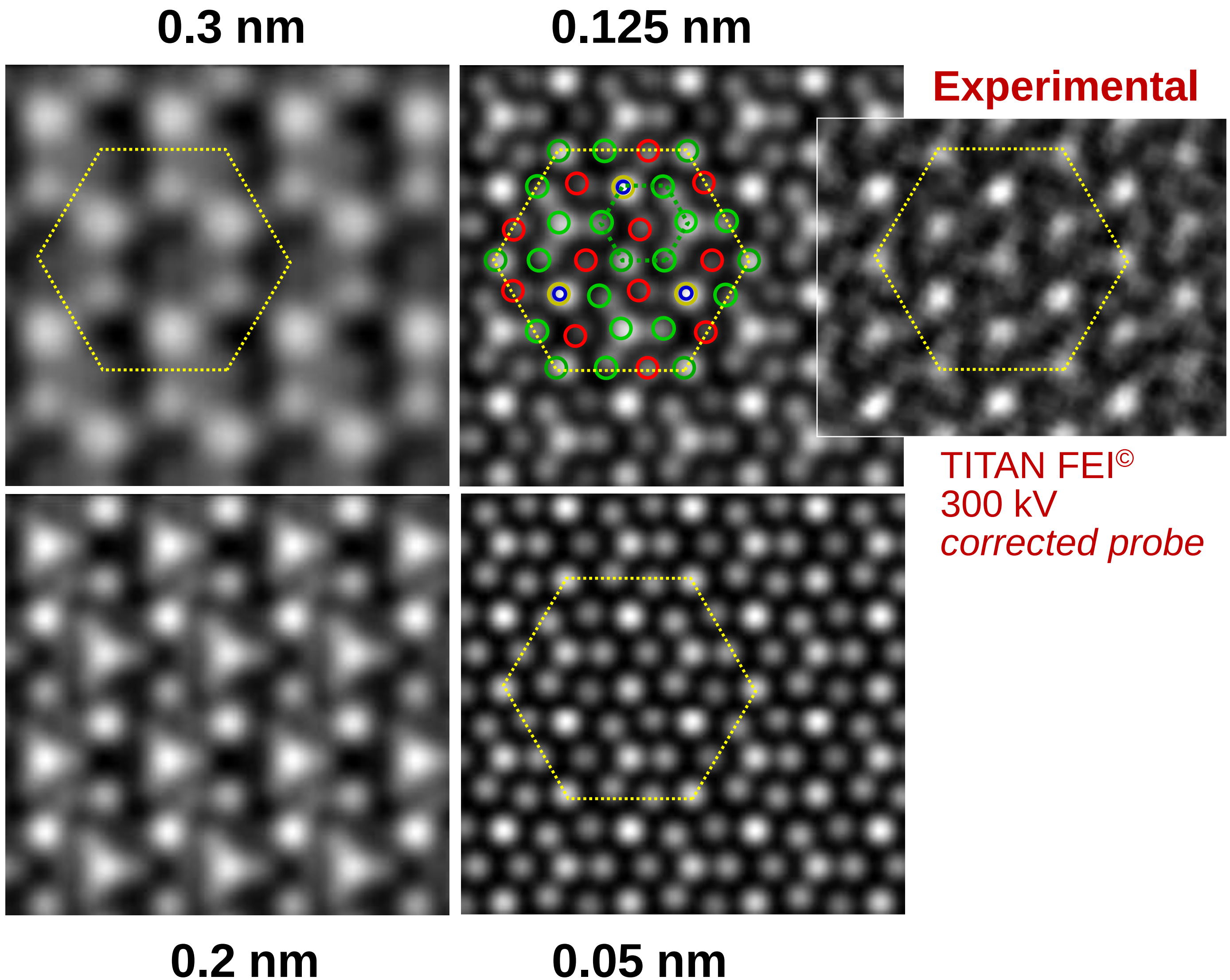
β' hexagonal P$\bar{6}$2m

a = 0.71 nm,

c = 0.405 nm

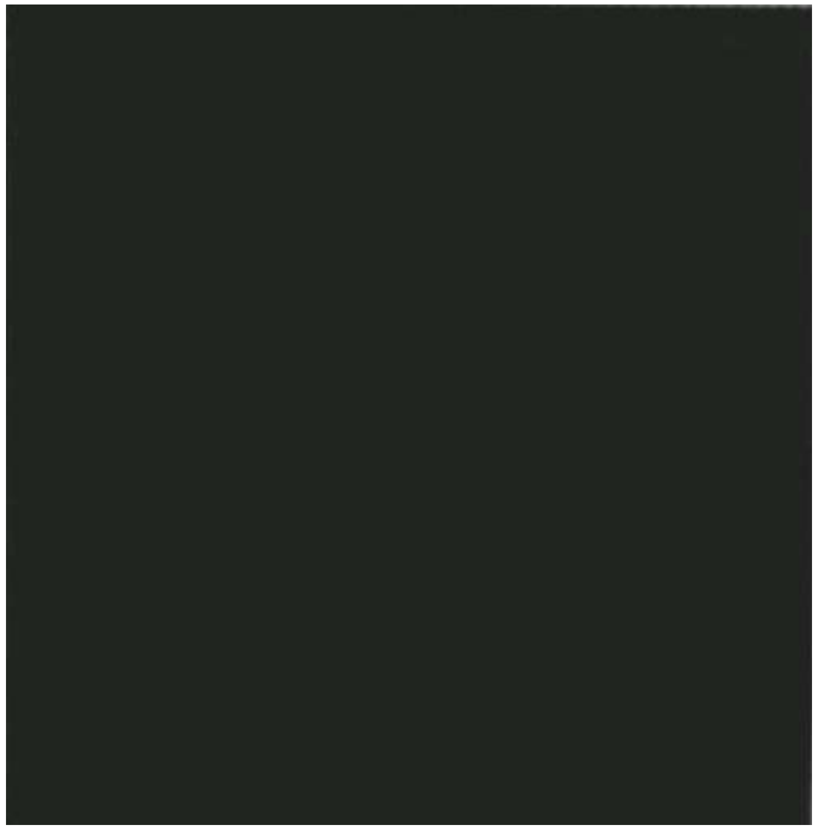
[C. CAYRON, P.A. BUFFAT, *Acta Mater.*, **48**, (2000), 2639]

[0001] // $[001]_{Al}$



TITAN FEI©
300 kV
corrected probe

STEM-HAADF at the ATOMIC LEVEL

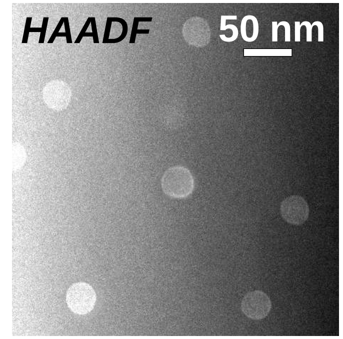


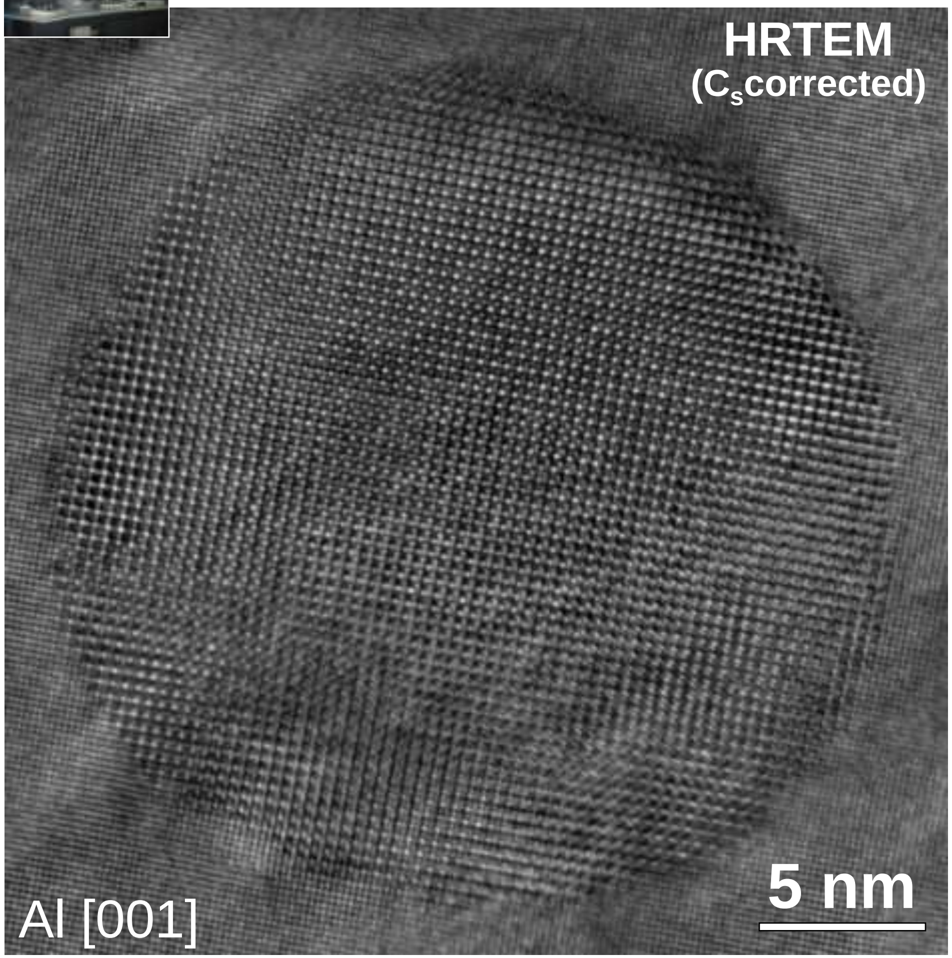
Q *(or λ)* **$Al_4Mg_8Si_7Cu_2$**

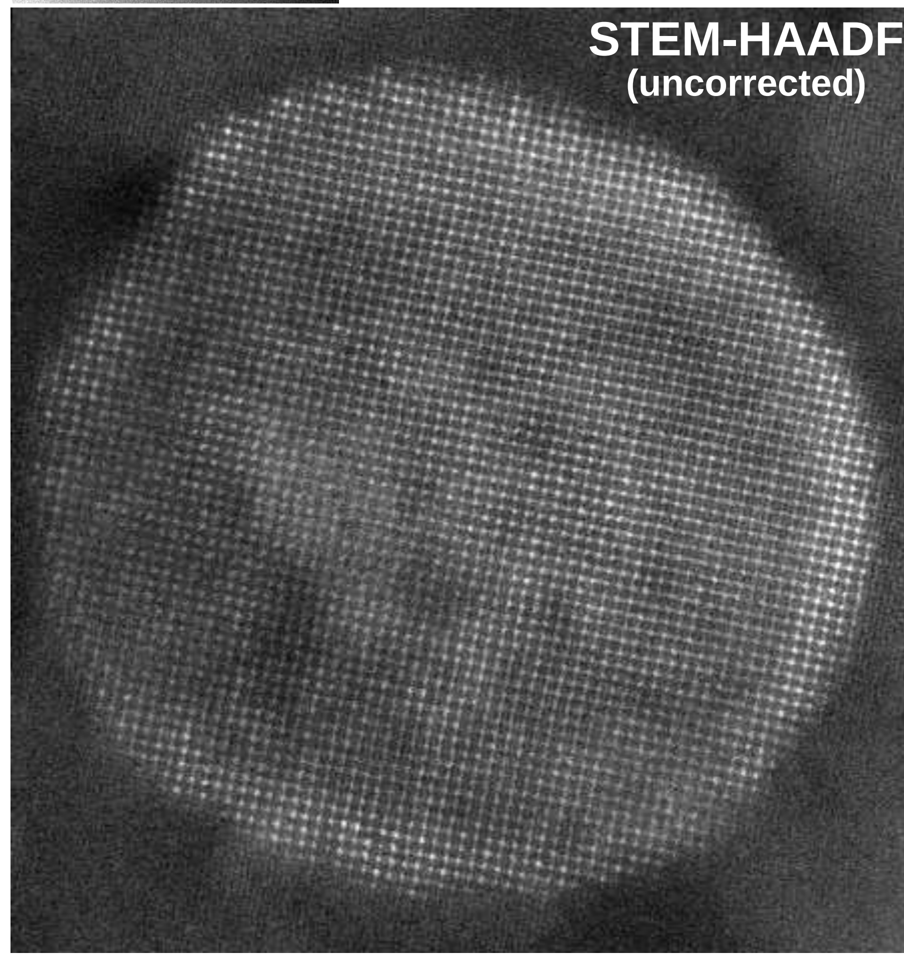
hexagonal P6: **a = 1.039 nm, c = 0.402 nm**

FEI TITAN *300 kV*

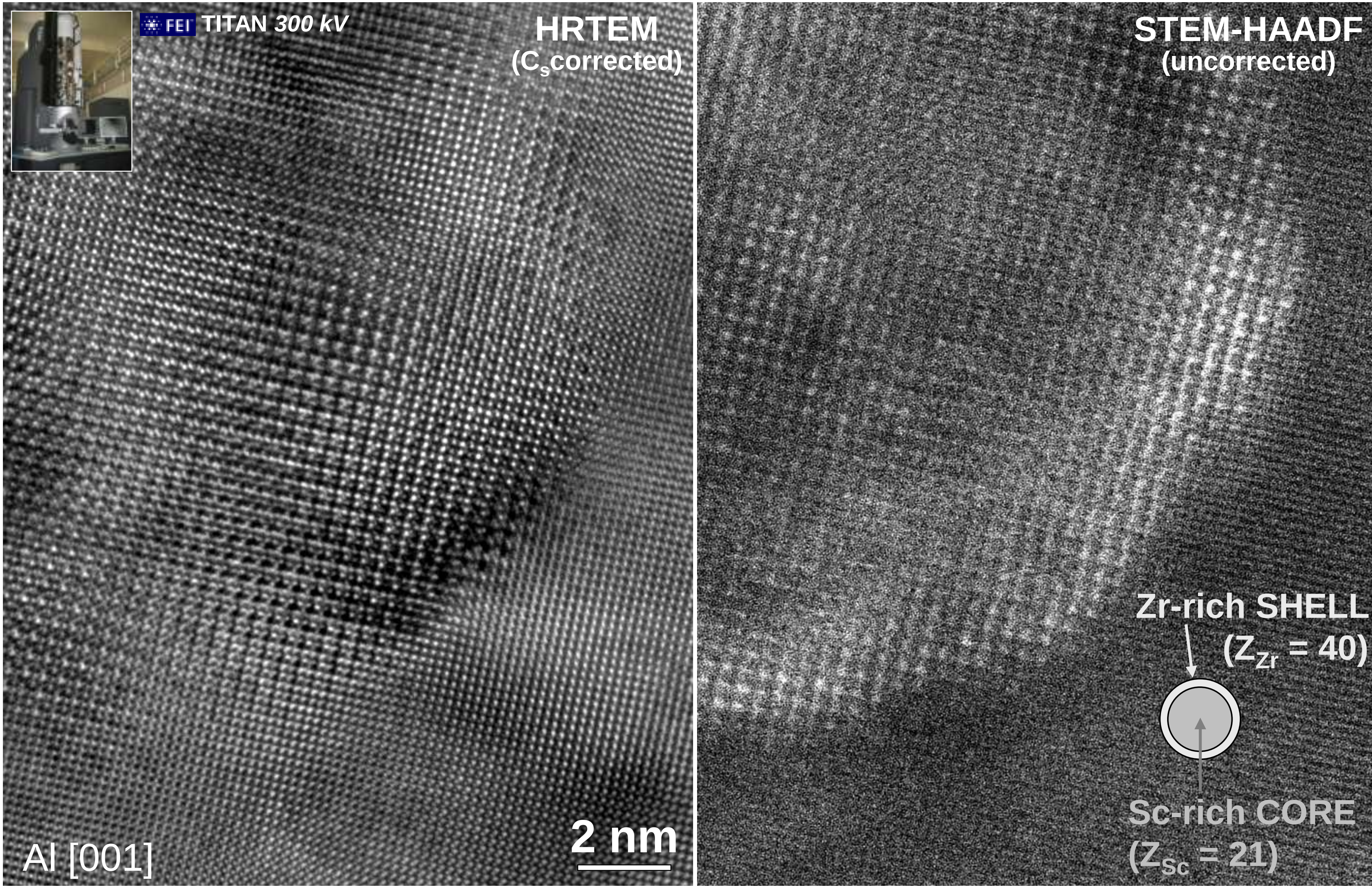
High Resolution TEM vs. *atomic HAADF*





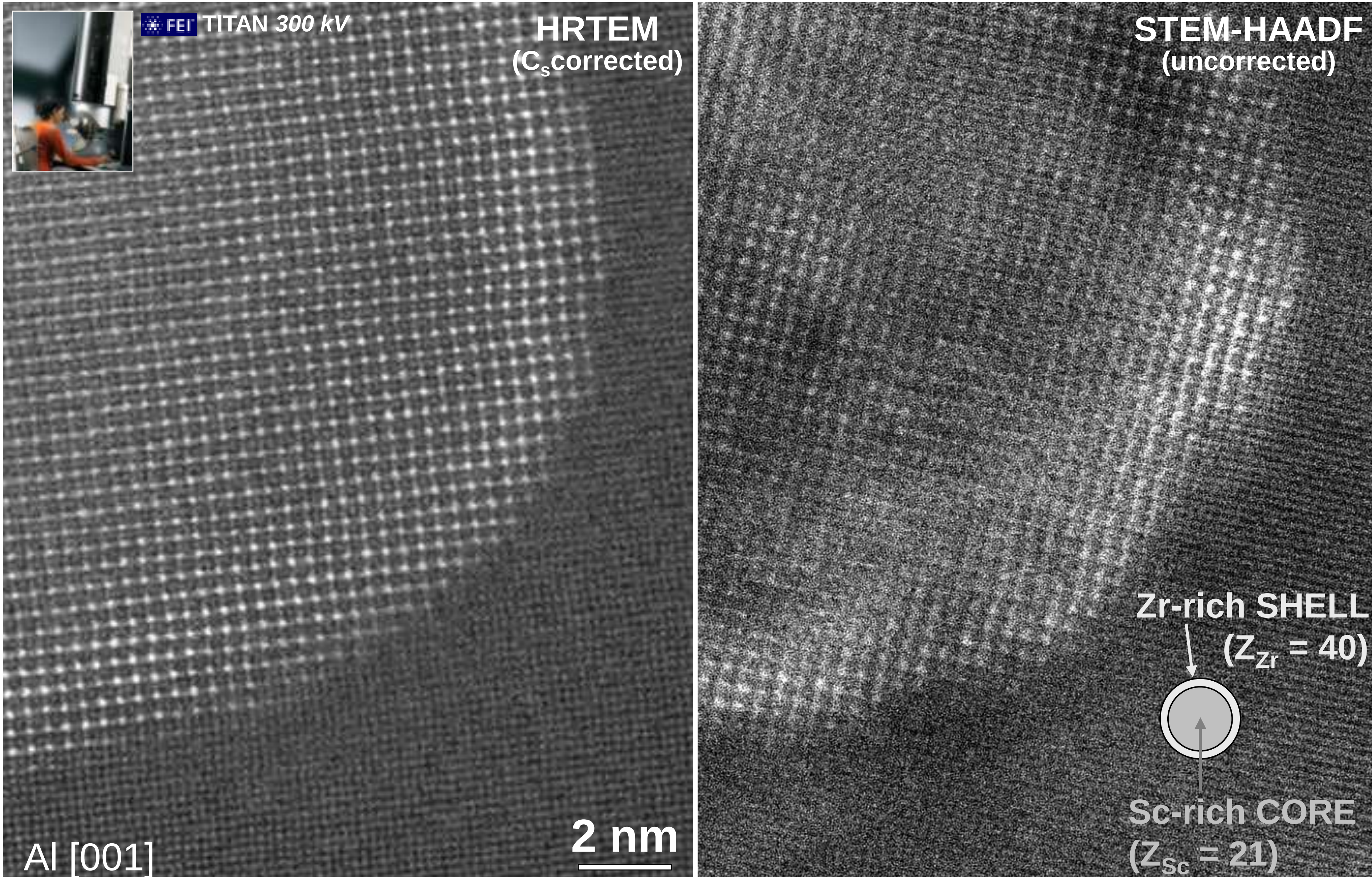


$Al_3(Zr,Sc)$ $L1_2$ precipitates in Al [T. EPICIER, K. SATO, T. KONNO, *unpublished*, (2009)]



FEI TITAN 300 kV
HRTEM
(C_s corrected)
Al [001]
2 nm
STEM-HAADF
(uncorrected)
Zr-rich SHELL
(Z_{Zr} = 40)
Sc-rich CORE
(Z_{Sc} = 21)

300 kV, FEI Titan (STEM-HAADF, corrected probe, *FWHM* ≈ 1 Å), *CEA-Grenoble, Minatec*



The precipitation sequence in Al 6XXX alloys

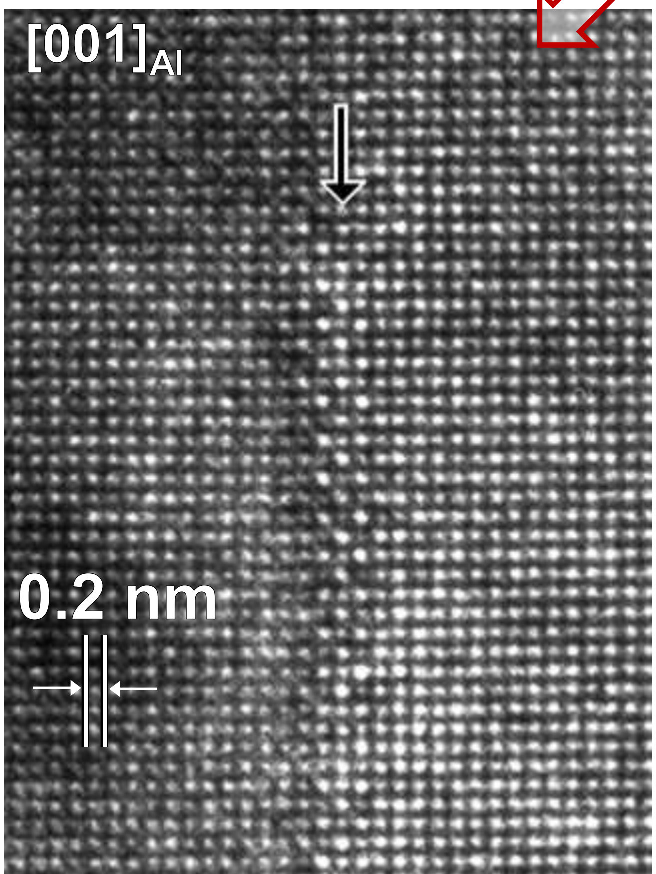
[M. MURAYAMA et al., *Mater. Sci. Eng.*, **A250** (1998), 127]

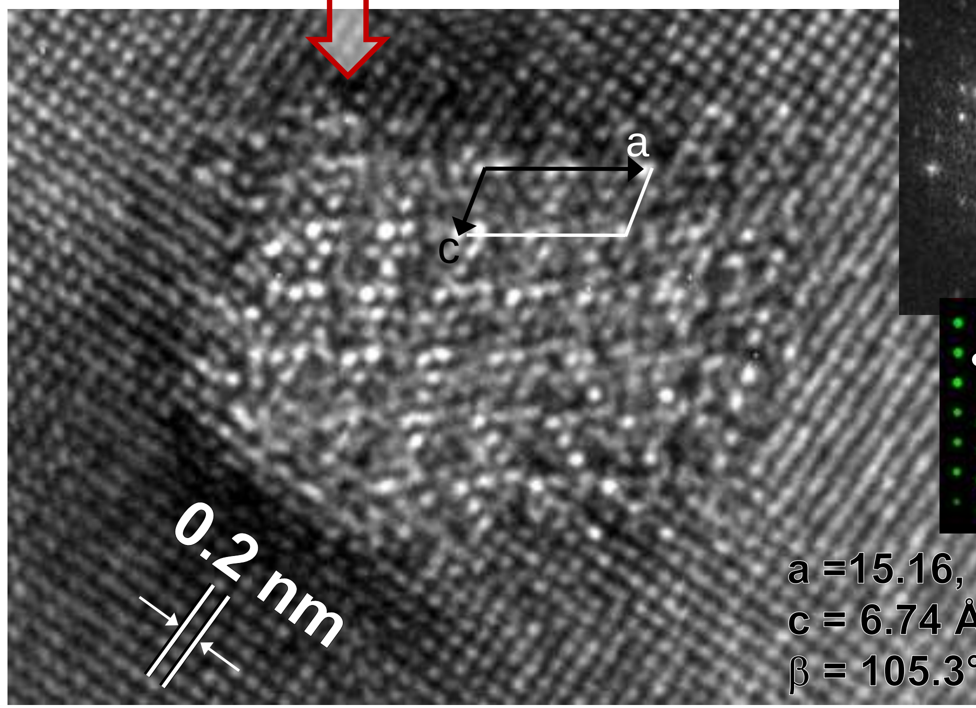
◆ **metastable precipitation sequence**

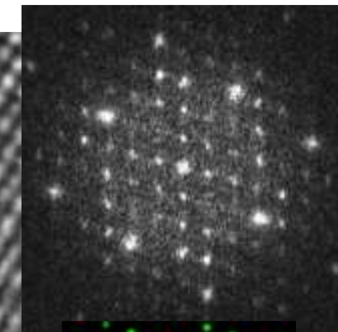
Pseudo binary alloy Al-Mg_2Si

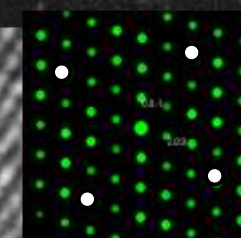
Mg: 0.83, Si: 0.59, Cu: 0.002 (wt. %)

SuperSaturated Sol. Sol. → clusters → **GP zones** *(type I)* → needles β'' **(monoclinic)** → rods β' **(hexagonal)** → precipitates **β-Mg_2Si** **(cubic)**







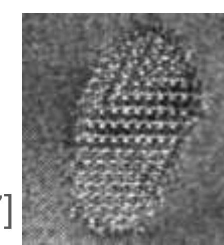


a =15.16, b = 4.05, c = 6.74 Å β = 105.3° (C2/m)

[S.J. ANDERSEN et al., *Acta Mater.* **46** 9 (1998), 3283, H.K. HASTING et al., *Surf. Interface Anal.* **39** (2007), 189]

Other crystallographic forms

[K. MATSUDA et al., *J. Mater. Sci.* **35** (2000), 179]
[S.J. ANDERSEN et al., *Mat. Sci. & Eng.* **A444** (2007), 157]



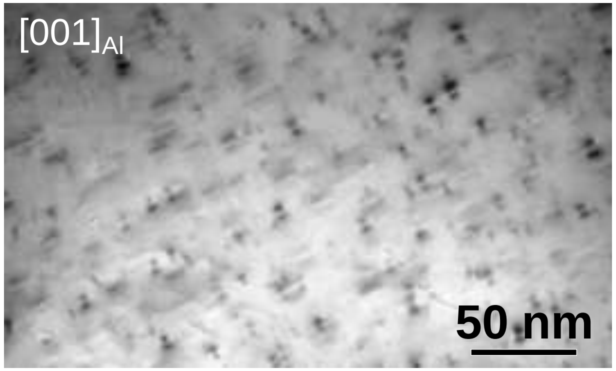
The precipitation sequence in Al 6XXX alloys

- **metastable precipitation sequence**

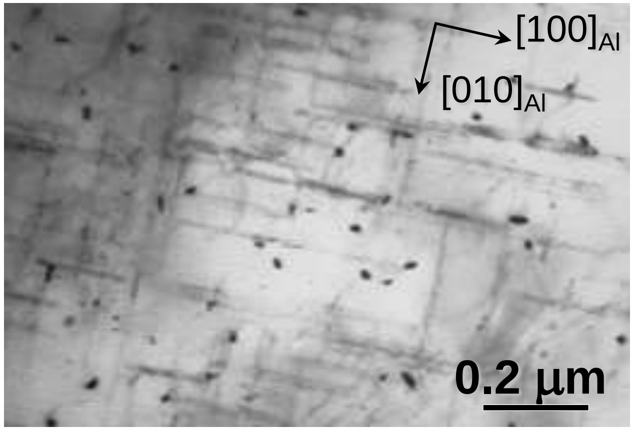
Pseudo binary alloy Al-Mg_2Si
Mg: 0.83, Si: 0.59, Cu: 0.002 (wt. %)

→ needles **β"** **(monoclinic)** → rods **β'** **(hexagonal)** → precipitates **β-Mg_2Si** **(cubic)**

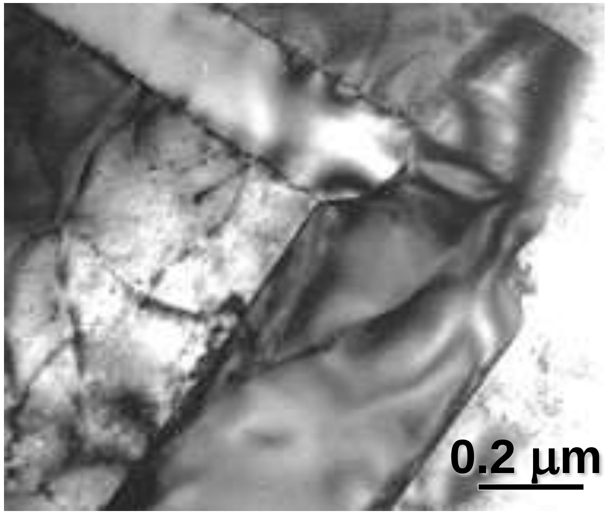
15', 200°C



5', 300°C



2 weeks, 300°C



- **influence of a small Cu addition**

e.g. [MASSARDIER V., EPICIER T., *Mat. Sci. Forum*, **396-402**, (2002), 851-856]

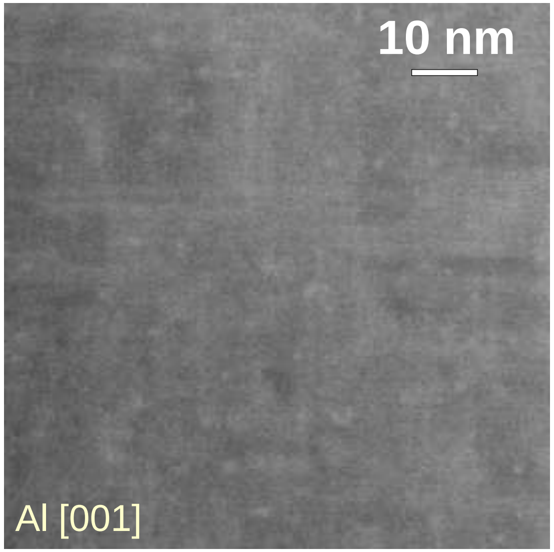
6061 alloy Al-Mg,Si,Cu
Mg: 1.0, Si: 0.6, Cu: 0.25 (wt. %)

needles **β"** **(monoclinic)** ⇢ rods β' (hexagonal) ⇢ precipitates **β-Mg_2Si** **(cubic)**

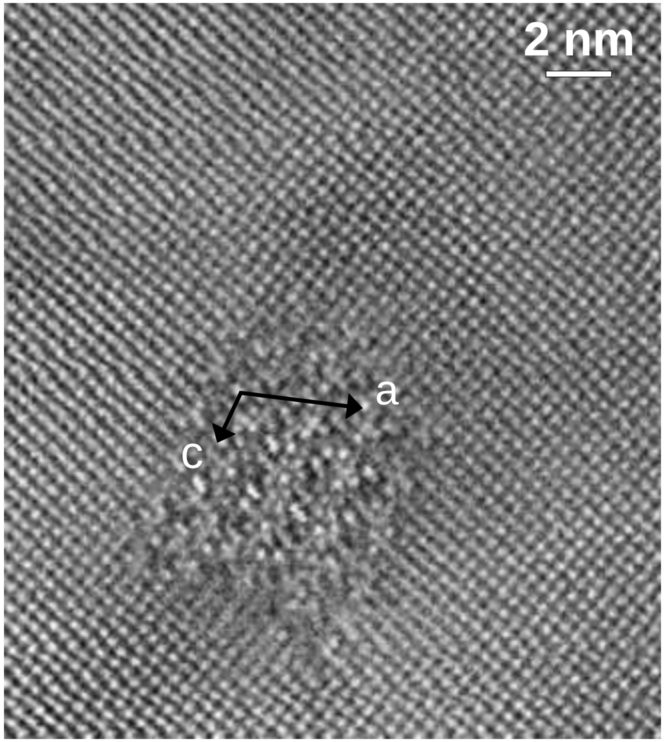
needles β" (monoclinic) → **QP** *(β'_0)* **(hexagonal)** → **QC** *(β'_I)* **(hexagonal)** → **Q'** *(λ', β'_{II})* **(hexagonal)** ⇢ precipitates β-Mg_2Si (cubic)

6061 alloy Al-Mg,Si,Cu: treatments @ 200°C

20' @ 200°C



HAADF

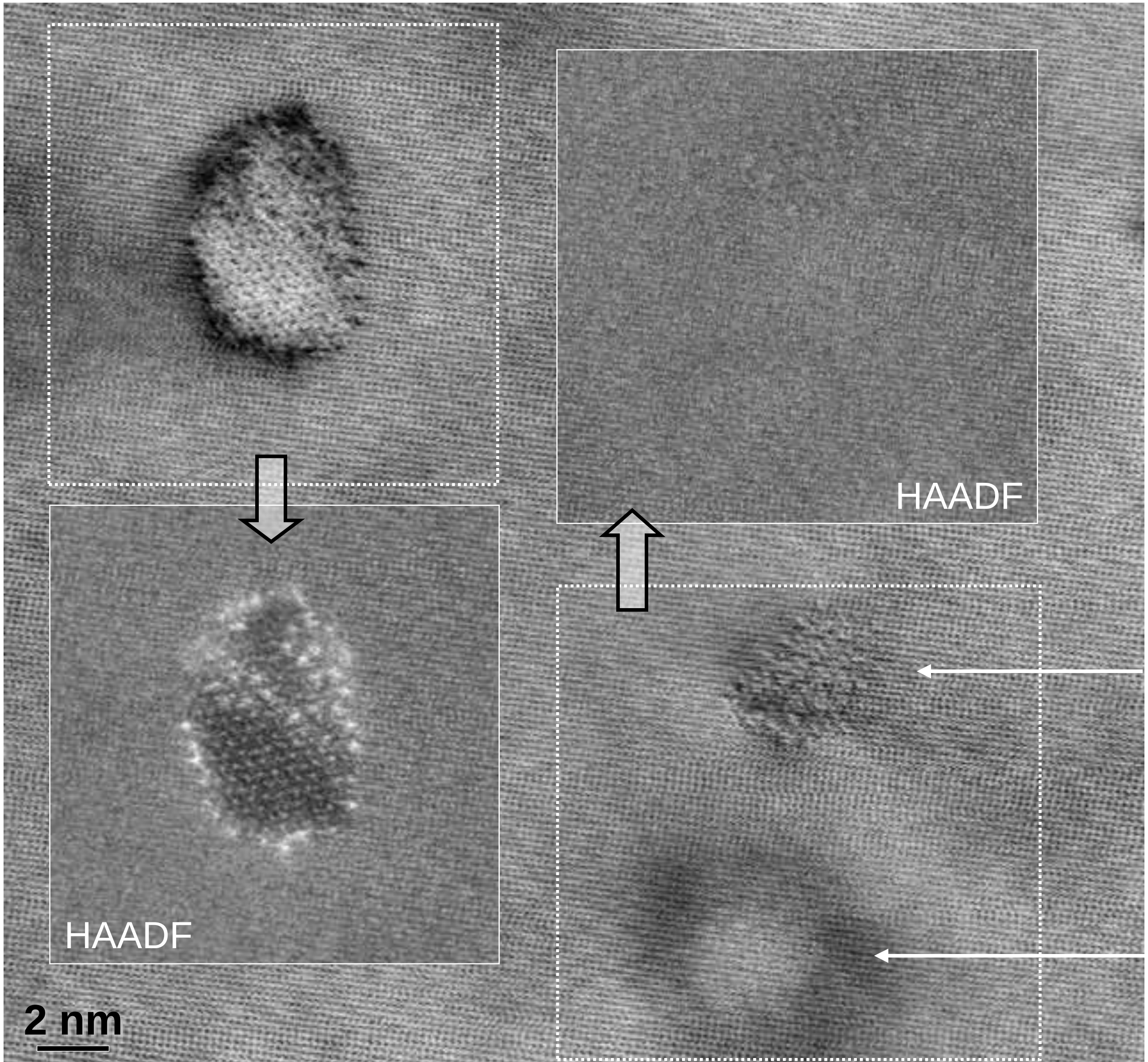


ordered β"
monoclinic phase

disordered *pre-β"*
contains Cu

STEM-BF

24 hrs @ 200°C



β'$_I$ (QC)
contains Cu

ordered (?) **β''**
no (few) ***Cu?***

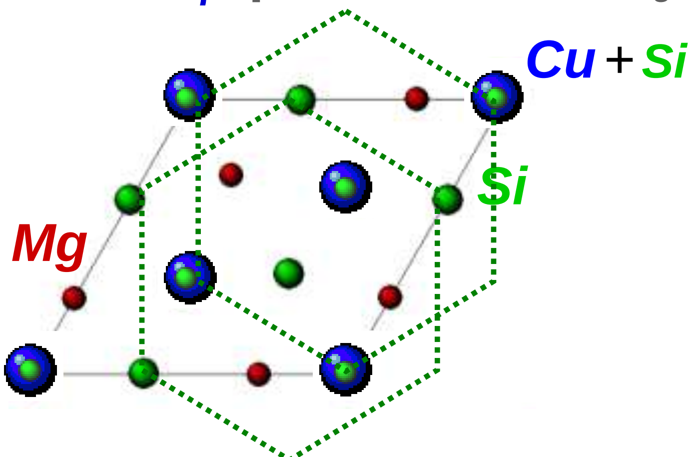
cluster
(pre-β''?)
no Cu

◆ the QC (β'_I) and the Q' (β'_{II}, λ') phase

hexagonal $P\bar{6}2m$:

a = 0.705 nm (< *0.7 nm with Cu*), c = 0.405 nm

based on **β'** [JACOBS M.H., *Phil. Mag.* **26** (1972), 1]



[CAYRON C., BUFFAT P., *Acta Mater.*, **48**, (2000), 2639-2653]

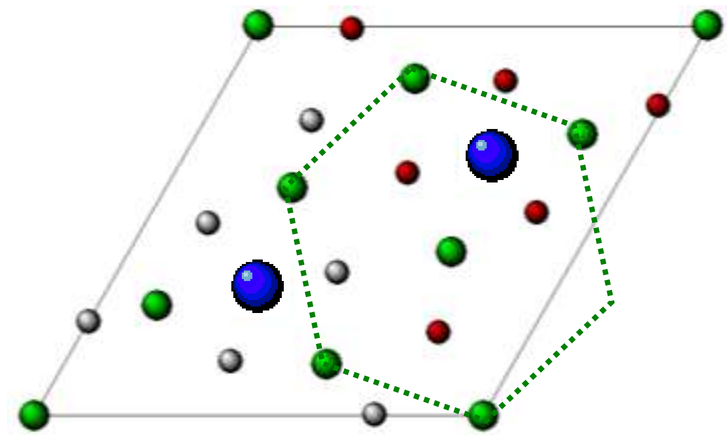
$Mg_{0.342}Si_{0.580}Cu_{0.079}$
(EDX measurements)

[MASSARDIER V., EPICIER T., *Mat. Sci. Forum*, **396-402**, (2002), 851-856]

Mg: 0.28, 0, 1/2, *1*
Si: 0, 0, 0, *0.39*
Cu: 0, 0, 0, *0.39*
Si: 0.36, 0.36, 0, *1*
Si: 1/3, 2/3, 1/2, *0.85*
Cu: 1/3, 2/3, 1/2, *0.15*

Q *(or λ)* **$Al_4Mg_8Si_7Cu_2$**

hexagonal $P\bar{6}$: **a = 1.039 nm, c = 0.402 nm**

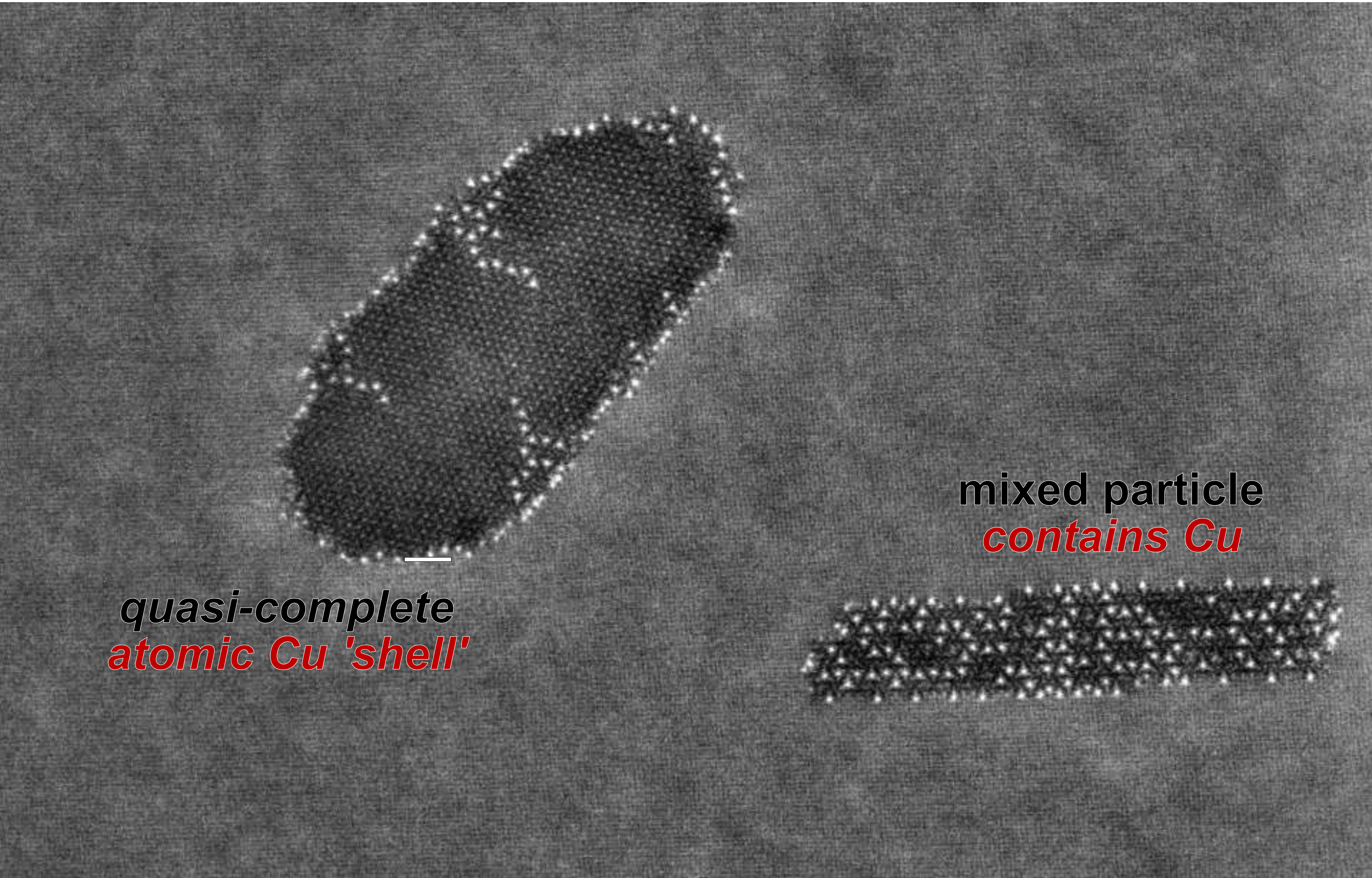


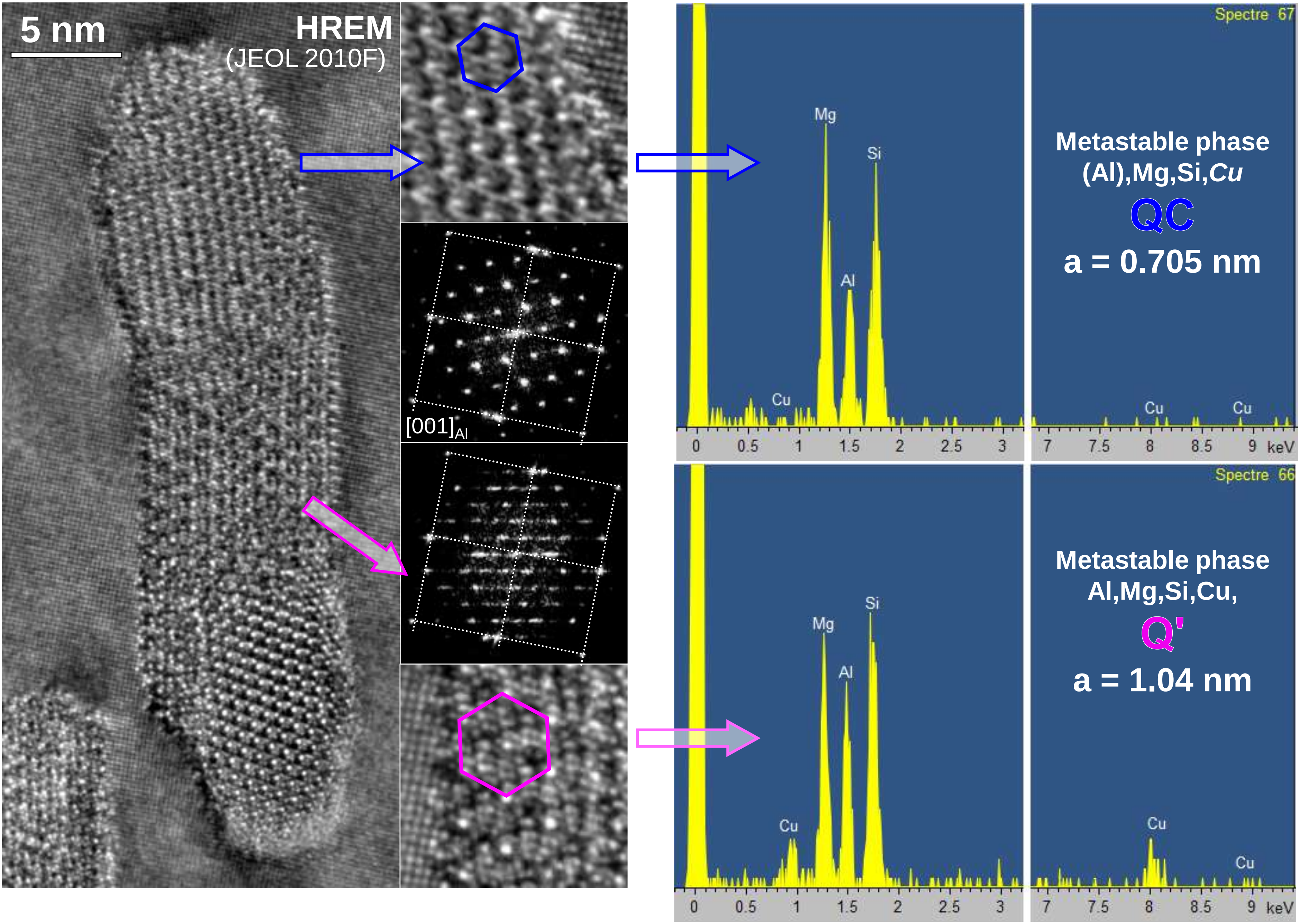
[ARNBERG L., AURIVILLIUS B., *Acta Chem. Scand.*, **A34**,(1980), 1-5]

$Al_{0.191}Mg_{0.381}Si_{0.333}Cu_{0.095}$

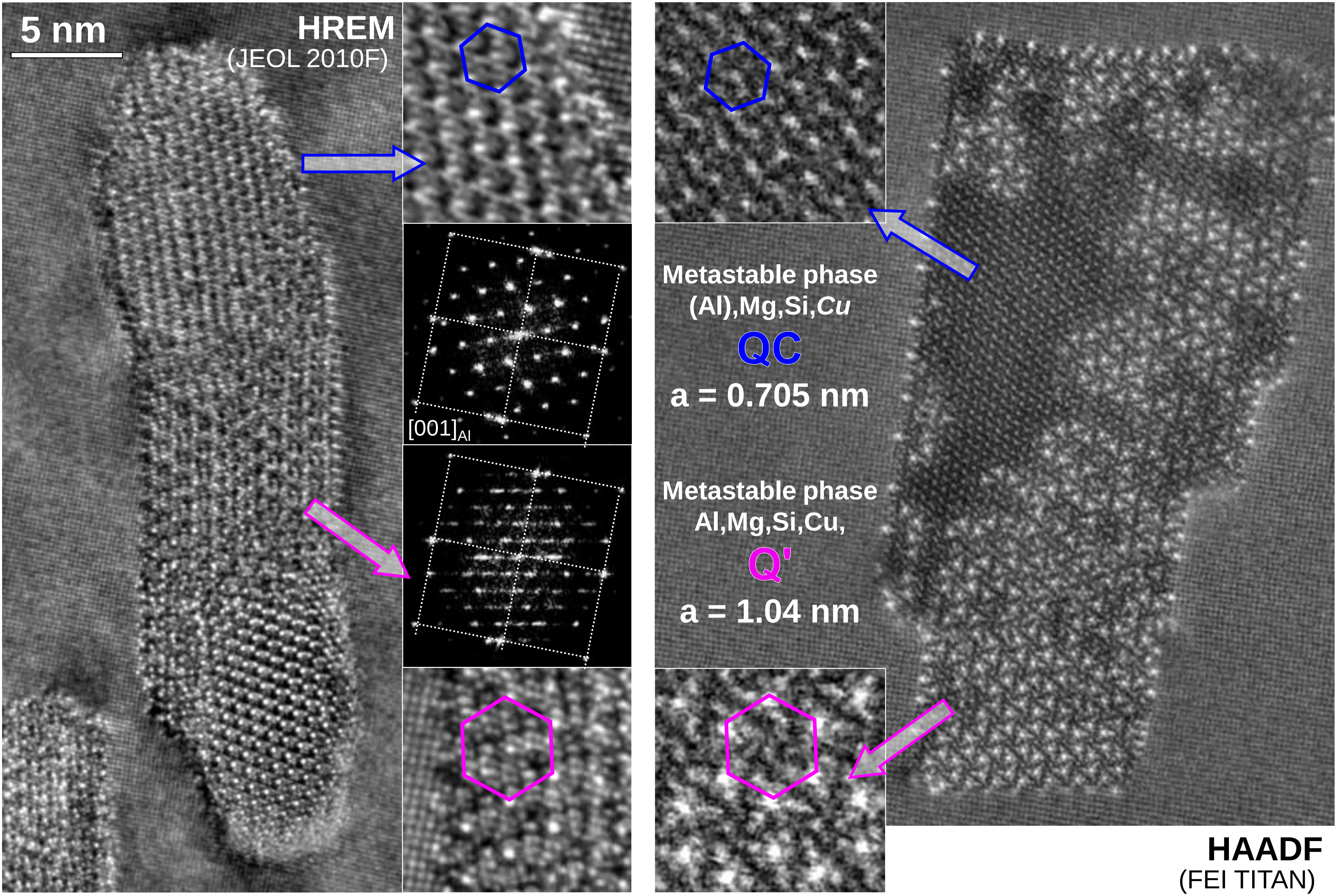
(Al,Mg): 0.2425, 0.002, 0
(Al,Mg): 0.6332, 0.1405, 0
(Al,Mg): 0.7878, -0.0080,1/2
(Al,Mg): 0.3790, 0.8587 ,1/2
Si_1: 0, 0, 0
Si_2: 0.5822, 0.8621, 0
Si_3: 0.4156, 0.1325, 1/2
Cu_1: 1/3, 2/3, 0
Cu_2: 2/3, 1/3, 1/2

6061 alloy Al-Mg,Si,Cu: 5' @ 300°C

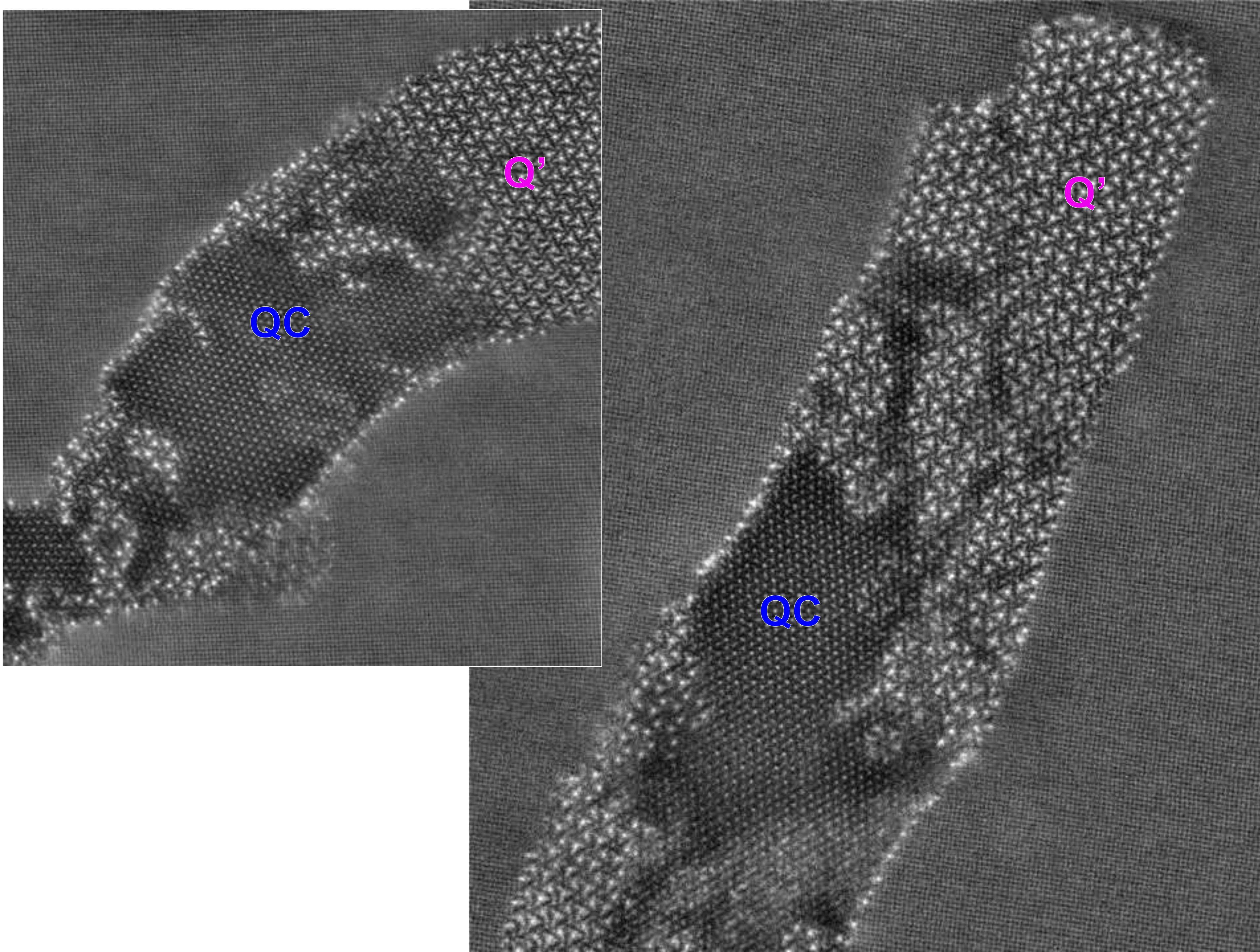




5 nm
HREM
(JEOL 2010F)
[001]Al
Mg
Si
Al
Cu
0
0.5
1
1.5
2
2.5
3
7
7.5
8
8.5
9
keV
Spectre 67
Metastable phase
(Al),Mg,Si,Cu
QC
a = 0.705 nm
Spectre 66
Metastable phase
Al,Mg,Si,Cu,
Q'
a = 1.04 nm

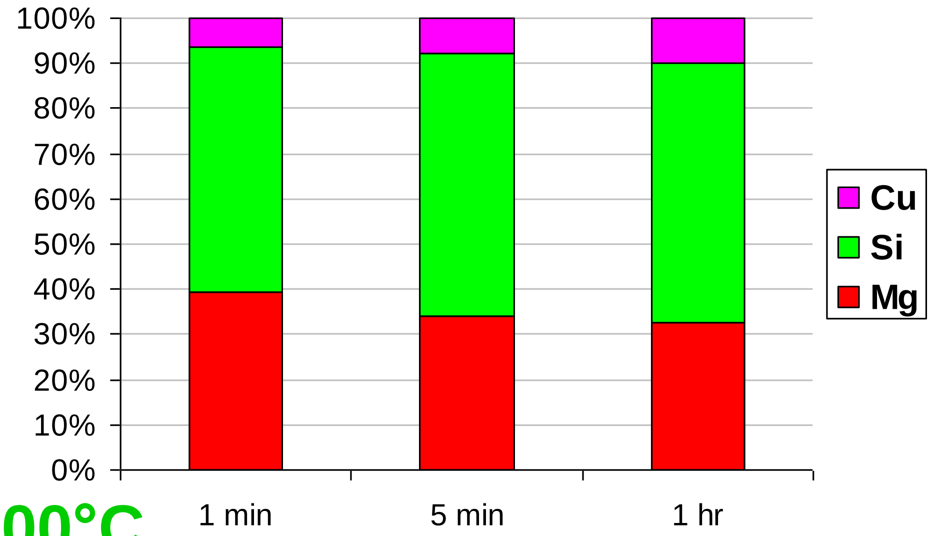


5 nm
HREM
(JEOL 2010F)
[001]Al
Metastable phase
(Al),Mg,Si,Cu
QC
a = 0.705 nm
Metastable phase
Al,Mg,Si,Cu,
Q'
a = 1.04 nm
HAADF
(FEI TITAN)


Q'
QC
Q'
QC

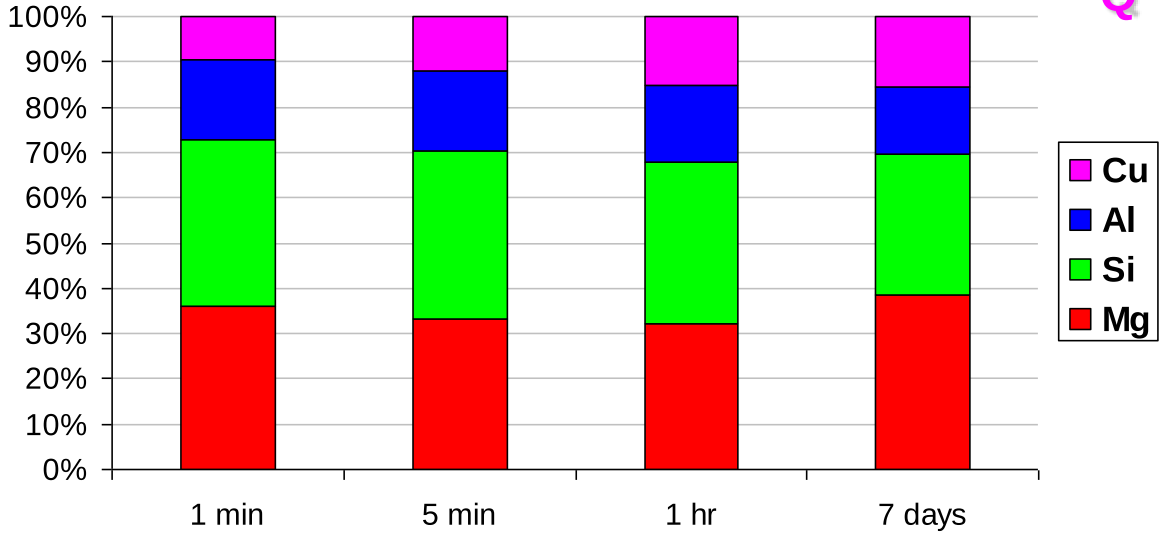
EDX Chemical analysis [MASSARDIER V., EPICIER T., *Mat. Sci. Forum*, **396-402**, (2002), 851-856]

QC

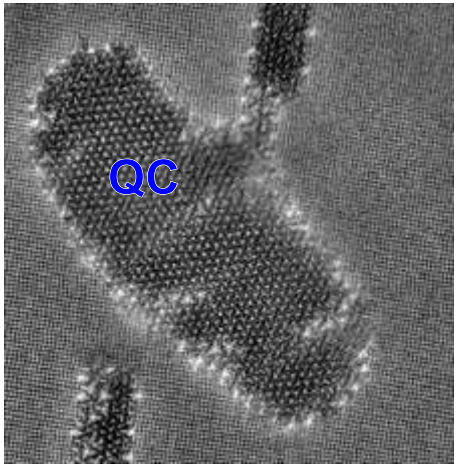


@ 300°C

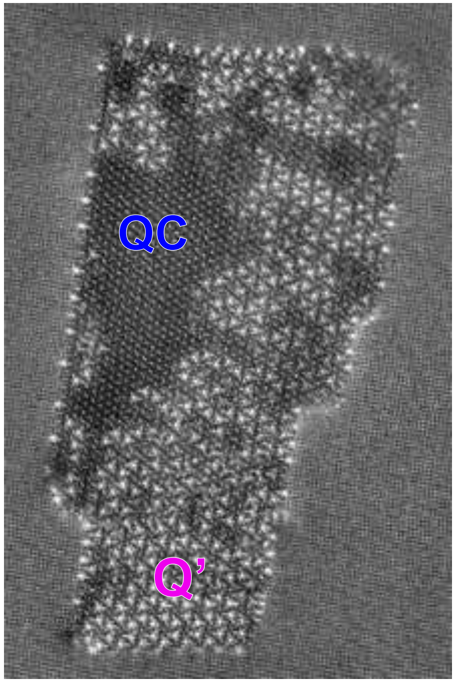
Q'

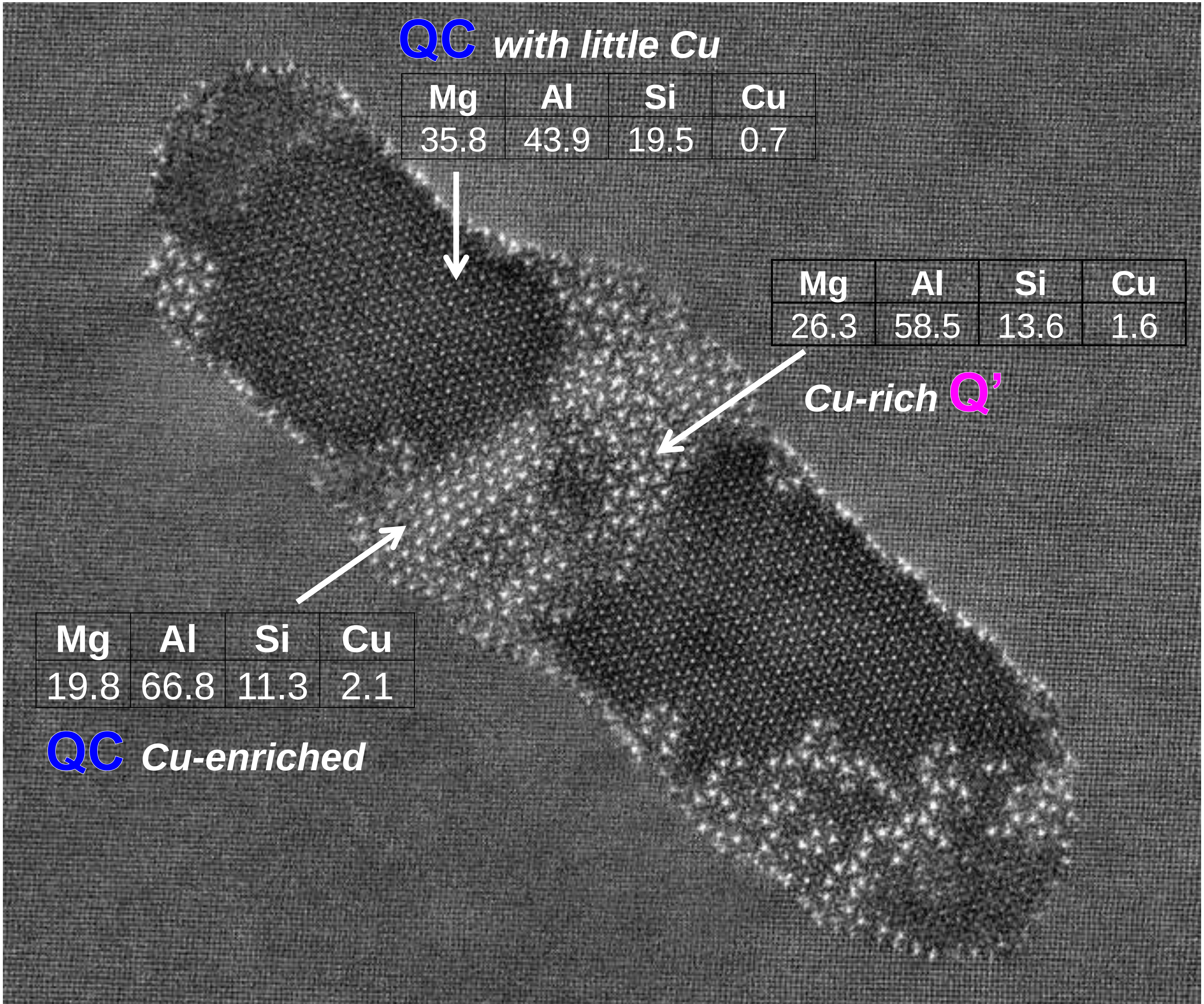


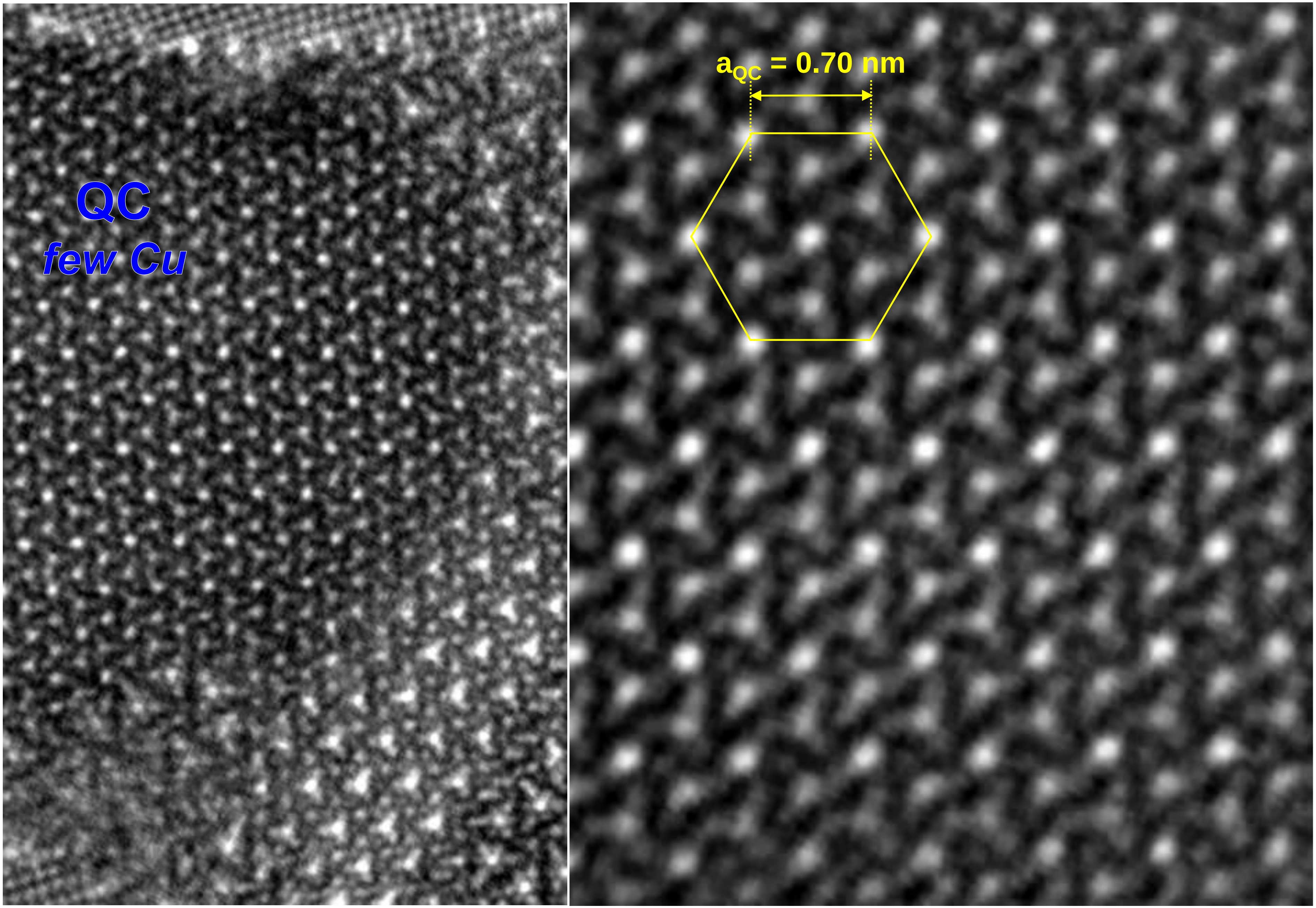
QC
+ *Cu "shell"*

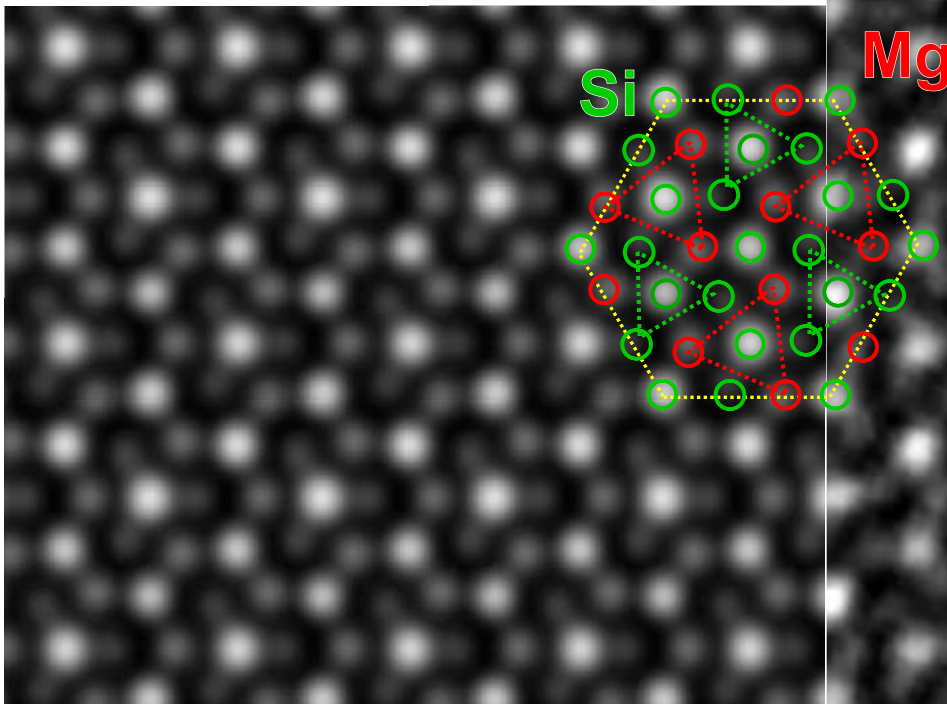


Cu-enriched QC
transformed into
Q'

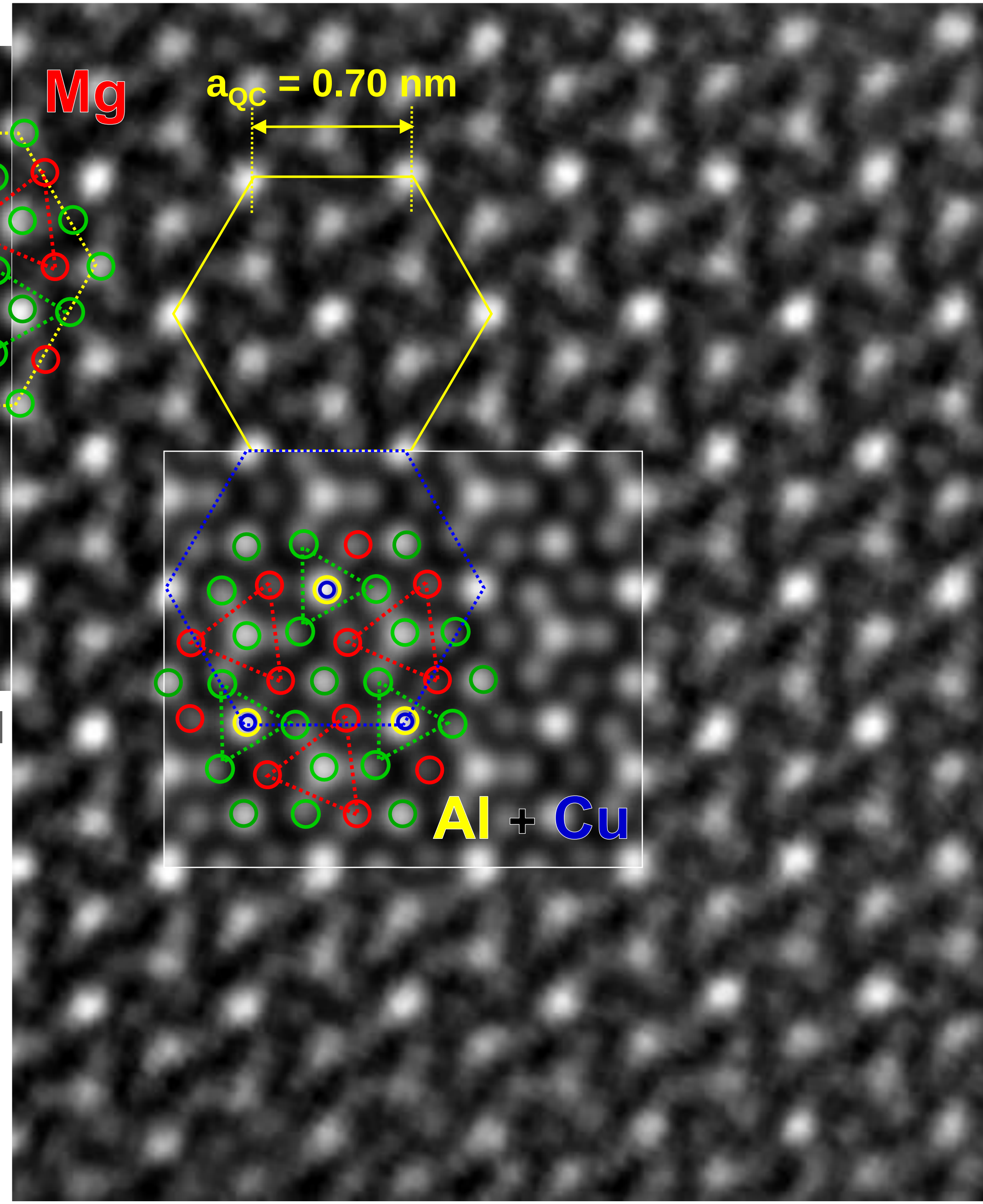



QC with little Cu
Mg Al Si Cu
35.8 43.9 19.5 0.7
Mg Al Si Cu
26.3 58.5 13.6 1.6
Cu-rich Q'
Mg Al Si Cu
19.8 66.8 11.3 2.1
QC Cu-enriched


QC
few Cu
a_{QC} = 0.70 nm



QC [CAYRON C., BUFFAT P., *Acta Mater* (2000)]



t ≈ *10 nm*

EDX

Mg	Al	Si	Cu
35.8	43.9	19.5	0.7

small amount of ordered Cu…

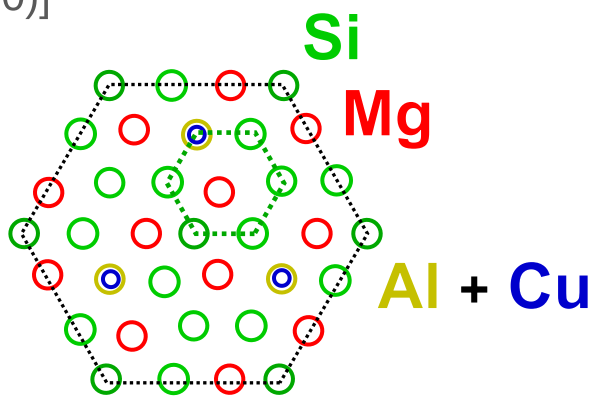
Mg	Al	Si	Cu
30.5	47.2	21.5	0.7

***QSTEM* simulations**

[KOCH CT., *PhD thesis*, ASU-USA, (2002)]

QC

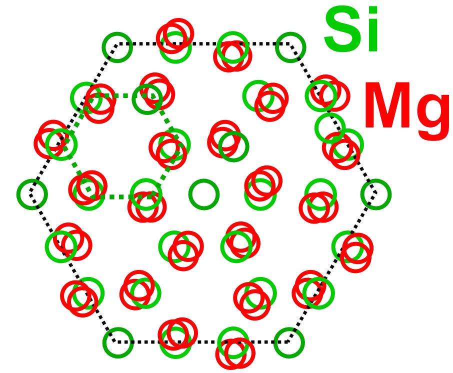
[C. CAYRON C., P. BUFFAT, *Acta Mater* (2000)]



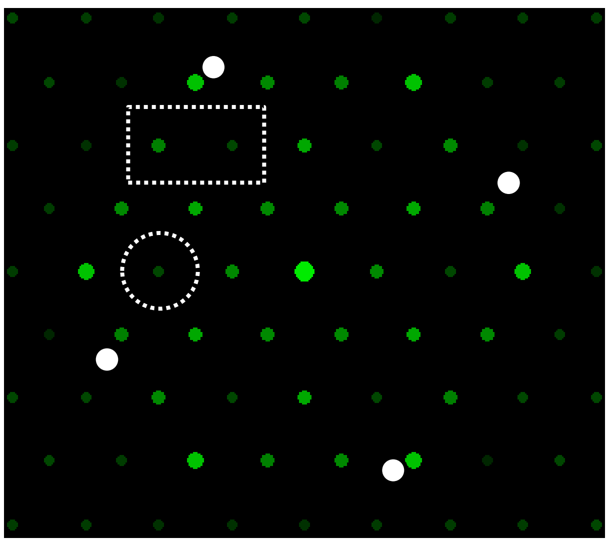
β' Mg_9Si_5 (disordered)

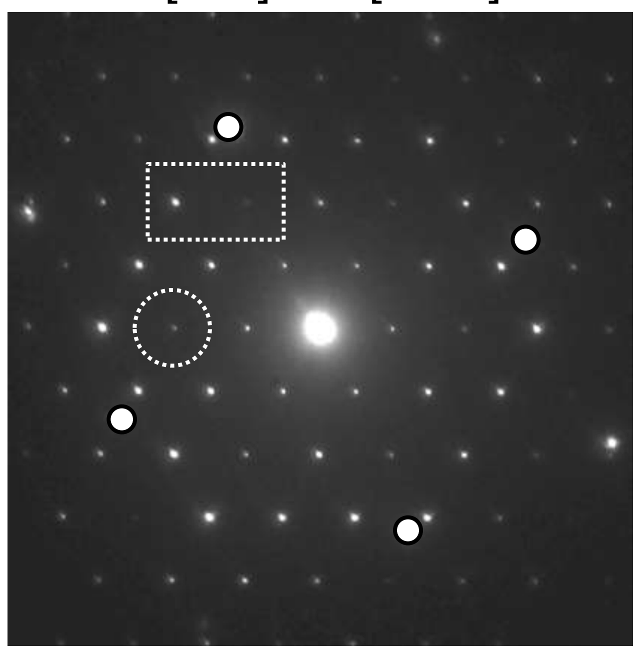
hexagonal P63/m, a = 0.705 nm, c = 0.405 nm

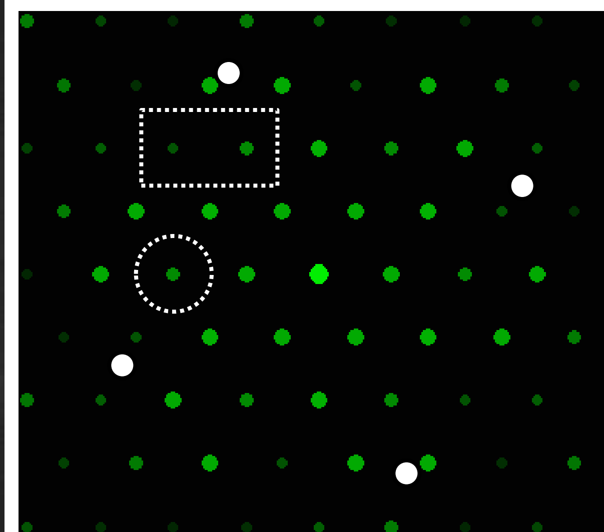
[R. VISSERS et al., *Acta Materialia*, **55** (2007), 3815–3823]

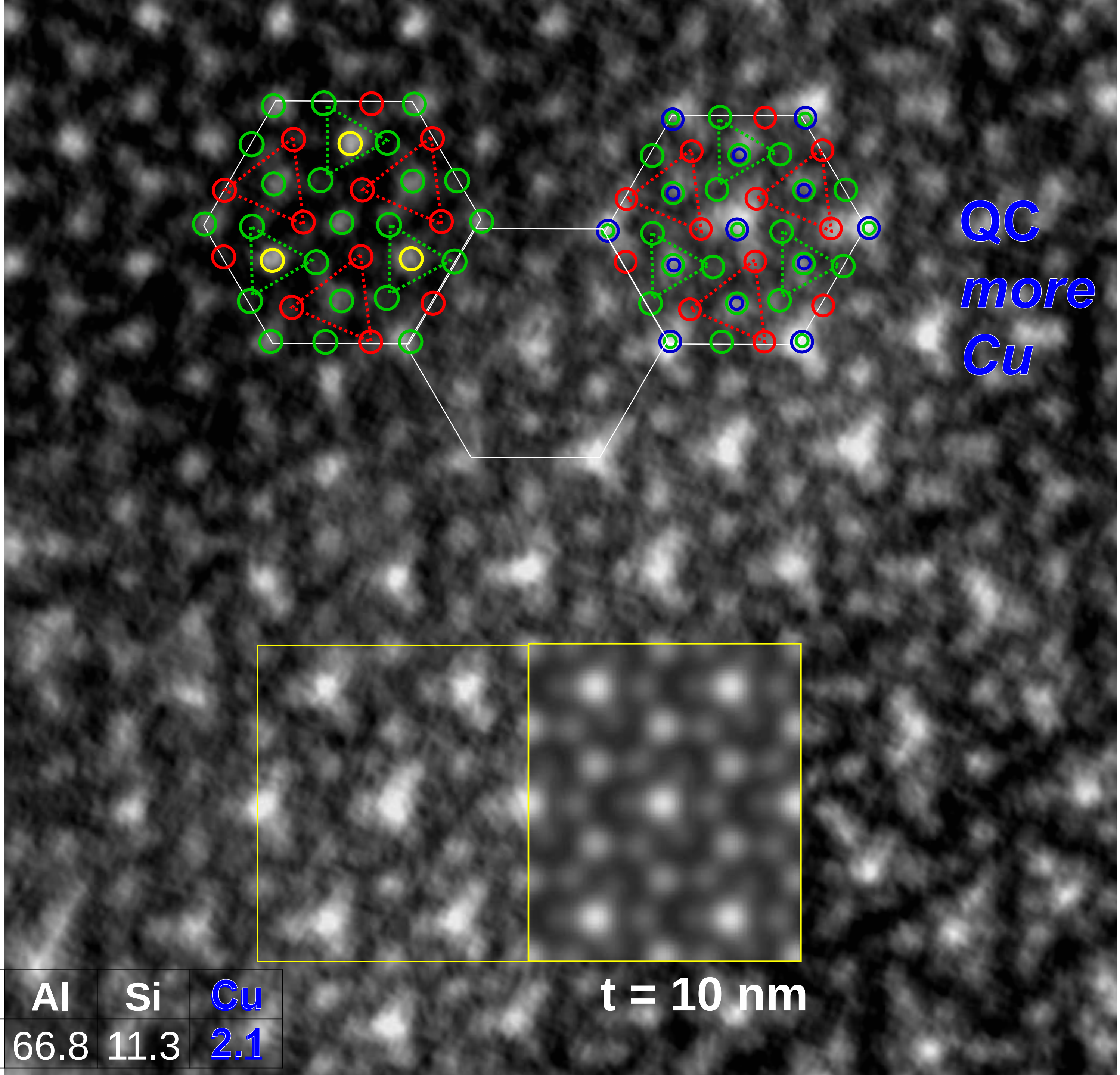


Al [001] // P [0001]

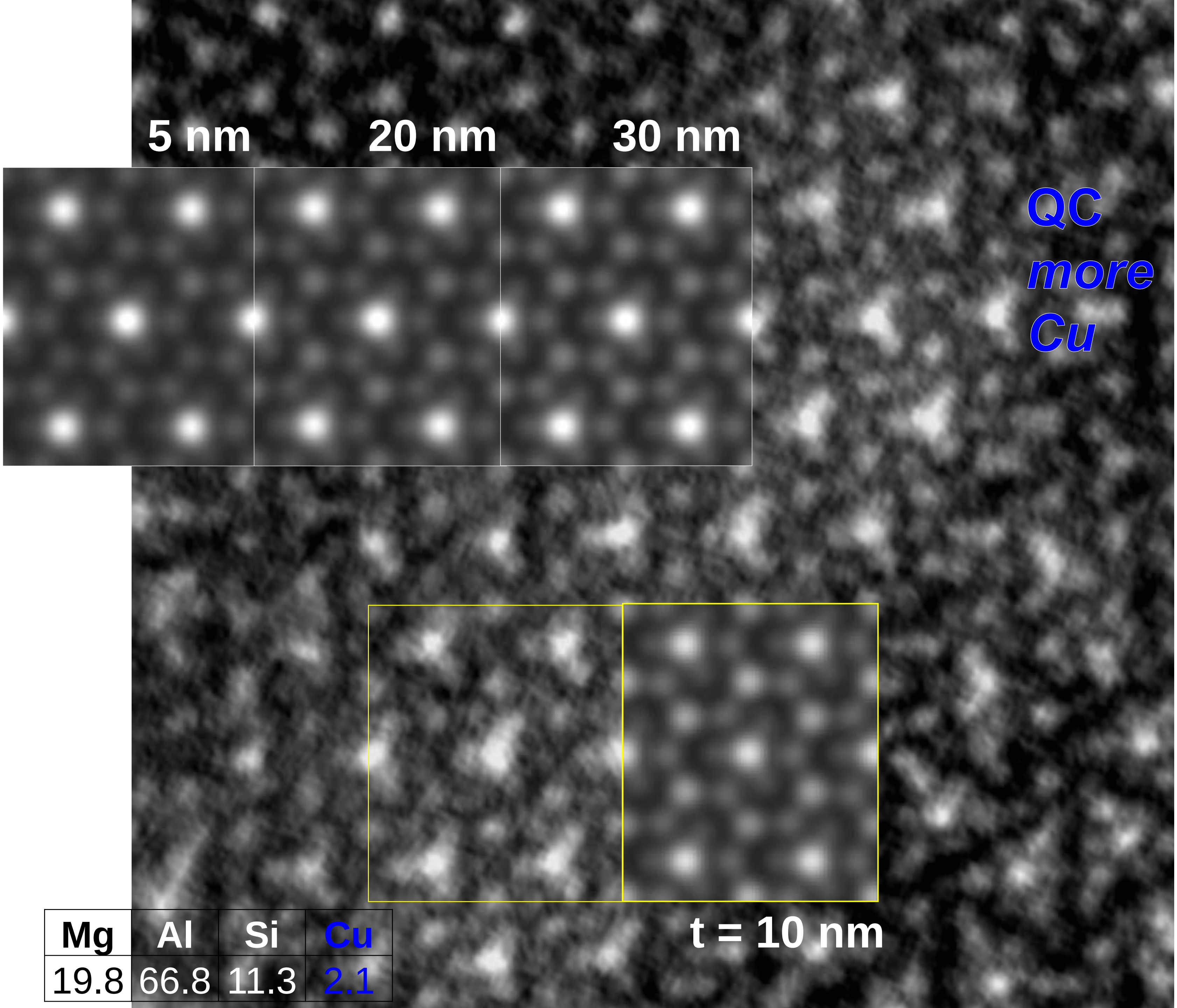






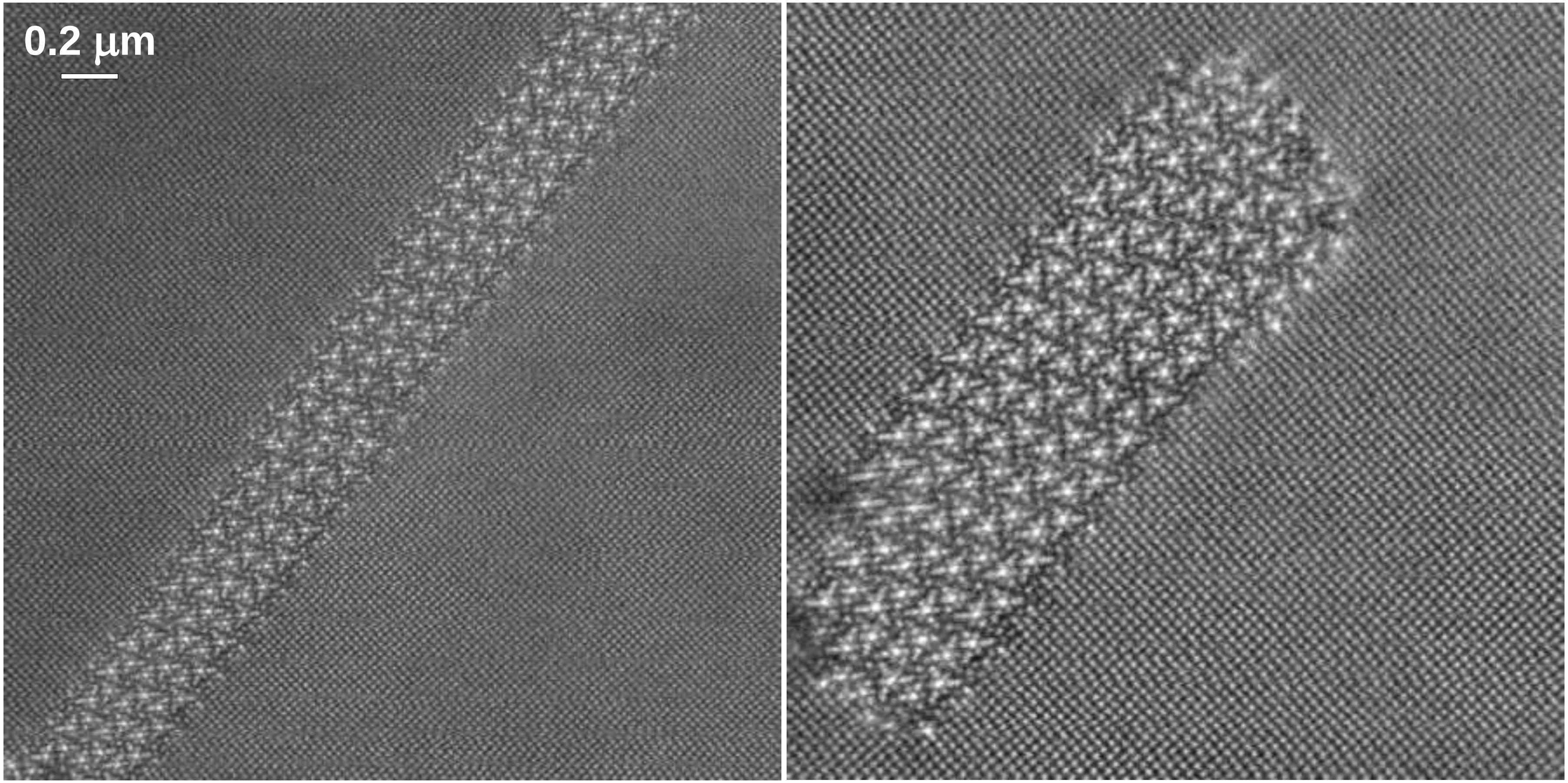


Mg	Al	Si	Cu
19.8	66.8	11.3	2.1



Mg	Al	Si	Cu
19.8	66.8	11.3	2.1

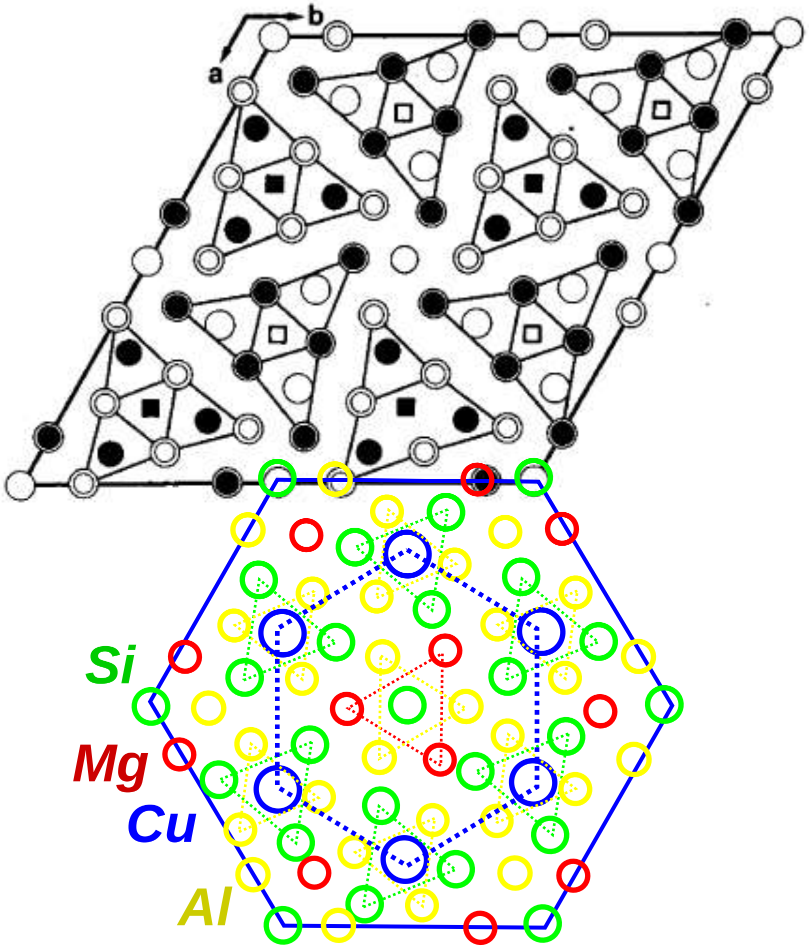
6061 alloy Al-Mg,Si,Cu: 1 hr @ 300°C

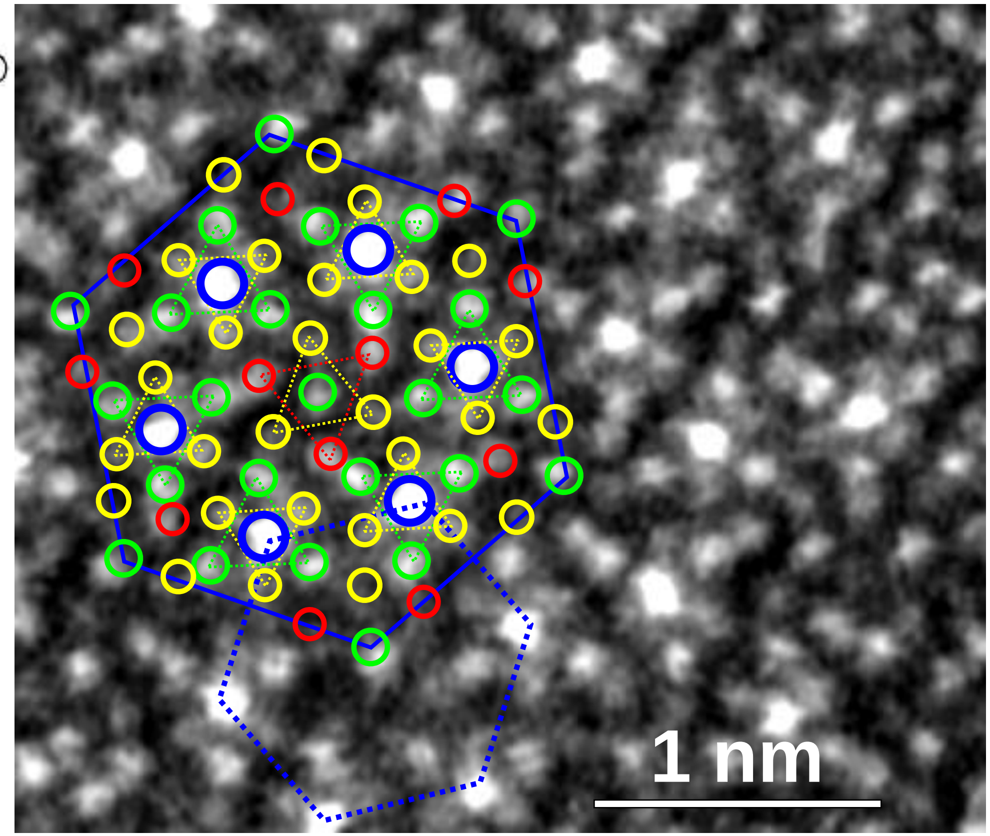


fully ordered β'_{II} **Q’ particles *with Cu***

The structure of the Q' phase

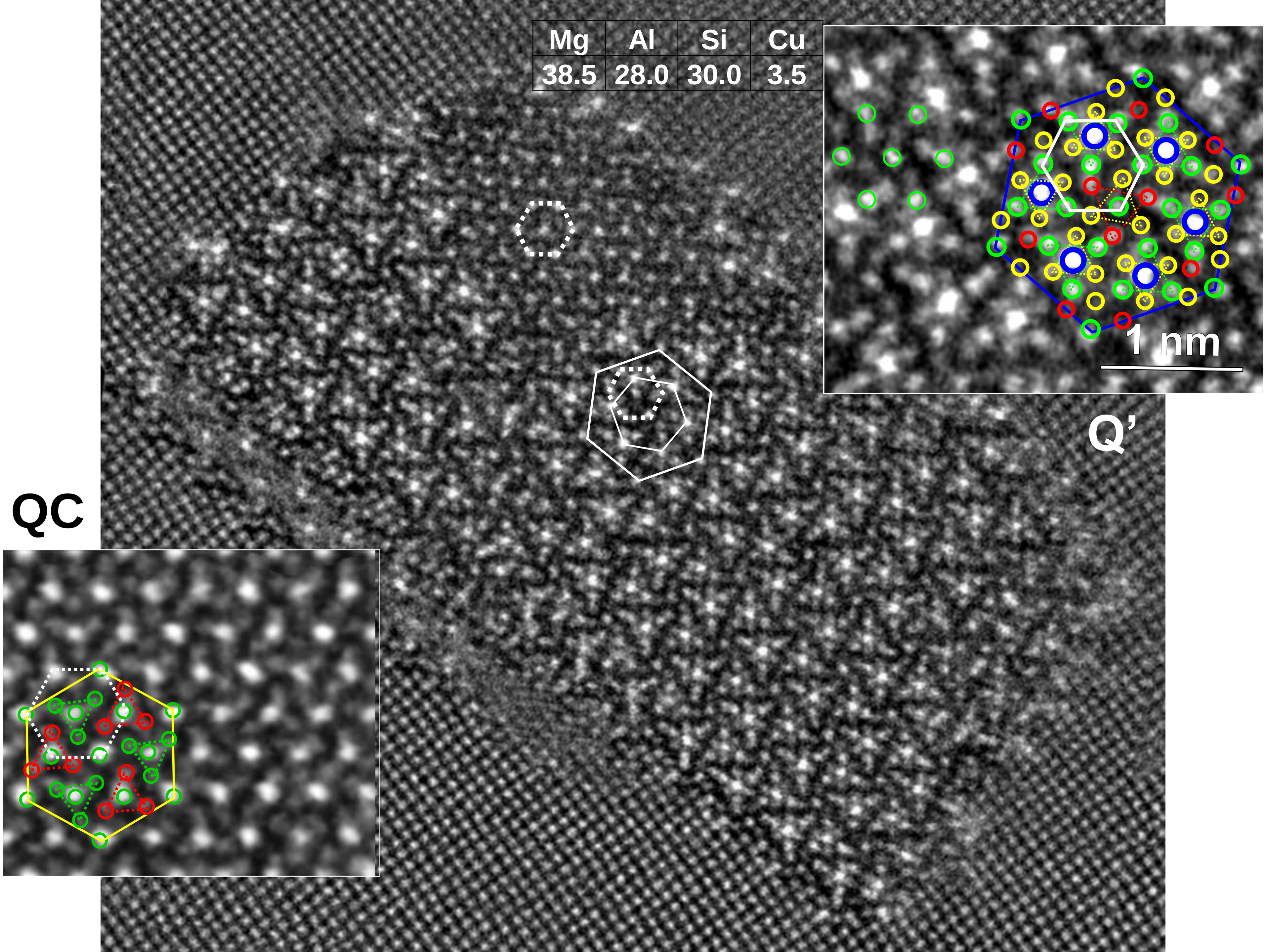
stable Q phase **$Al_4Cu_2Mg_8Si_7$**





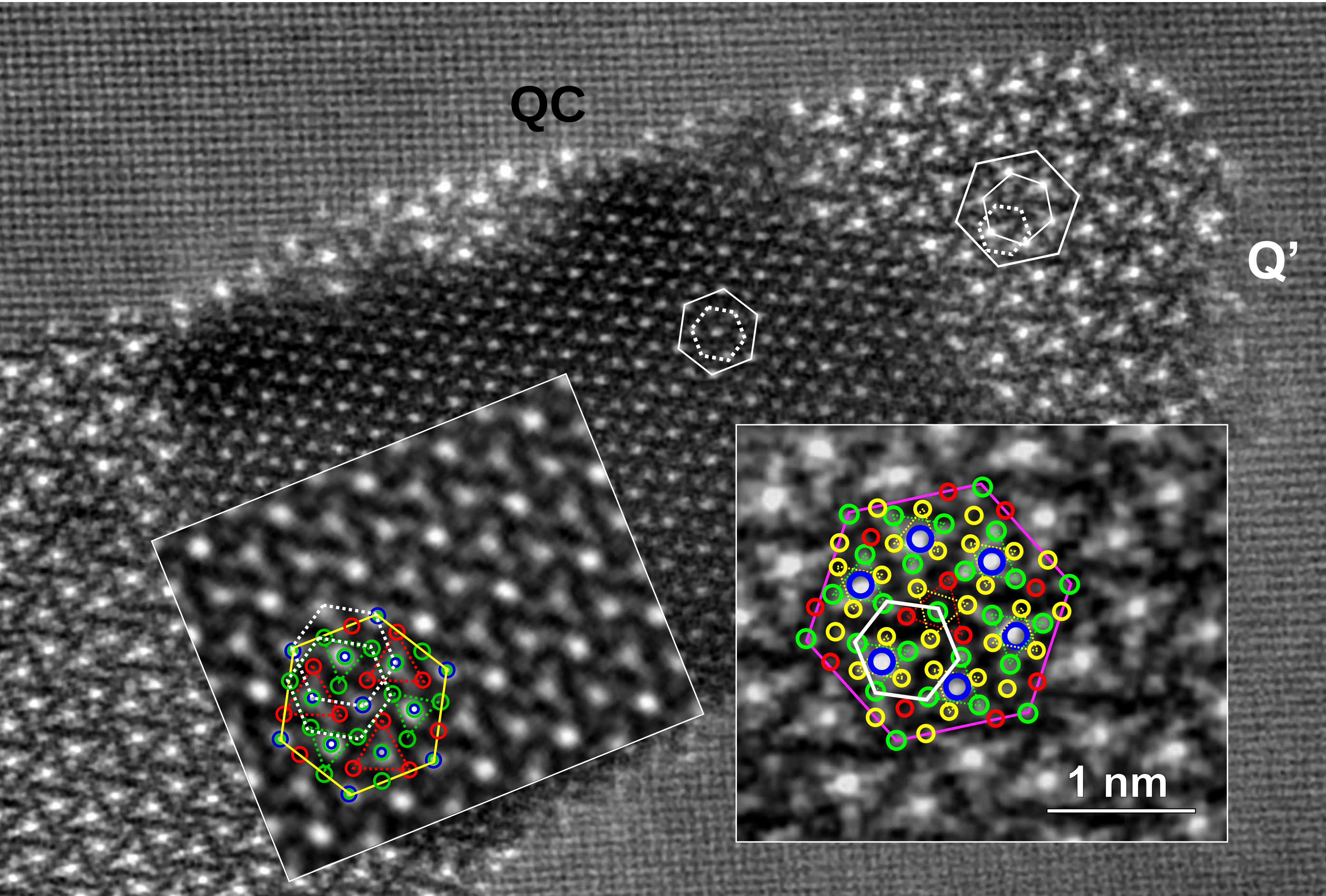
hexagonal P6, a = 1.039 nm, c = 0.402 nm

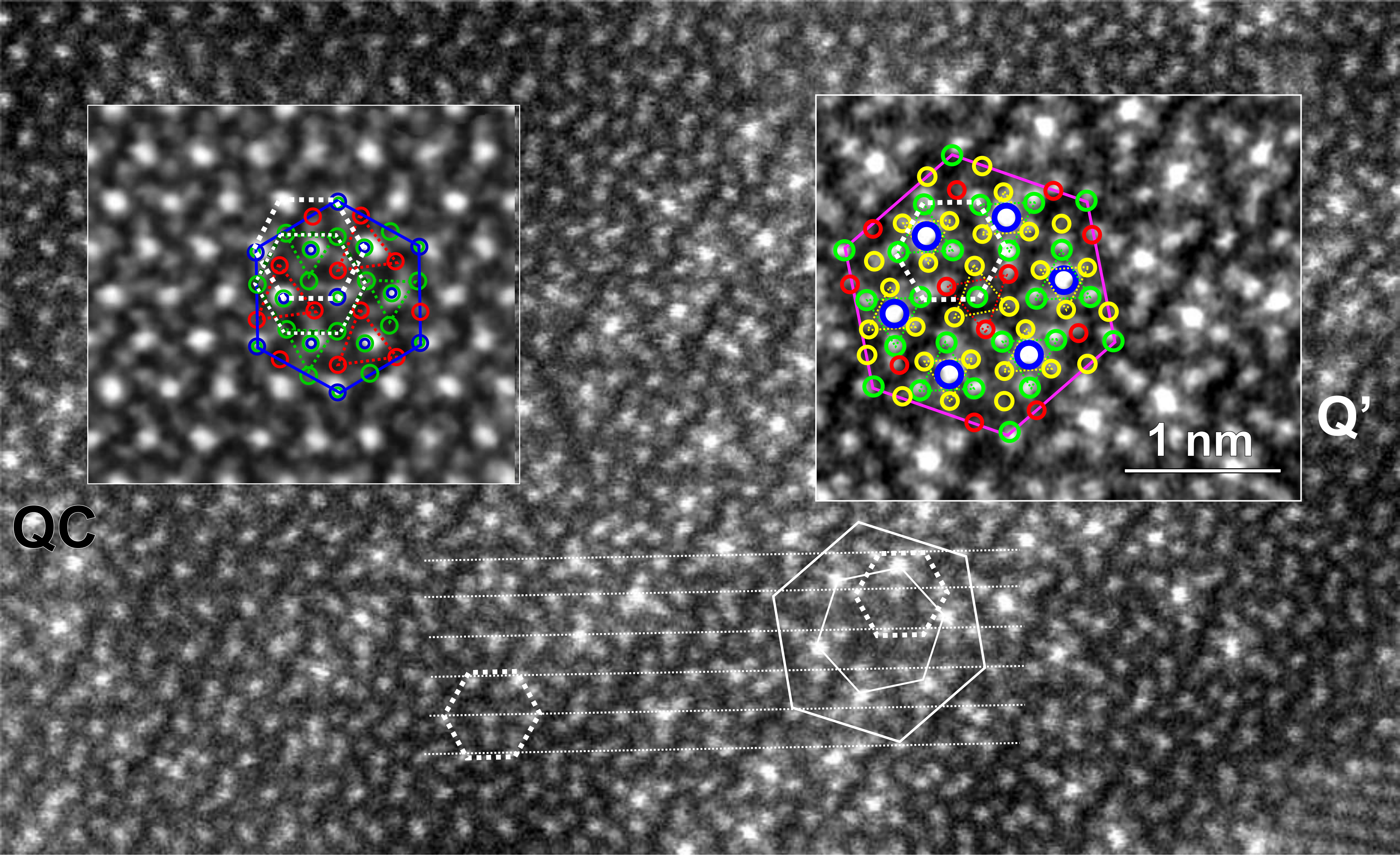
[L. ARNBERG and B. AURIVILLIUS, *Acta Chem. Scand.*, **A34**,(1980), 1-5]



Mg Al Si Cu
38.5 28.0 30.0 3.5
1 nm
Q'
QC

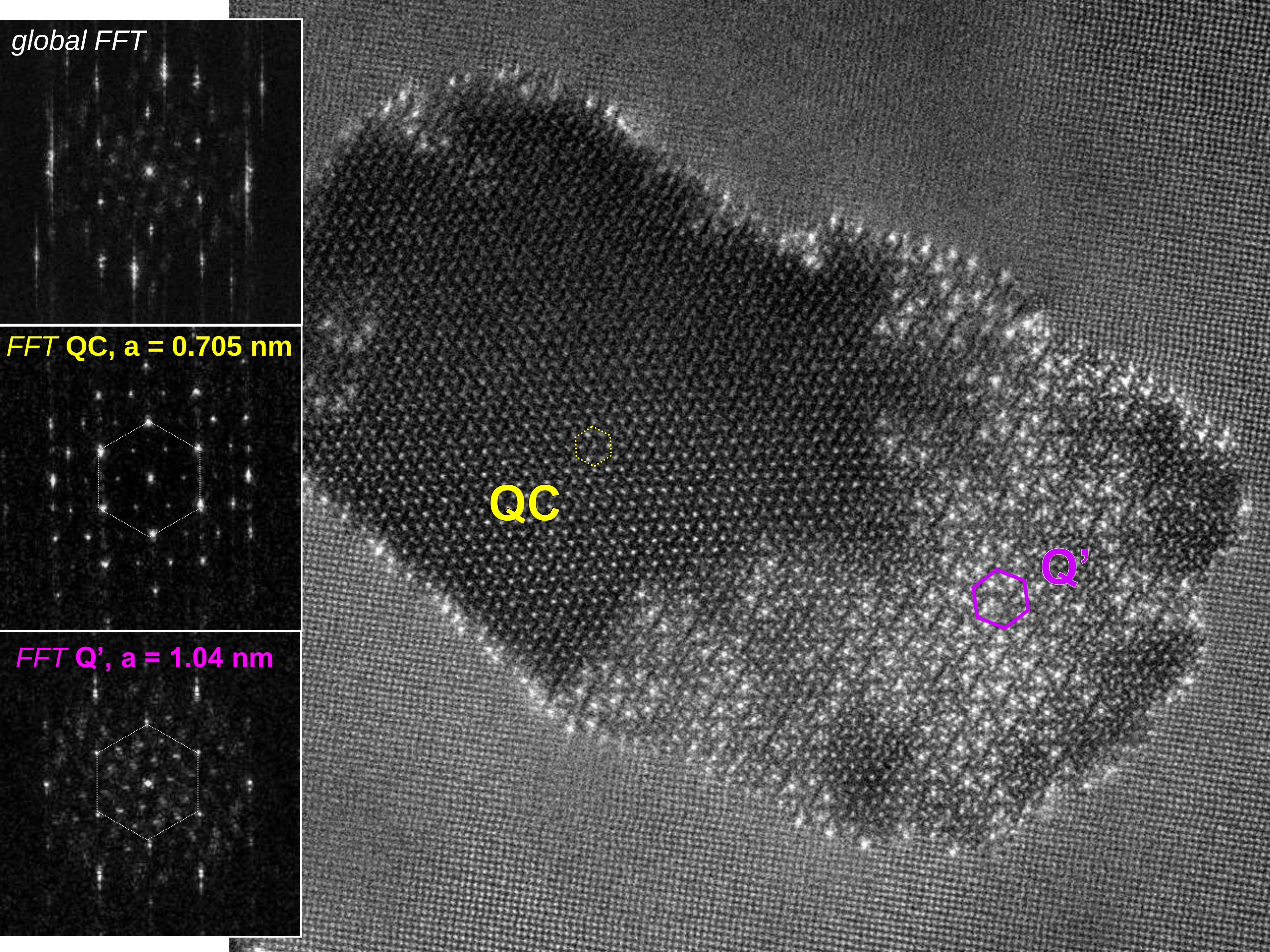
Transformation QC → Q' (5' @ 300°C)





Lattice continuity between QC vs. Q' phases:

- identified by [C. CAYRON C., P.A. BUFFAT, *Acta Mater.*, **48**, (2000), 2639]
- confirmed by [C.D. MARIOARA et al., *Philos. Mag.*, **87**, 23, (2007),3385]


global FFT
FFT QC, a = 0.705 nm
FFT Q', a = 1.04 nm
QC
Q'

SUMMARY

- HAADF C_s-corrected images have been obtained from QC and Q' (mixed-)precipitates in a 6061 alloy aged 5' and 1 hr. at 300°C

- a resolution of ≈ 0.12 nm is required to solve the structure of these phases:
  - the **QC phase** adopts the hexagonal structure proposed by CARYON & BUFFAT [*Acta Mater.*, **48**, (2000)]
  - the **Q' phase** appears to be isostructural *(identical?)* to the stable Q phase in the quaternary system AlCuMgSi identified by ARNBERG & AURIVILLIUS [*Acta Chem. Scand.*, (1980)]

- Cu-segregation occurs around the QC precipitates before transformation into Q' phase

- The transformation QC ➔ Q' via **Cu-diffusion into the QC hexagonal lattice**, leaving a common Si ≈ hexagonal sub-lattice between both phases.

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