Chemical Quantification of Atomic scale EDS Maps

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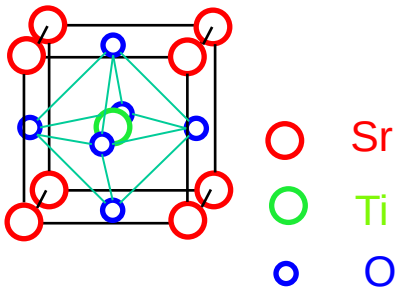

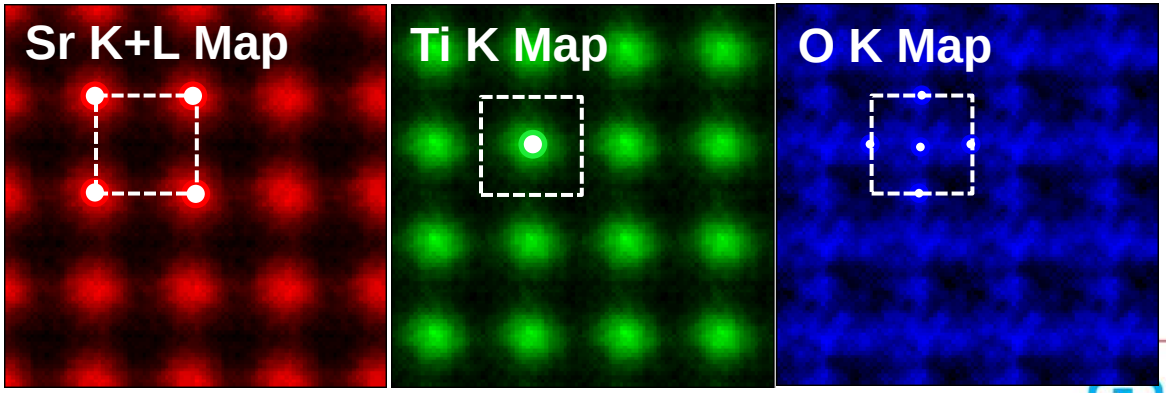

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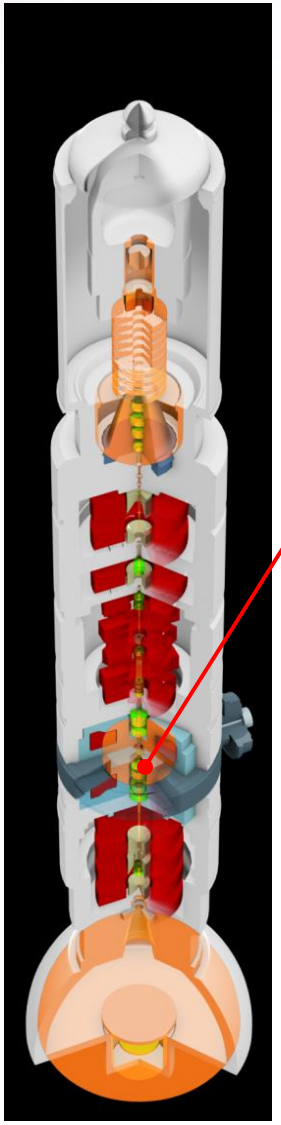
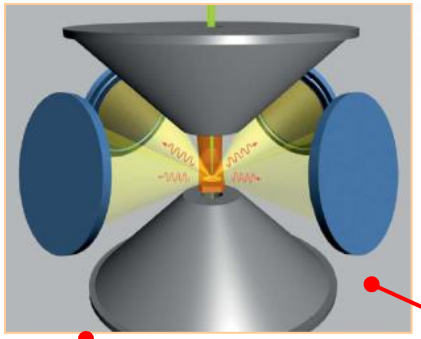
Sandia's AC-STEM capability

X-FEG

DCOR (CEOS)

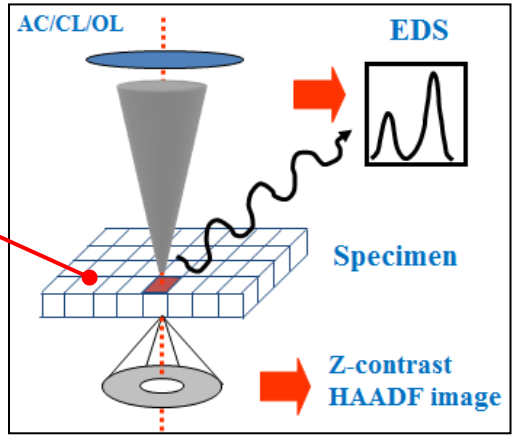
Super-X





- 4 SDD geometry around the sample

Aberration correction and four in-lens EDS X-ray detector technologies.



Small, intense electron probe + Super efficient EDS detector

- **Sub-atomic-scale STEM imaging (80pm at 200 kV; 120pm at 80 kV)**
- **Atomic-scale chemical mapping by Energy X-ray Dispersive Spectroscopy (EDS)**

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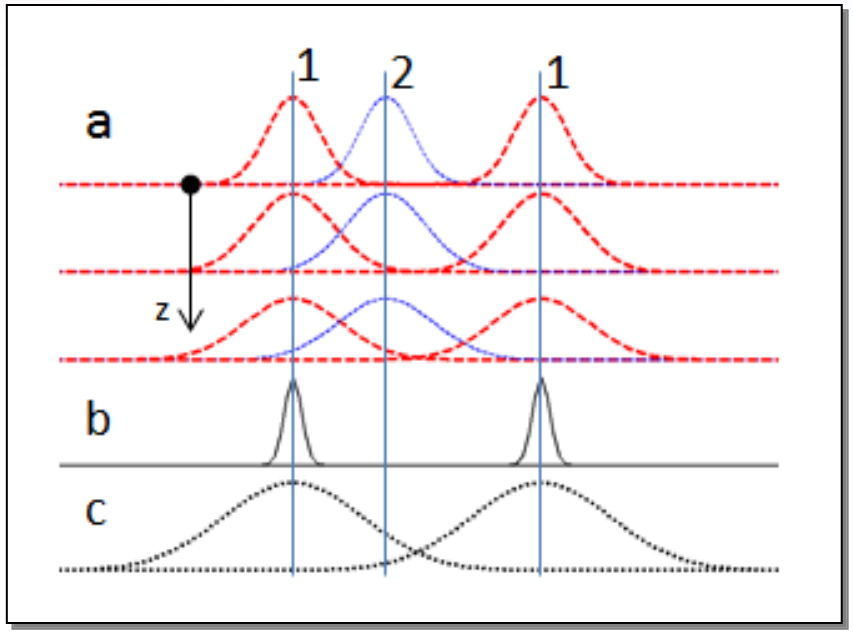
X-ray generation process in STEM-EDS



Incoherent mode

$$\sigma(\boldsymbol{R},t)=\frac{4\pi}{h\upsilon J}\sum_{j=1}^{J}\int_{0}^{t}\int_{A}|\psi_j(\boldsymbol{R},\boldsymbol{r}_\perp,z)|^2V(\boldsymbol{r}_\perp)d\boldsymbol{r}_\perp dz. \quad (1)$$

$$V(\boldsymbol{r}_\perp)=\frac{2\pi m}{h^2t_c}\sum_{n}\frac{1}{k_n}|H_{n0}(\boldsymbol{r}_\perp)|^2, \quad (2)$$

(A.J. D'Alfonso *et al.* , Physical Review B 81, 100101 (2010))

Beam broadening, channeling, de-channeling, "cross-talk"

When
(1) specimen is very thin (<20nm) and
(2) the EDS scattering potential is highly localized.
➔ Fit the x-ray counts from the atomic column with a Gaussian function

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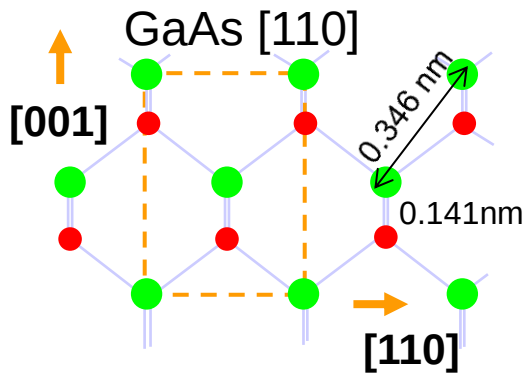
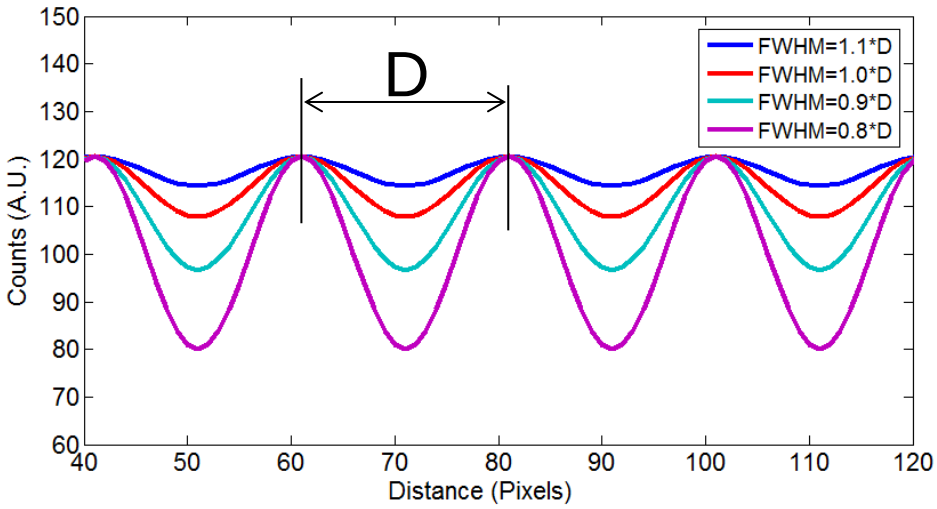
Spatial Resolution of Chemical Mapping

- The shortest lateral distance between same type of atoms in the projection



➔ ~0.346 nm to resolve all atomic columns in this projection

- The FWHM of the Gaussian peak vs Spatial resolution



If $\Delta S/N>3$

FWHM<0.86D

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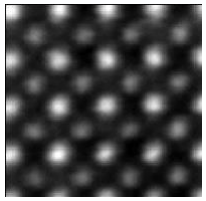
Effect of specimen thickness

Thickness

HAADF

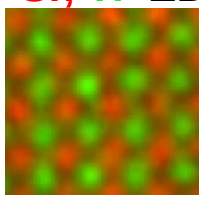


t/λ =0.15

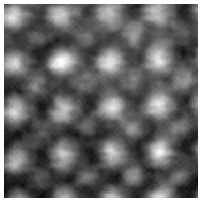
or

17nm

Sr, Ti EDS



HAADF

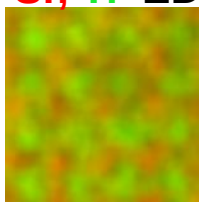


t/λ =0.44

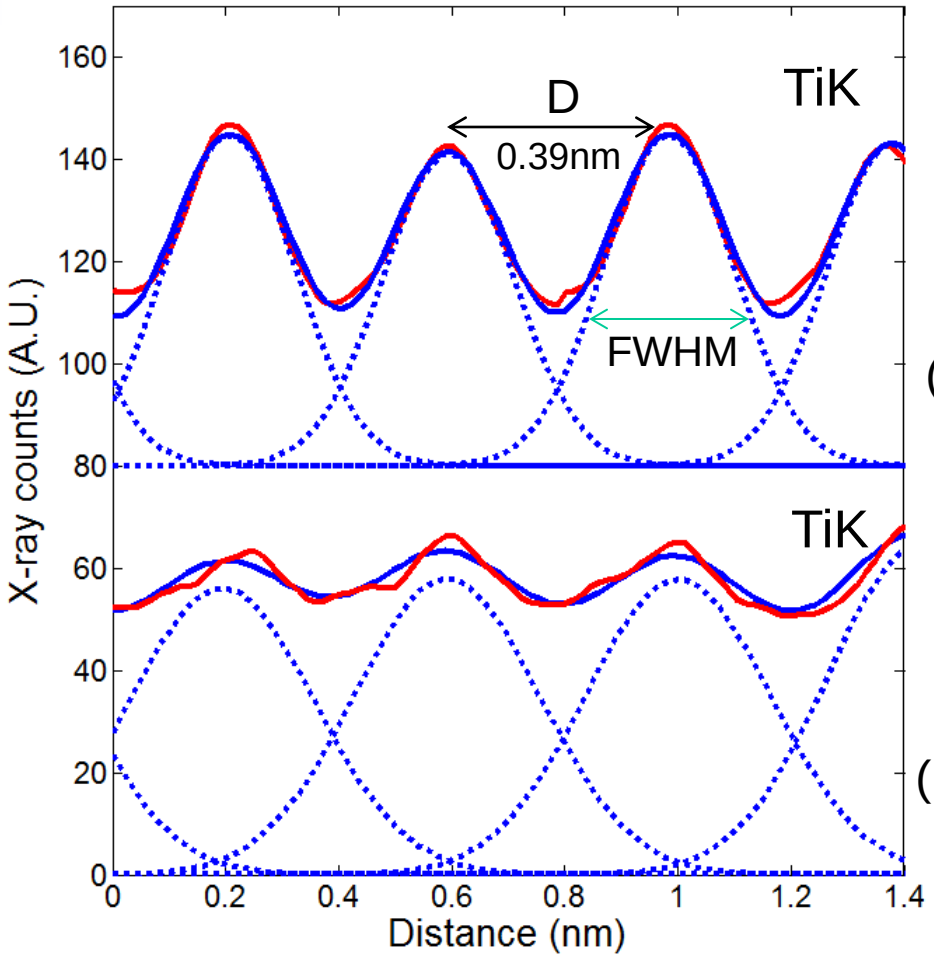
or

51nm

Sr, Ti EDS



EDS Map line profile along [100] direction



FWHM:
0.263 nm

(FWHM/D =0.67)

FWHM:
0.374 nm

(FWHM/D =0.95)

➔ The thinner specimen, the better for the quantification

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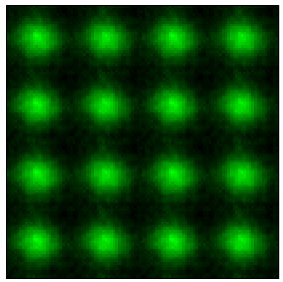
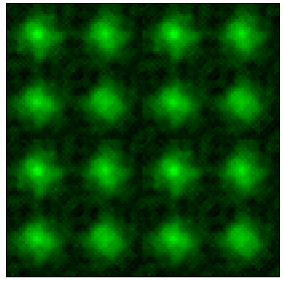
Effect of X-ray energy, TiK vs TiL

t/λ =0.15

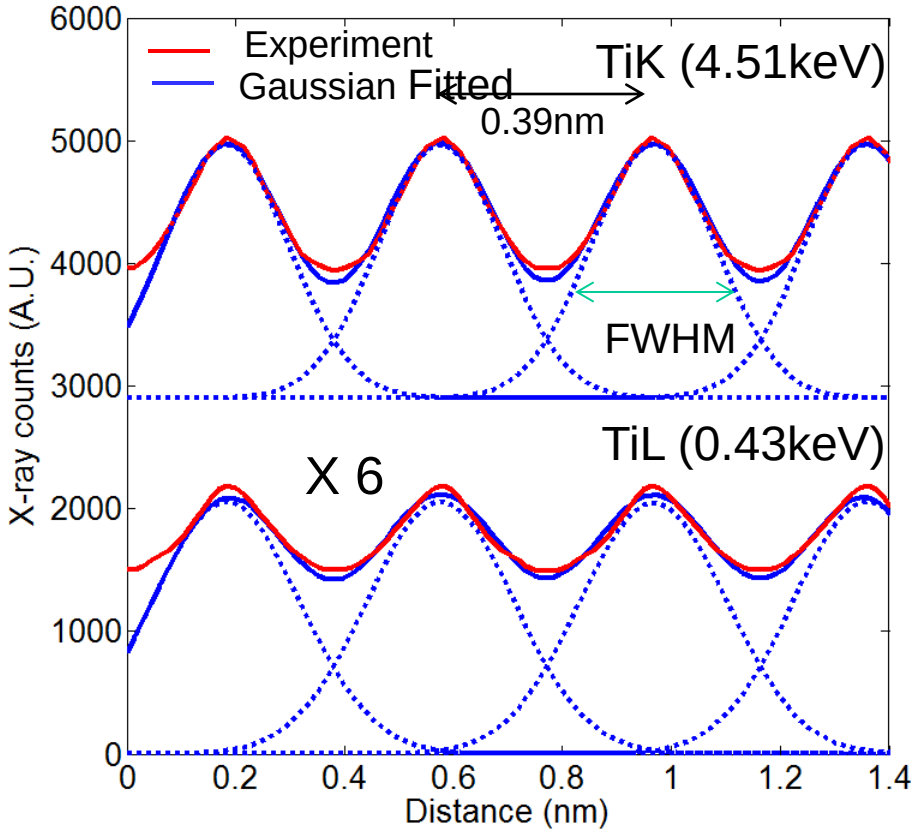
Ti K map



Ti L map



EDS Map line profile along [100] direction



FWHM:
0.266 nm
(FWHM/D =0.68)

FWHM:
0.317 nm
(FWHM/D =0.813)

➔The ionization potentials become less localized as the energy of the ejected electron decreases to below 1kV.

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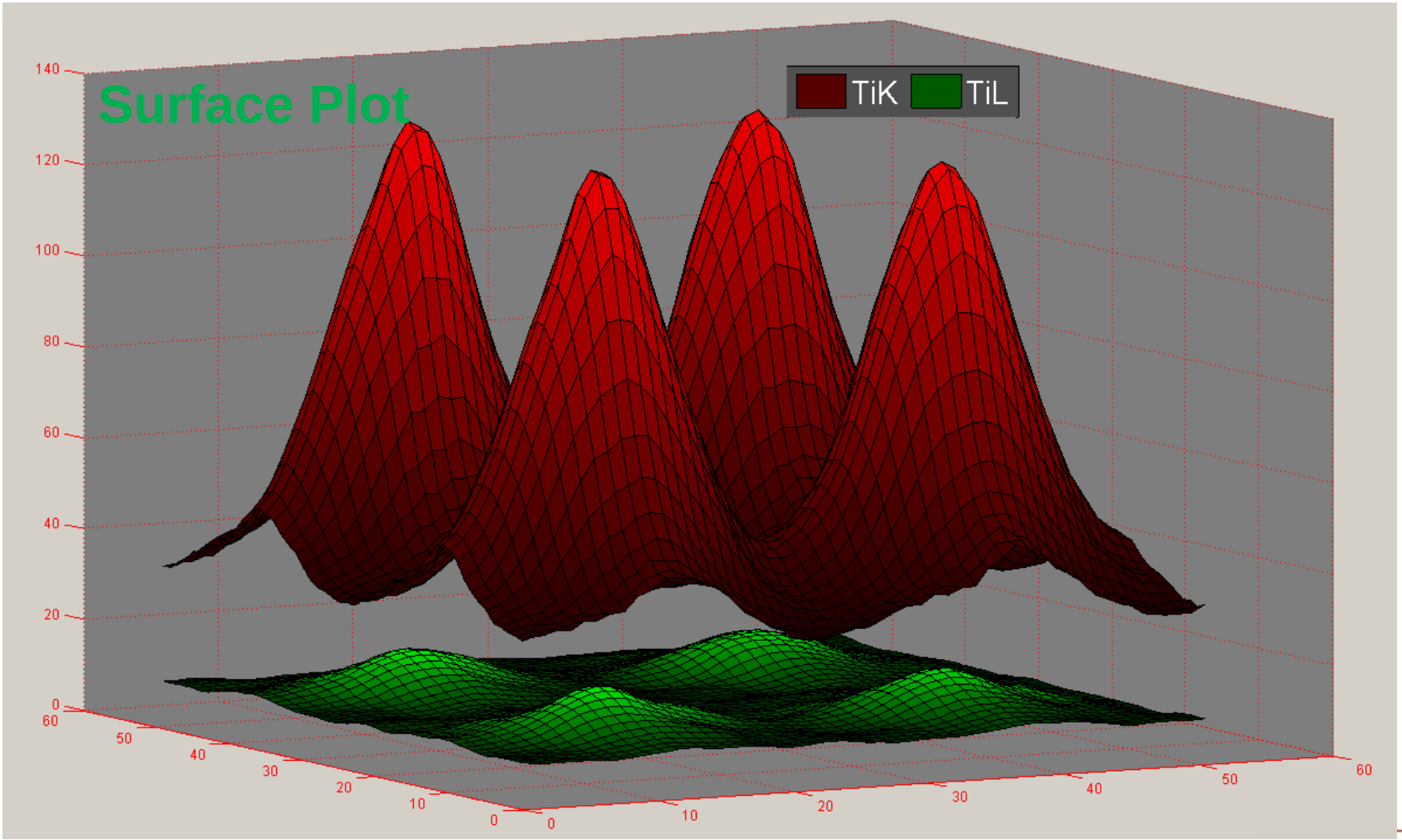
Effect of X-ray energy, TiK vs TiL



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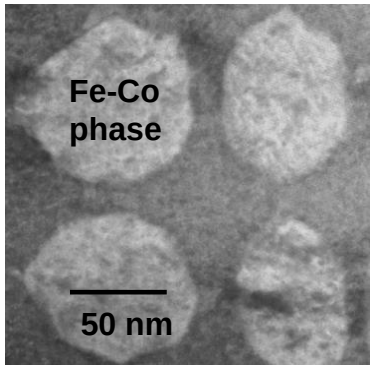
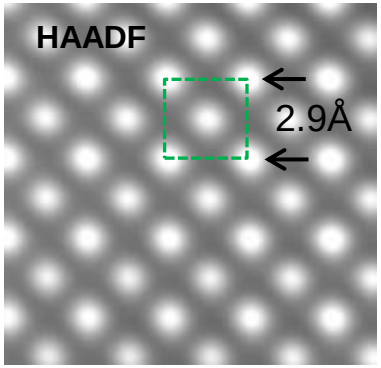
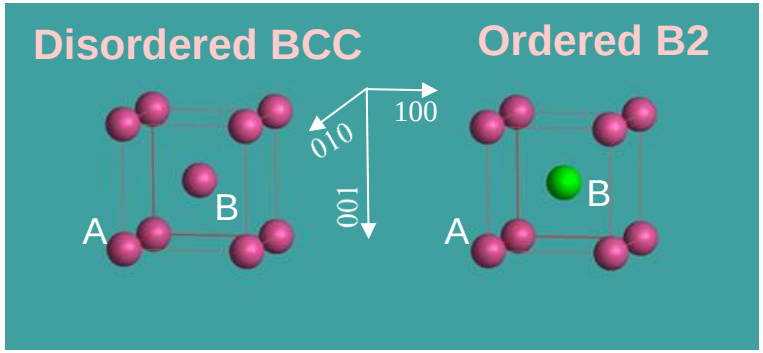
Example 1- Ordering-disordering in Fe-Co intermetallic phase

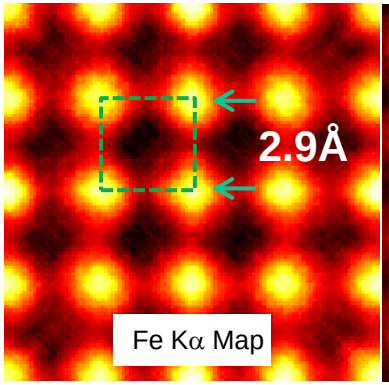
Fe-Co phase of an “alnico” alloy from a spinodal decomposition

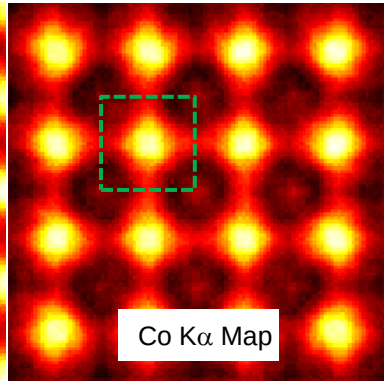


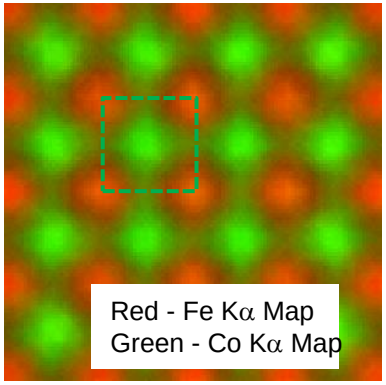




“Permanent magnet alloys”







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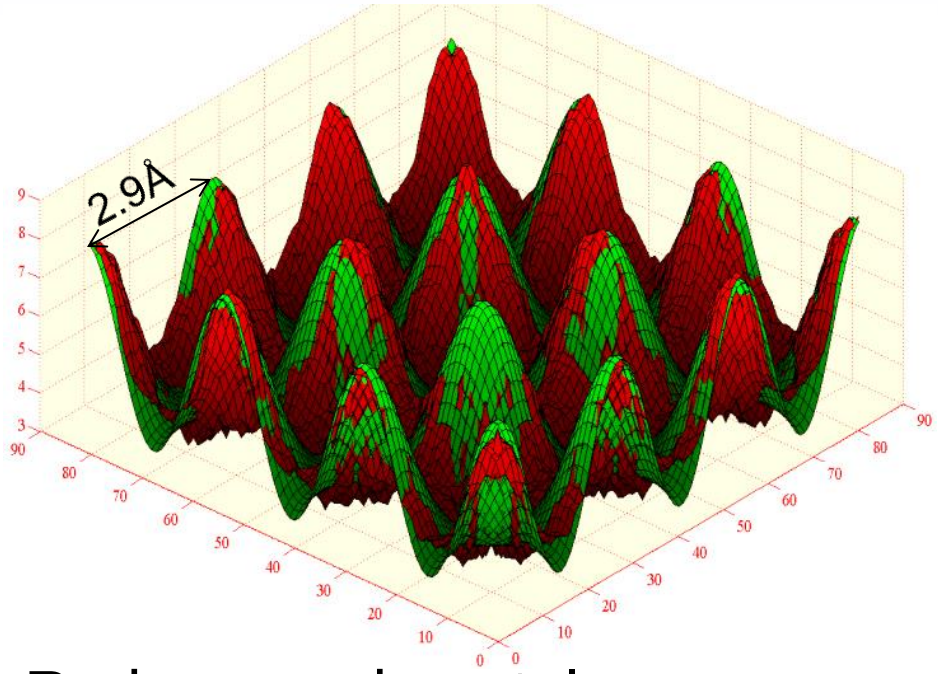
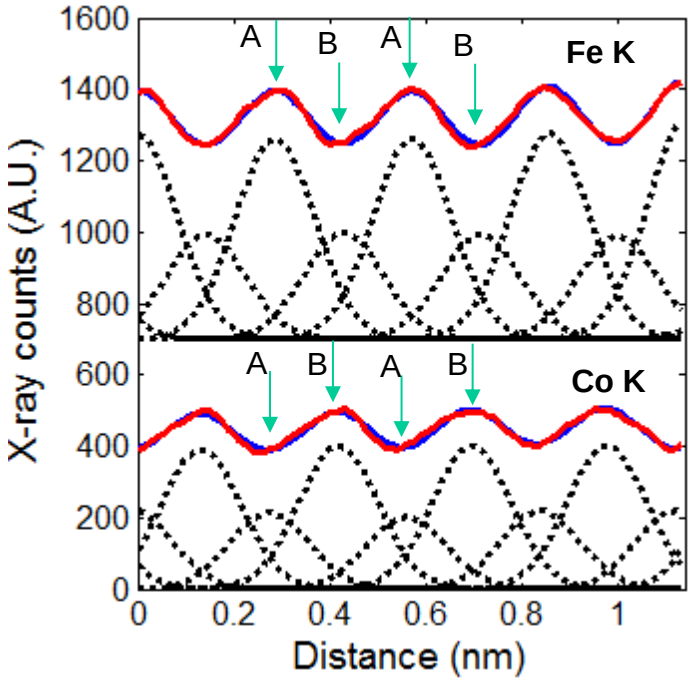
Ordering-disordering in Fe-Co intermetallic phase

3-D surface plot for Fe K_α



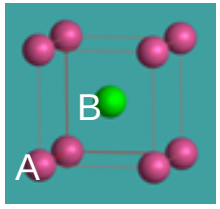
Line-profile in [100]



Red – experimental

Green – Gaussian fitted

(a constrained nonlinear optimization routine)



➔ A: $Fe_{0.76}Co_{0.24}$; B: $Fe_{0.40}Co_{0.60}$

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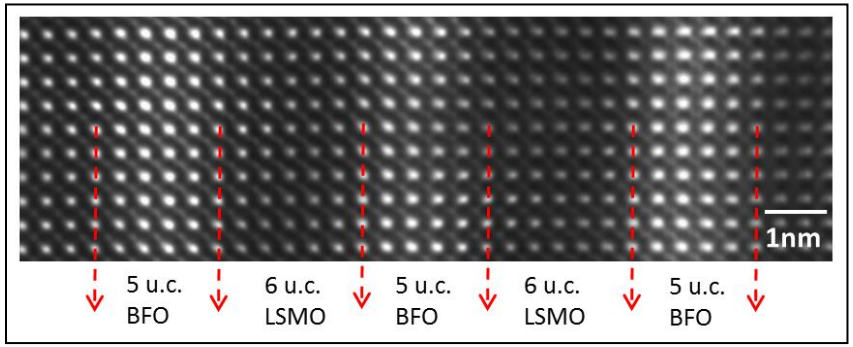
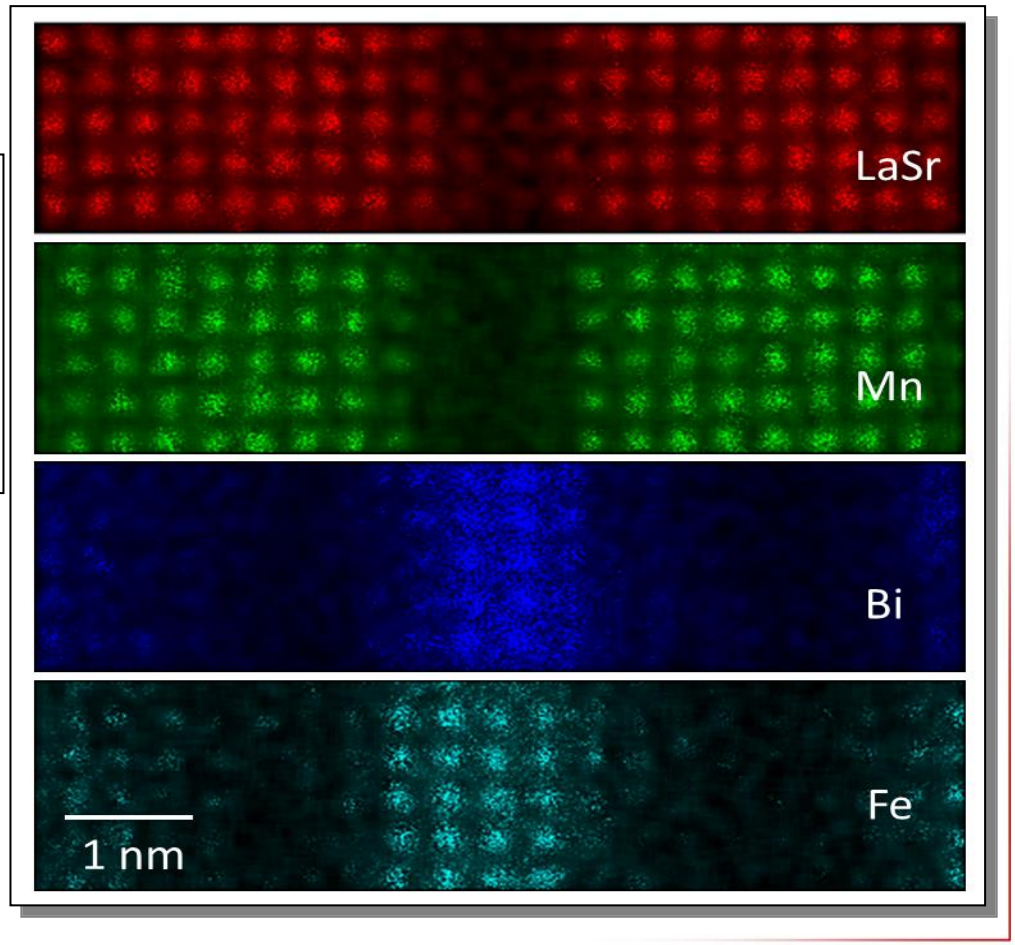
Example 2- $La_{0.7}Sr_{0.3}MnO_3$\$BiFeO_3$ quantum structure

EDS Map

HAADF





Pulsed Laser Deposition (PLD) on STO

$La_{0.7}Sr_{0.3}MnO_3$ - Ferromagnetic
$BiFeO_3$ - Antiferromagnetic

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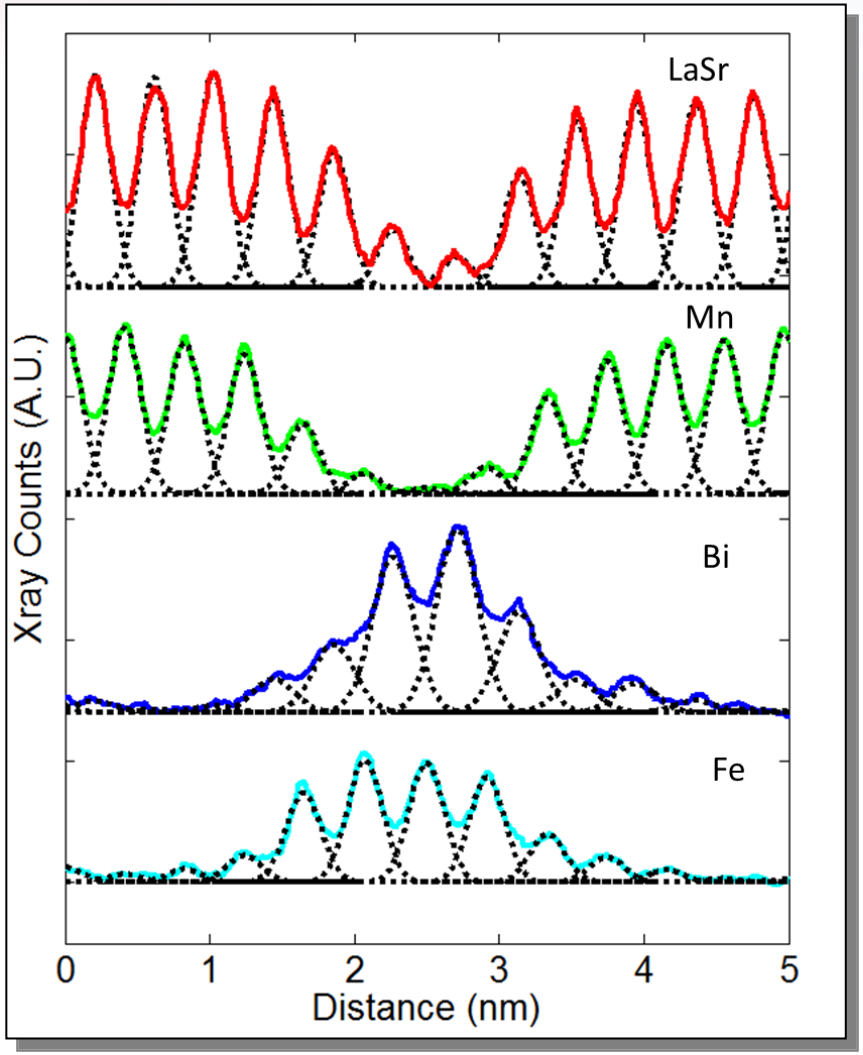
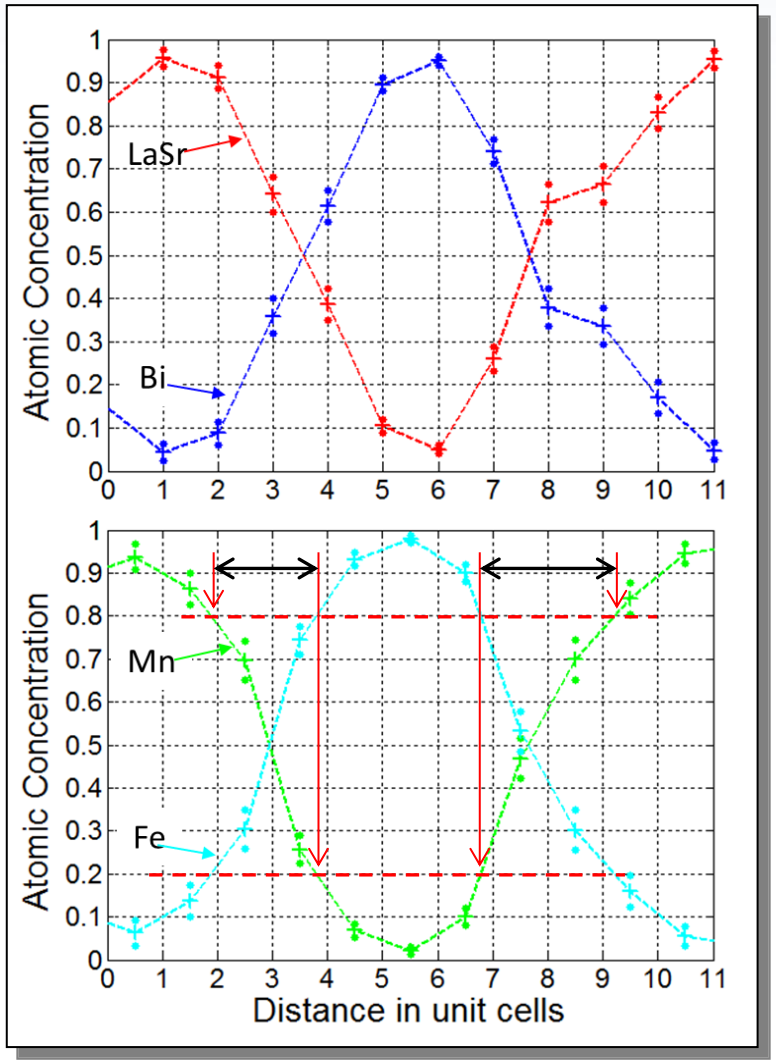
$La_{0.7}Sr_{0.3}MnO_3\backslash BiFeO_3$ quantum structure





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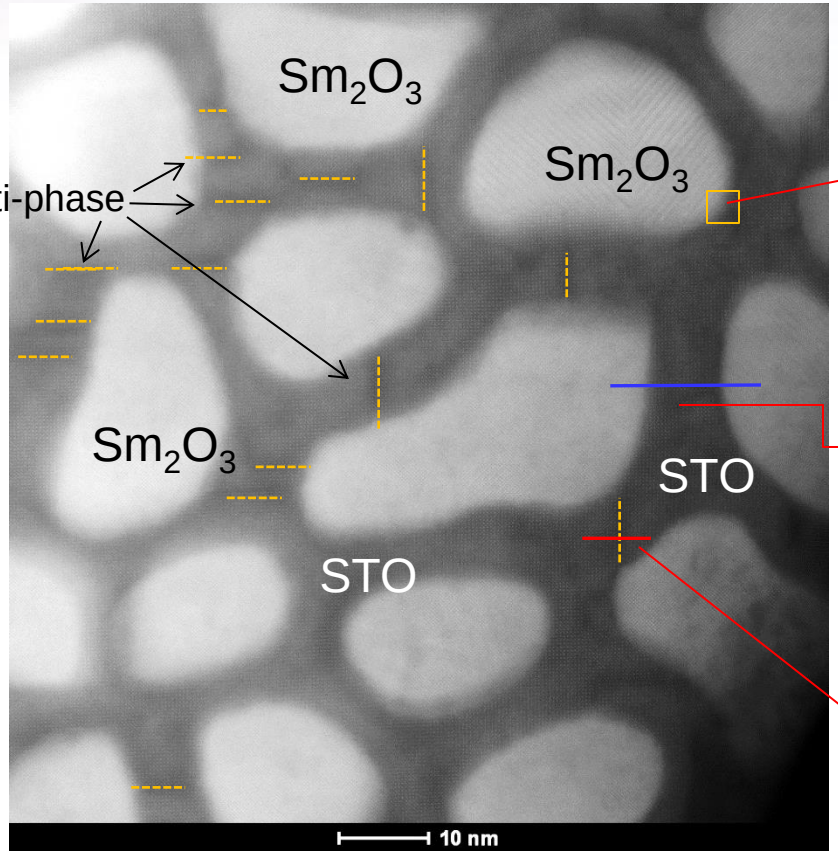
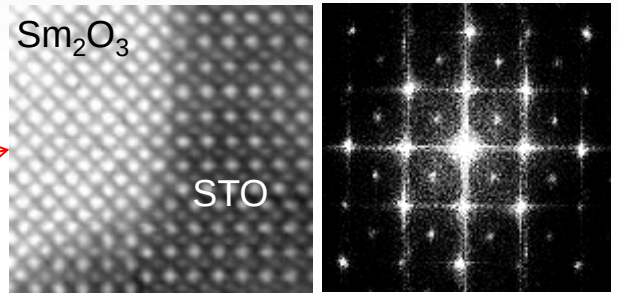
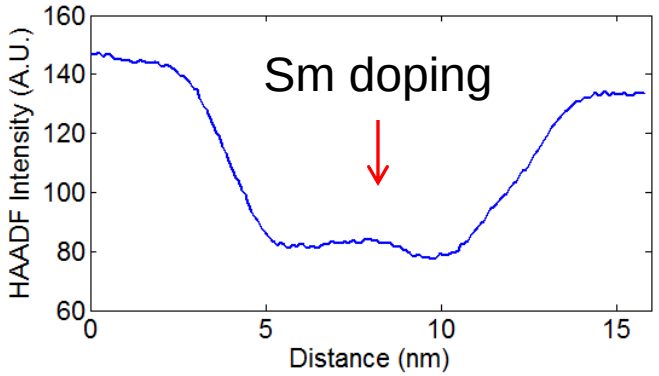
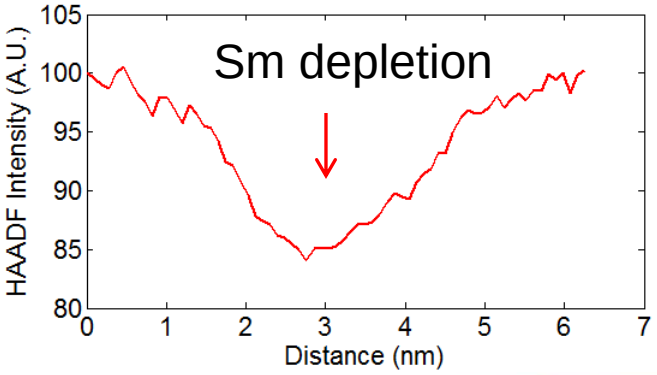
Example 3- Sm doping in $SrTiO_3$









Sm_2O_3 and $SrTiO_3$ co-deposited by PLD on STO substrate

"Nanoscaffold memristor"

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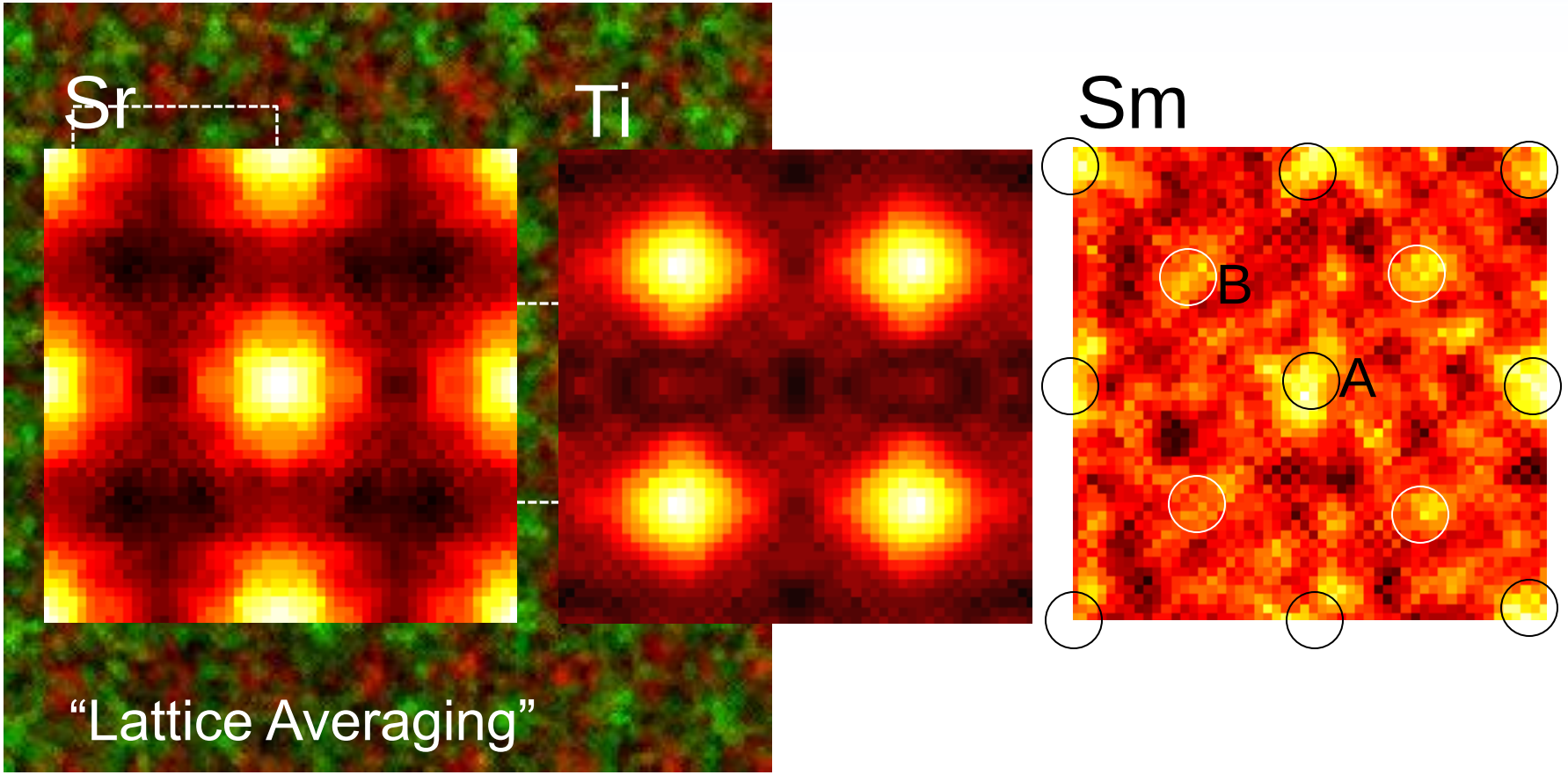
Sm doping in $SrTiO_3$



Lattice-Averaging can be used to improve S/N statistic!

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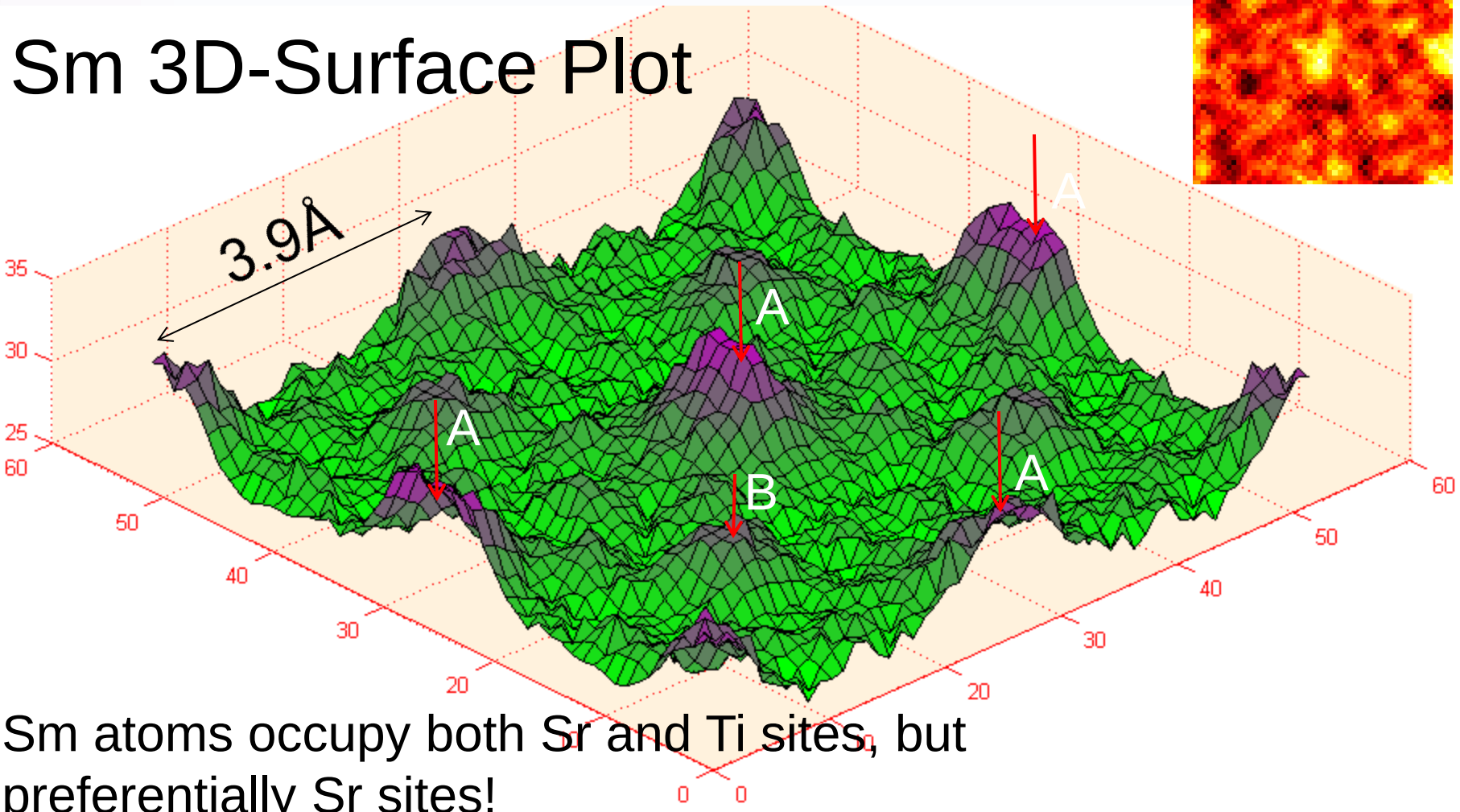
Sm 3D-Surface Plot



Sm atoms occupy both Sr and Ti sites, but preferentially Sr sites!

$Sm_xSr_{1-x}Sm_yTi_{1-y}O_3$
with x=0.08, y=0.03

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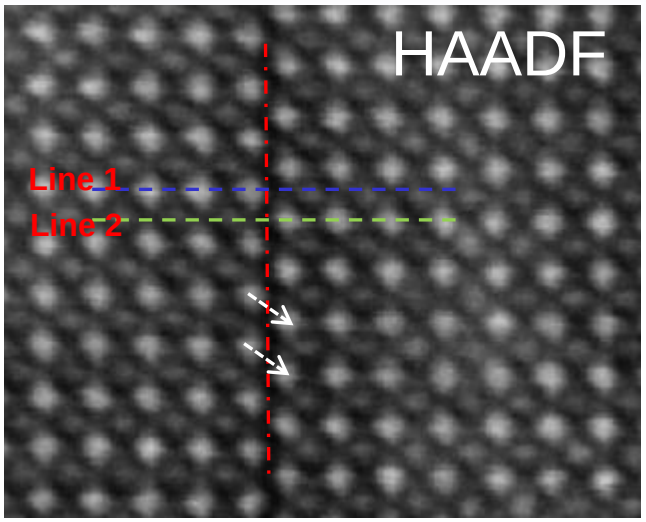
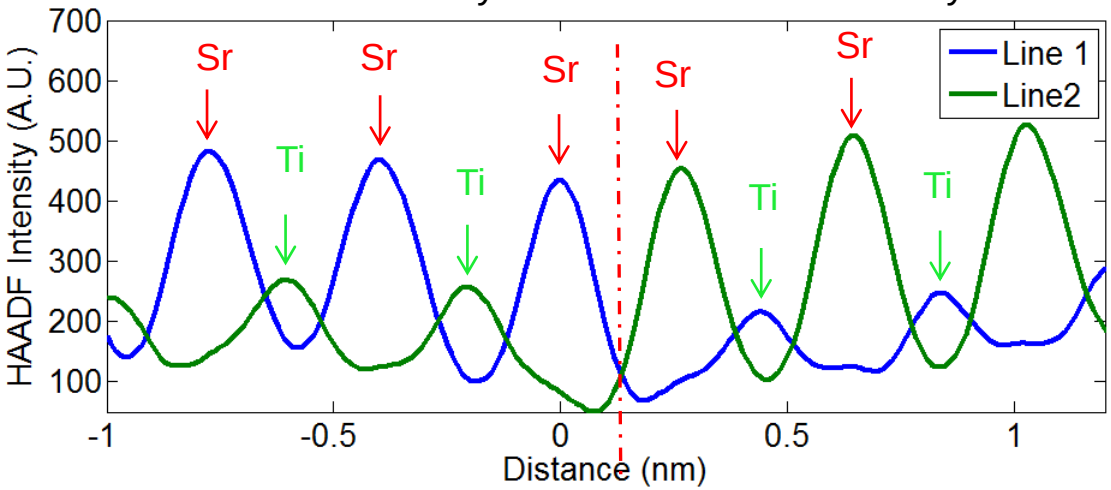
Anti-phase Boundaries



HAADF intensity decreases as it approaches the boundary!

HAADF Intensity Profile Across the Boundary



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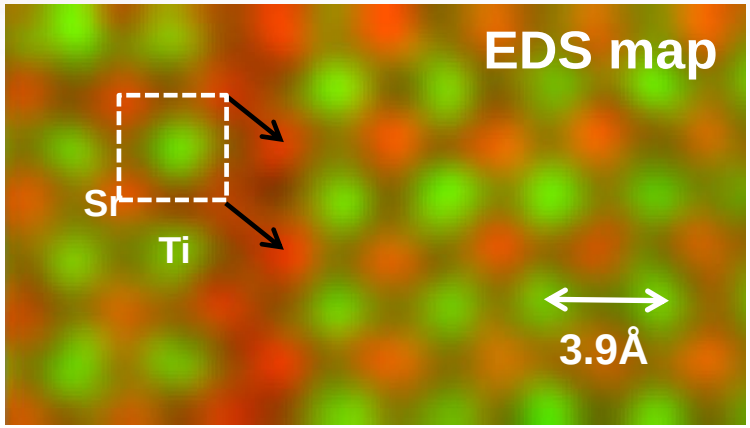
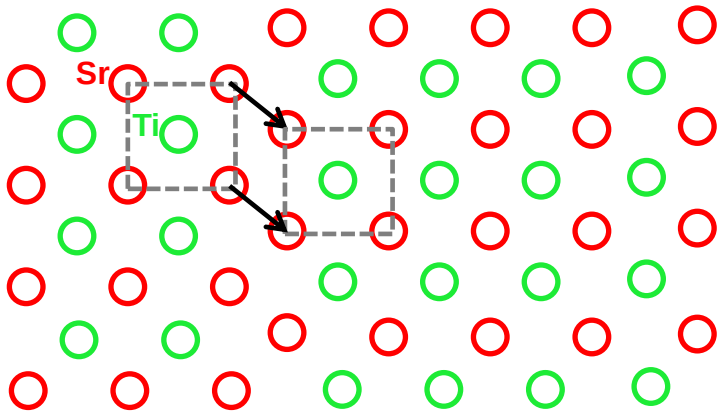
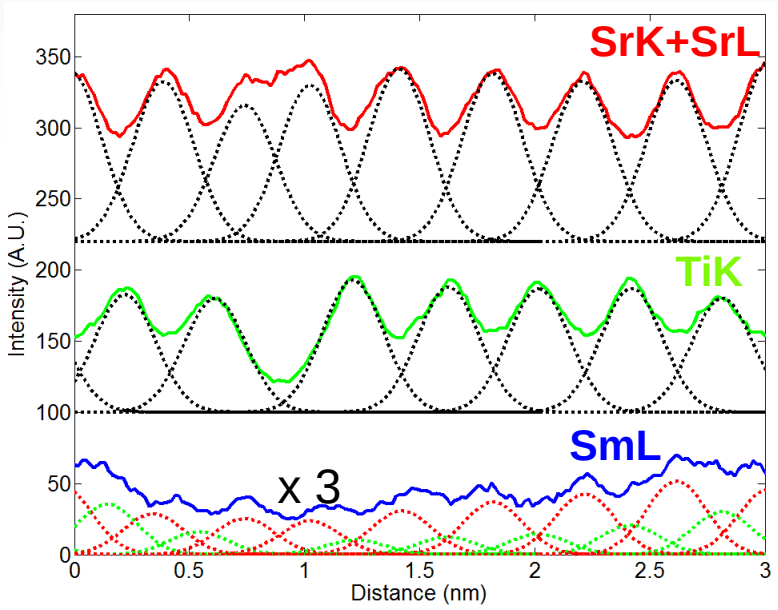
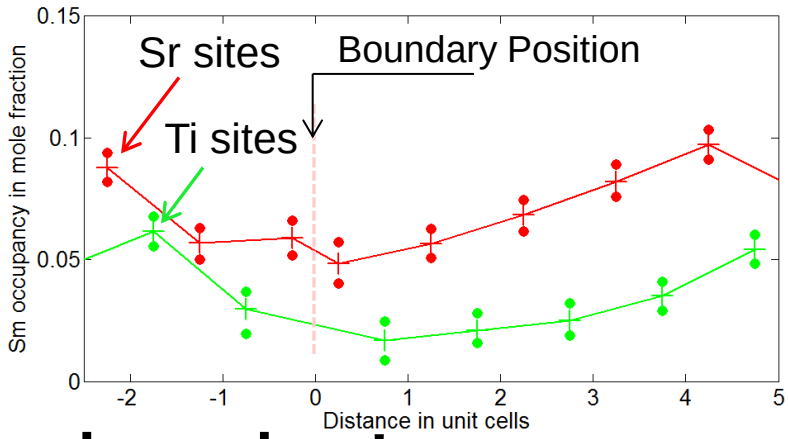
Anti-phase Boundaries









- **Sm atoms are depleted at the boundary!**
- **Likely, this is due to the strain effect.**

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Conclusions

- STEM-EDS maps can be properly quantified when specimen is thin and EDS scattering potential is localized such that the x-rays from each individual column is localized.
  - Thickness < 20 nm
  - X-ray energy > 1keV
  - Gaussian fitting the x-ray counts to account the x-rays from each atomic column and column-by-column quantification by Cliff-Lorimer method
- STEM-EDS provides a powerful approach to investigate structures chemically in real space at atomic-scale.
  - Ordering-disordering in a Fe-Co intermetallic (the technique developed in this study appears to be only way!)
  - Chemical quantification of oxide interfaces
  - Defect structure and doping concentration studies in oxide ceramics

Other collaborators:

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