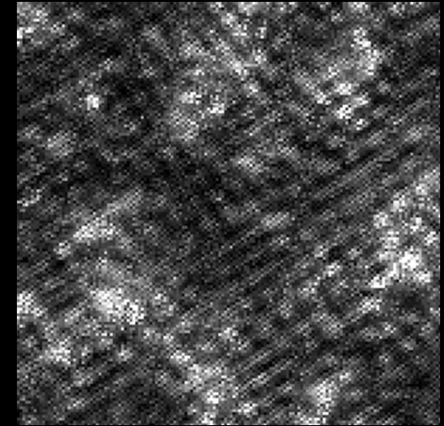
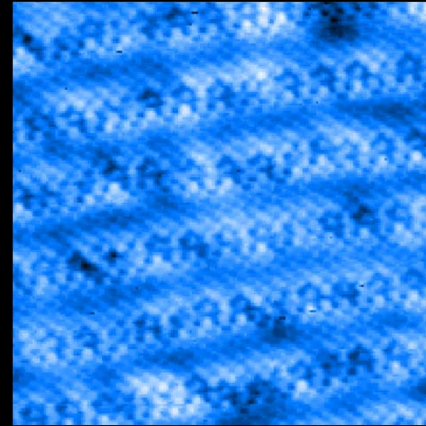
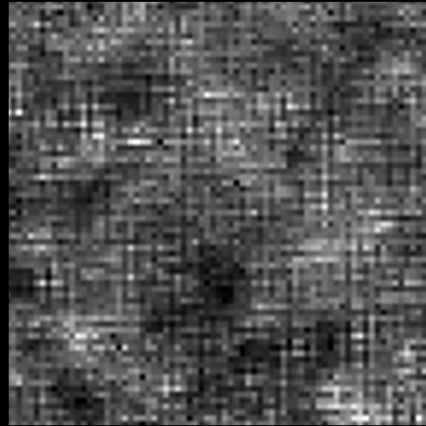
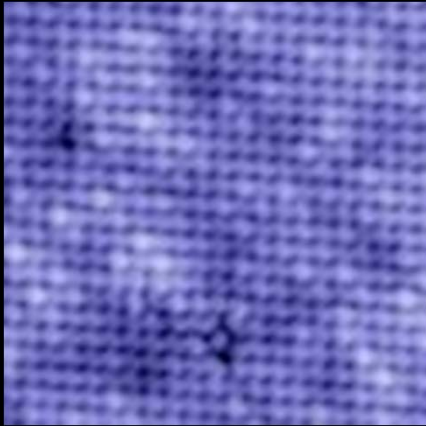


# STM imaging of broken symmetry states in cuprate superconductors



## STM Experiments:

Ilija Zeljkovic

Liz Main

Tess Williams

Yi Yin

Martin Zech

Jenny Hoffman

*Harvard Physics*

Michael Boyer

Kamalesh Chatterjee

Doug Wise

Eric Hudson

*MIT Physics*

## Bi-2212 Samples:

Zhijun Xu

Genda Gu

*Brookhaven*

Takeshi Kondo

## Bi-2201 Samples:

T. Takeuchi

Hiroshi Ikuta

*Nagoya University*

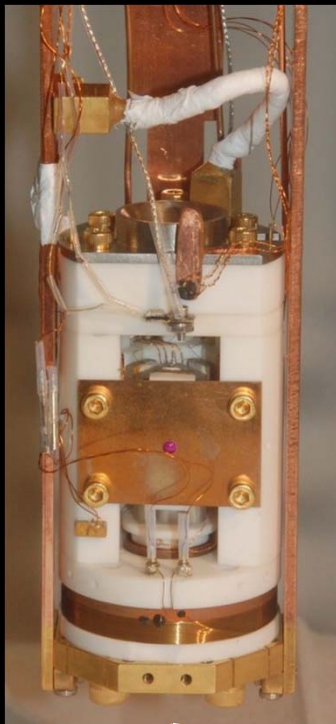
Thanks to:



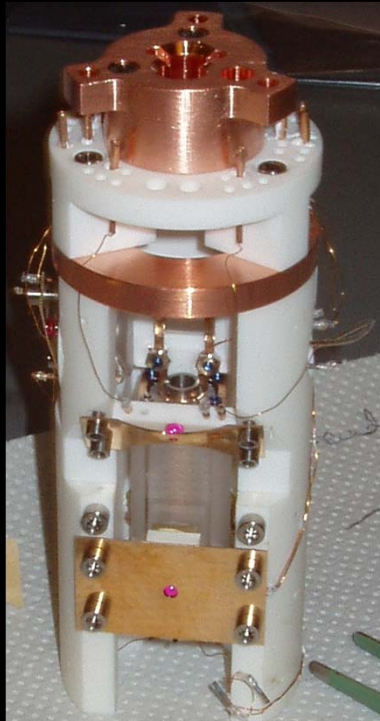
# Hoffman/Hudson Lab Local Probes



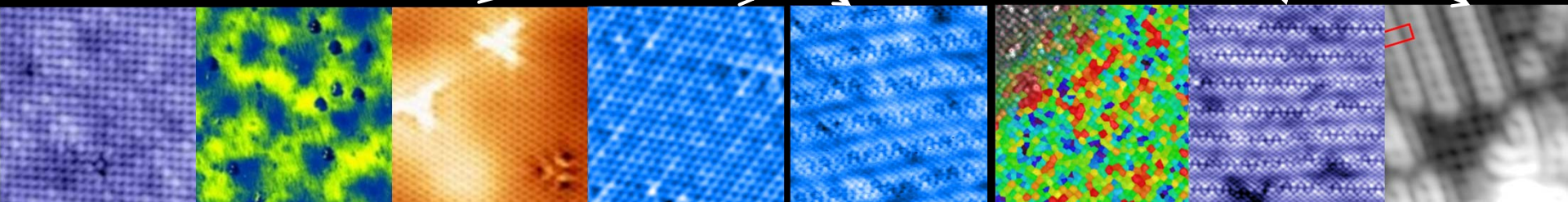
Hoffman Lab STM  
(9T v, 3T h; 1-40K)



Hoffman Lab UHV STM  
(9T v, 3T h; 2-80K)



Hudson Lab UHV STM  
(4-120K)



Bi-2201

Ba-122 iron  
pnictide

topological  
insulator

NbSe<sub>2</sub>

Bi-2212

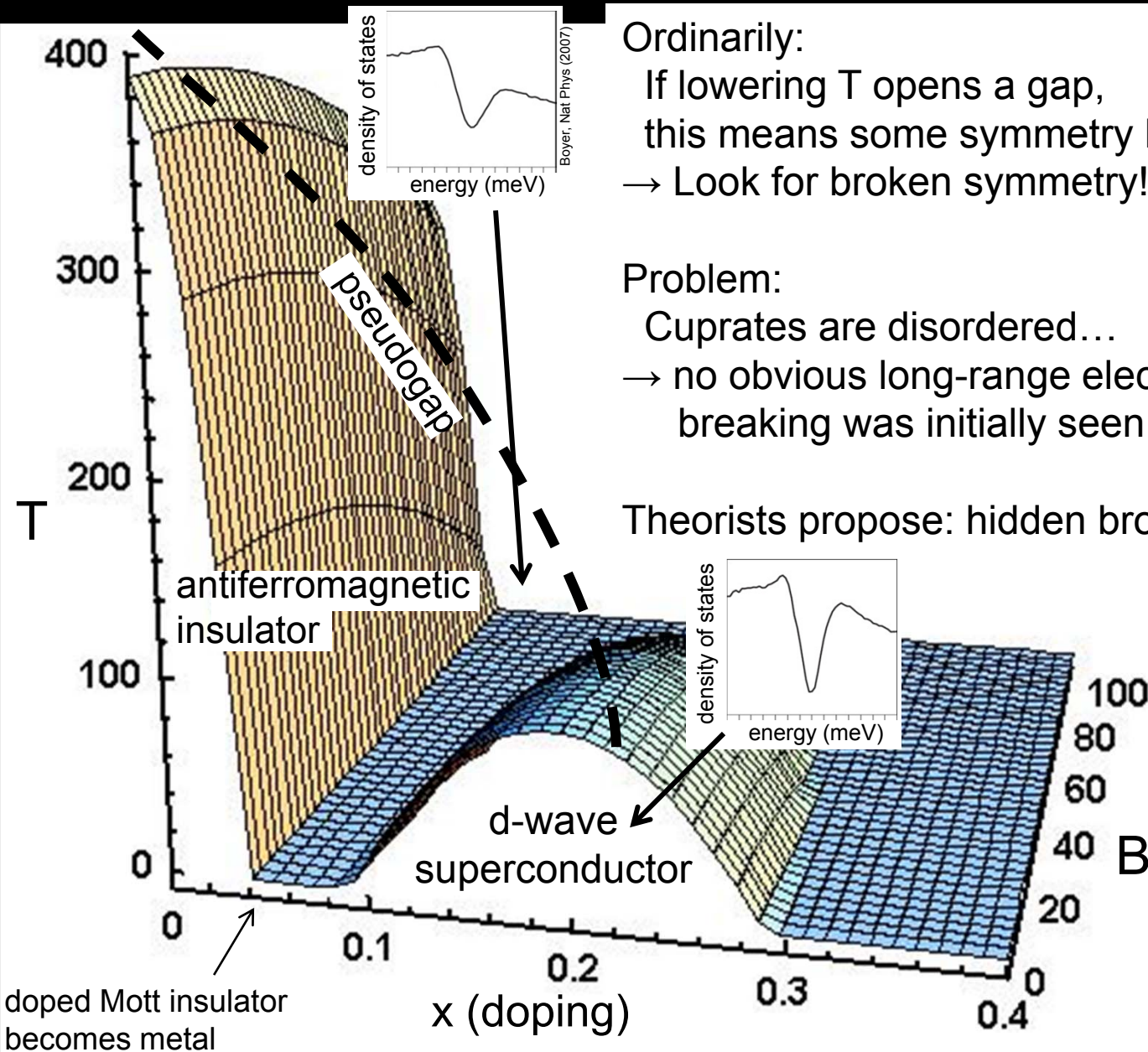
Bi-2201

Bi-2212

Sr-122 iron  
pnictide



# Cuprate Phase Diagram



Ordinarily:

If lowering  $T$  opens a gap,  
this means some symmetry has been broken.  
→ Look for broken symmetry!

Problem:

Cuprates are disordered...  
→ no obvious long-range electronic symmetry  
breaking was initially seen experimentally

Theorists propose: hidden broken symmetries!

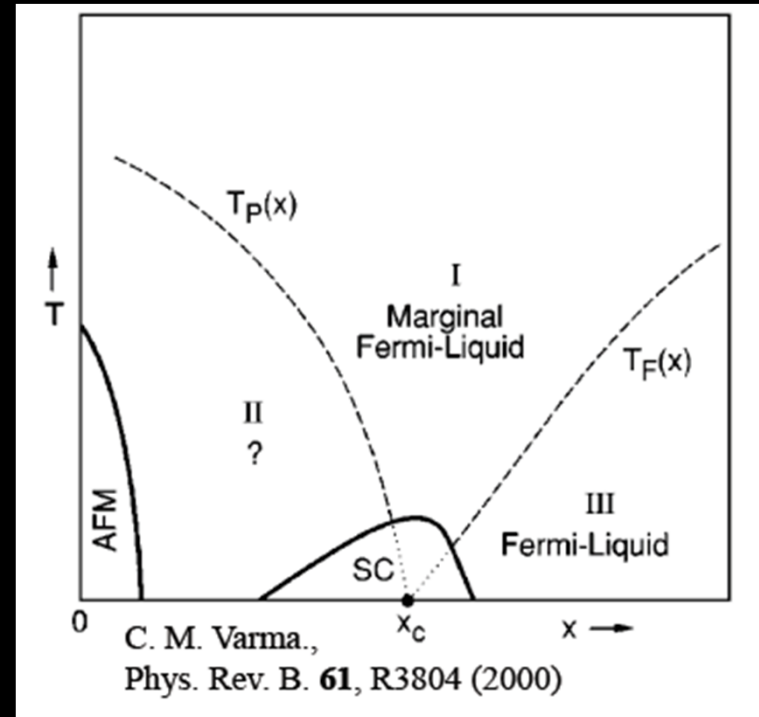
# Varma: sub-unit-cell orbital ordering



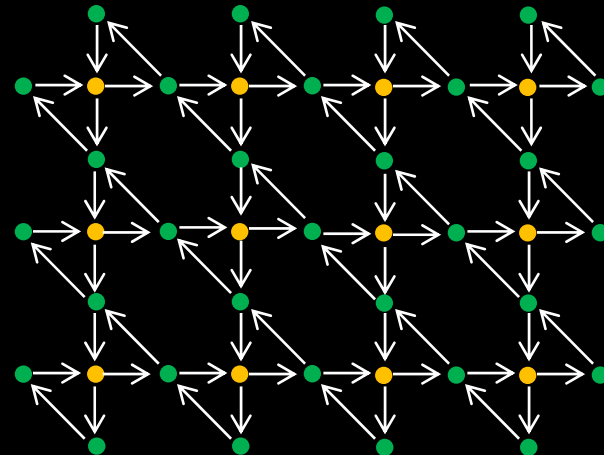
Underdoped cuprates have a hitherto undetected broken symmetry phase which does not break translation symmetry.

The non-Fermi liquid “normal” state is the **quantum critical regime**, in which order parameter fluctuations strongly scatter the quasiparticles.

The critical fluctuations “mediate” d-wave pairing.



Breaks **time-reversal**  
and **inversion**  
but not the produce of TI.

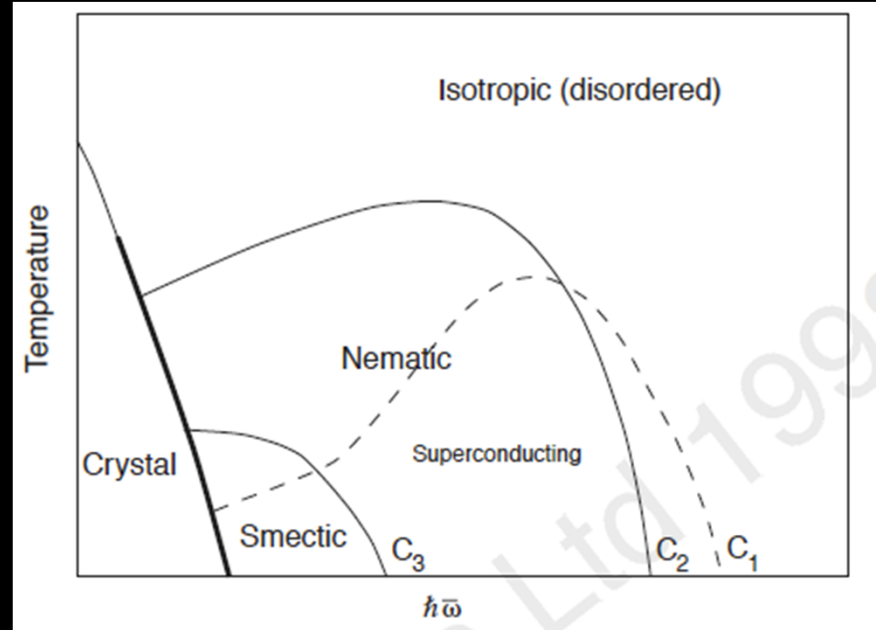




# Kivelson, Fradkin: stripy liquid crystal phases

Fluctuating stripes play to role of the “nematogens” which allows for the formation of various “electronic liquid crystalline phases” in the pseudo-gap regime.

Local stripe order may enhance pairing, but stripe order certainly suppresses superfluid stiffness.



Crystal



Nematic



Smectic



Isotropic

Nematic:

breaks long-range **rotation**

Smectic:

breaks long-range **rotation & translation**

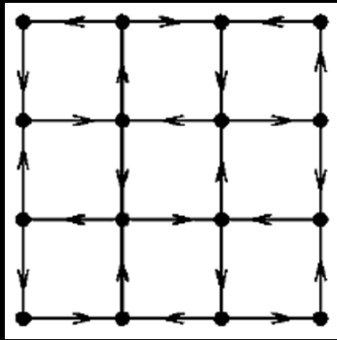
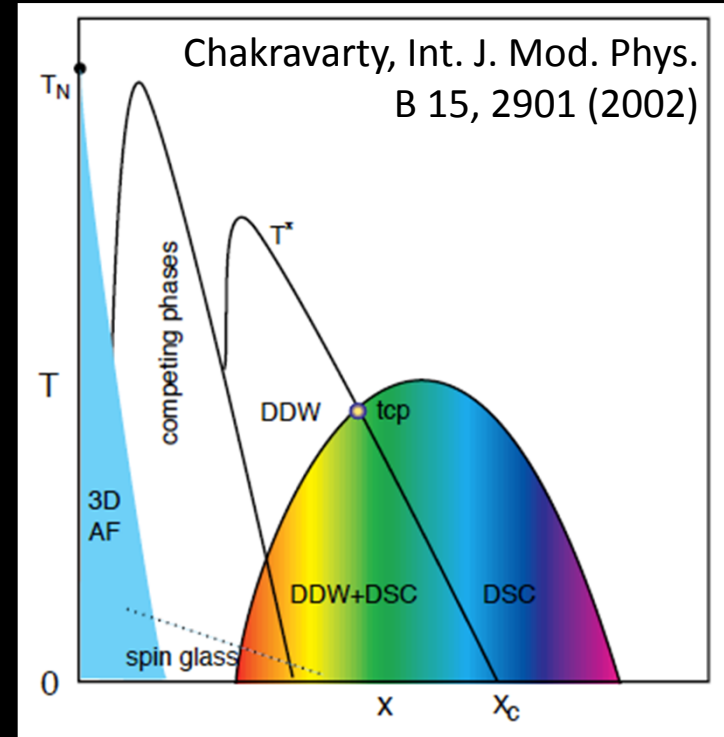
# Nayak & Chakravarty: d-density wave



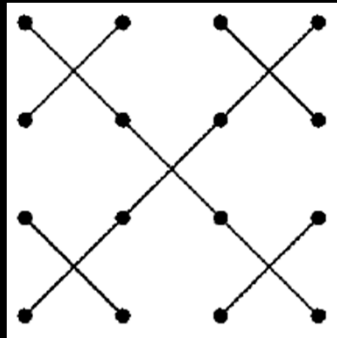
The pseudo-gap has broken translational symmetry and a corresponding partial gapping and restructuring of the FS.

The order parameter is “hidden” in the sense that it is intrinsically difficult to see directly in experiment.

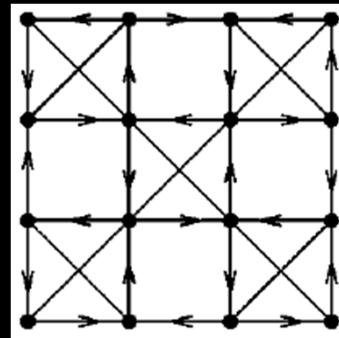
Breaks **time reversal** and **translational** symmetry, but preserves the product.



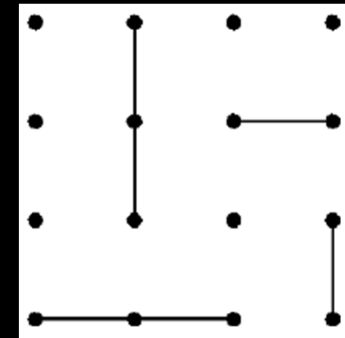
$$d_{x^2-y^2}$$



$$d_{xy}$$



$$d_{x^2-y^2} + id_{xy}$$



incommensurate,  
T-preserving  $d_{x^2-y^2}$

## Some broken symmetry states in the pseudo-gap

(for which there is direct experimental evidence):

**Electron Nematic:** Uniform (translation symmetry unbroken)  
Fluid (metallic or superconducting)  
With spontaneously broken point group symmetry  
(e.g. electronic orthorhombicity)

**Electron smectic:** Unidirectional metallic (or superconducting)  
charge density wave

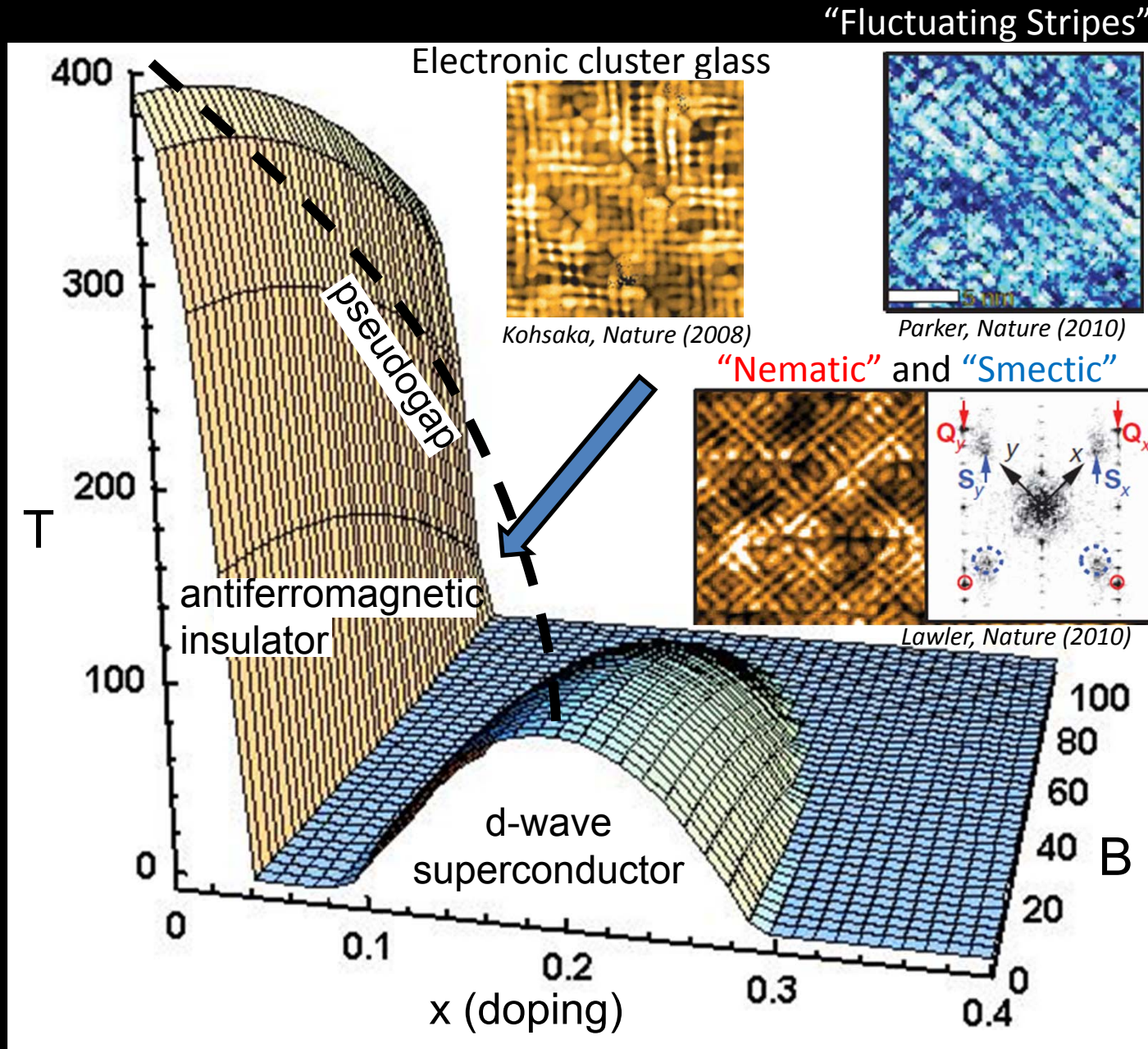
**Stripe phase:** Unidirectional colinear spin density wave with  
coexisting CDW with  $\frac{1}{2}$  the wavelength  
(Both insulating and conducting versions)  
In the presence of weak disorder, this becomes a “cluster  
spin-glass” with only short-range stripe order.

**Intra-unit cell antiferromagnet:** Breaks time-reversal and some  
point-group symmetries (Chandra’s-loops)

**d-density wave:** Breaks time reversal and translational symmetry,  
but preserves the product.



# Lots of candidates for pseudogap from STM

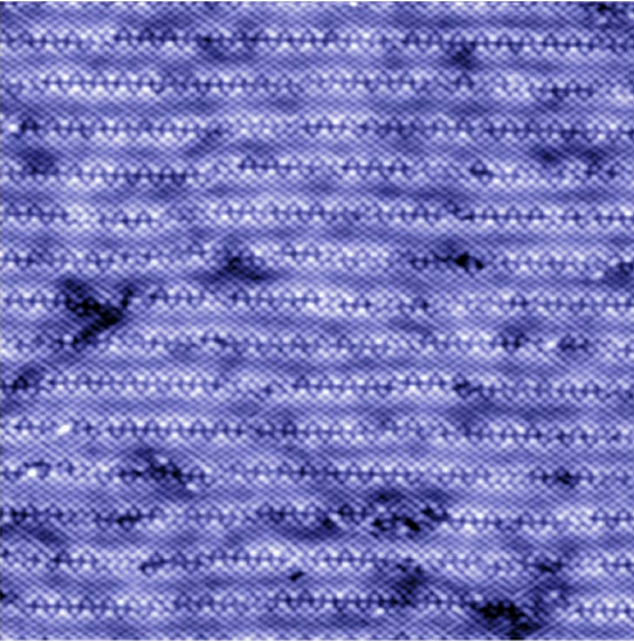




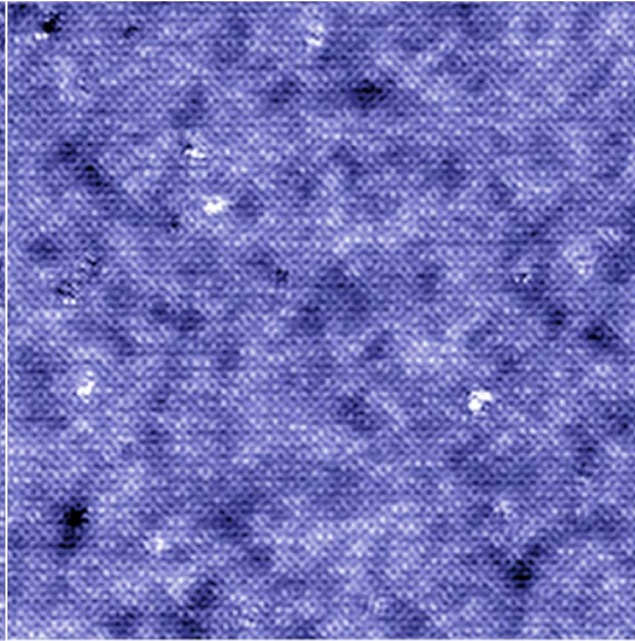
# ? Structural $\leftrightarrow$ Electronic ?



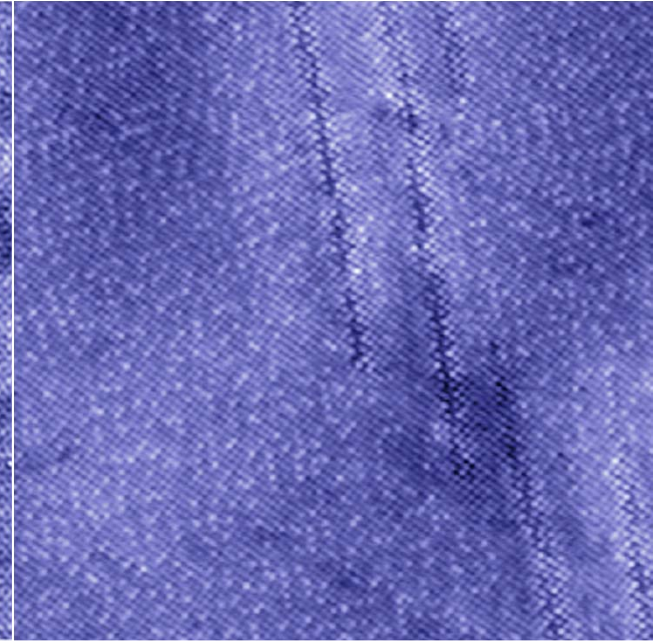
Bi-2212



Bi-2201, Pb-doped



another Bi-2201, Pb-doped

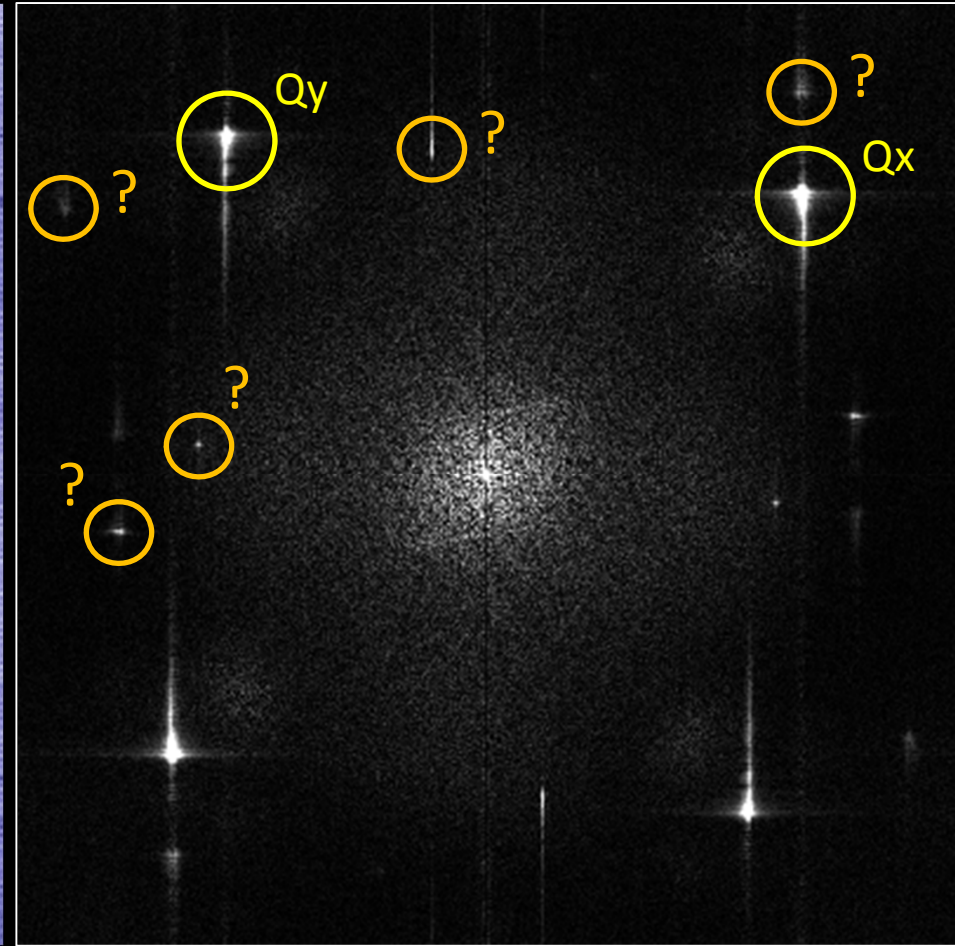
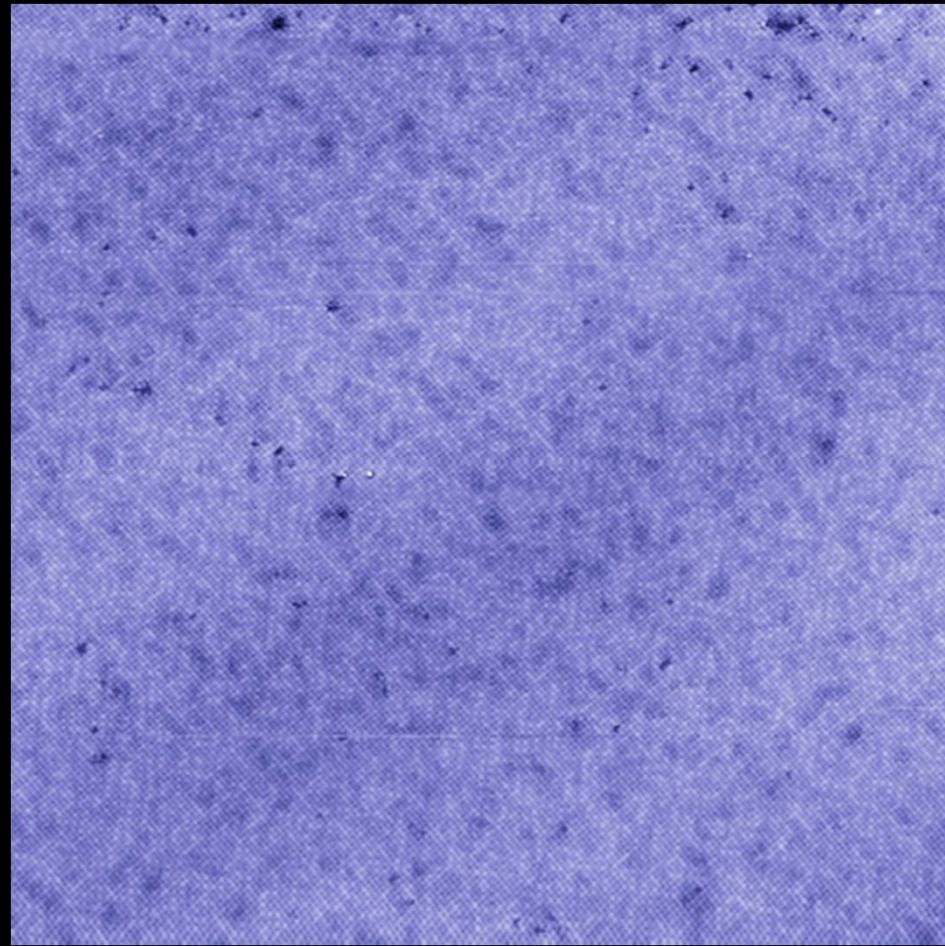




# Raw data



(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



66x66 nm<sup>2</sup>

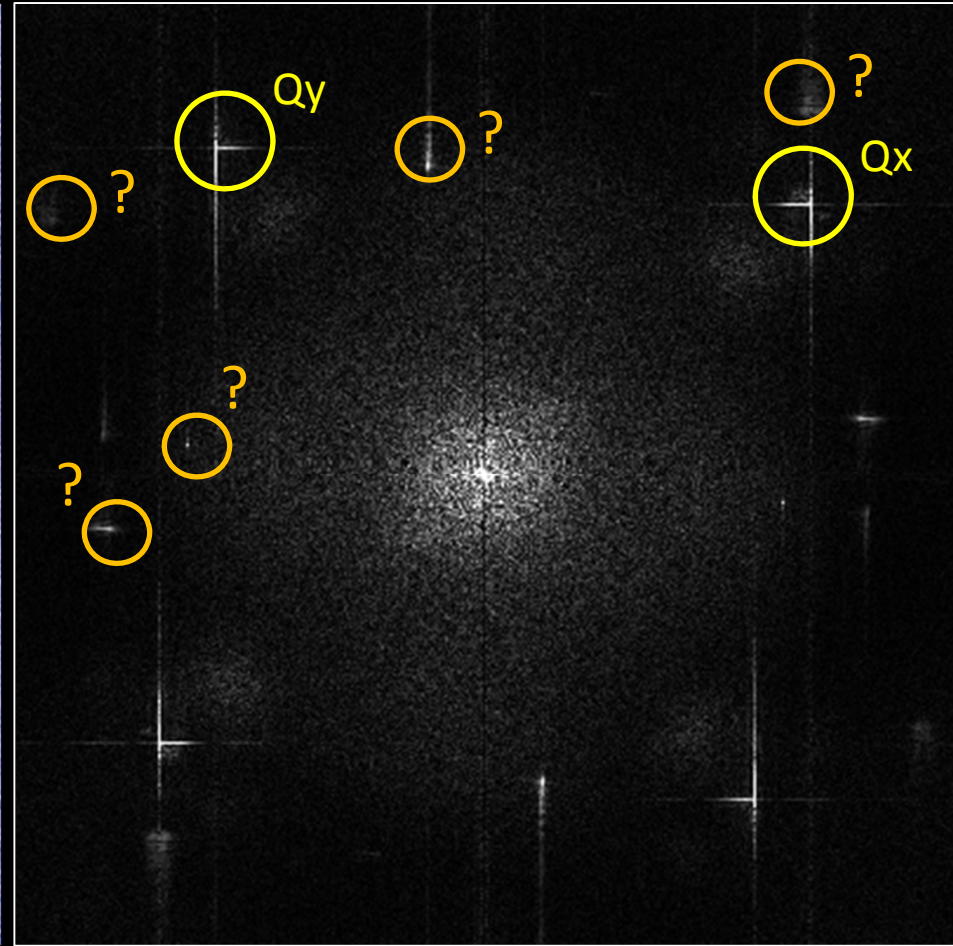
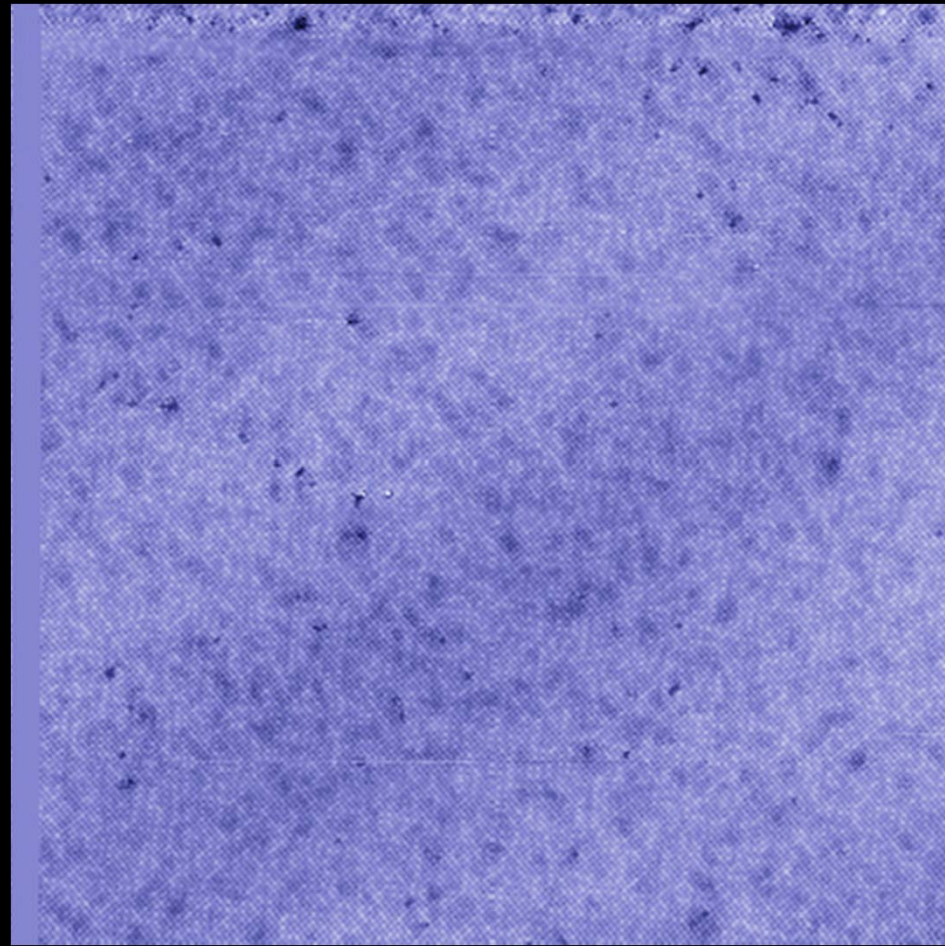
Bragg peaks are blurred  $\rightarrow$  need to apply Lawler algorithm to drift-correct!



# Drift-corrected data



(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



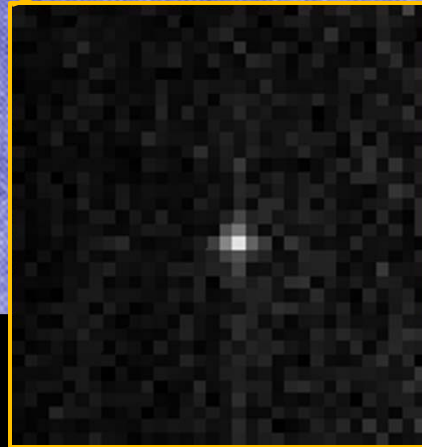
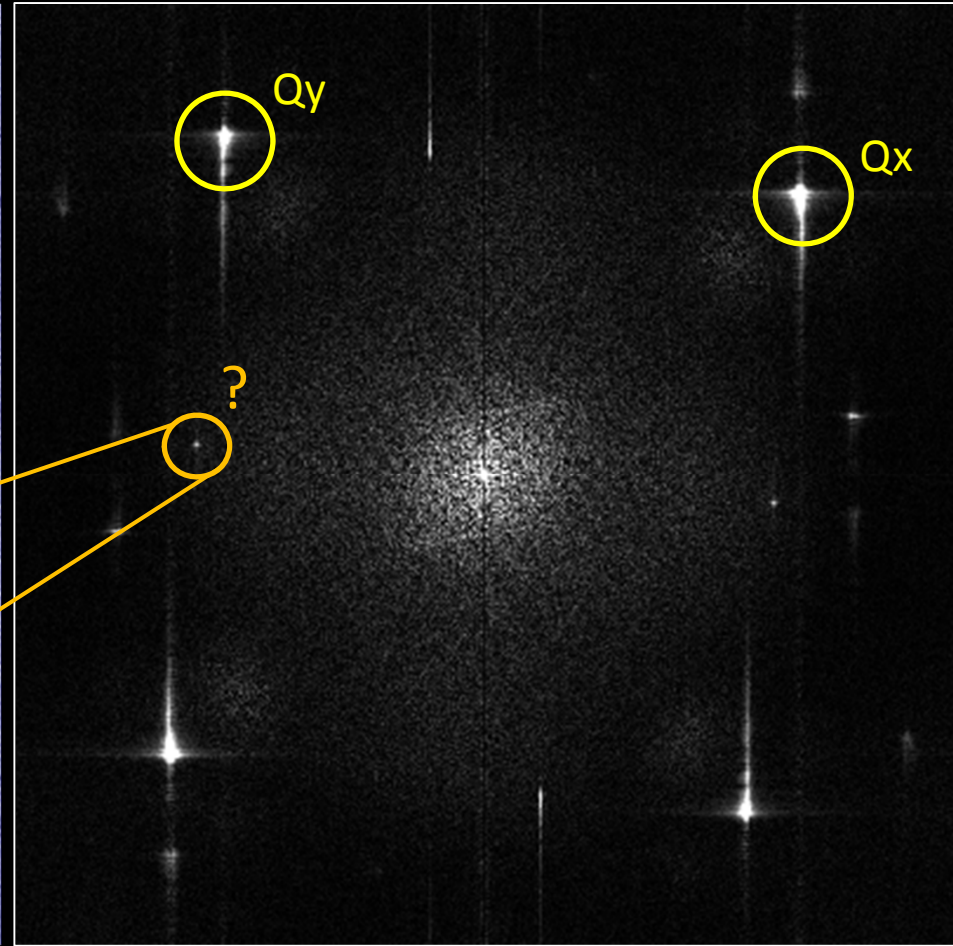
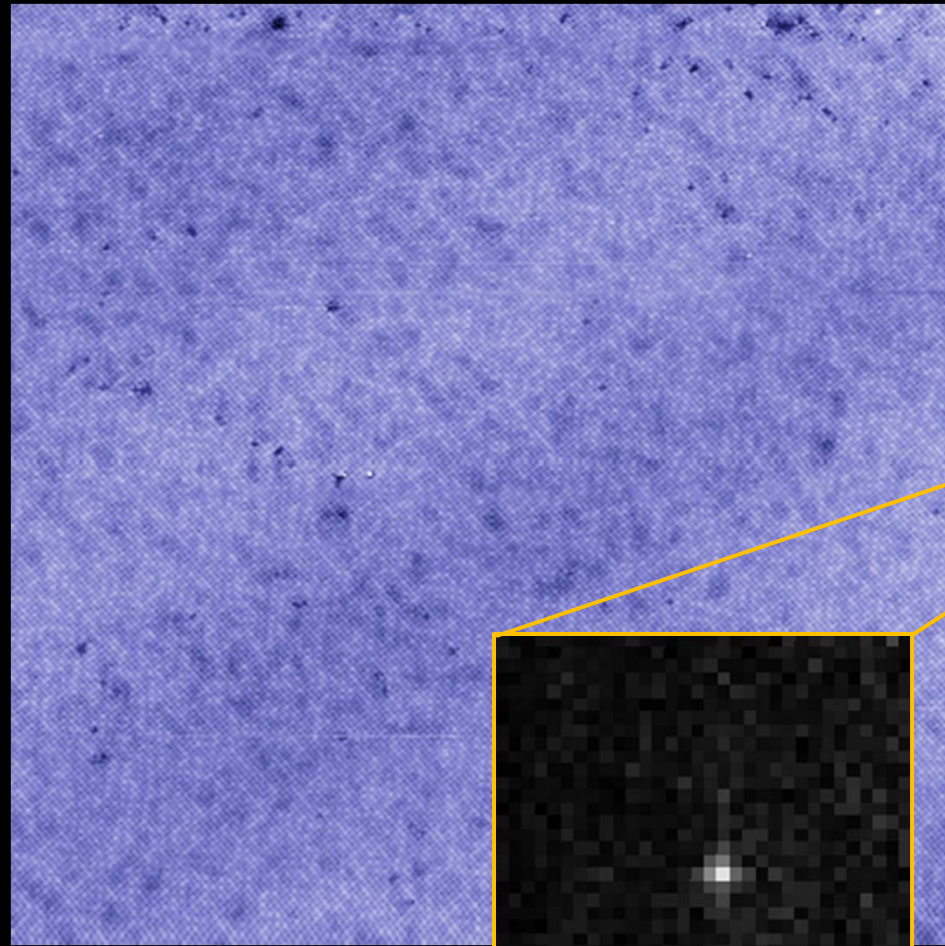
Bragg peaks sharpen up  $\rightarrow$  they are true structure  
Most other peaks broaden out  $\rightarrow$  they are noise



# Raw data



(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



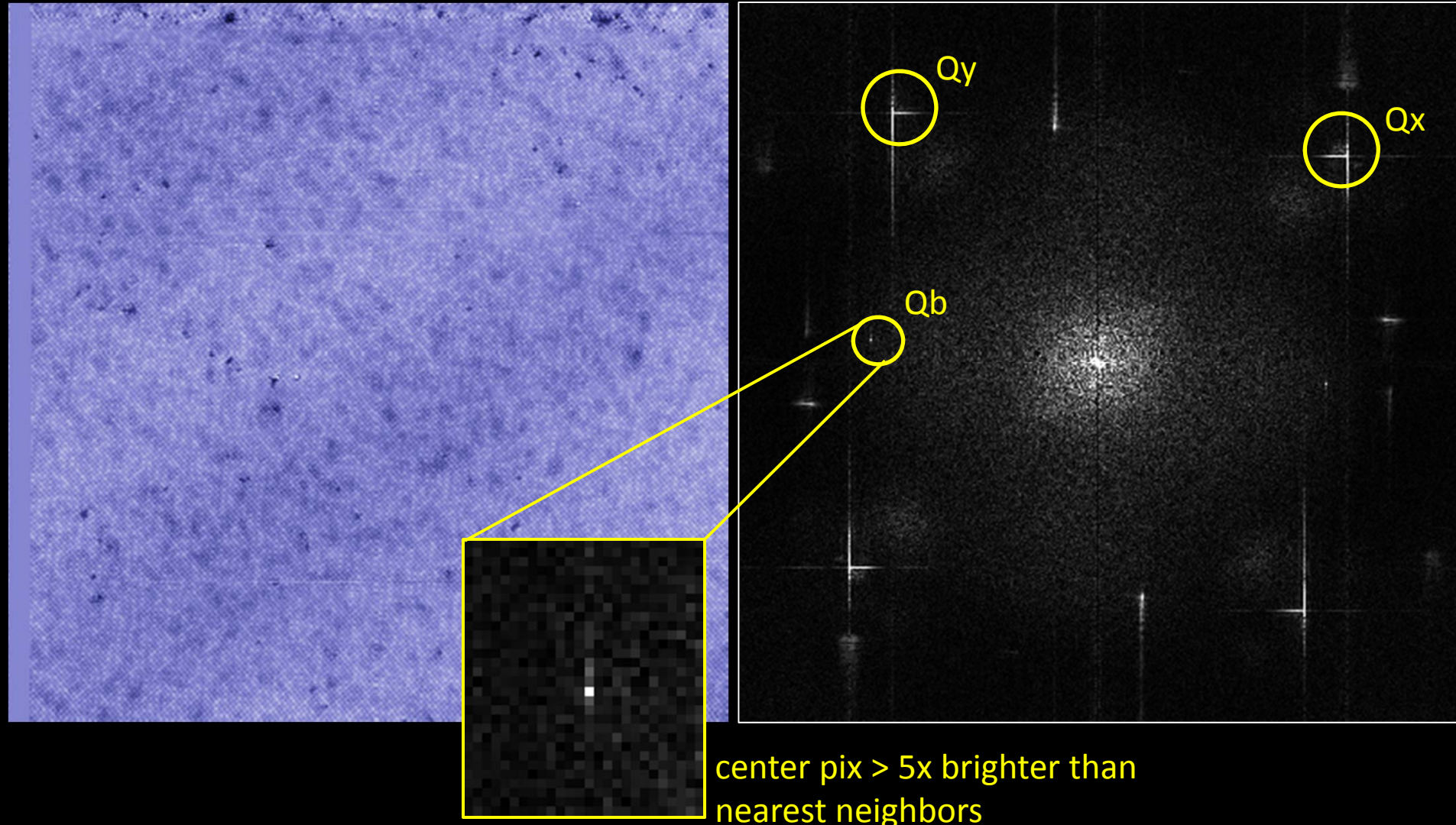
center pix only 20% brighter than nearest neighbors



# Drift-corrected data



(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



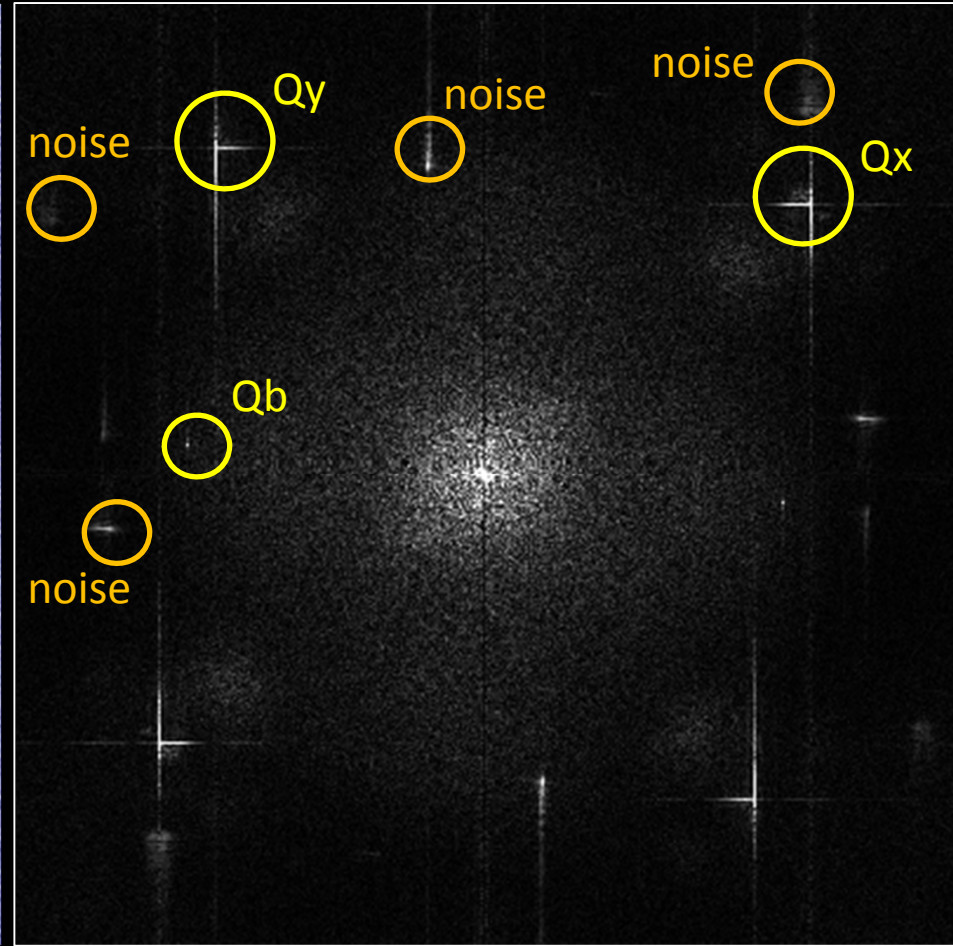
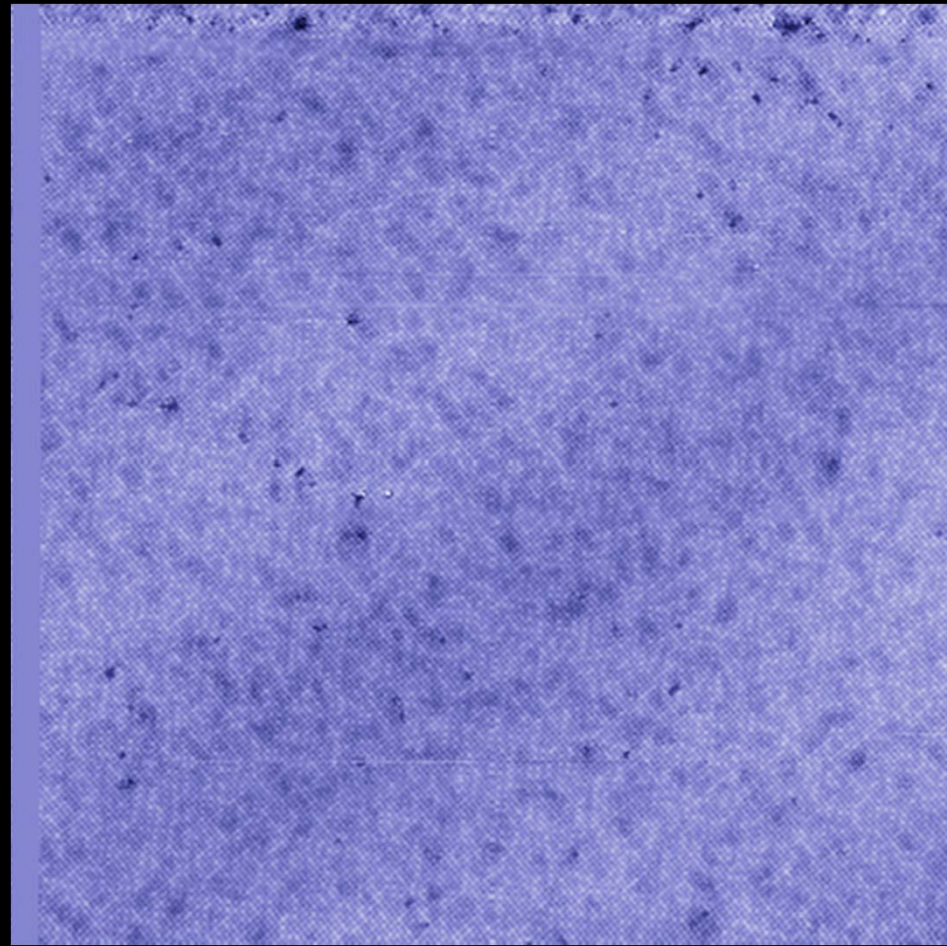
center pix > 5x brighter than  
nearest neighbors



# Drift-corrected data



(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)

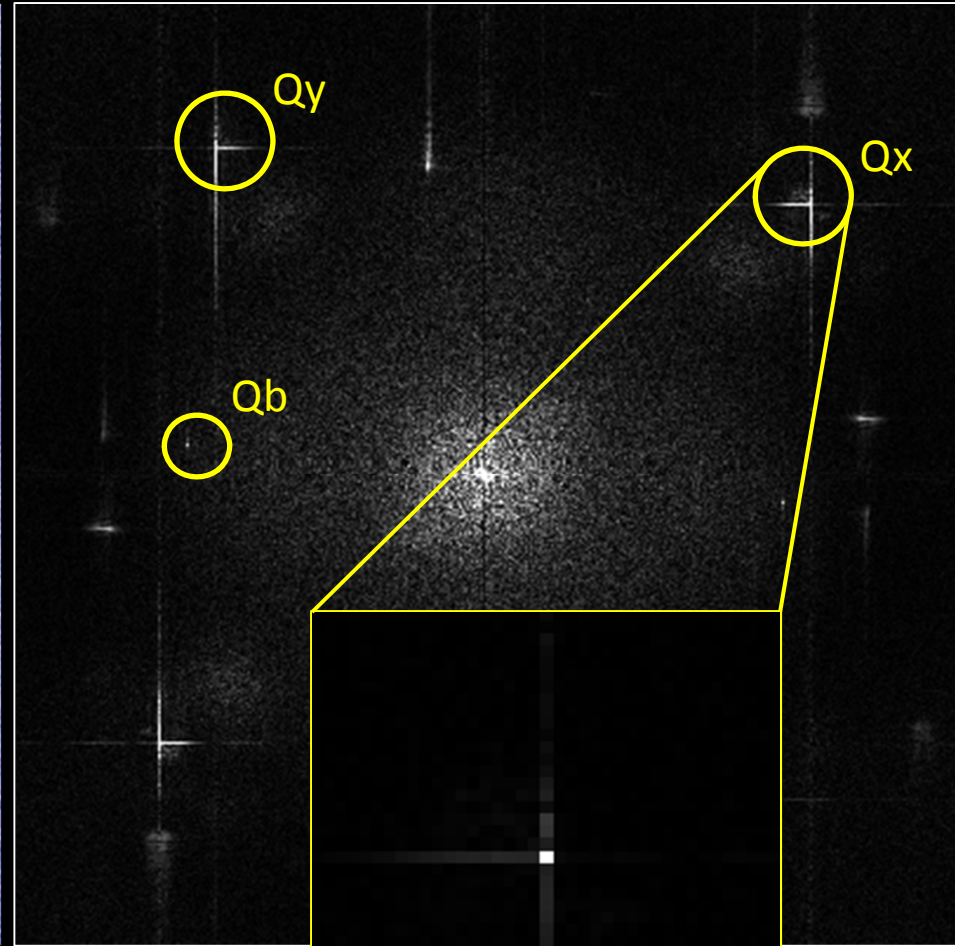
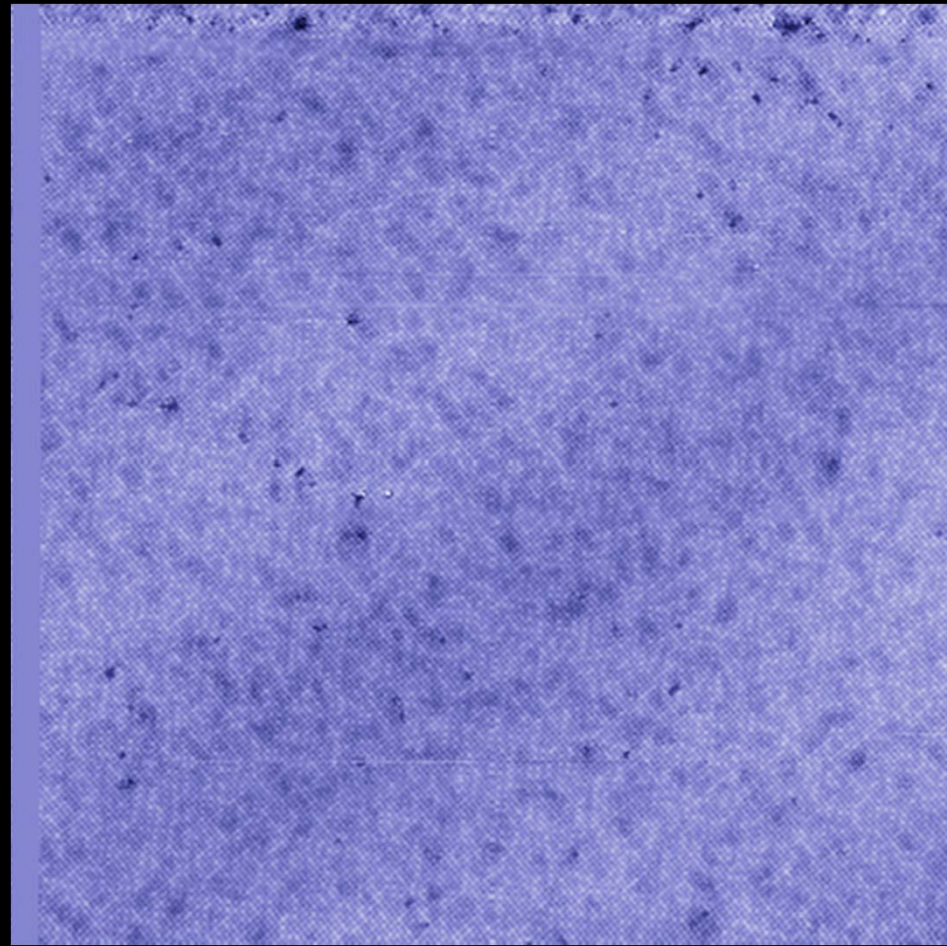




# Drift-corrected data



(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



> 10x brighter than neighboring pixels

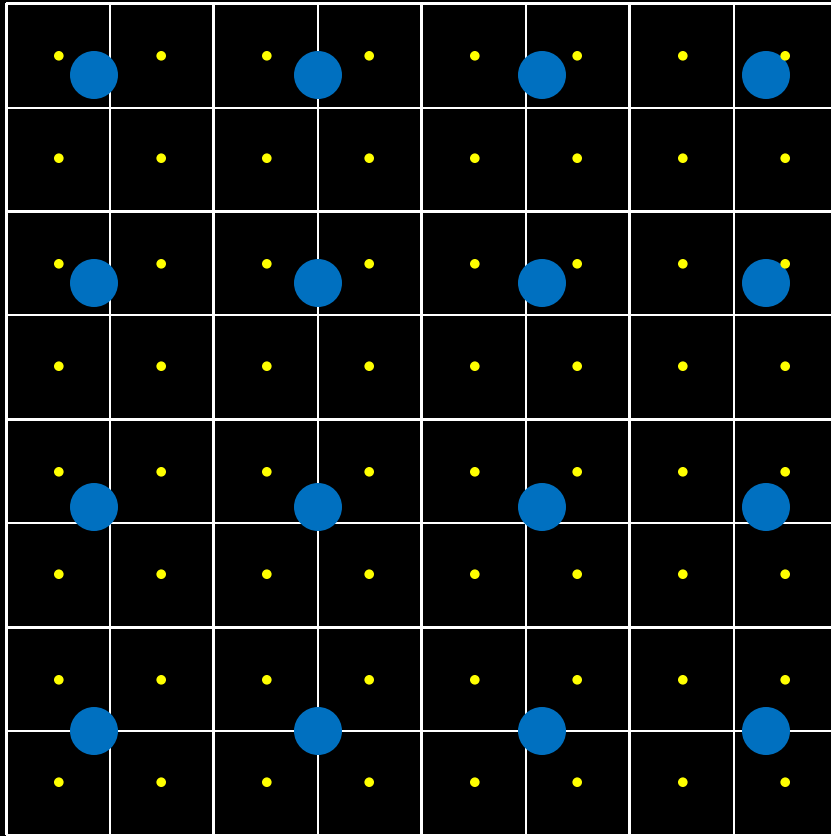
# Make Average Unit Cell



— Pixel grid

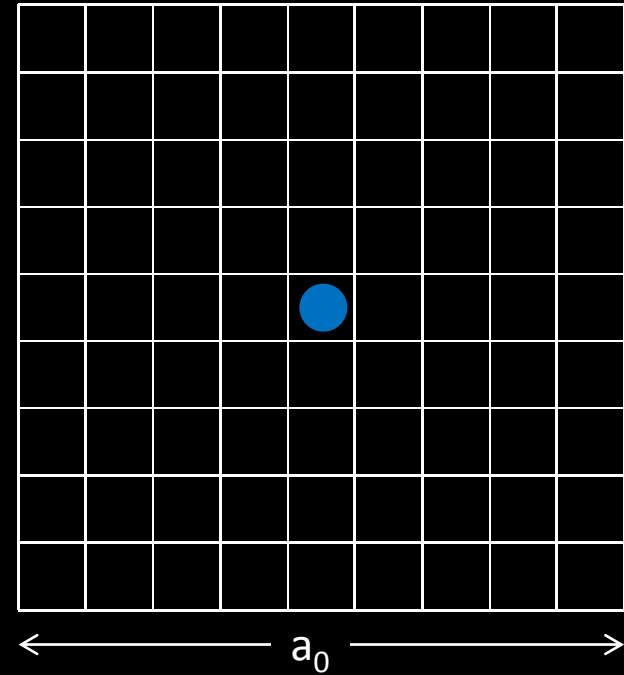
• exact tip location when data acquired

● Bi atom



Make a new grid, one unit cell, but with more pixels than we have in raw data.

Center Bi in center of this unit cell.



Note: data acquisition only slightly better than Nyquist frequency for atoms!

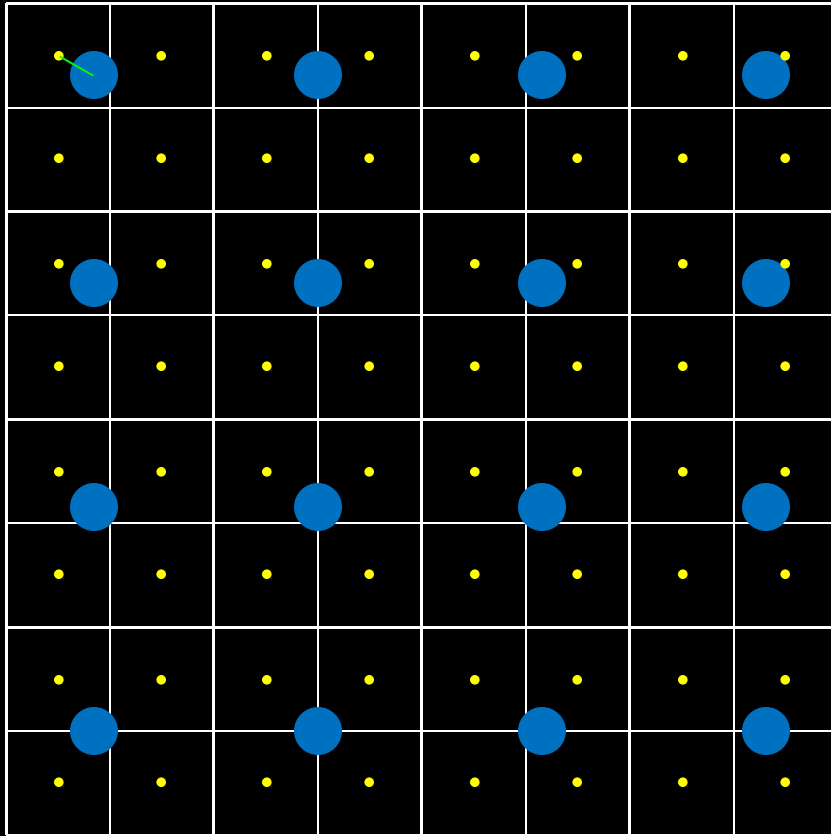
# Make Average Unit Cell



— Pixel grid

• exact tip location when data acquired

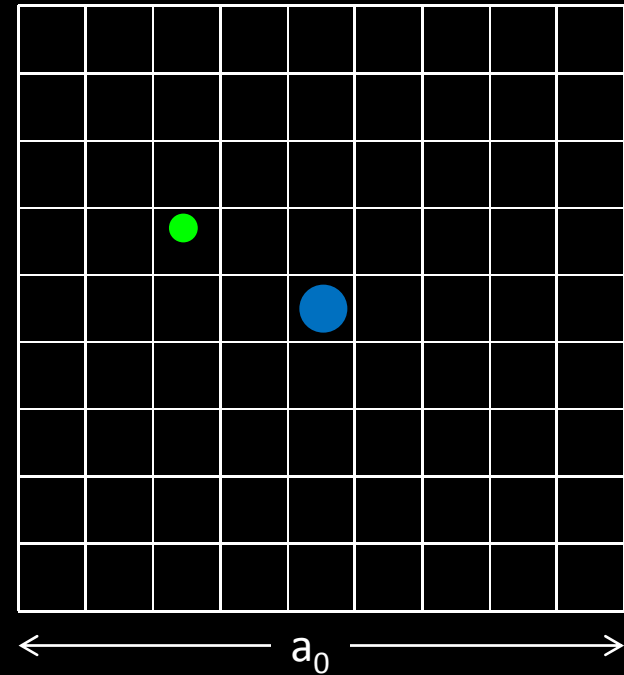
● Bi atom



Make a new grid, one unit cell, but with more pixels than we have in raw data.

Center Bi in center of this unit cell.

Build up a histogram of weight at each sub-unit-cell-resolved location.



Note: data acquisition only slightly better than Nyquist frequency for atoms!



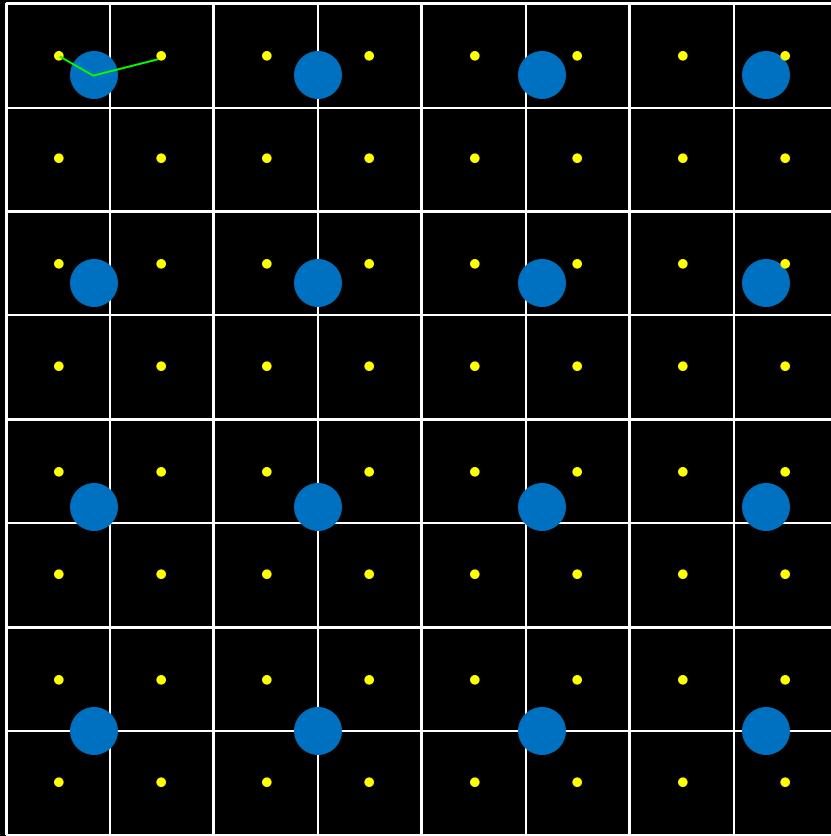
# Make Average Unit Cell



— Pixel grid

• exact tip location when data acquired

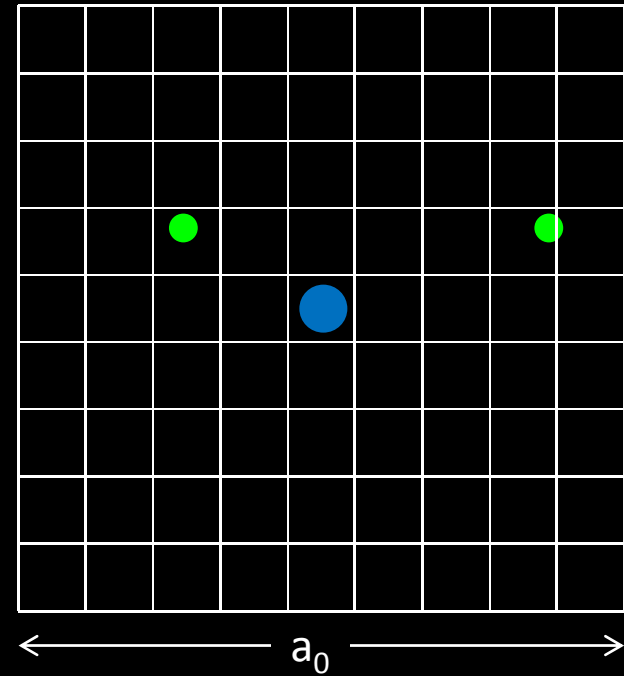
● Bi atom



Make a new grid, one unit cell, but with more pixels than we have in raw data.

Center Bi in center of this unit cell.

Build up a histogram of weight at each sub-unit-cell-resolved location.



Note: data acquisition only slightly better than Nyquist frequency for atoms!

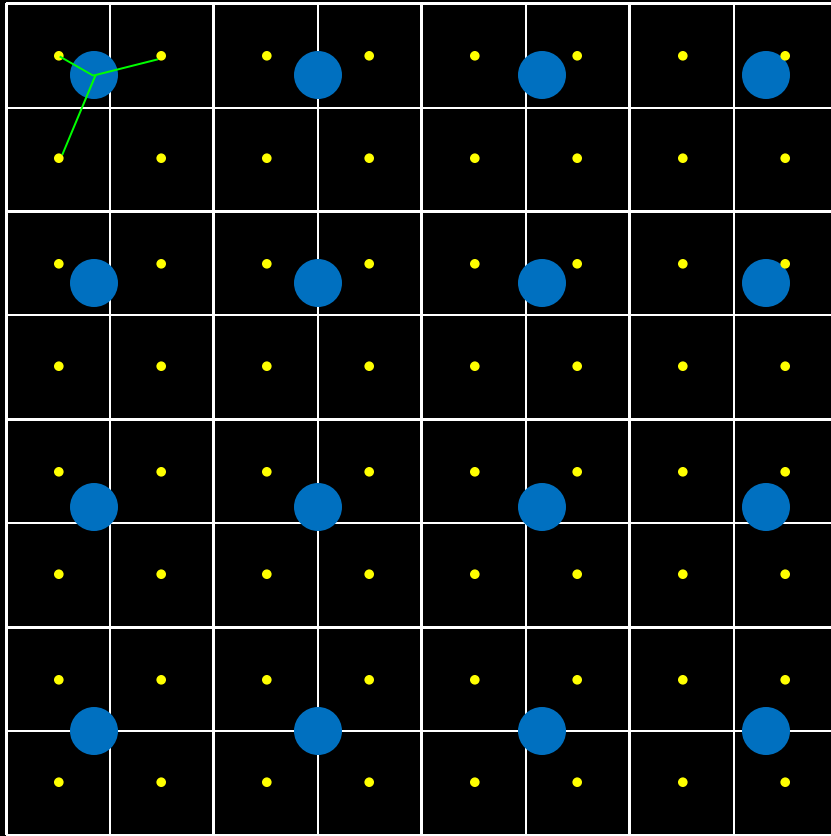
# Make Average Unit Cell



— Pixel grid

• exact tip location when data acquired

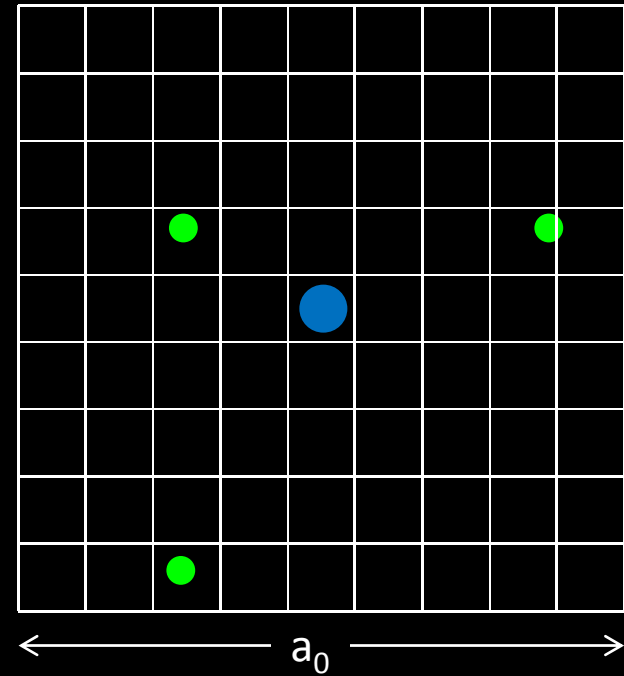
● Bi atom



Make a new grid, one unit cell, but with more pixels than we have in raw data.

Center Bi in center of this unit cell.

Build up a histogram of weight at each sub-unit-cell-resolved location.



Note: data acquisition only slightly better than Nyquist frequency for atoms!

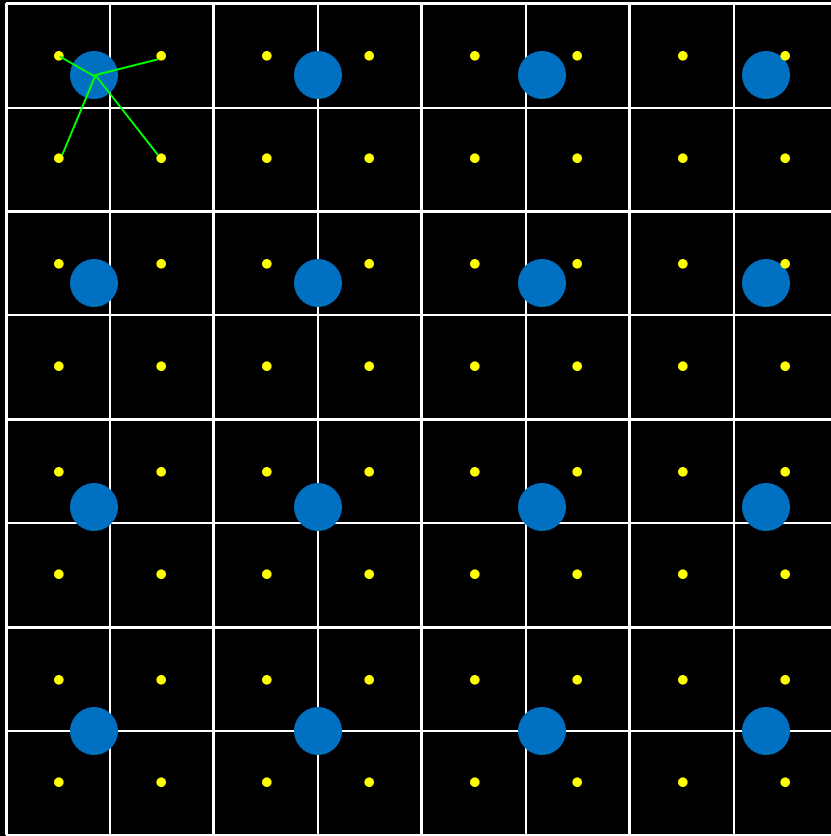
# Make Average Unit Cell



— Pixel grid

- exact tip location when data acquired

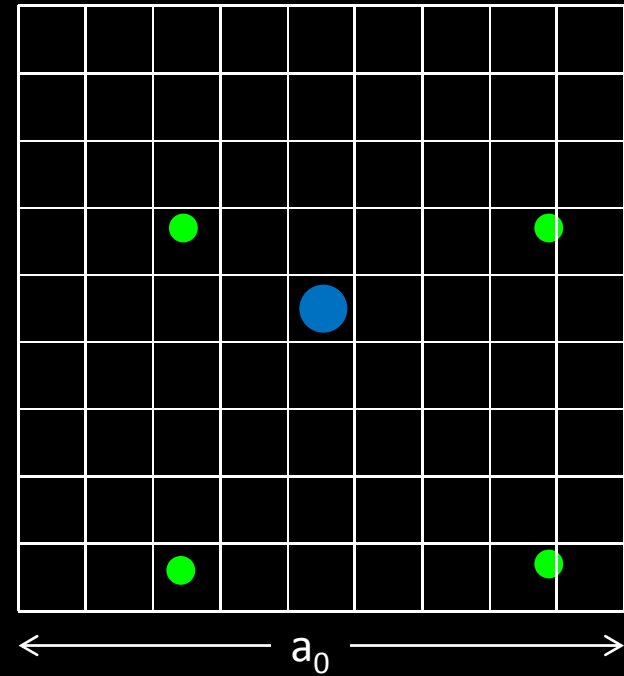
● Bi atom



Make a new grid, one unit cell, but with more pixels than we have in raw data.

Center Bi in center of this unit cell.

Build up a histogram of weight at each sub-unit-cell-resolved location.



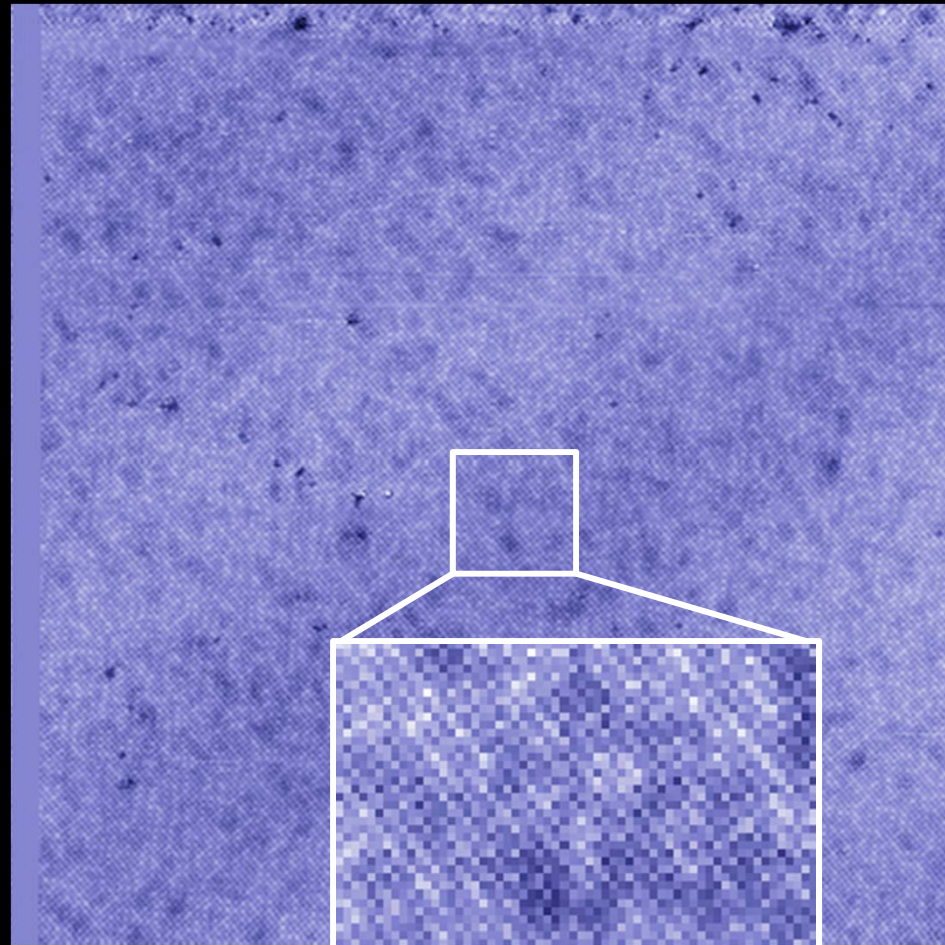
Note: data acquisition only slightly better than Nyquist frequency for atoms!

Perfect registry allows sub-unit-cell resolution!



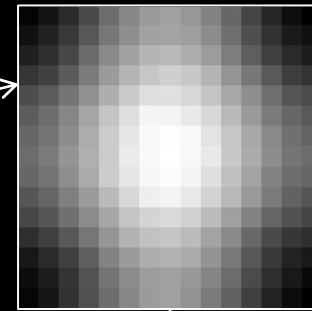
# Make Average Unit Cell

(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)

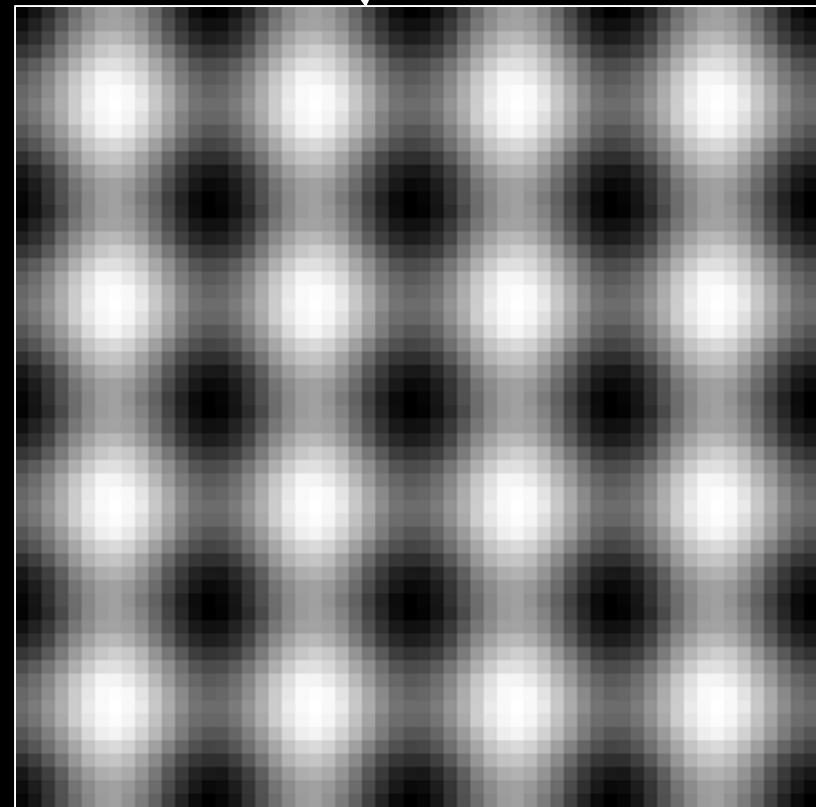


66x66 nm<sup>2</sup>

make average  
unit cell

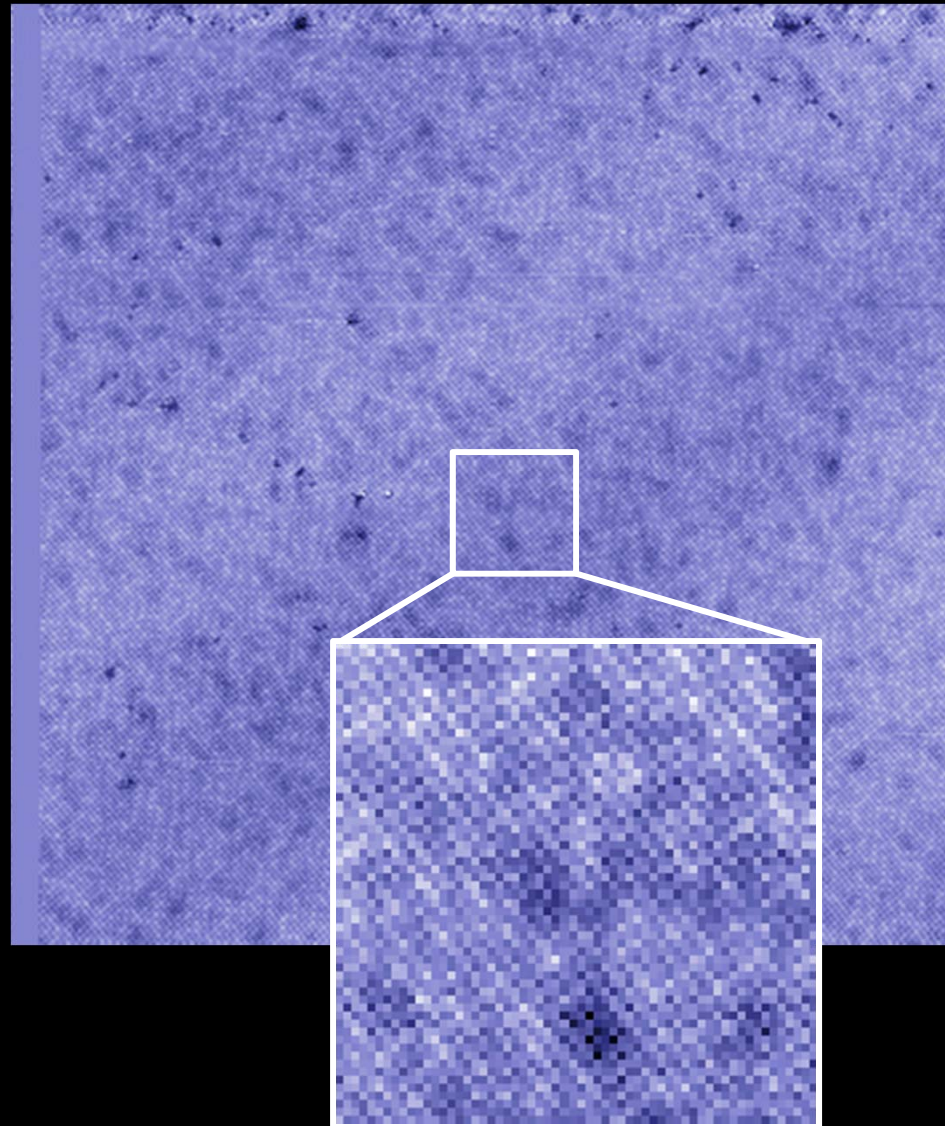


tile 4x4

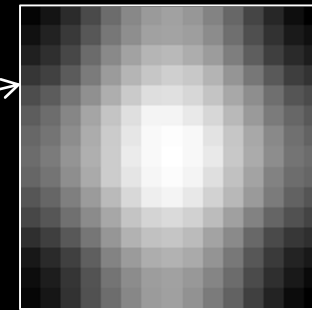


# Make Average Unit Cell

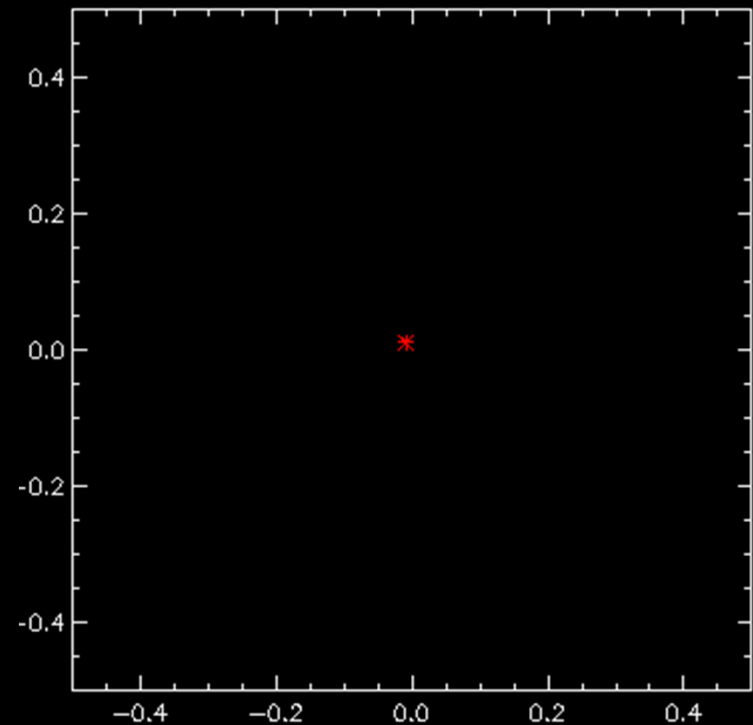
(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



make average  
unit cell



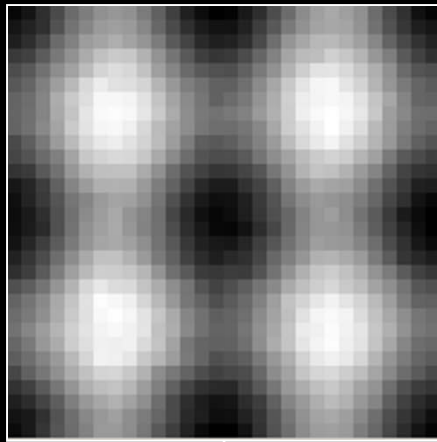
fit to make sure Bi is at center,  
where we think it should be



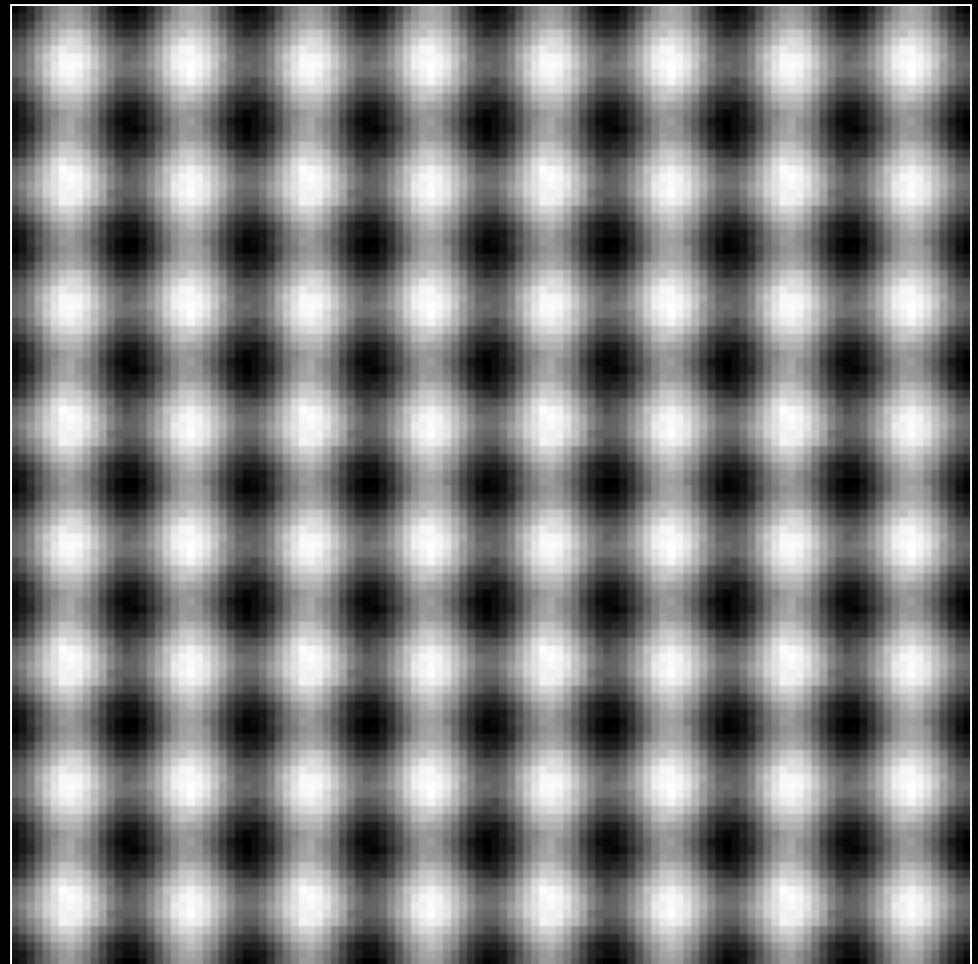
# Make Average Supercell: 2x2



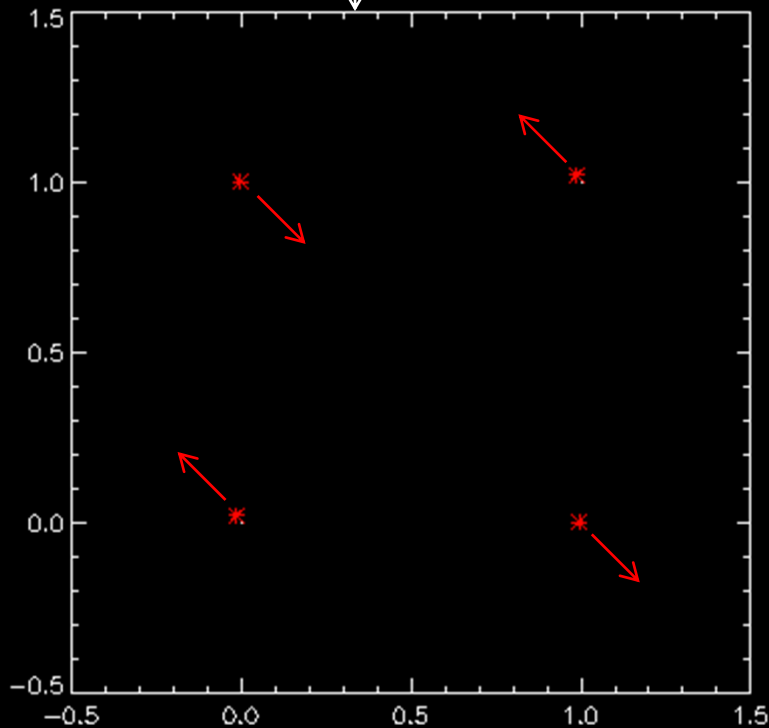
(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



→ tiled



↓ fit

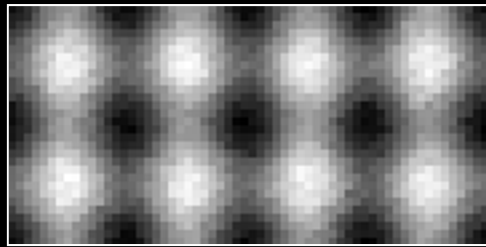


shift by  $\sim 1\%$  of unit cell

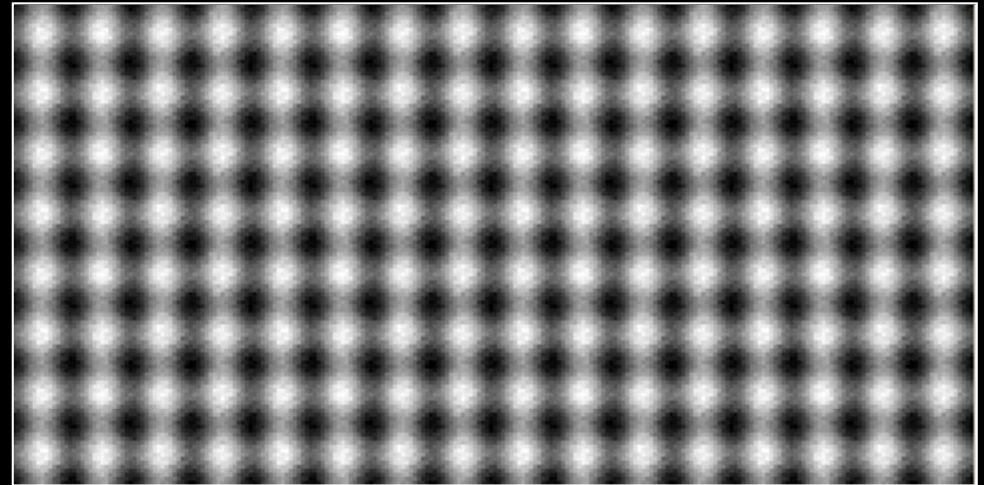


# Make Average Supercell: 4x2

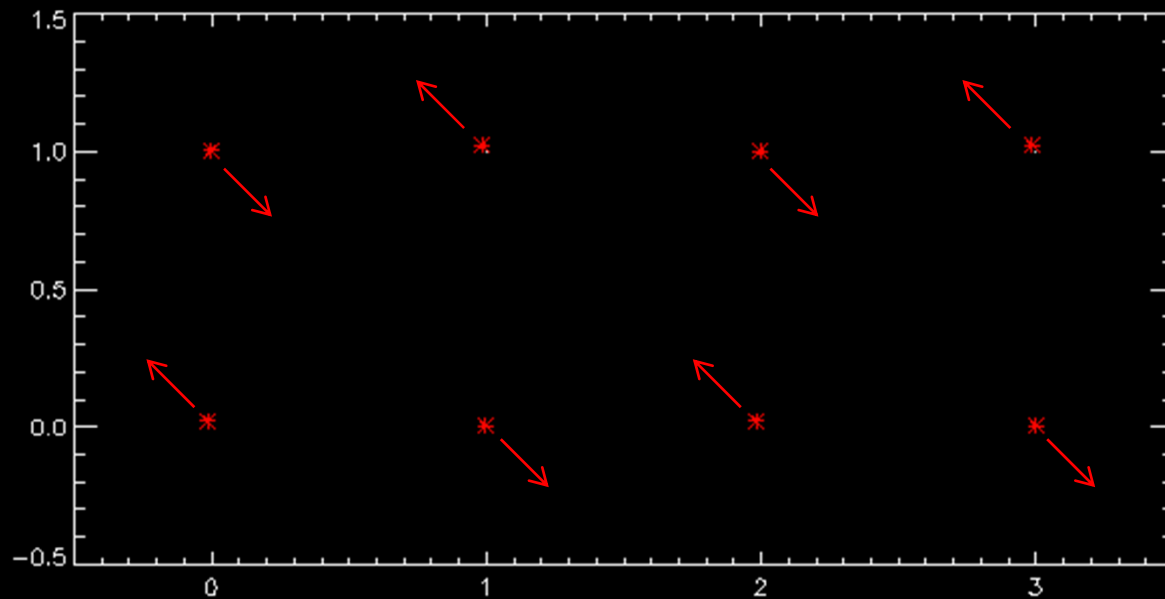
(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



tiling



fit

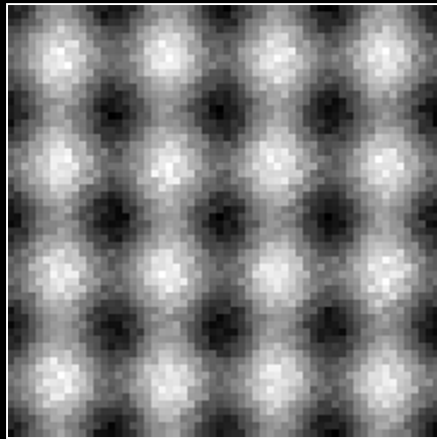




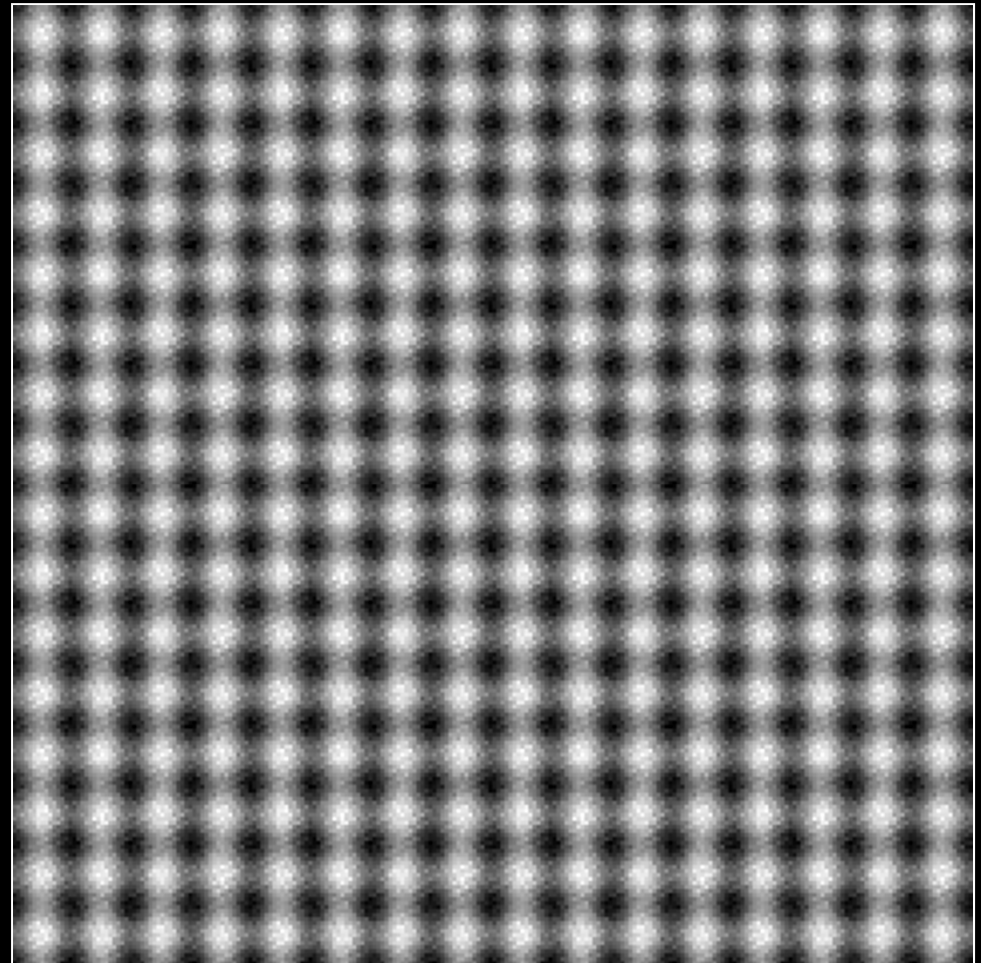
# Make Average Supercell: 4x4



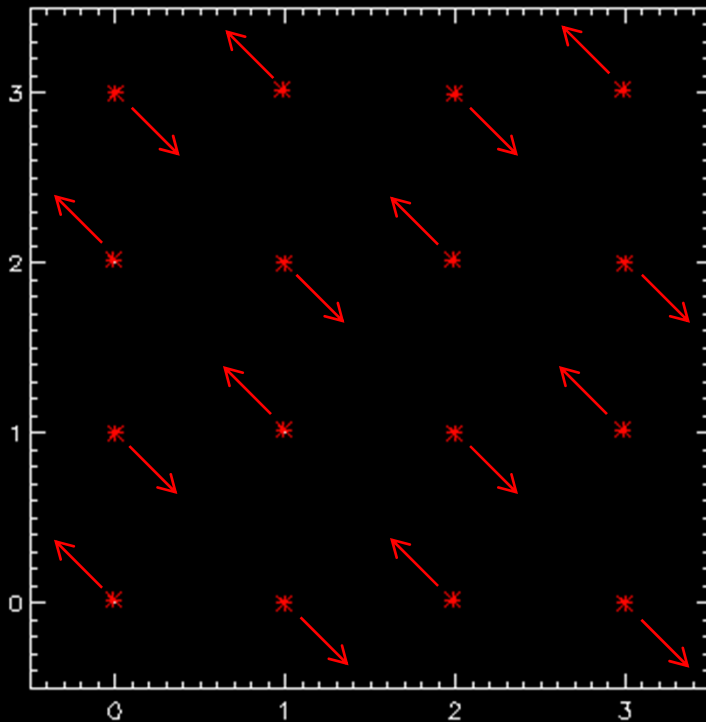
(Bi-2201,  $T_c=32\text{K}$ , slightly underdoped)



tiling



fit



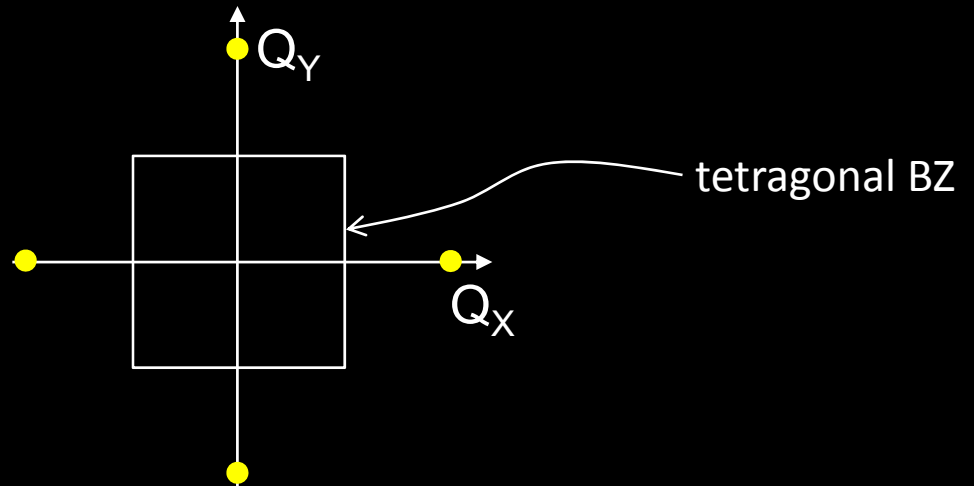
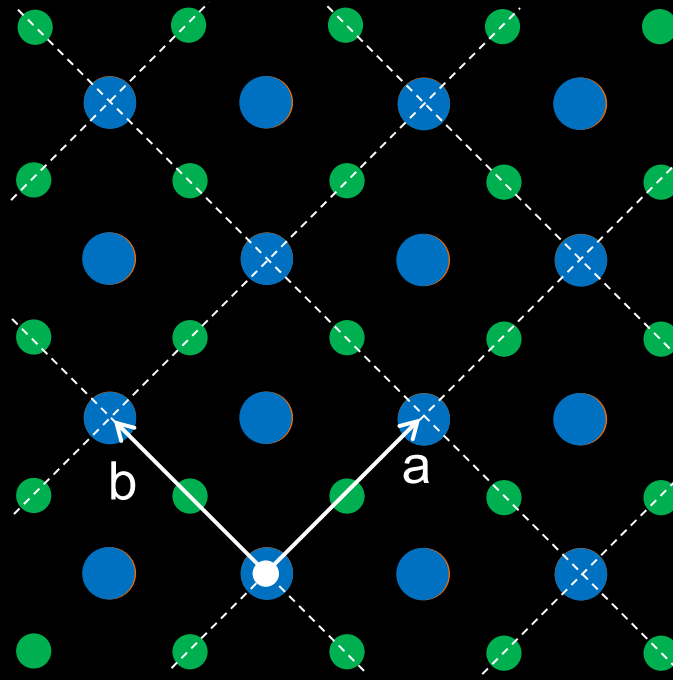
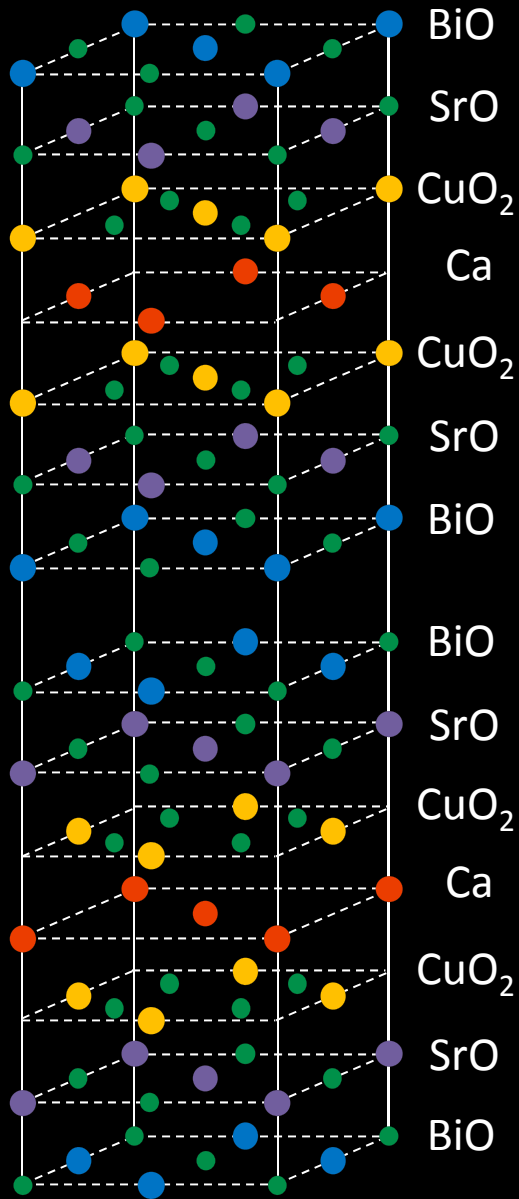
16 inequivalent sites:

average displacement: 1.1%

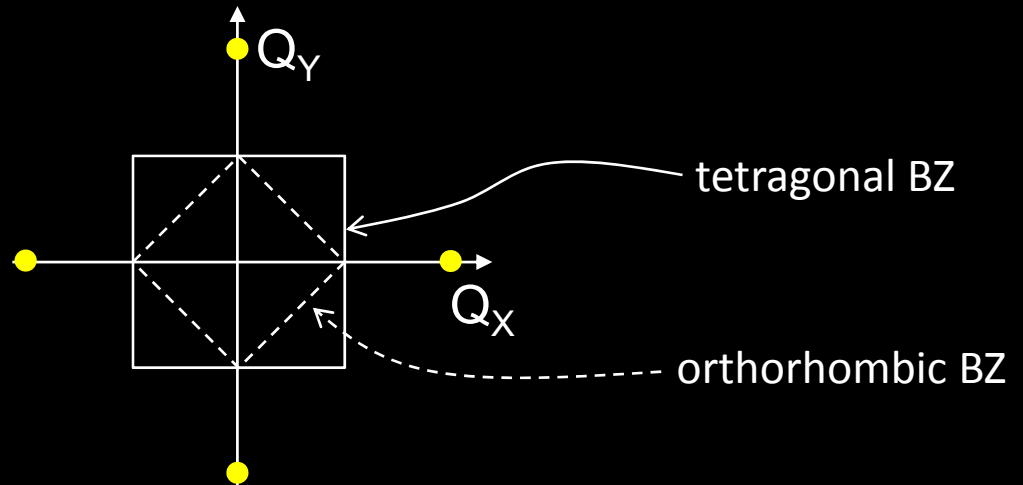
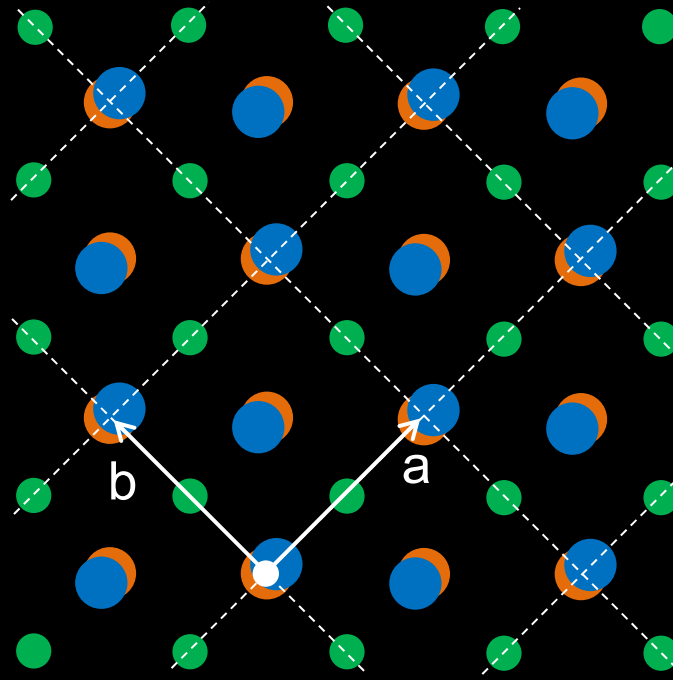
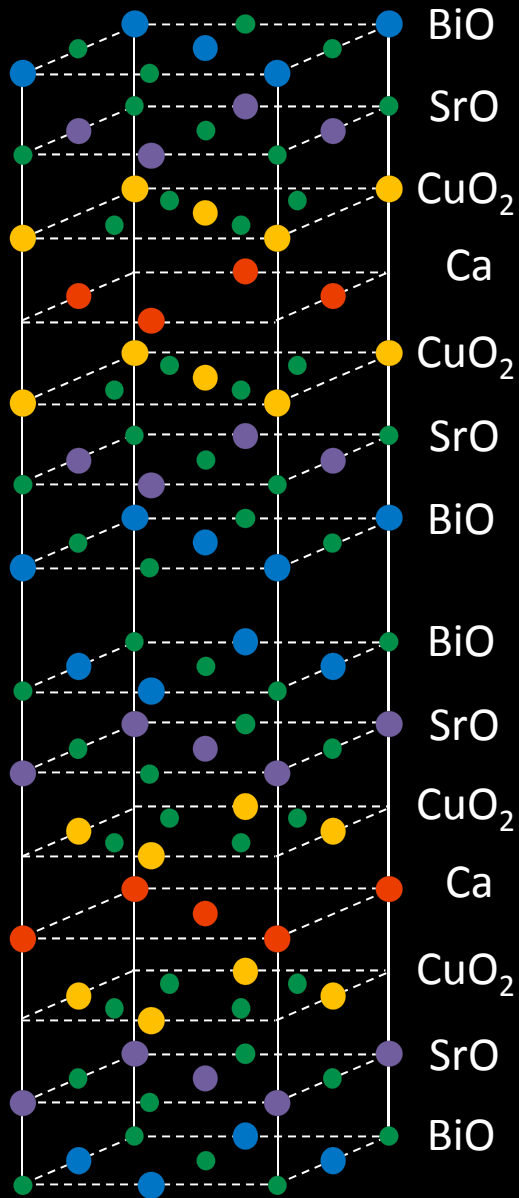
standard deviation: 0.36%

(error bar  $\sim 1/3$  of effect  $\rightarrow$  inconsistent with zero)

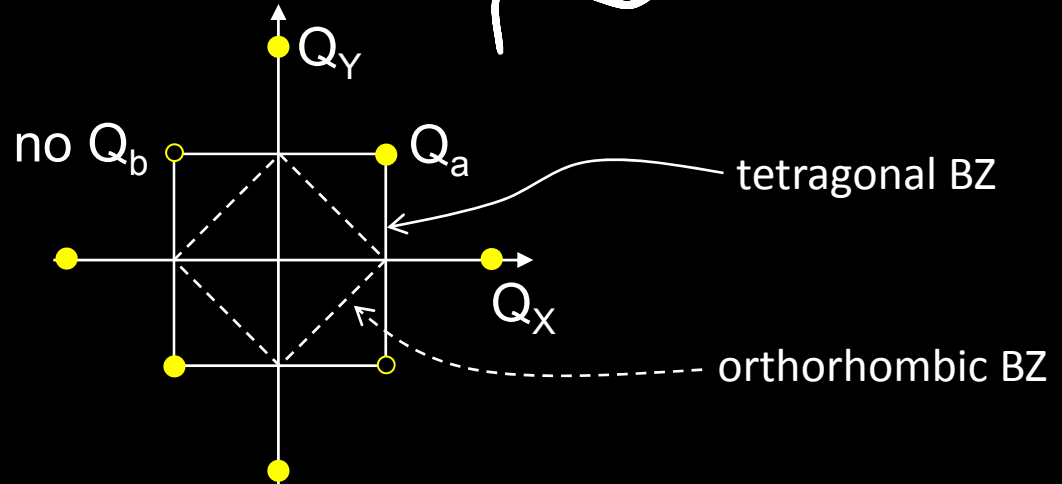
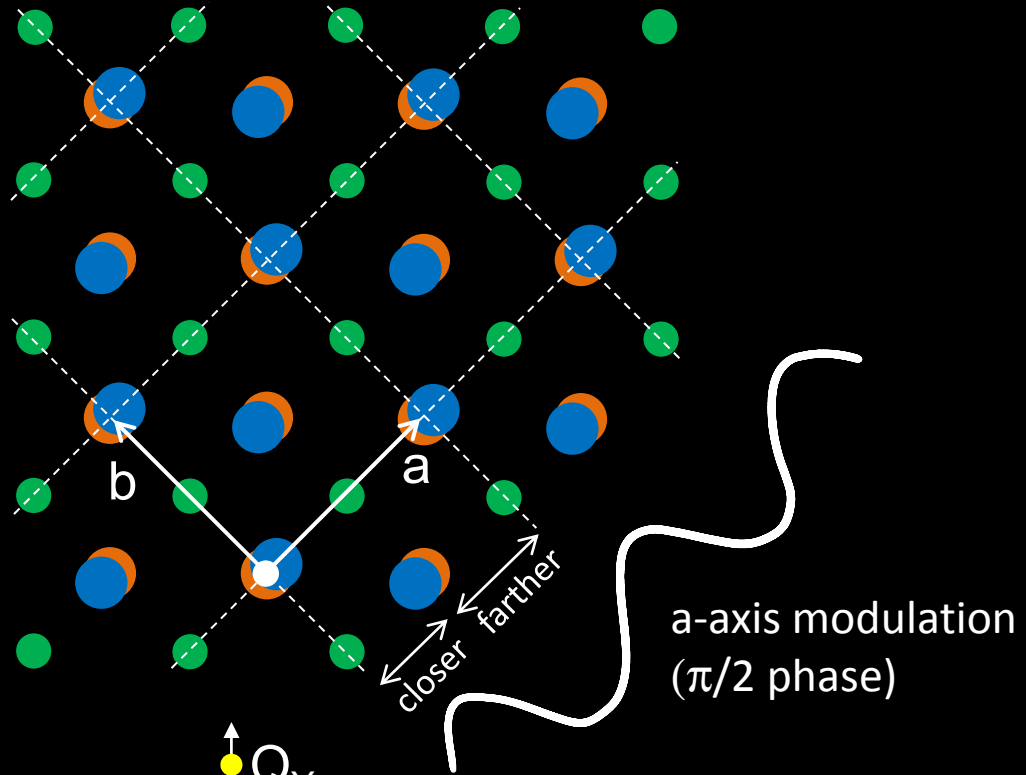
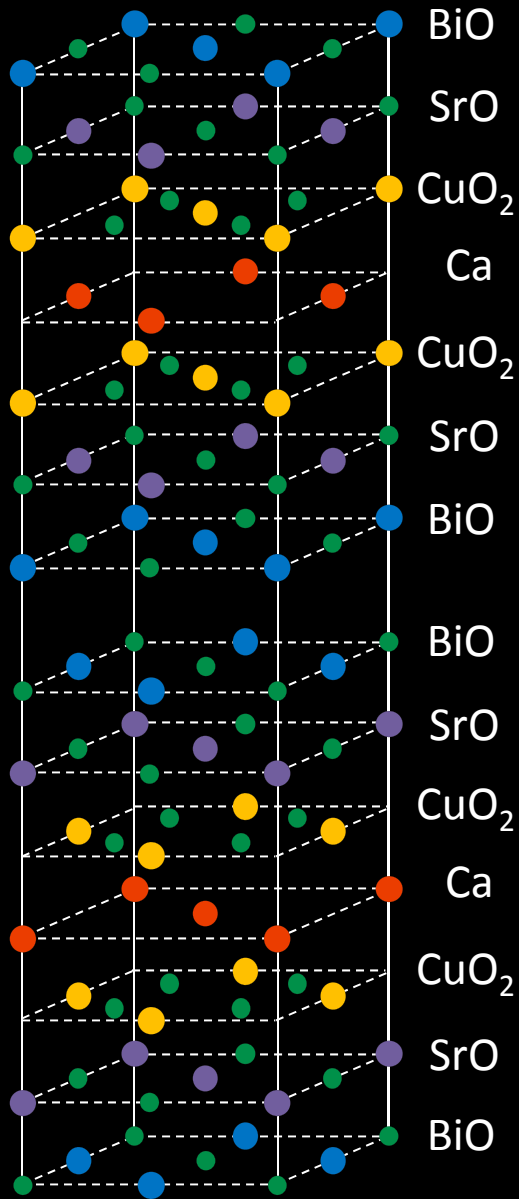
# Crystal Structure



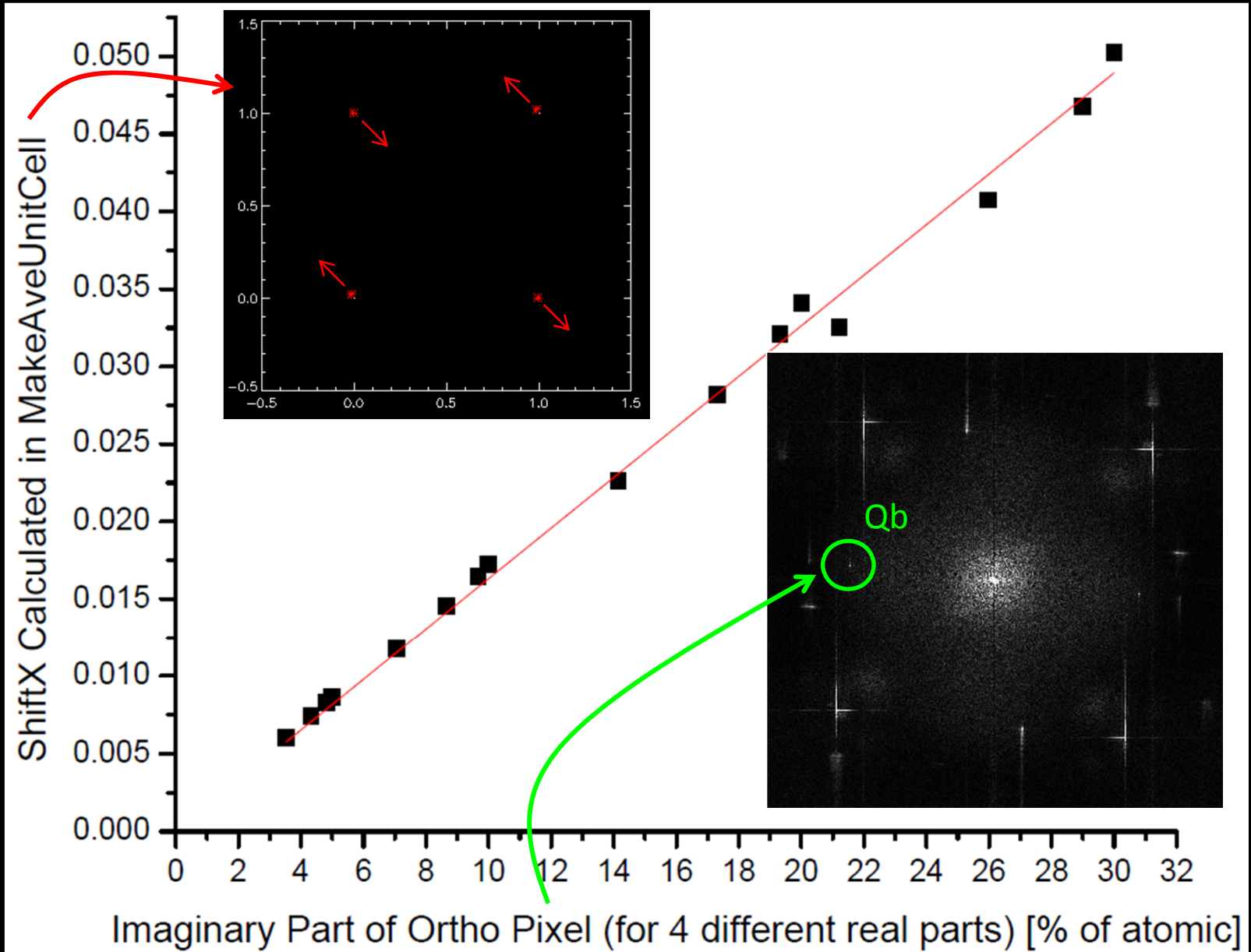
# Crystal Structure



# Crystal Structure

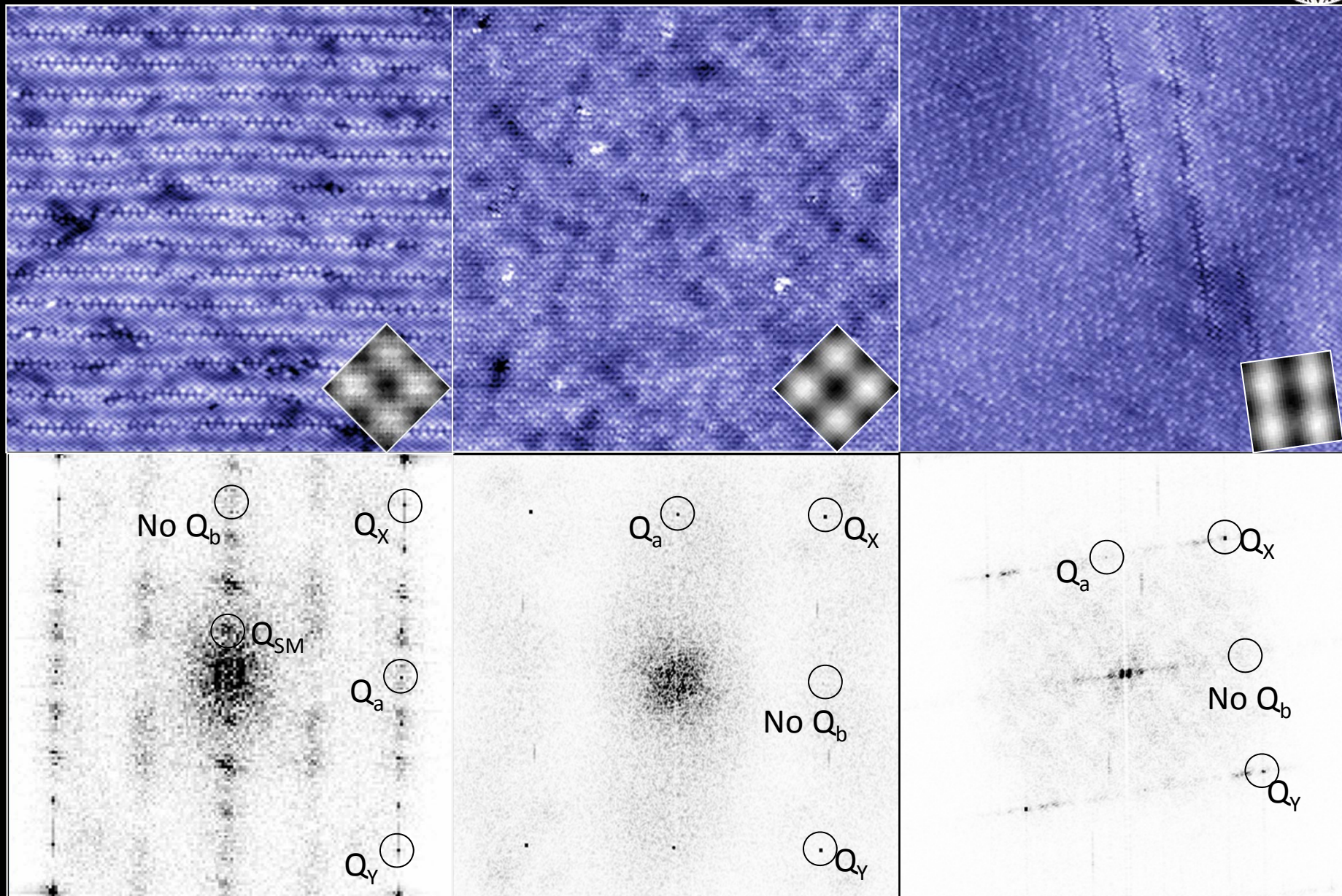


# Back to q-space: does it check out?

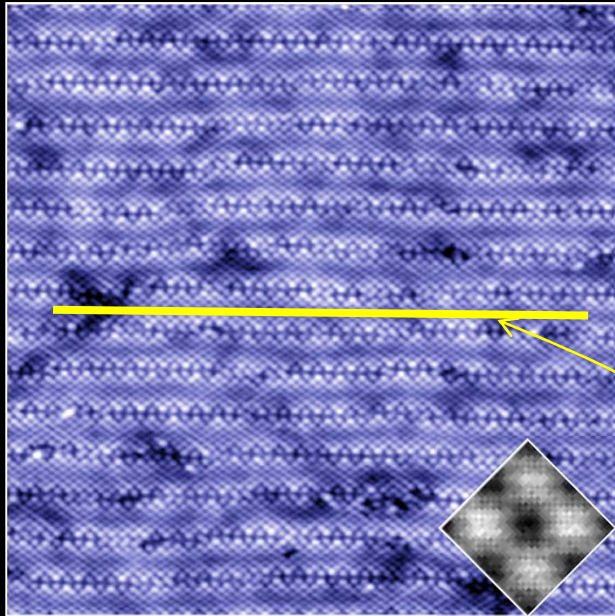




# Apply 2 methods to many samples



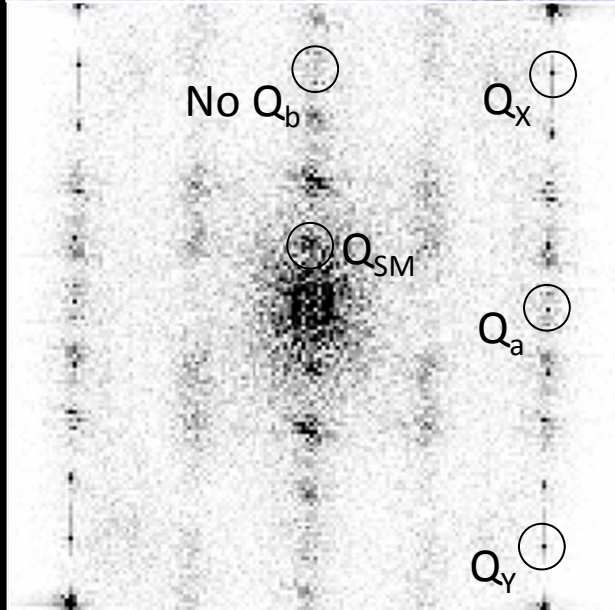
# 8 different Bi-2212 samples



$Q_{SM} \equiv$  crystalline b axis

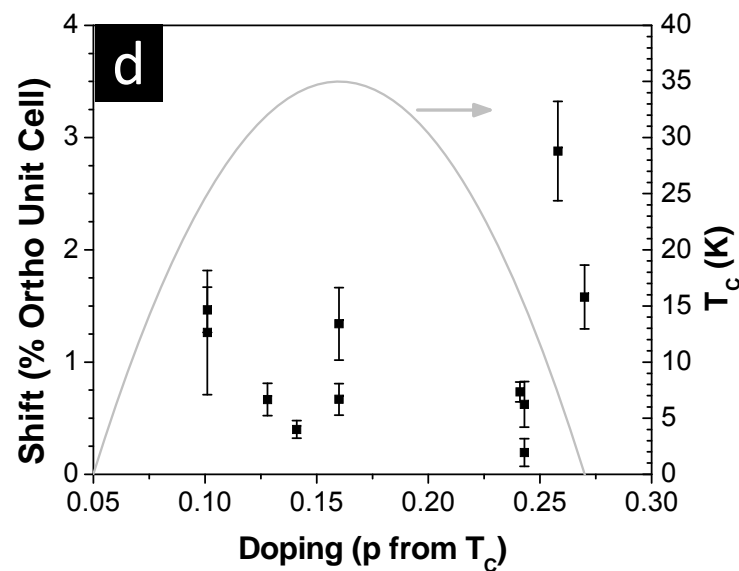
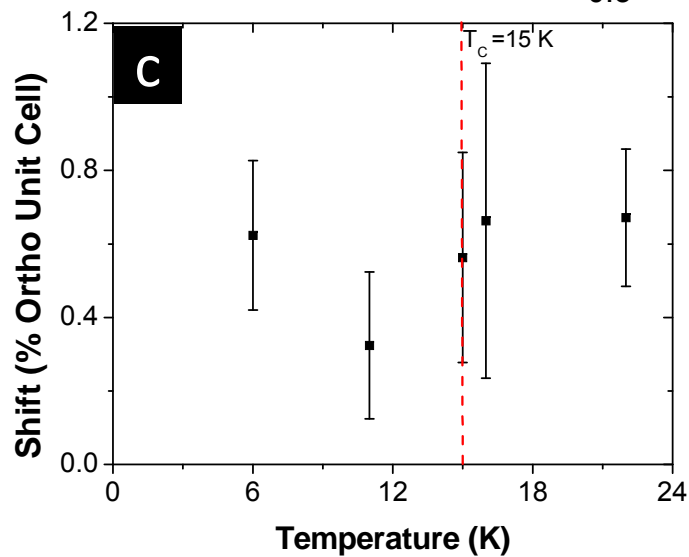
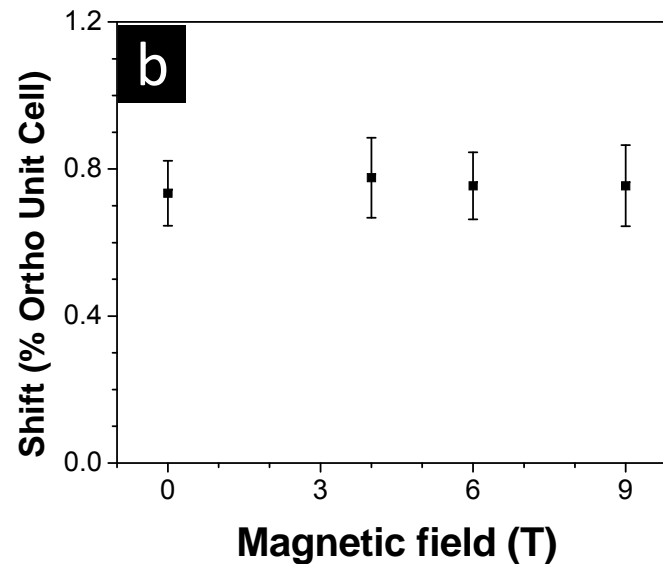
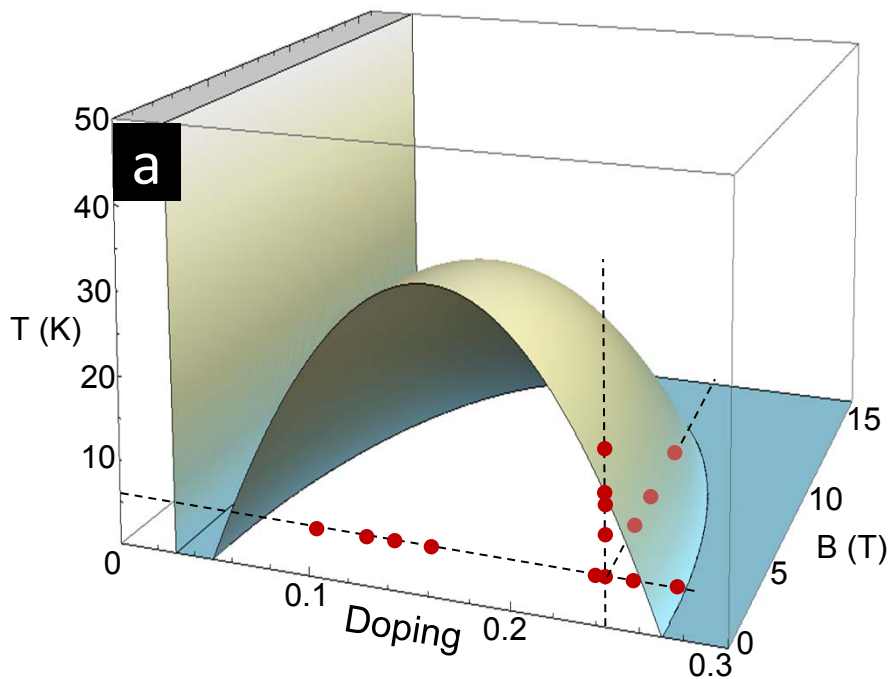
8 samples: ortho distortion along a axis

mirror plane always chooses this axis





# Bi-2201 throughout the SC dome





# Historical: Structure from Scattering

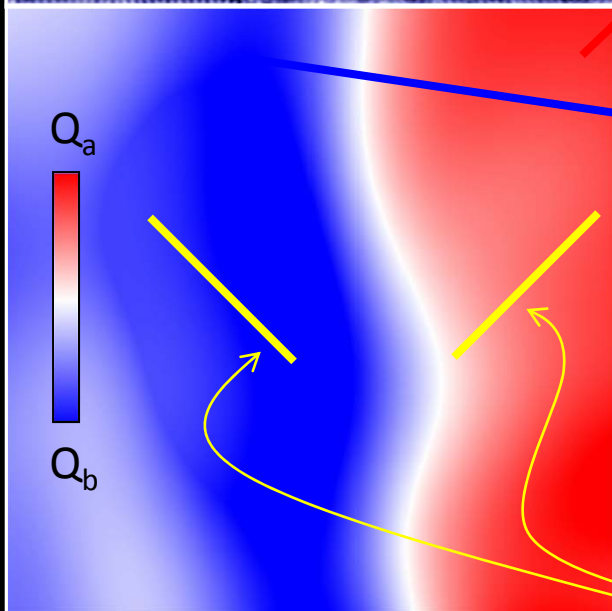
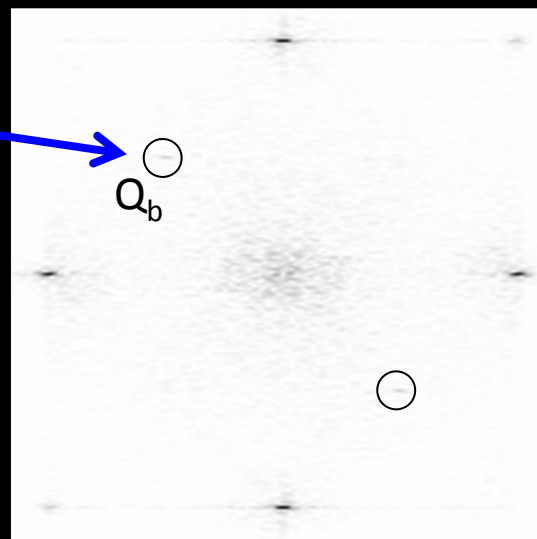
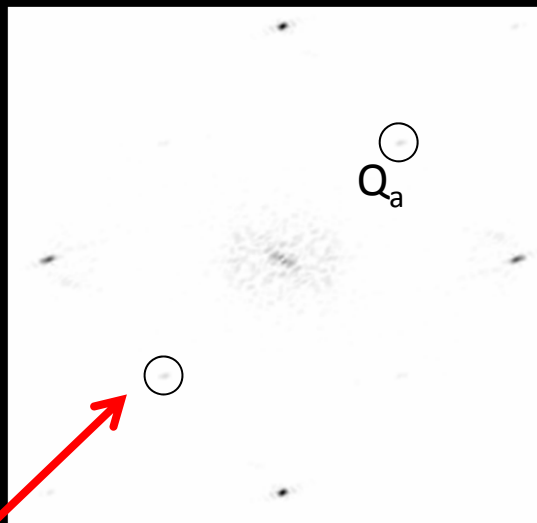
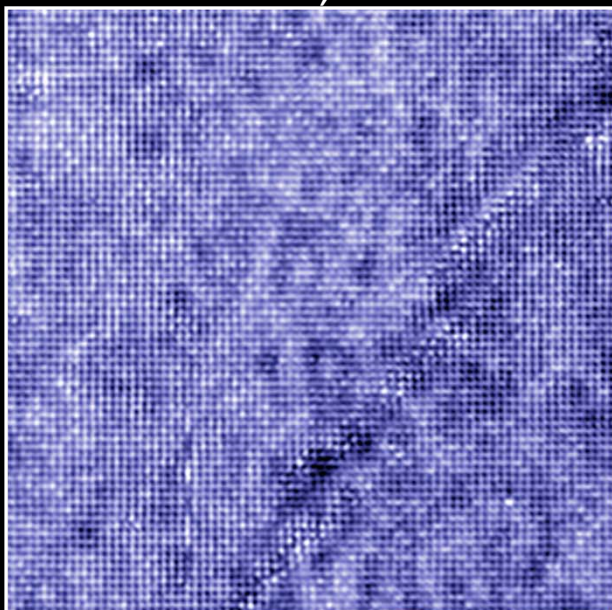


Material	Pb?	Technique	Bi distortion	Cu distortion	Ref
Bi-2223	no	XRD	2.22% (b axis)	-0.01% (b axis)	Subramanian, Science (1988)
Bi-2201	no	XRD	2.58% (b axis)	none	Torardi, PRB (1998)
Bi-2212	no	neutrons	2.55% (a axis)	-0.07% (a axis)	Miles, Physica C (1998)
Bi-2201	yes	XRD	1.82% (a axis) 6.34% (b axis)	none	Ito, PRB (1998)
Bi-2212	yes	XRD	1% (a axis) 1.65% (b axis)	2.57% (a axis) -0.02% (b axis)	Calestani, Physica C (1998)
Bi-2212	yes	XRD	1.1% (a axis) 1.53% (b axis)	0.08% (b axis)	Gladyshevskii, PBR (2004)
Bi-2201	yes and no	LEED, ARPES	one axis only	can't determine	Mans, PRL (2006)

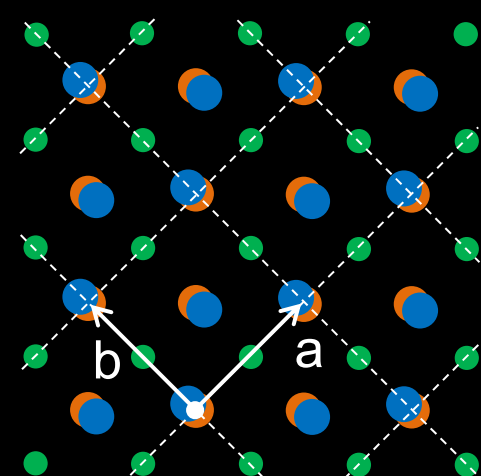
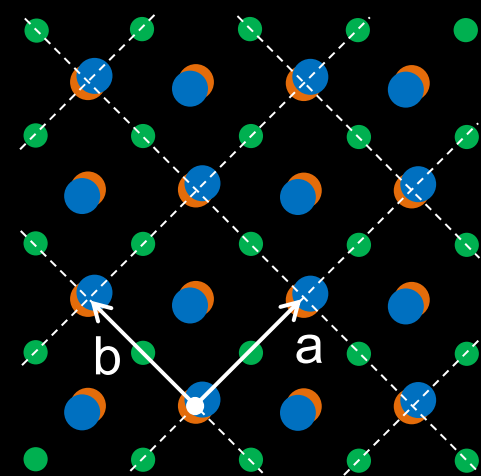
# STM adds: *LOCAL* symmetry determination



Bi-2201:  $T_c=25\text{K}$ , UD



local mirror planes!



# Historical: Structure from Scattering



Material	Pb?	Technique	Bi distortion	Cu distortion	Ref
Bi-2223	no	XRD	2.22% (b axis)	-0.01% (b axis)	Subramanian, Science (1988)
Bi-2201	no	XRD	2.58% (b axis)	none	Torardi, PRB (1998)
Bi-2212	no	neutrons	2.55% (a axis)	-0.07% (a axis)	Miles, Physica C (1998)
Bi-2201	yes	XRD	1.82% (a axis) 6.34% (b axis)	none	Ito, PRB (1998)
Bi-2212	yes	XRD	1% (a axis) 1.65% (b axis)	2.57% (a axis) -0.02% (b axis)	Calestani, Physica C (1998)
Bi-2212	yes	XRD	1.1% (a axis) 1.53% (b axis)	0.08% (b axis)	Gladyshevskii, PBR (2004)
Bi-2201	yes and no	LEED, ARPES	one axis only	can't determine	Mans, PRL (2006)

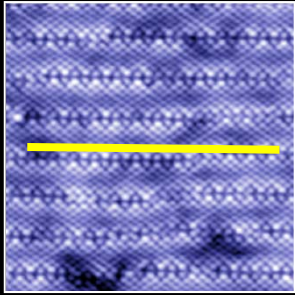
In the absence of supermodulation, there can be twin boundaries  
→ leads to the appearance of shifts along 2 axes



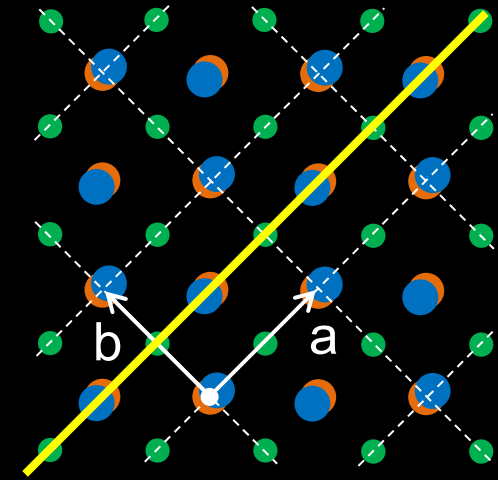
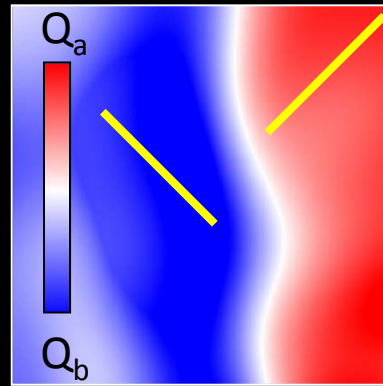
# Conclusions



1. structural distortion in BiO plane breaks inversion symmetry at the Bi site, **but preserves mirror plane**



2. **mirror plane** is always aligned with supermodulation

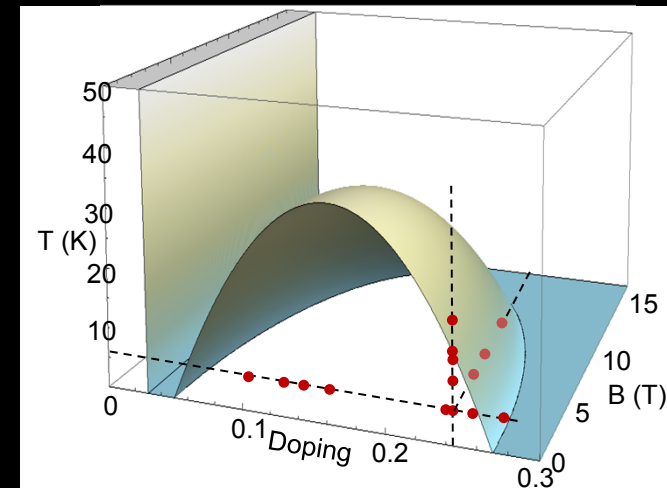


3. can image the **local mirror plane**

4. resolve long discrepancies in the bulk scattering literature:

- supermodulated samples → no ortho twinning;
- Pb-doped samples → can have ortho twinning

5. orthorhombic distortion present across large regions of Bi-2201 phase diagram



# Implications



1. Algorithms: we extend Lawler's algorithm for 4 additional purposes
  - a. discriminating between noise (broadens) and signal (sharpens)
  - b. make average unit cell: can arbitrarily exchange large area for high resolution
  - c. make average supercell: can detect any commensurate modulation
  - d. use Fourier methods to locally track any structural modulation
  
2. Structural vs. electronic:
  - a. We also see inversion "symmetry breaking" in the electronic signal. It appears larger than structural, but we haven't found a way to make ourselves confident that it is not a normalization artifact.
  - b. Investigations of local electronic "symmetry breaking" should take care to state which structural symmetries are already broken, and to compare the magnitudes of electronic and structural symmetry breaking.
  - c. If electronic "symmetry breaking" states just reinforce structural symmetries, but can be shown to follow  $T^*$  line, then of course they are important and interesting.