

Lecture 19: Linear Methods for Spectroscopy and Imaging

Instructor: Sergei V. Kalinin

General linear unmixing

$$S(\mathbf{x}, \mathbf{R}) = \sum_i a_i(\mathbf{x}) w_i(\mathbf{R}) + N$$

We start with:

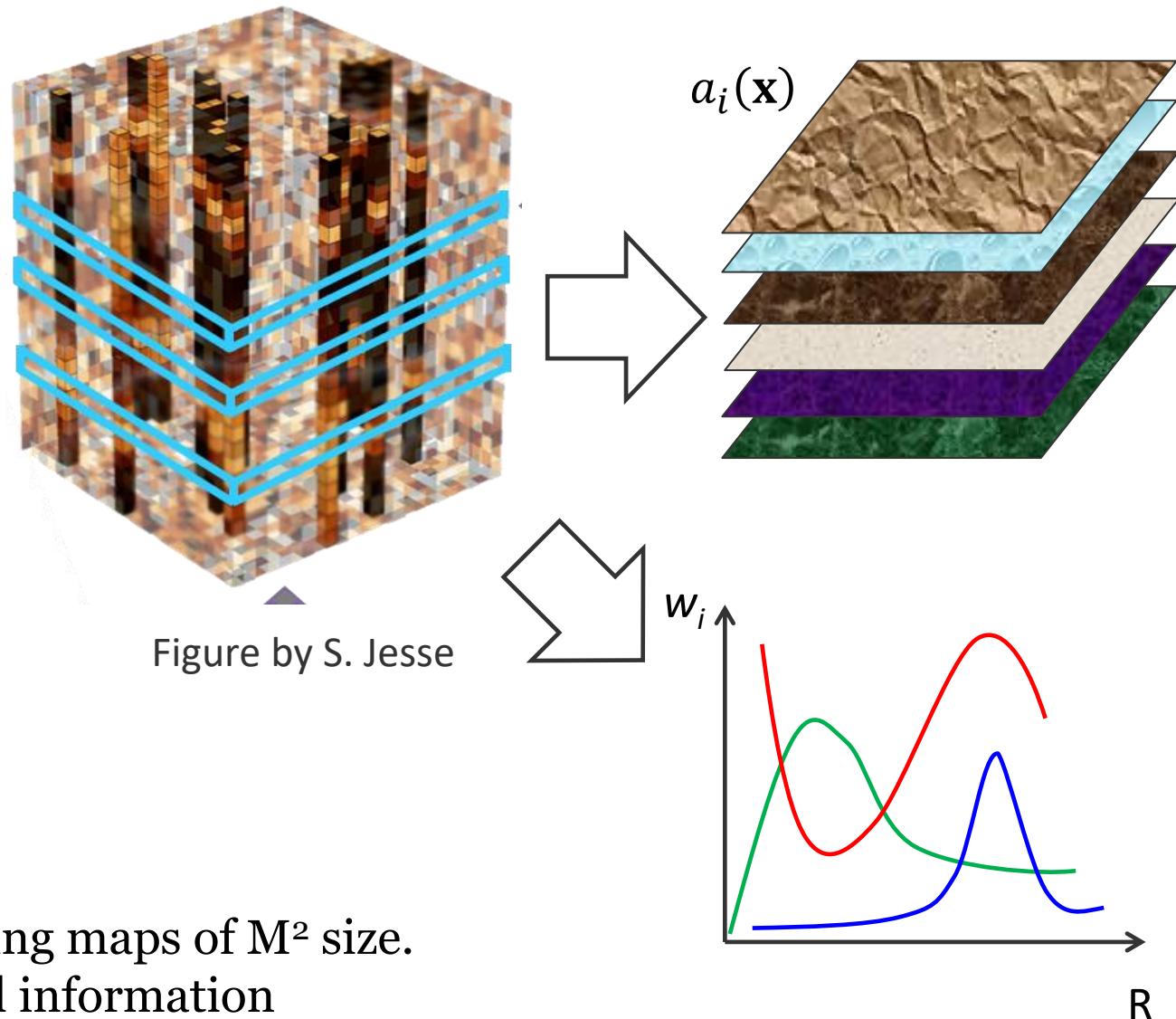
- \mathbf{x} is the spatial variable, $\mathbf{x} = (x, y)$
- \mathbf{R} is the (vector) parameter variable
- N is noise

Overall, for $M \times M$ image and P point in spectra, we have $M^2 P$ data points

We aim to get:

- $a_i(\mathbf{x})$ are loading maps
- $w_i(\mathbf{R})$ are endmembers/eigenvectors

Overall, we can have (maximum) P loading maps of M^2 size.
However, not all of them will have useful information



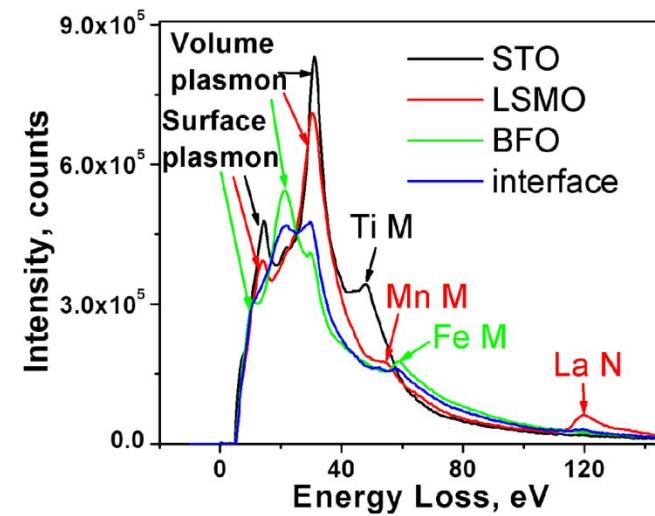
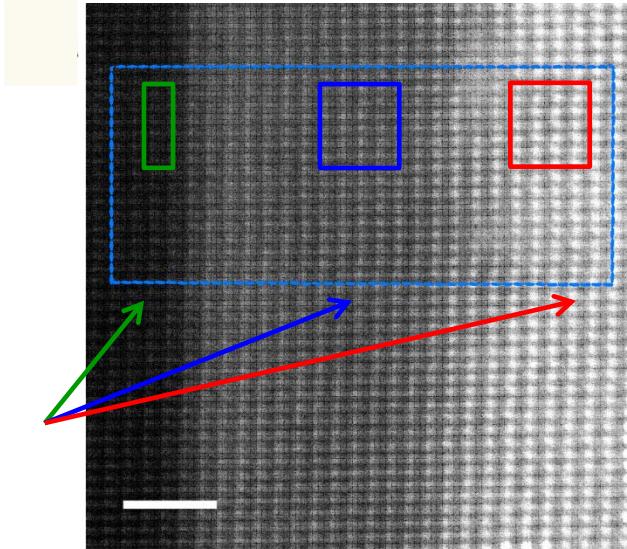
Multiple Linear Regression

Linear mixing $S(\mathbf{x}, \mathbf{R}) = \sum_i a_i(\mathbf{x}) w_i(\mathbf{R}) + N$ but $w_i(\mathbf{R})$ are known

STEM of STO/LSMO/BFO interface

Low-loss EELS spectra of three components

Standard spectra



A.Y. BORISEVICH ET AL,
*Suppression of Octahedral
Tilts and Associated
Changes in Electronic
Properties at Epitaxial
Oxide Heterostructure
Interfaces*, Phys. Rev. Lett.
105, 087204 (2010).

“Chemistry”:
35 to 125 eV



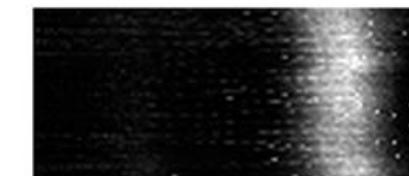
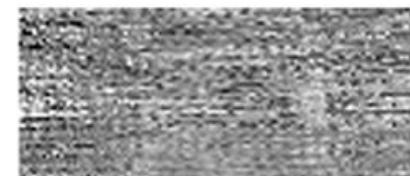
“Plasmons”
5 to 35 eV



Fit coefficient map

residuals map

χ^2 map



Principal Component Analysis

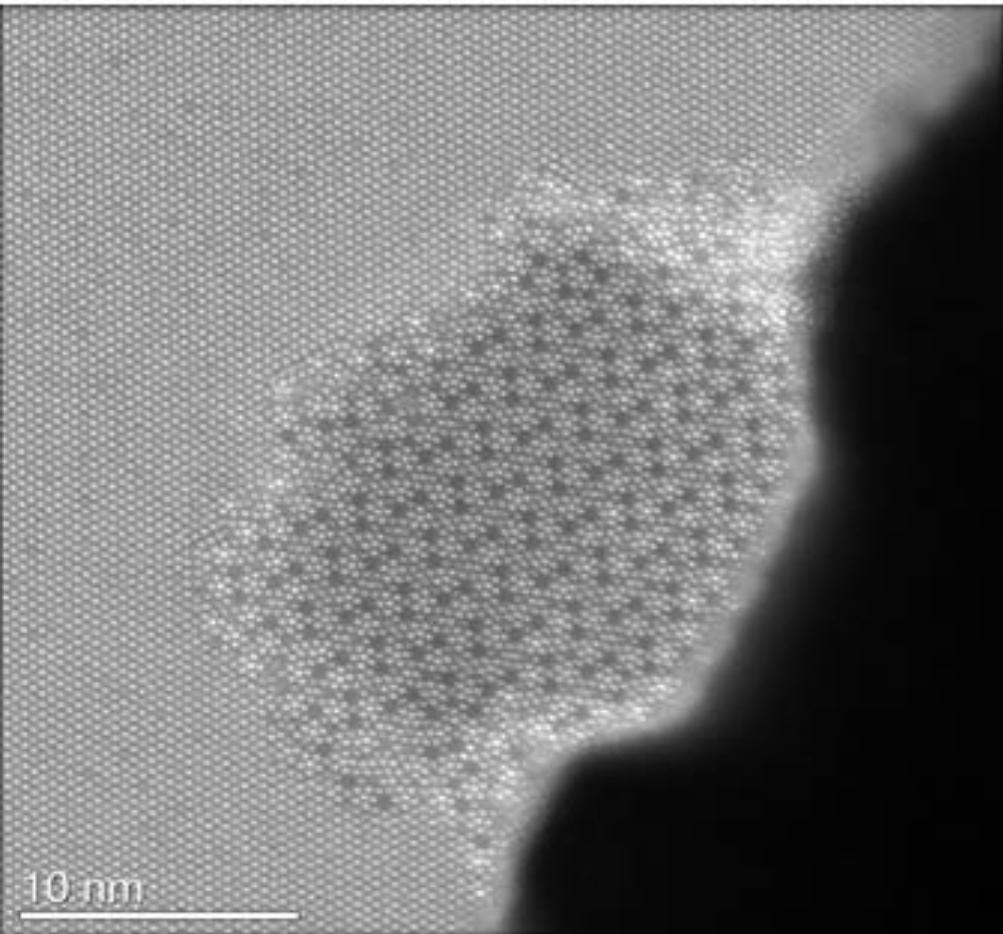
$$S(\mathbf{x}, \mathbf{R}) = \sum_i a_i(\mathbf{x}) w_i(\mathbf{R})$$

- In PCA, the eigenvectors $w_i(\mathbf{R})$ are orthonormal and are arranged such that corresponding eigenvalues are placed in descending order by variance
- Can be used to separate “real data” from “noise” – but needs cut-off/selection criteria
- PCA eigenvectors generally do not have defined physical meaning
- PCA is a starting point for many other unmixing methods

13_PCA_CL.ipynb

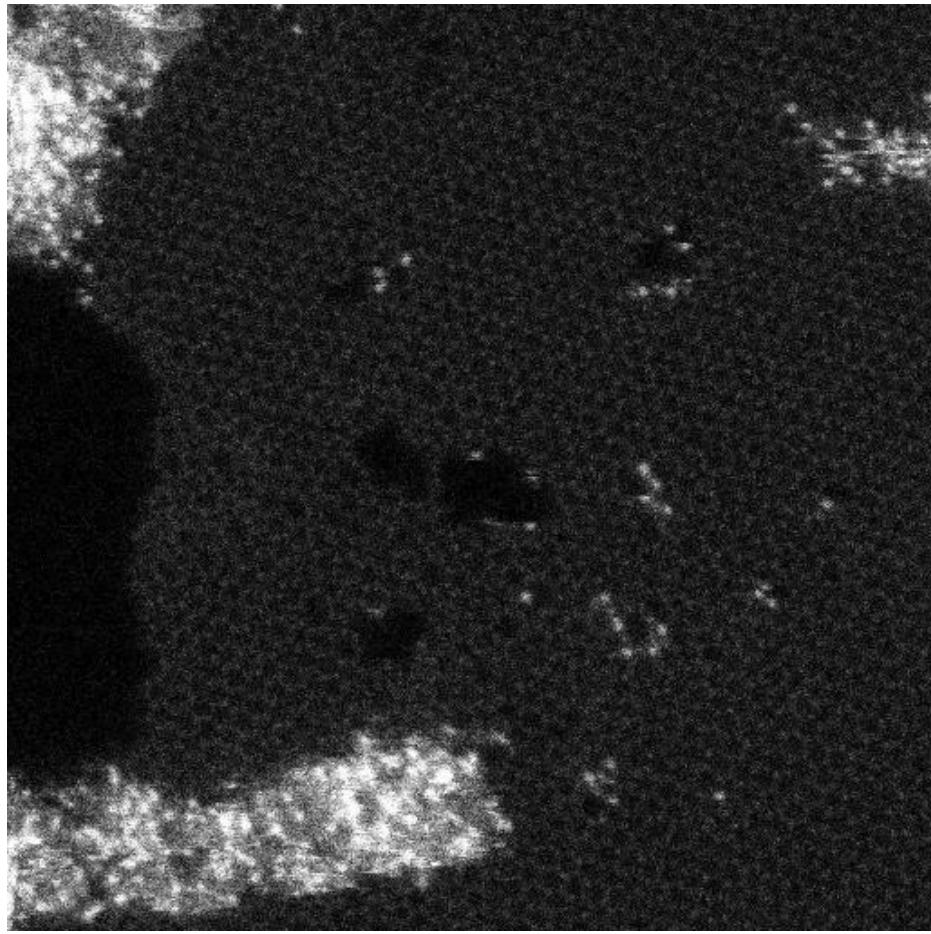
Chemically disordered systems

Mo-V-Ta complex oxide



Q. He et al, ACS Nano 9, 3470-3478

Si in graphene

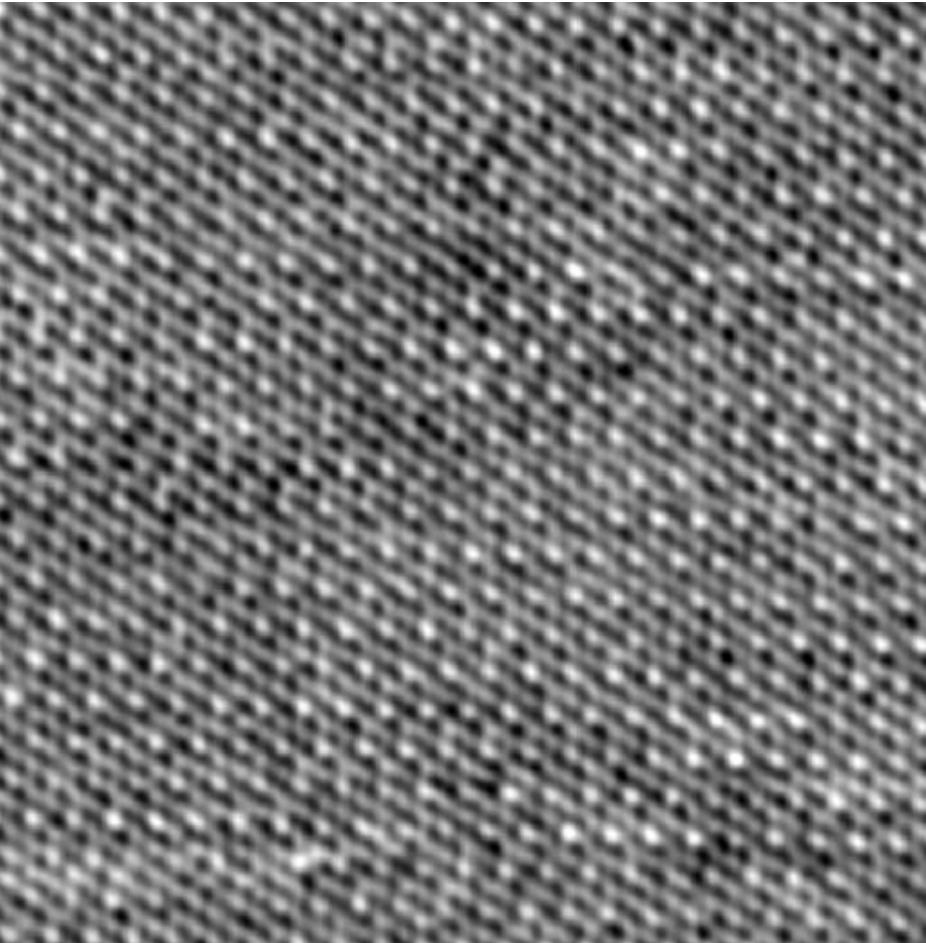


Data collected by O. Dyck (ORNL)

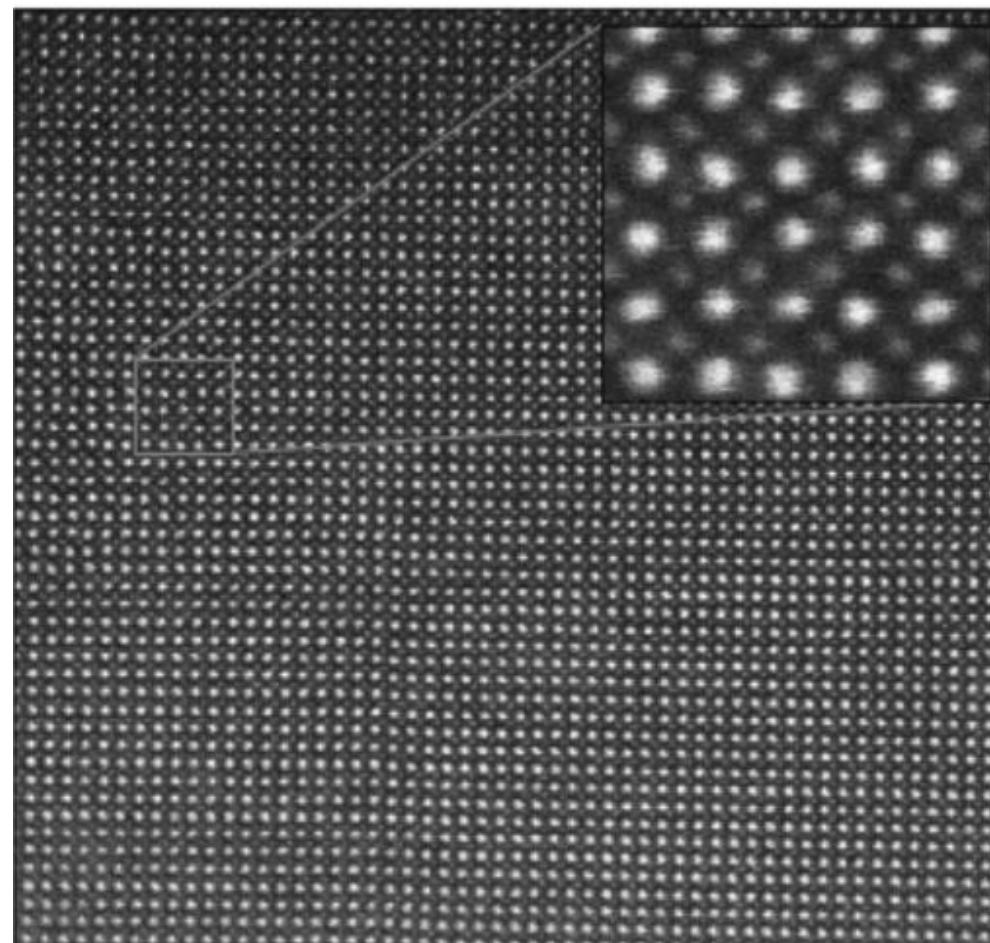
- What is the nature of the building blocks and relevant atomic configurations?
- Can we define single-phase regions and phase boundaries?

But what about subtle distortions?

Electronic structure in RuCl₃



BiFeO₃ on SrRuO₃



- Can we identify ferroelectric and ferroic variants and associated topological defects?
- What is the nature of the phases?

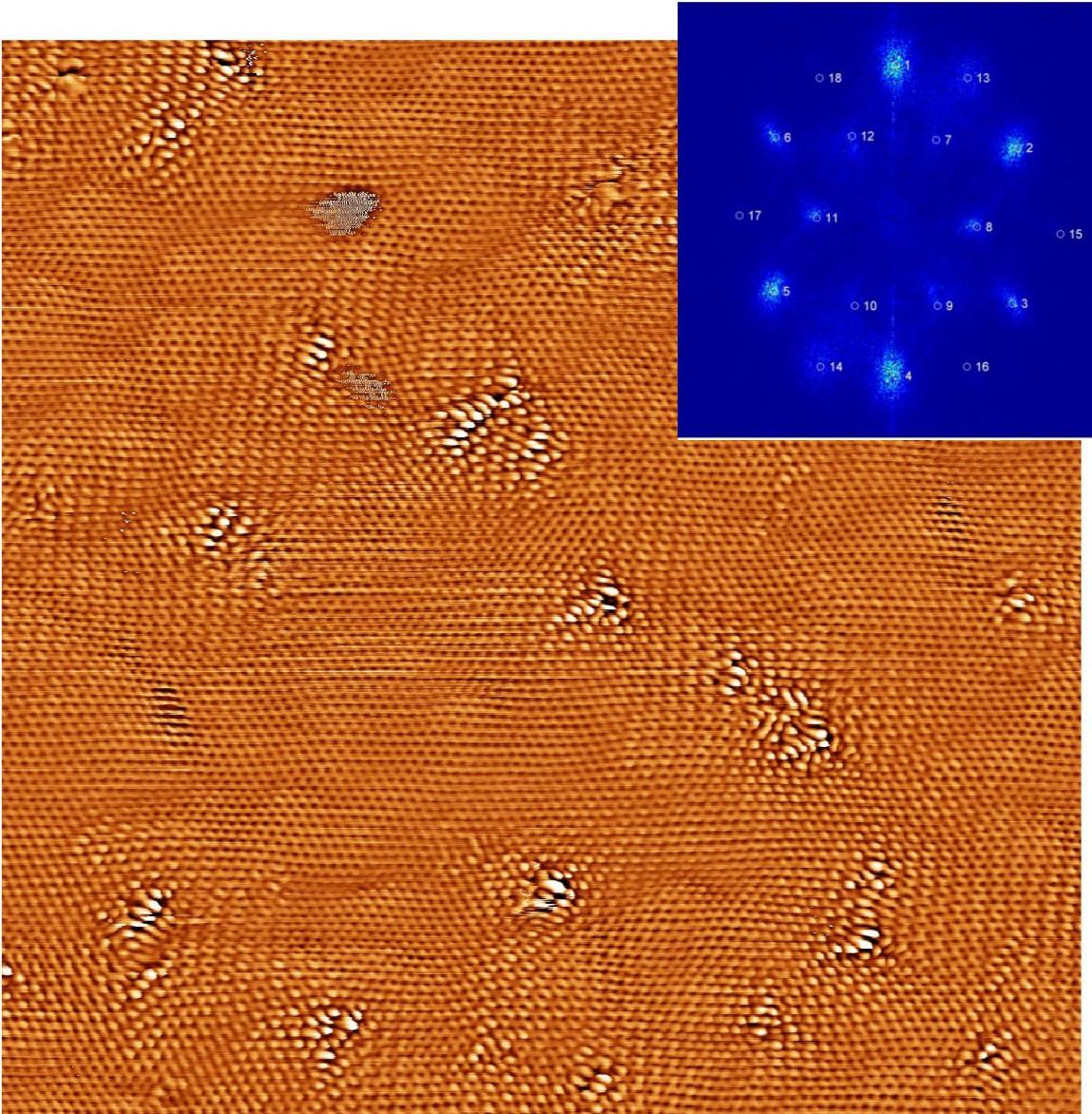
Can global FFT help?

- Global FFT – everything is averaged:
 - Drift
 - Extended defects
 - Multiple grains

We are averaging out all interesting phenomena except for small spatially uniform structural distortions

- Solution – sliding window approaches:
 - Fit FFT peaks: amplitudes, positions
 - Multivariate analysis

Note: window can be also tied to a specific feature, such a selected atom. Then we explore atomic neighborhood



General linear unmixing

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We start with:

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- \mathbf{R} is the (vector) parameter variable

We aim to get:

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- $w_i(\mathbf{R})$ are endmembers/eigenvectors
- N is noise

The M pixel 2D image is transformed to M/N pixel image of more complex structure.

Our loading map is 2D image, and
endmembers/eigenvectors are 2D images

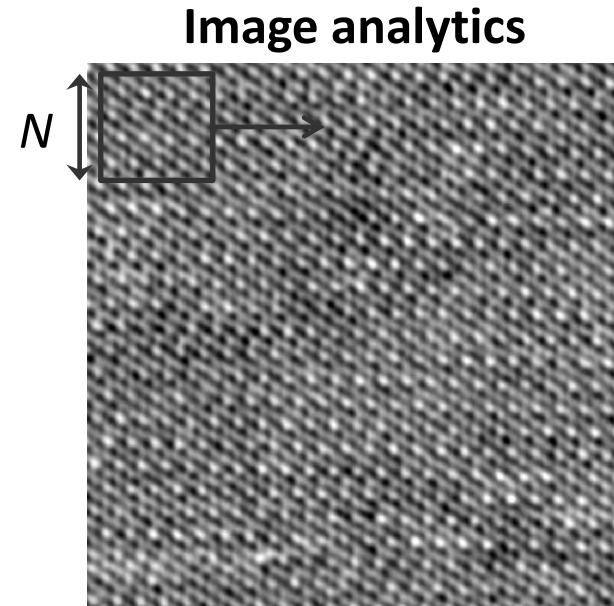
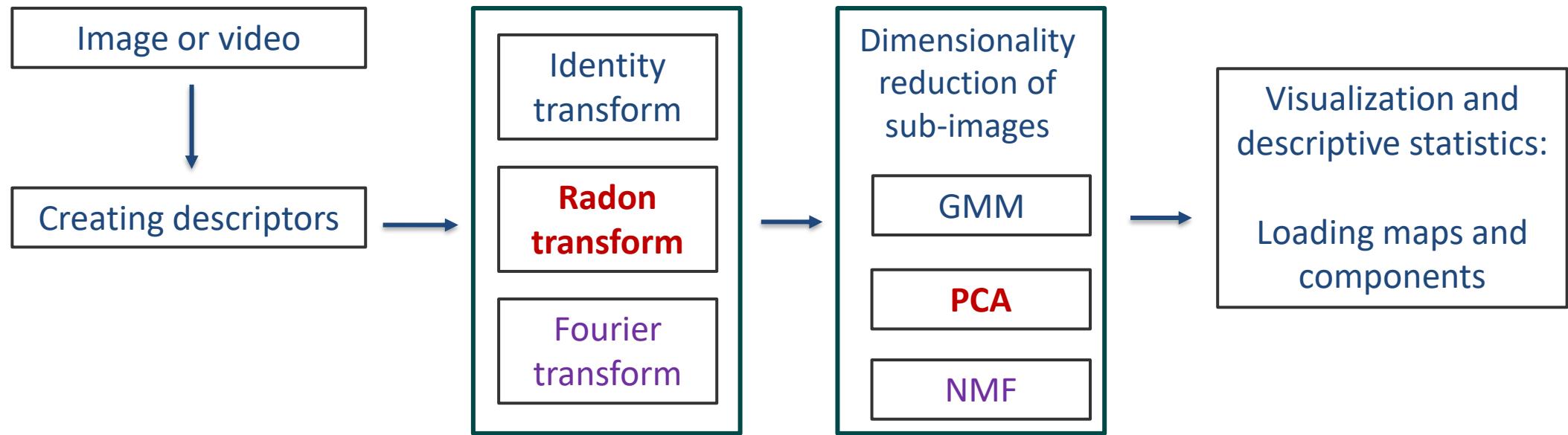


Figure by M. Ziatdinov

Sliding image transforms:

- Fast Fourier Transforms
- Correlation functions
- Intensity histograms
- Structural descriptors

Example of analysis pipeline



Pipelines are defined to

- Make analysis traceable, repeatable, explainable, and transferable
- Allow for hyperparameter tuning and optimization
- Efficiently use the memory

Sliding PCA-FFT

Can we use PCA of FFT transform in sliding windows to find periodicity?

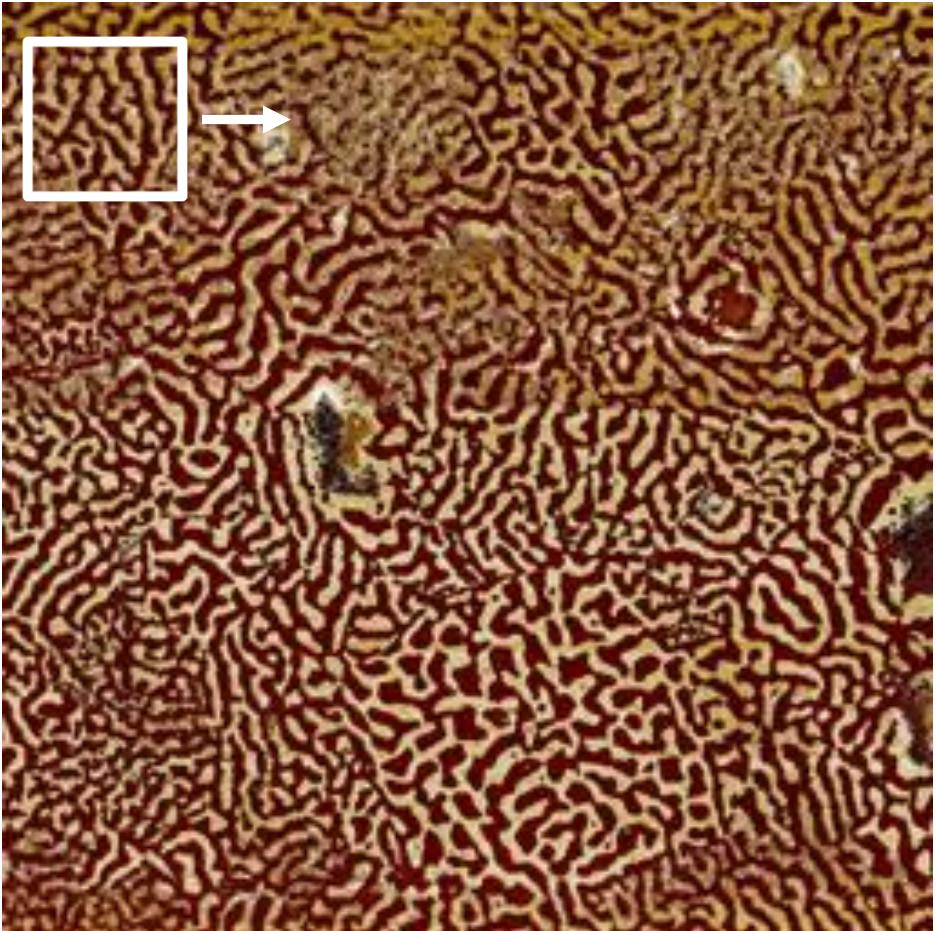
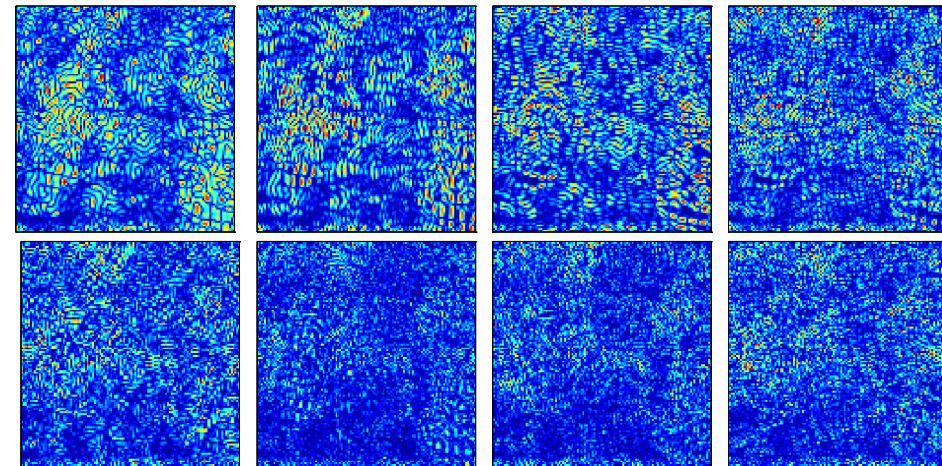
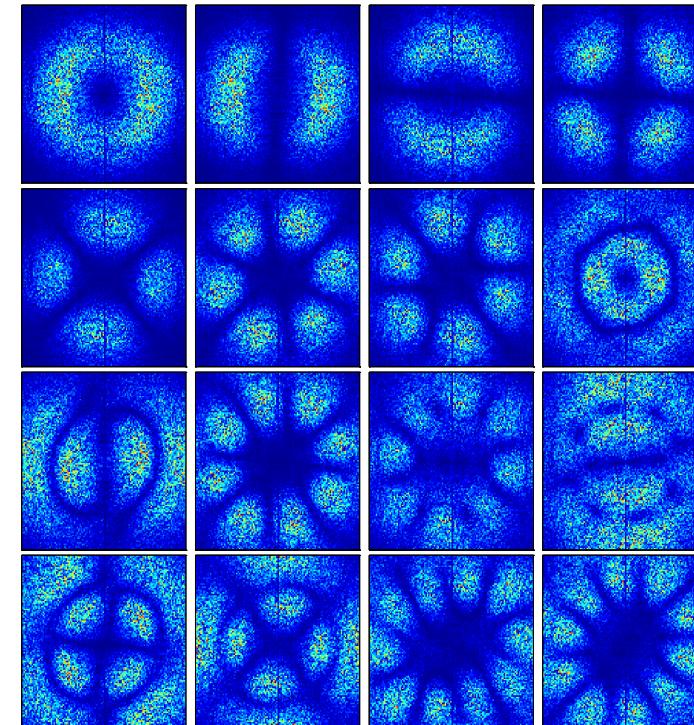


Figure by S. Jesse, data D. Gobellic

First 8 maps



First 16 eigenvectors



Spectral Unmixing: N-FINDR

Spectra for a given pixel is assumed to be a linear combination of the end-member spectra (+ Gaussian noise). The mixing proportions sum to 1

Physics constraint

$$p_{ij} = \sum_k e_{ik} c_{kj} + \varepsilon \quad \sum_k c_{kj} = 1$$

- Let E be the matrix of end-members (here, 3).

$$E = \begin{bmatrix} 1 \\ \vec{e}_1 & \vec{e}_2 & \vec{e}_3 \end{bmatrix} \quad V \left(\frac{1}{(l-1)!} \right) |\det(E)|$$

- Iteratively select endmembers, accepting the new selection if the volume increases

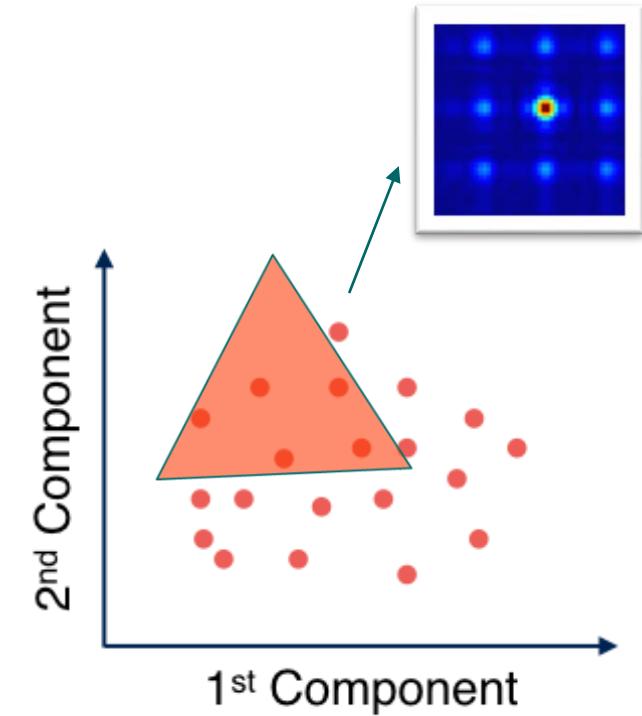


Figure by R. Vasudevan

Ideal test case

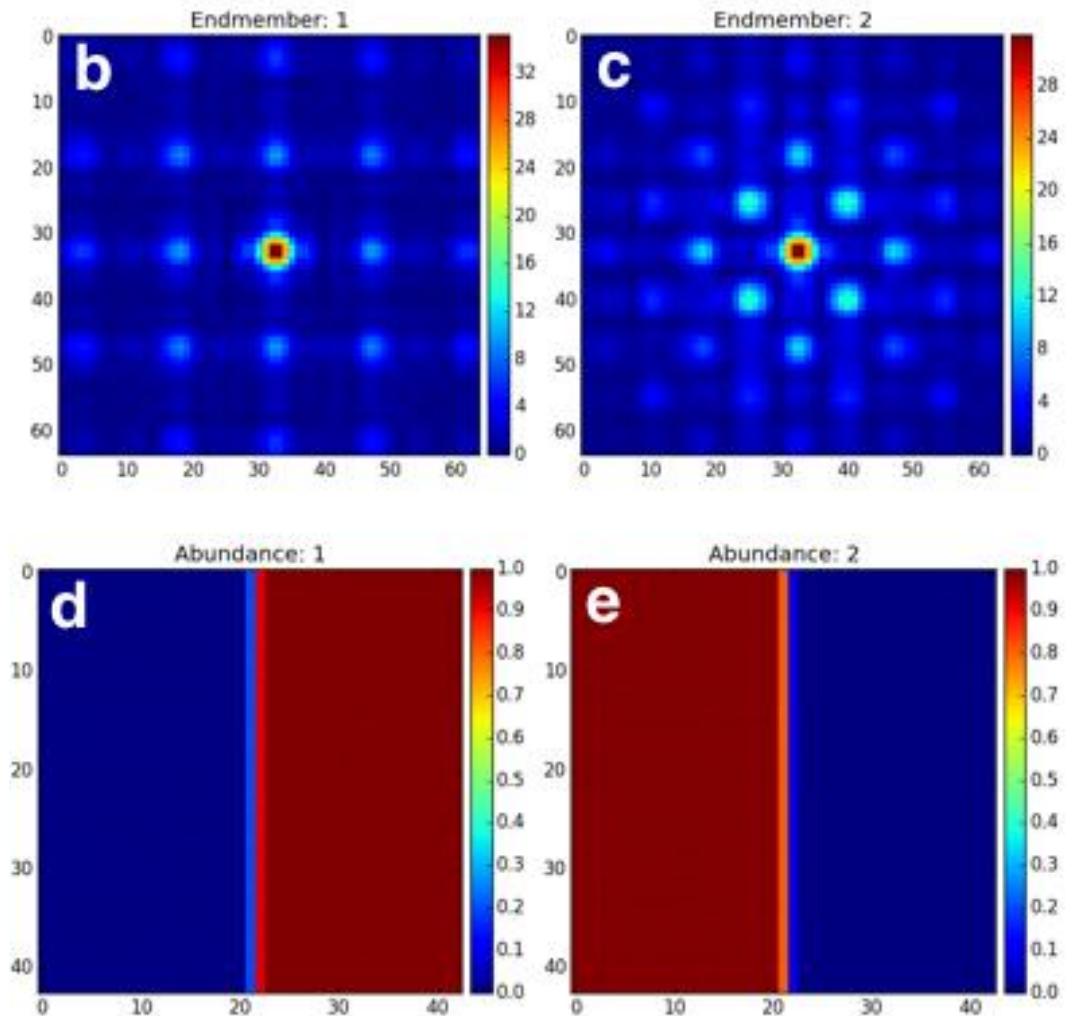
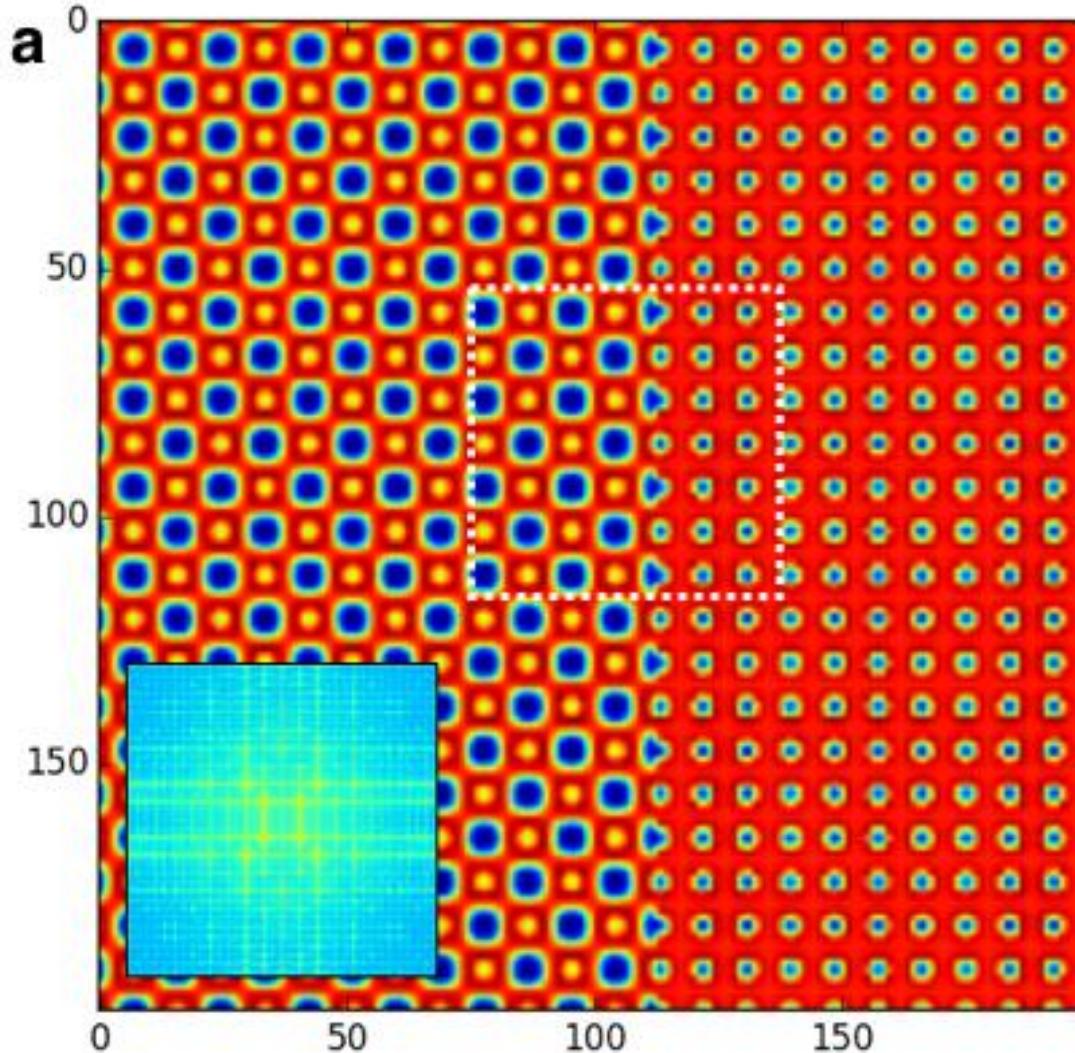
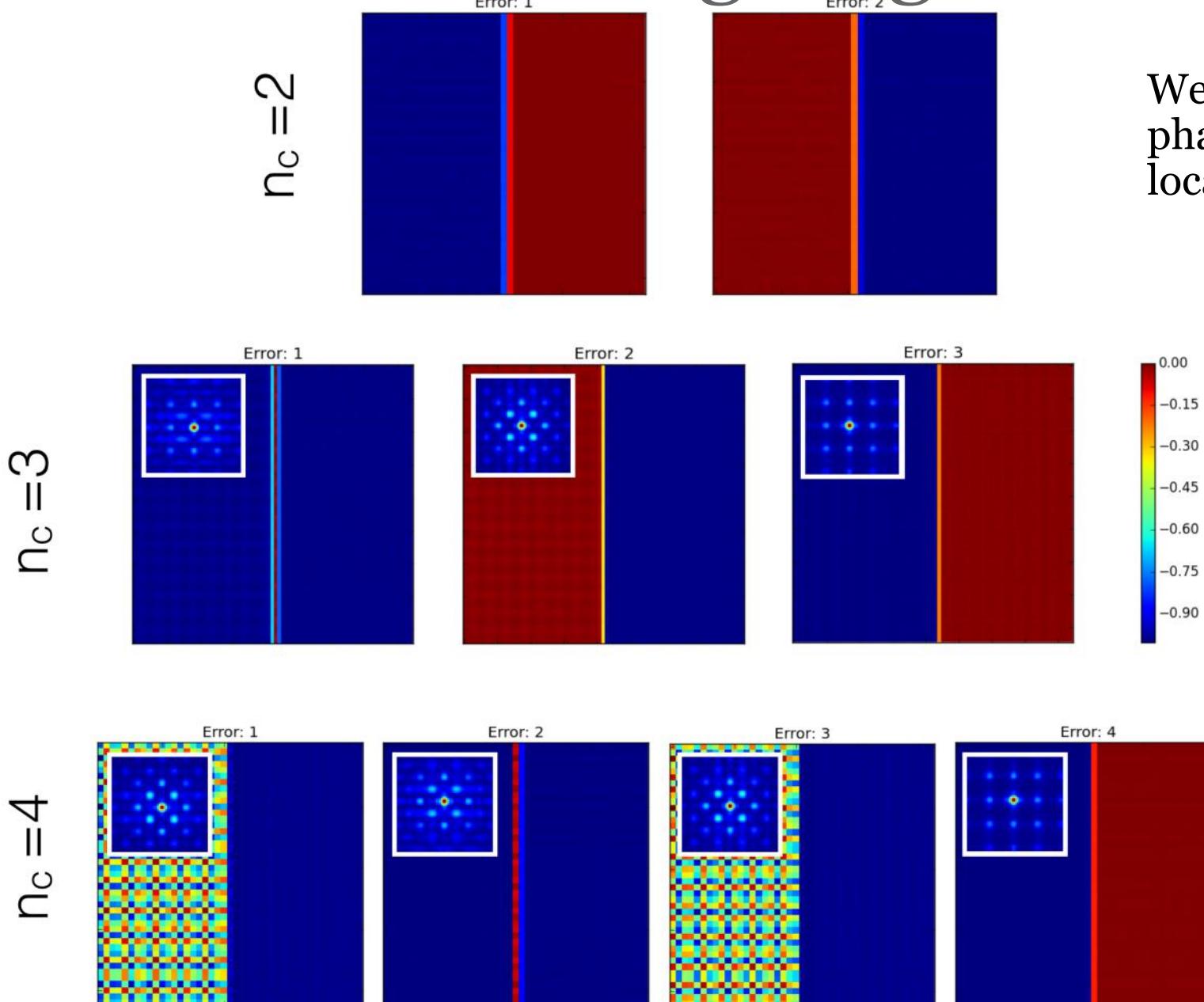


Figure by R. Vasudevan

Main idea:

- FFT amplitudes are non-negative;
- FFT removes translation

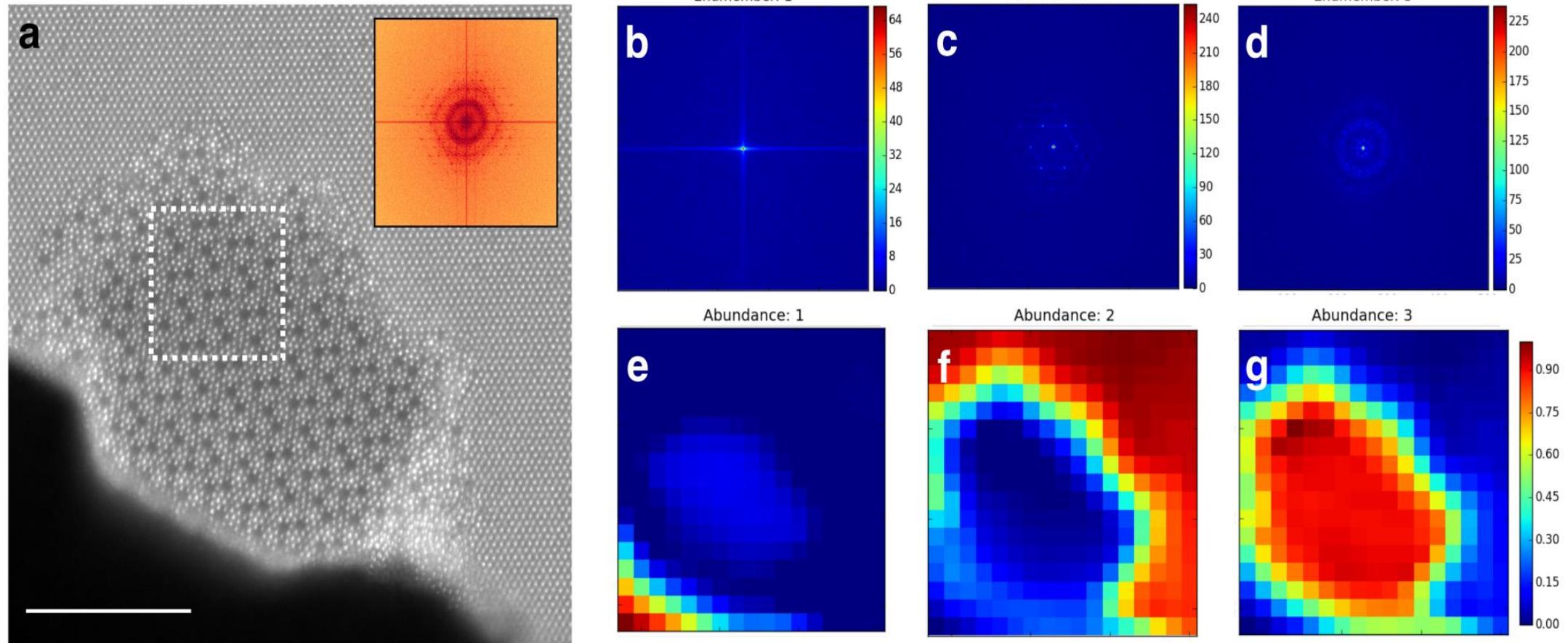
N-FINDR for image segmentation



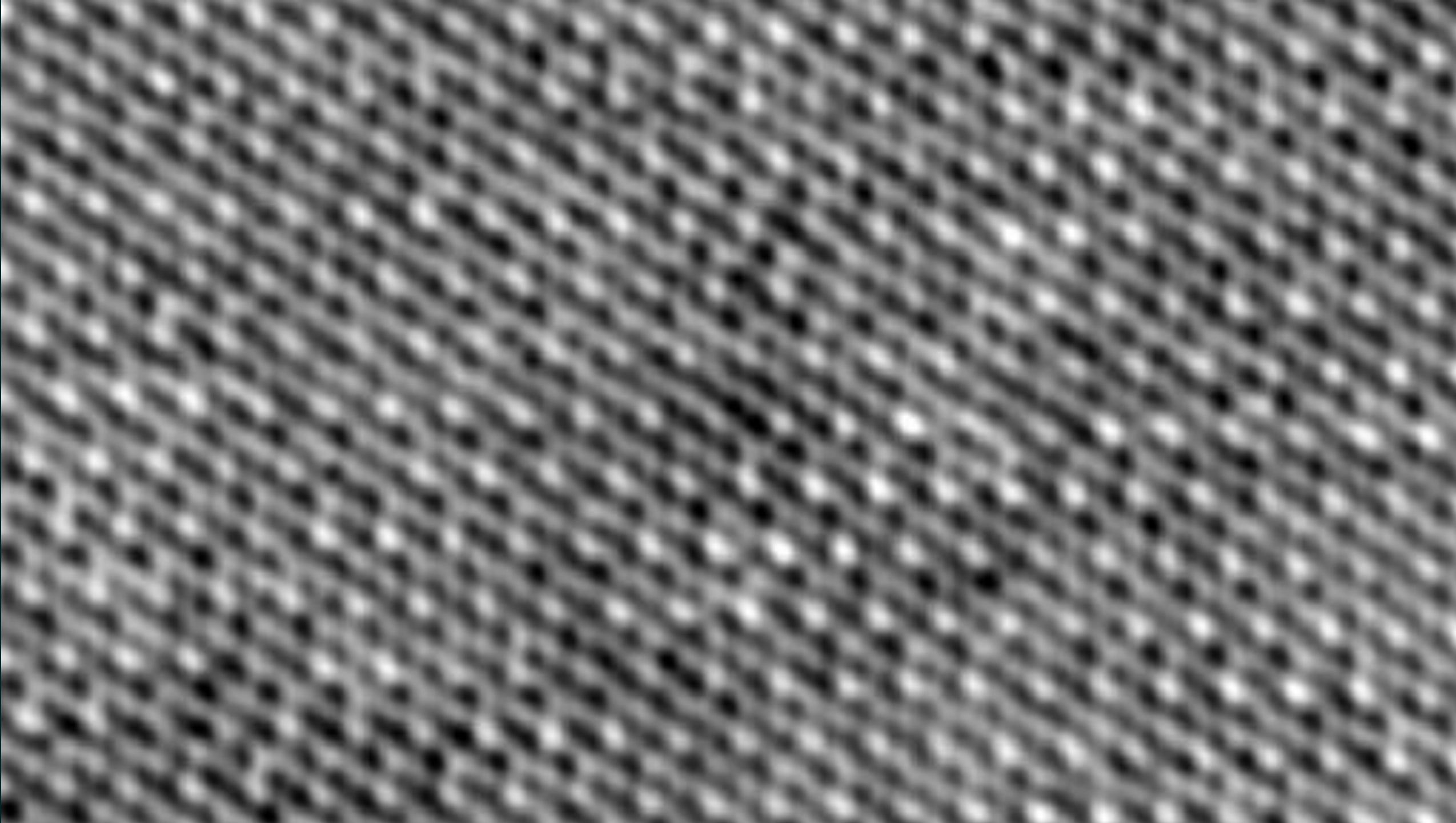
We can determine number of phases based on spatial localization and geometry

Figure by R. Vasudevan

N-FINDR for chemically separated images

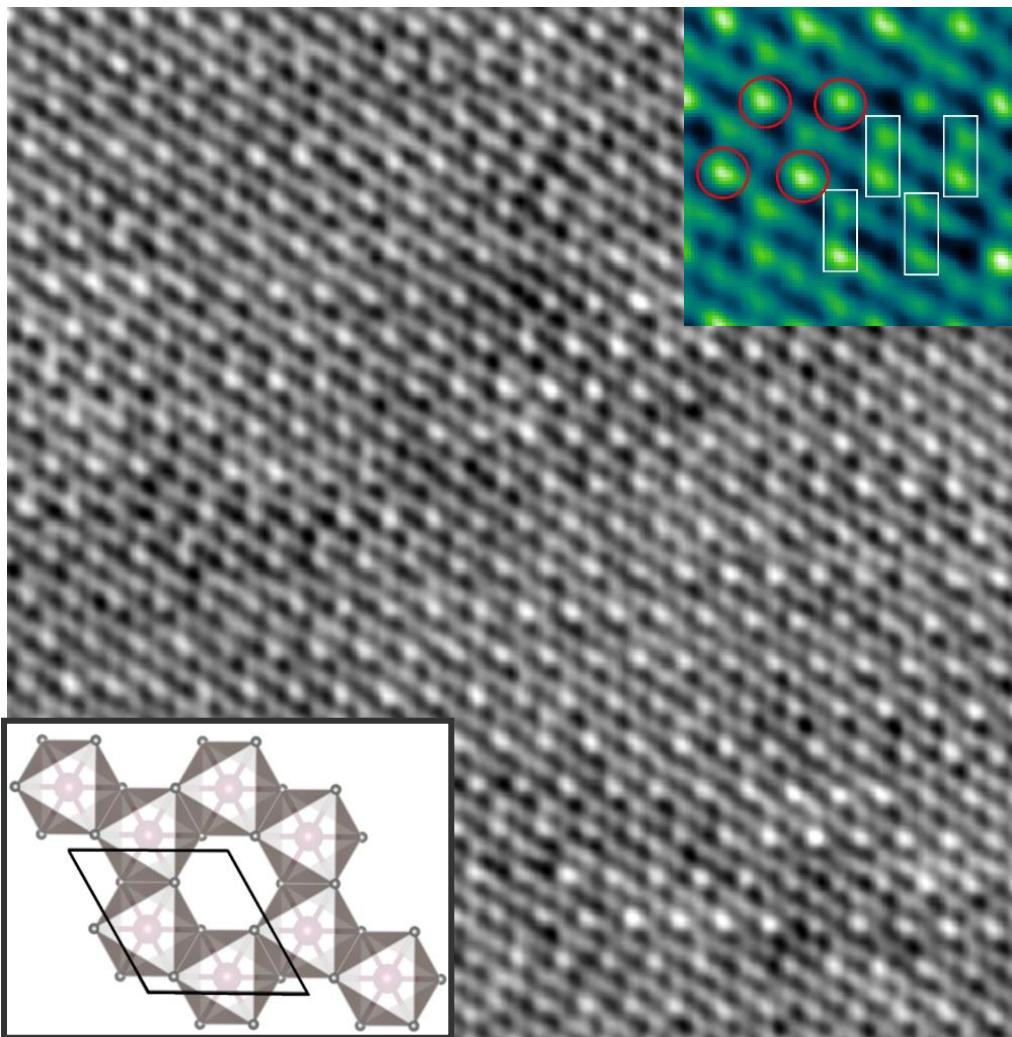


Q. He, J. Woo, A. Belianinov, V.V. Gulians, A.Y. Borisevich, *Better catalysts through microscopy: mesoscale M₁/M₂ intergrowth in Molybdenum–Vanadium based complex oxide catalysts for propane ammoxidation*, ACS Nano 9, 3470-3478

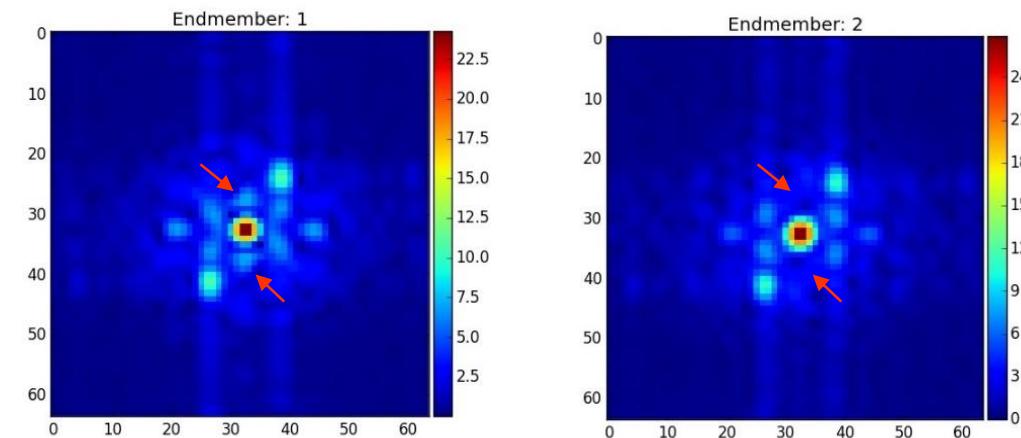


NFINDR for coexisting order parameters

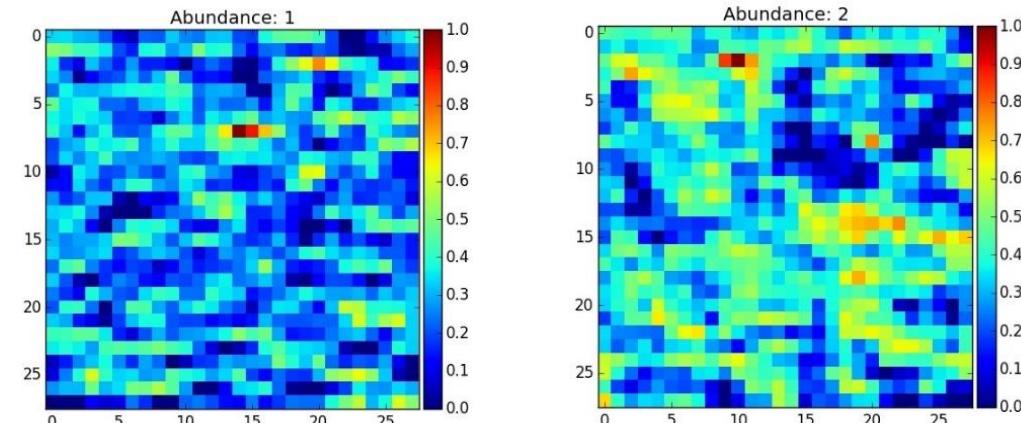
Input experimental image



FFT endmembers



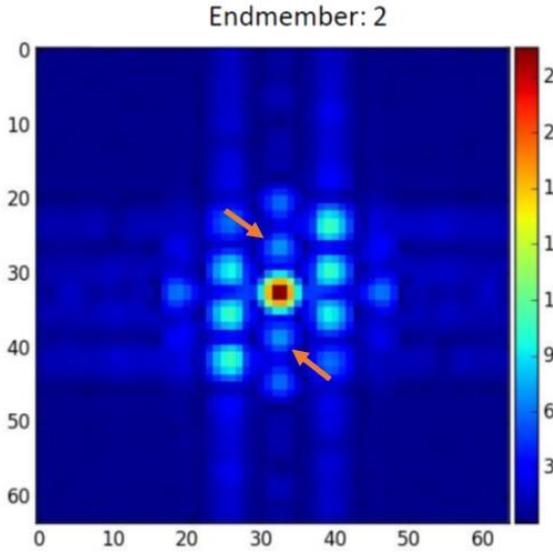
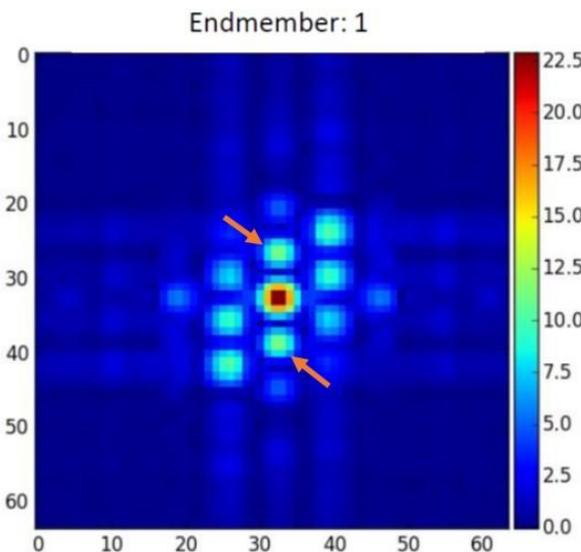
Real-space abundance maps



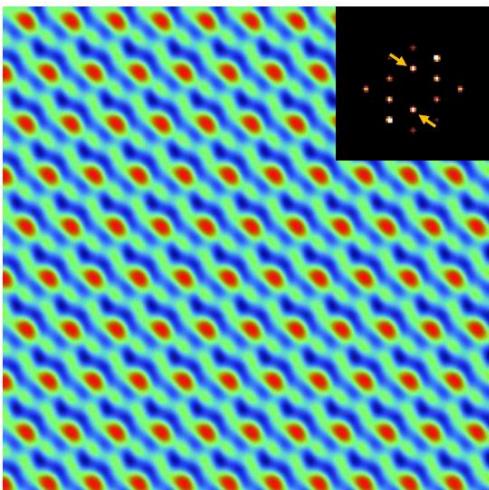
In a good agreement with test case, 2 spots in the “inner hexagon” are strongly suppressed in the 2nd component reflecting a fine structure of charge ordered pattern

NFIND-R for coexisting order parameters

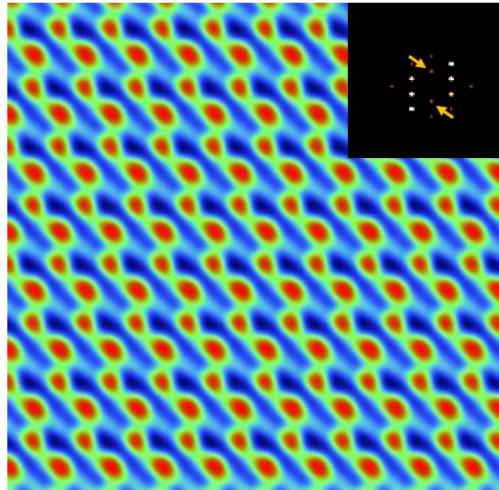
FFT endmembers



Real-space images of corresponding phases



Hexagonal superlattice



Dimer superlattice

In the 2nd component, 2 spots in the “inner hexagon” are strongly suppressed reflecting a fine structure of charge ordered pattern

M. ZIATDINOV, A. BANERJEE, A. MAKSOV, T. BERLIJN, W. ZHOU, H.B. CAO, J.Q. YAN, C.A. BRIDGES, D.G. MANDRUS, S.E. NAGLER, A.P. BADDORF, and S.V. KALININ, *Atomic-scale observation of structural and electronic orders in the layered compound α -RuCl₃*, Nature Comm. 7, 13774 (2016).

Sliding FFT:

- We always have a problem of window size:
 - too large – loose spatial resolution,
 - too small – FFT behaves poorly due to edge effects
- Interpretation of FFT data is complicated (too much data if fit each peak, unclear meaning of the unmixing components)
- Natural descriptor for atomically resolved images – atomic coordinates!

Local crystallography

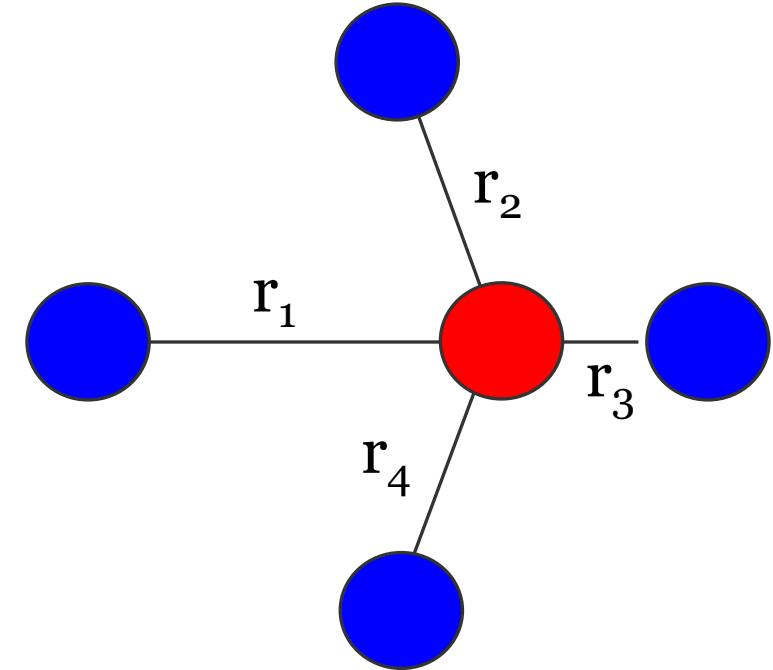
For each atom, define nearest neighbors and generate array of the corresponding radius-vectors of the form

$$NA_{ij} = (rx_1, ry_1, rx_2, ry_2, rx_3, ry_3, rx_4, ry_4)_{ij}$$

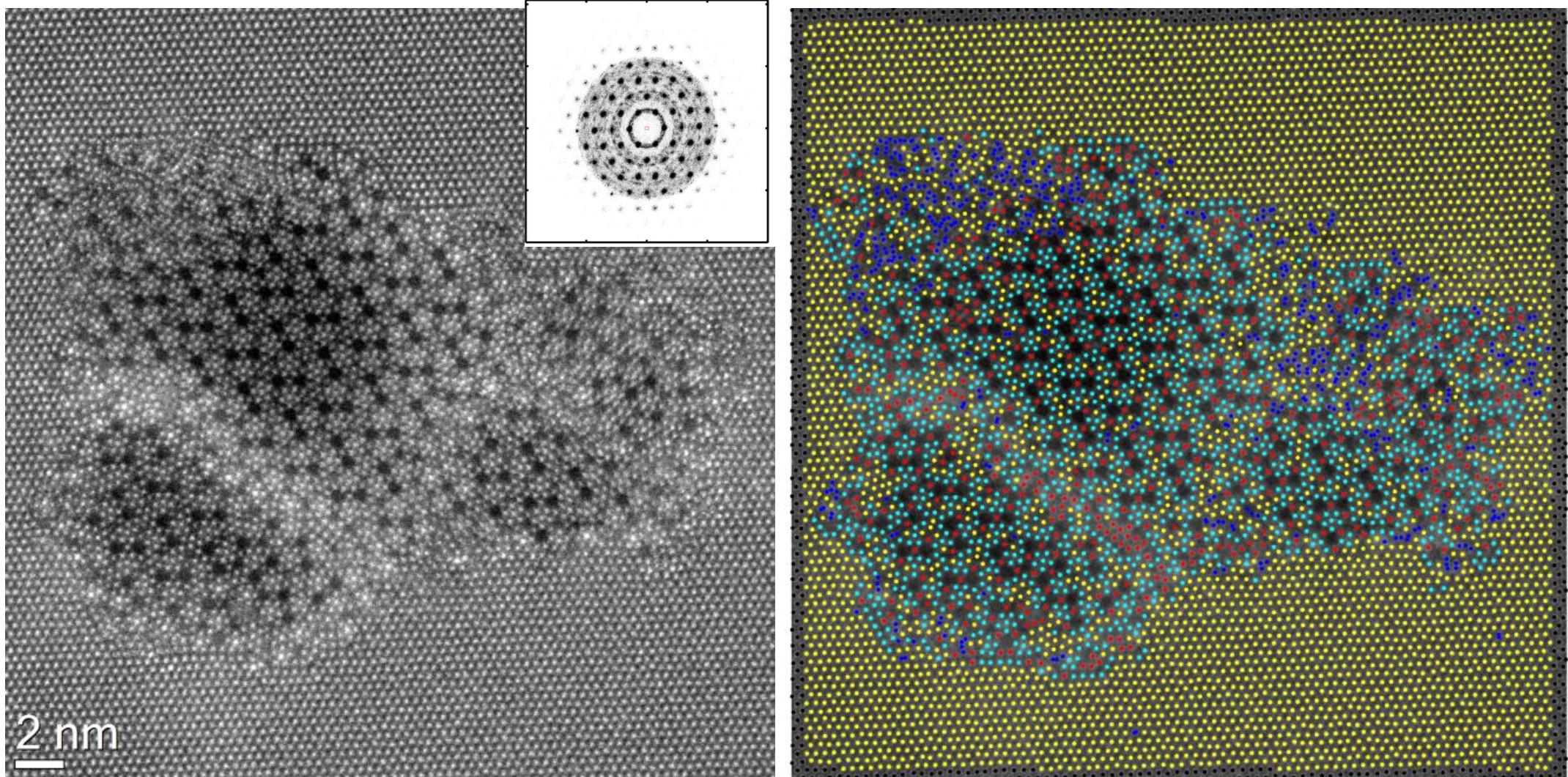
Indexes 1,2,3,4 are chosen in the same sense for all atoms
(generalization for different lattice and/or next coordination sphere obvious)

Then, phase/ferroic variant identification problem can be reduced to finding equivalent (in statistical sense) groups of nearest neighbors

We can also use group theory to make hypotheses, e.g.
add translation symmetry operations, i.e. $i \rightarrow i+1$ and $j \rightarrow j+1$ for lattice doubling)



Local crystallography: k-means



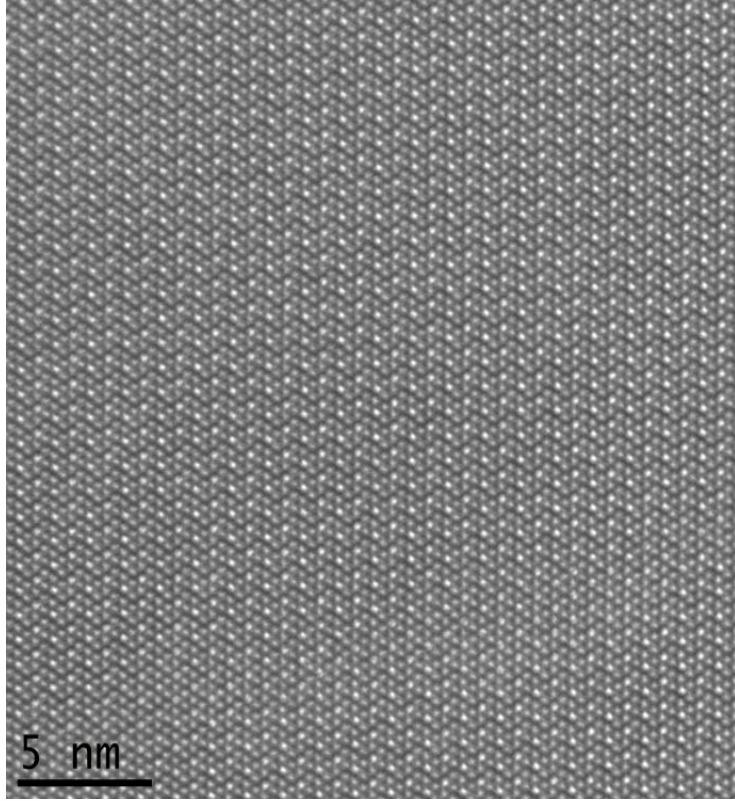
A. BELIANINOV, Q. HE, M. KRAVCHENKO, S. JESSE, A. BORISEVICH, and S.V. KALININ, *Identification of phases, symmetries, and defects through local crystallography*, Nat. Comm. **6**, 7801 (2015).

5 nm

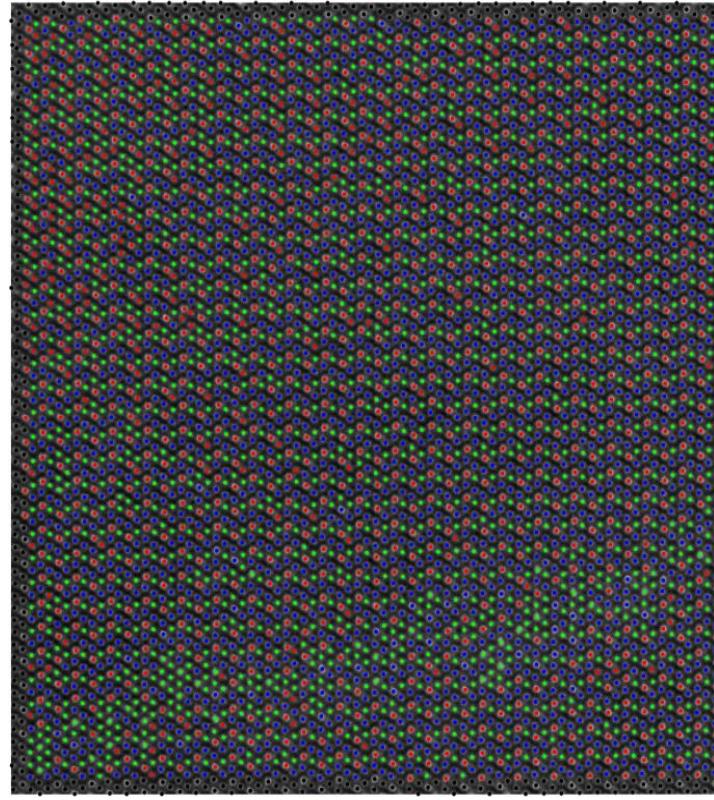
Local crystallography

THE UNIVERSITY OF TENNESSEE  KNOXVILLE

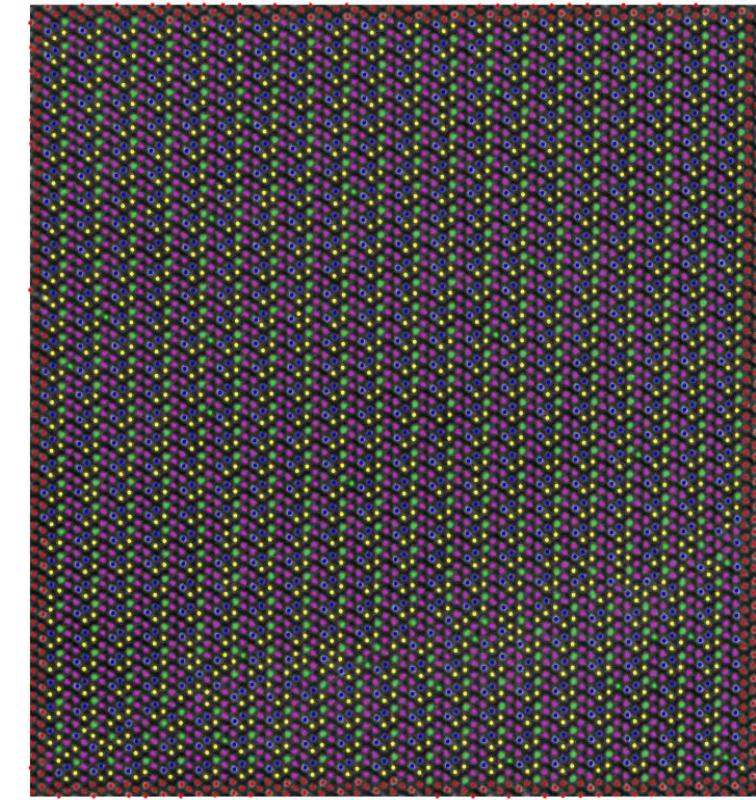
Image



K-means full vector



K-means angles



Normal modes: group theory

- **Group Representations** map group elements onto matrices, ensuring matrix multiplication aligns with the group operation.
- Molecules have **symmetries** defined by point groups linked to symmetry operations, such as rotations.
- Molecules have various **vibrational modes** with specific symmetries. Using the molecule's point group, one can deduce which modes are spectroscopically active.
- **Selection Rules:** Group representations dictate which vibrational modes appear in techniques like IR or Raman. Some modes may be IR-active but not Raman-active based on symmetry.
- **Vibrational frequencies** indicate energy differences between vibrational levels that are connected to group representations

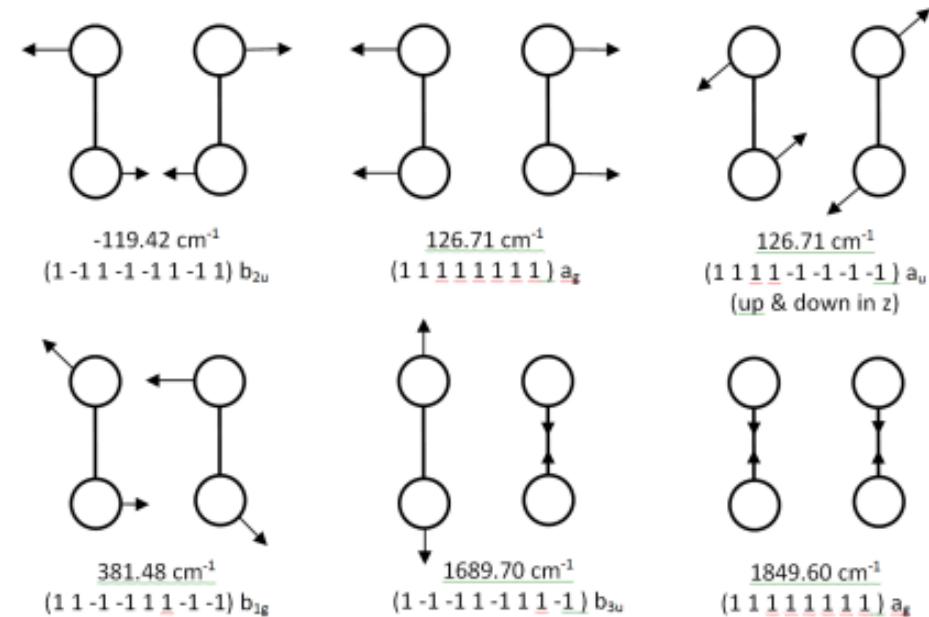
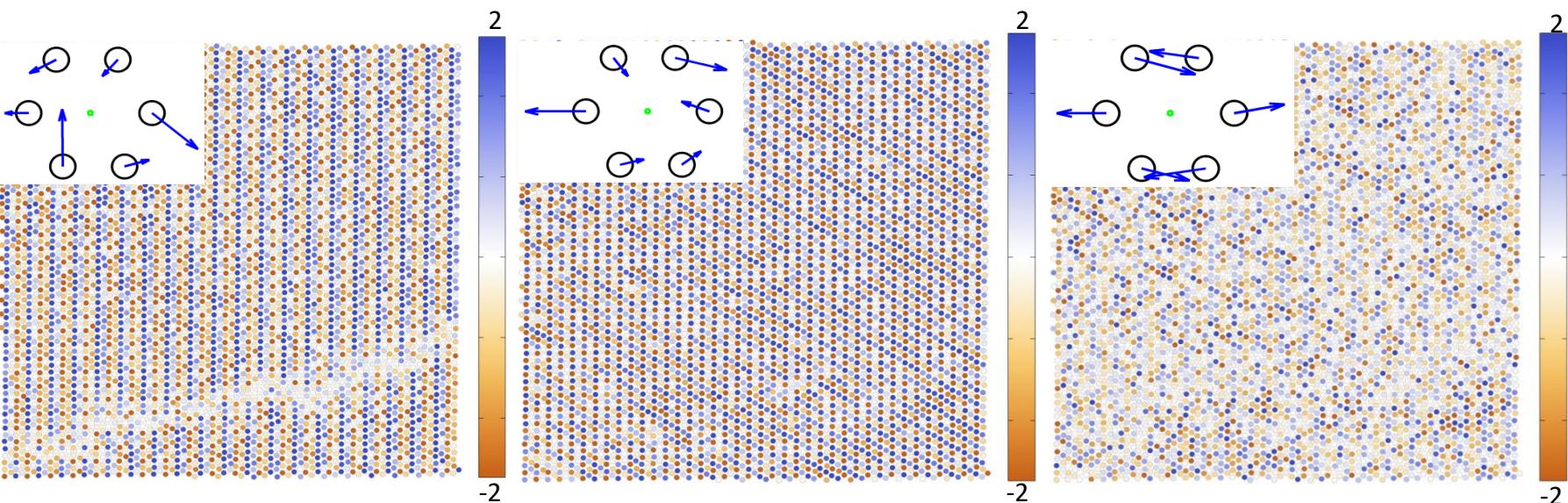
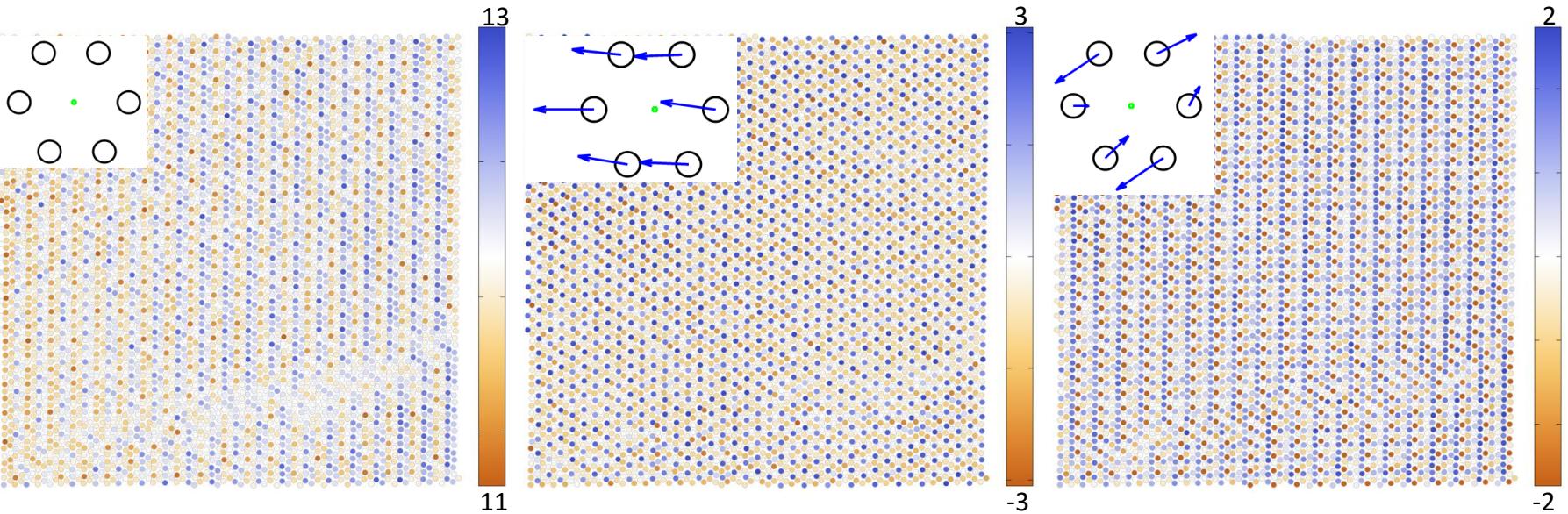


Figure 2: Sketches of Normal Modes of O_4^+

Table 2: Character Table for Point Group D_{2h}

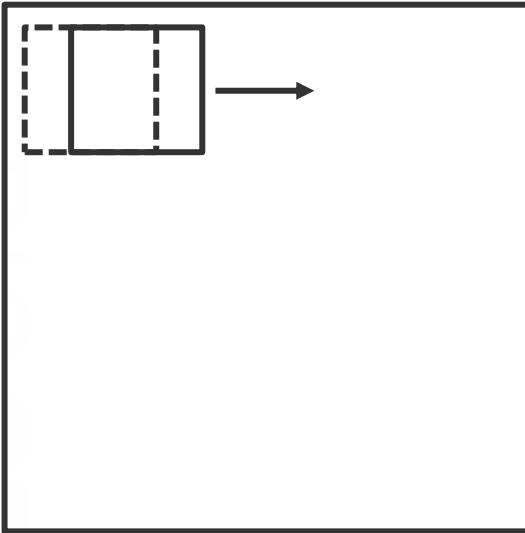
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2	
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

Local crystallography: PCA

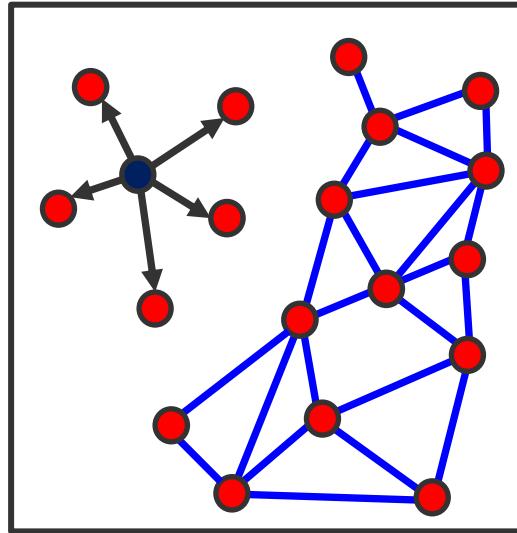


Constructing the descriptors

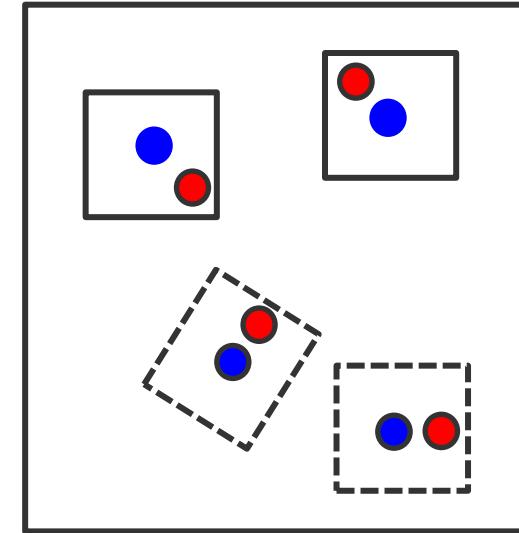
**Continuous
translational
symmetry**



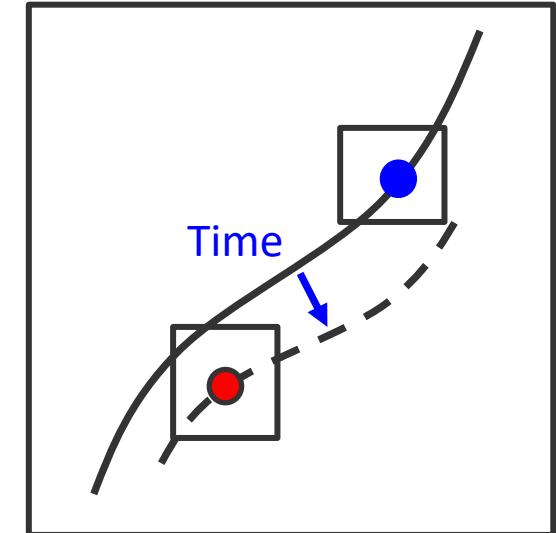
**Atom based
descriptions**



**Localized
sub-images**



**Time-delayed
descriptors**

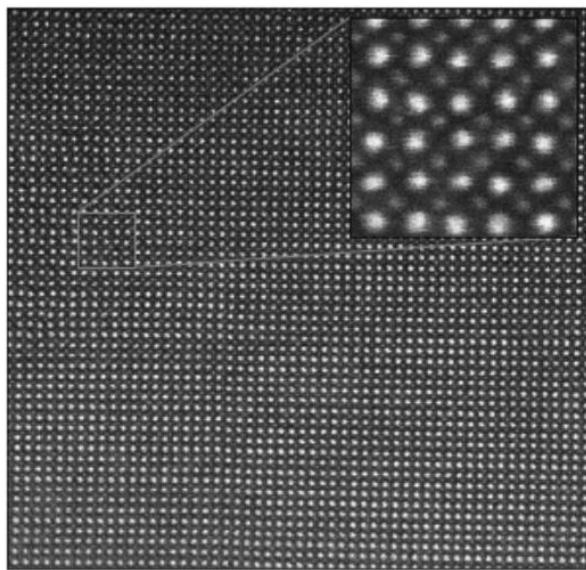


The choice of the descriptor:

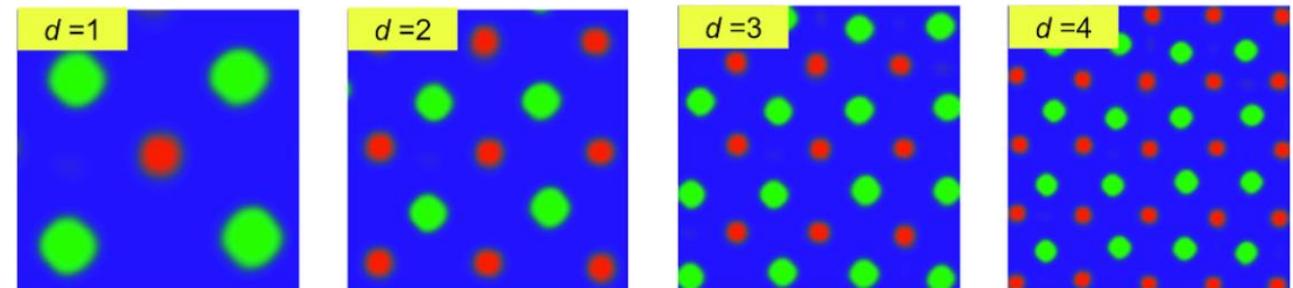
- Defines physical inferential biases and allows to introduce prior knowledge
- Determines the physical meaning of the analysis
- Establishes the analysis pipeline

Local crystallography: FerroNET

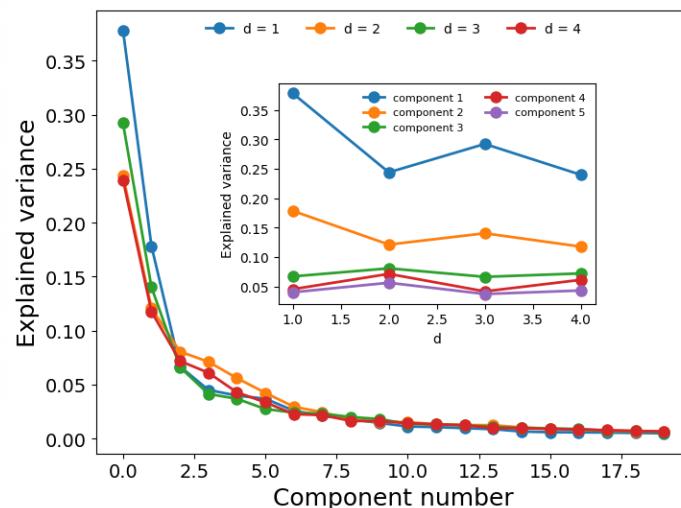
Experimental (LBFO film)



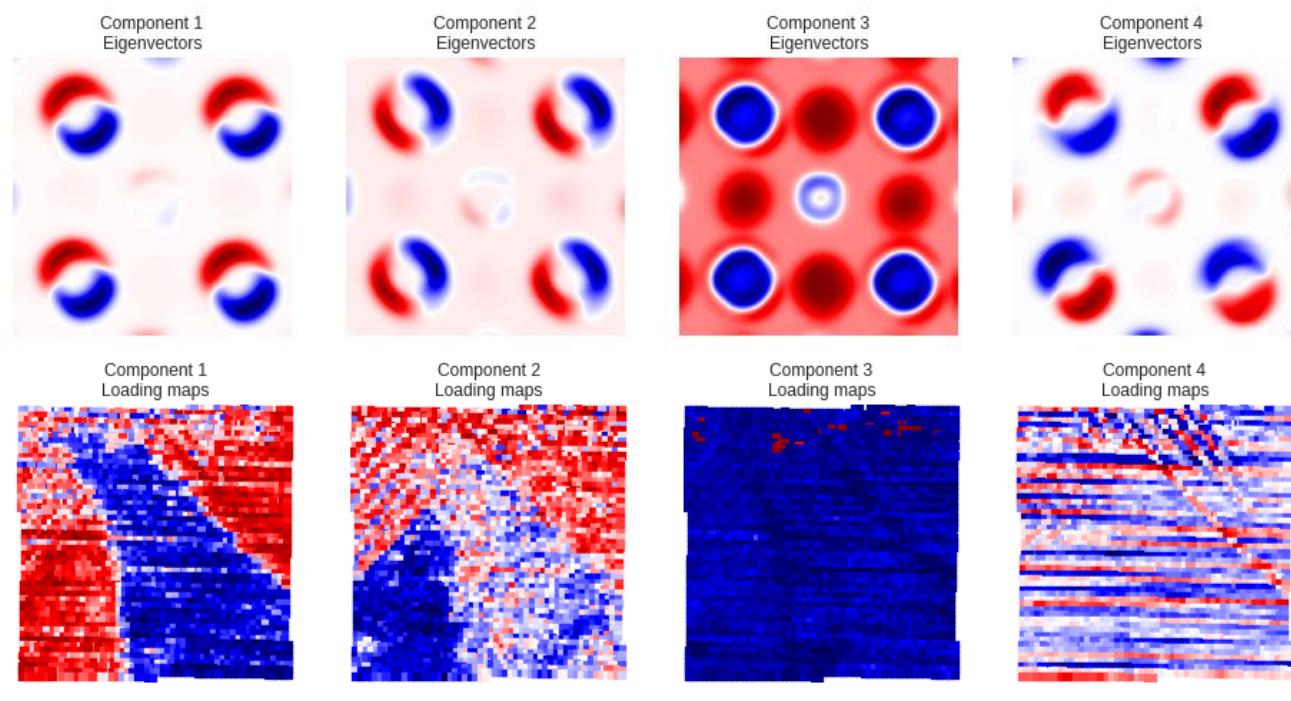
Building blocks (from neural network output)



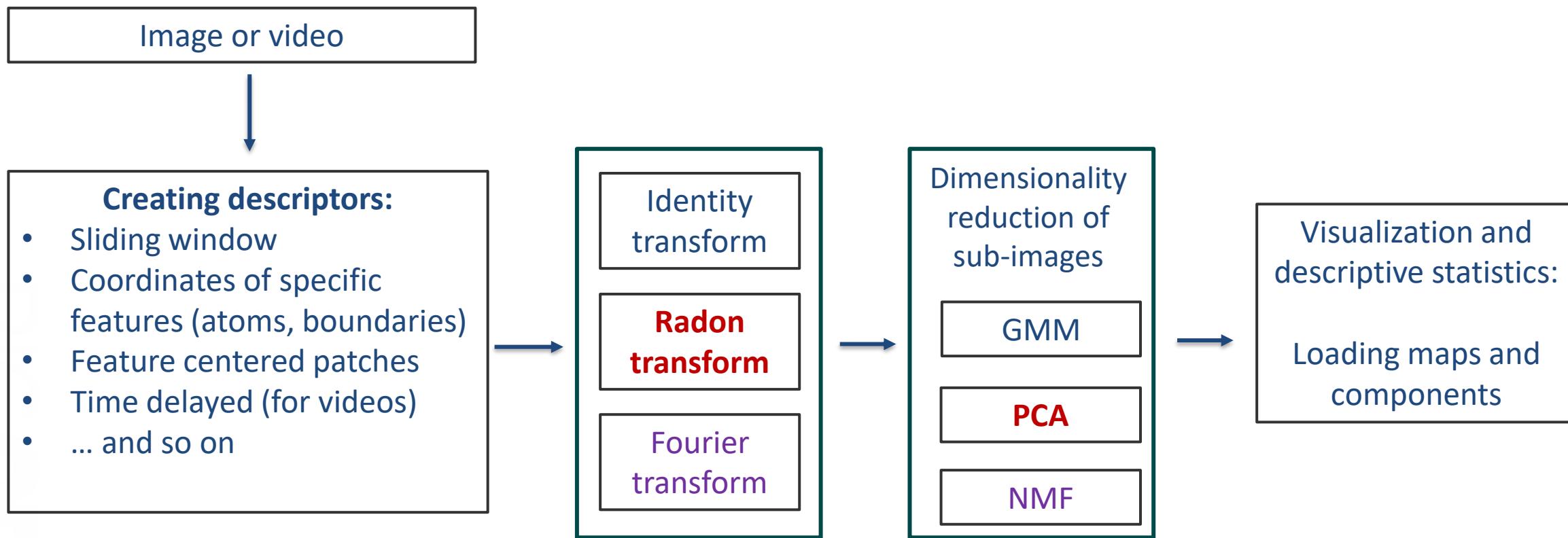
Information Content



PCA eigenvectors and loading maps



Example of analysis pipeline



Pipelines are defined to

- Make analysis traceable, repeatable, explainable, and transferable
- Allow for hyperparameter tuning and optimization
- Efficiently use the memory

How general should you be: depends on applications

14_FerroicBlocks_mockup_paper_v3a.ipynb

Next module: Bandit problem

