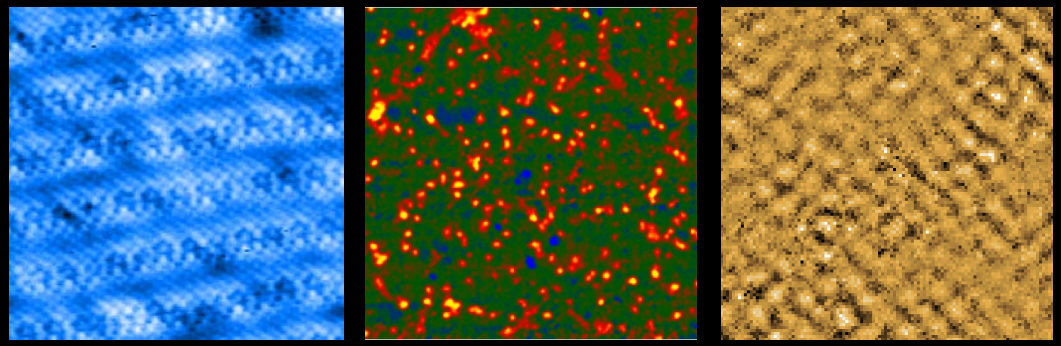
The effect of a single atom on high-T_c superconductivity

Jenny Hoffman



Experiments:

Liz Main
Adam Pivonka
Ilija Zeljkovic
Anjan Soumyanarayanan
Michael Yee
Yang He
Martin Blood-Forsythe
Lena Huefner
Yi Yin
Martin Zech
Tess Williams
Nick Litombe
Monica Chao
Can-Li Song
Dennis Huang
Eric Hudson

Harvard Physics

Samples:

Dillon Gardner
Young Lee
MIT

Zhijun Xu
Jinsheng Wen
Genda Gu
Brookhaven

Dirk Rahn
Kai Rossnagel
Kiel University

Paul Canfield
Matt Tillman
Ames Lab

Thanks to:

BSF

NSEC

HARVARD

NSF

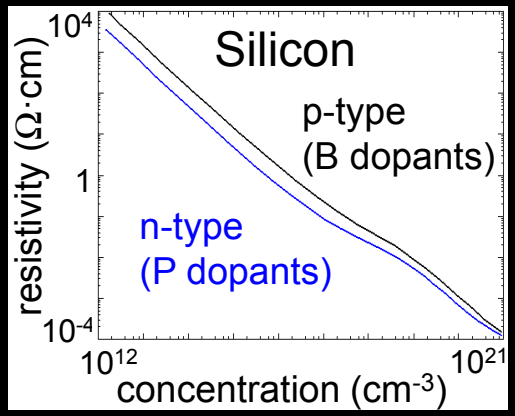
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

ALFRED P. SLOAN FOUNDATION 1934

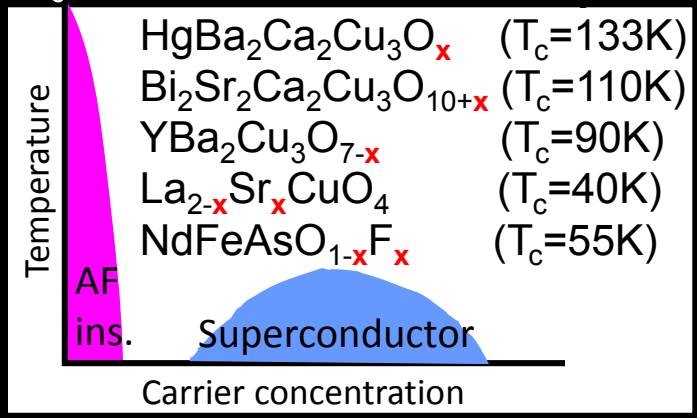
The importance of a single atom

Doping makes useless materials useful

Semiconductors:

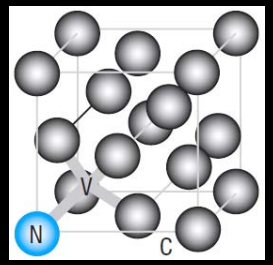


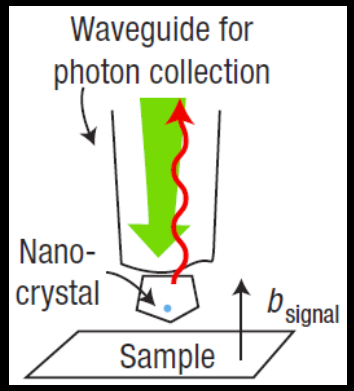
High-T_c superconductors:



Single atoms as computing or measurement tools

Diamond nitrogen-vacancy centers for qubits or sensitive magnetic measurements

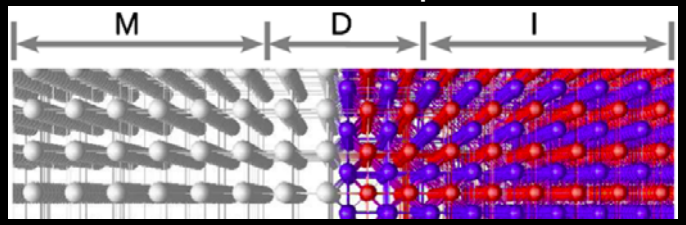




Taylor, … Yacoby, Walsworth, Lukin, Nat. Phys. 4, 810 (2008)

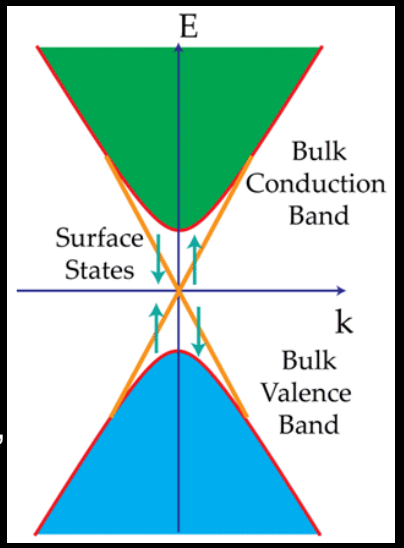
Impurities lead to unwanted effects

Decoherence: 5×10^{17} m^{-2} spins at M-I interface



Choi, … Clarke, PRL 103, 197001 (2009)

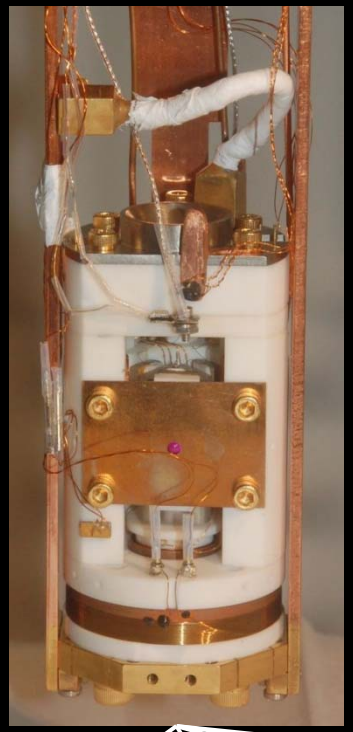
Electrical shorts, e.g. topological "insulators" have conducting bulk



Analytis et al, Nat. Phys. 6, 960 (2010)

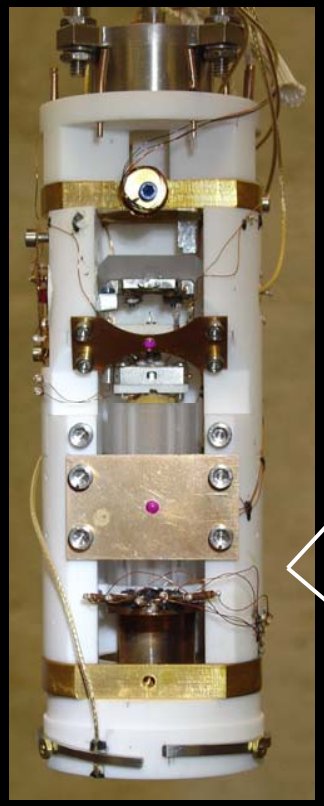
Hoffman Lab Local Probes

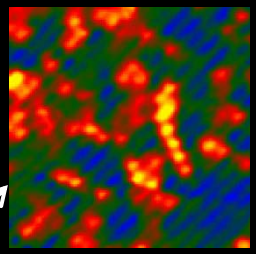
Scanning Tunneling Microscope



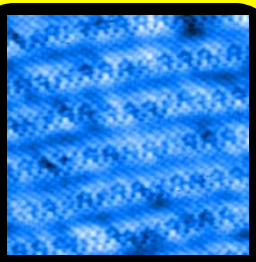
Force Microscope

Ultra-high vacuum STM

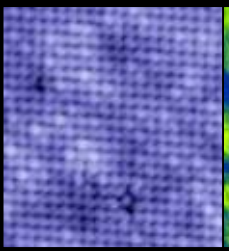




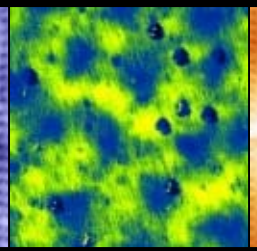
$Pr_xCa_{1-x}Fe_2As_2$



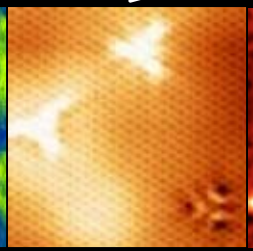
Bi-2212



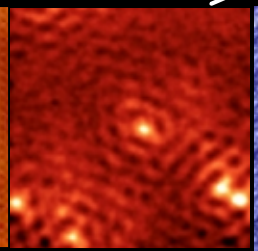
Bi-2201



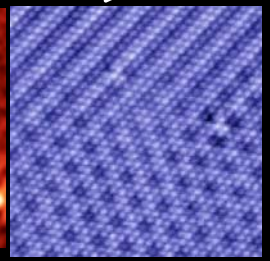
122 iron pnictide



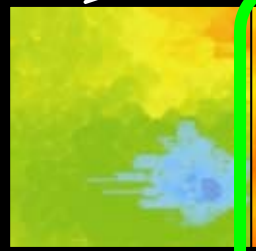
topological Bi_2Se_3



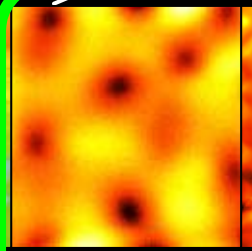
topological Sb(111)



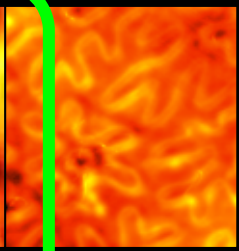
$NbSe_2$



metal-insulator transition in VO_2



1111 iron pnictide



$Nd_2Fe_{14}B$

Outline

Superconductors: 100 Year History

Part I: Pseudogap in cuprates:

- Competing or collaborating?
  (introduction to scanning tunneling microscopy)
- Nanoscale inhomogeneity: energy & charge modulation
  → what is the hidden variable??
- Previous studies of chemical disorder
  → hidden variable remains mysterious…
- STM imaging of oxygen dopants & vacancies
  → we found the hidden variable!!

Part II: Vortex pinning in iron-based superconductors:

- MFM imaging of $NdFeAsO_{1-x}F_x$, in-plane anisotropy
- Single atoms → collective pinning

Outline

Superconductors: 100 Year History

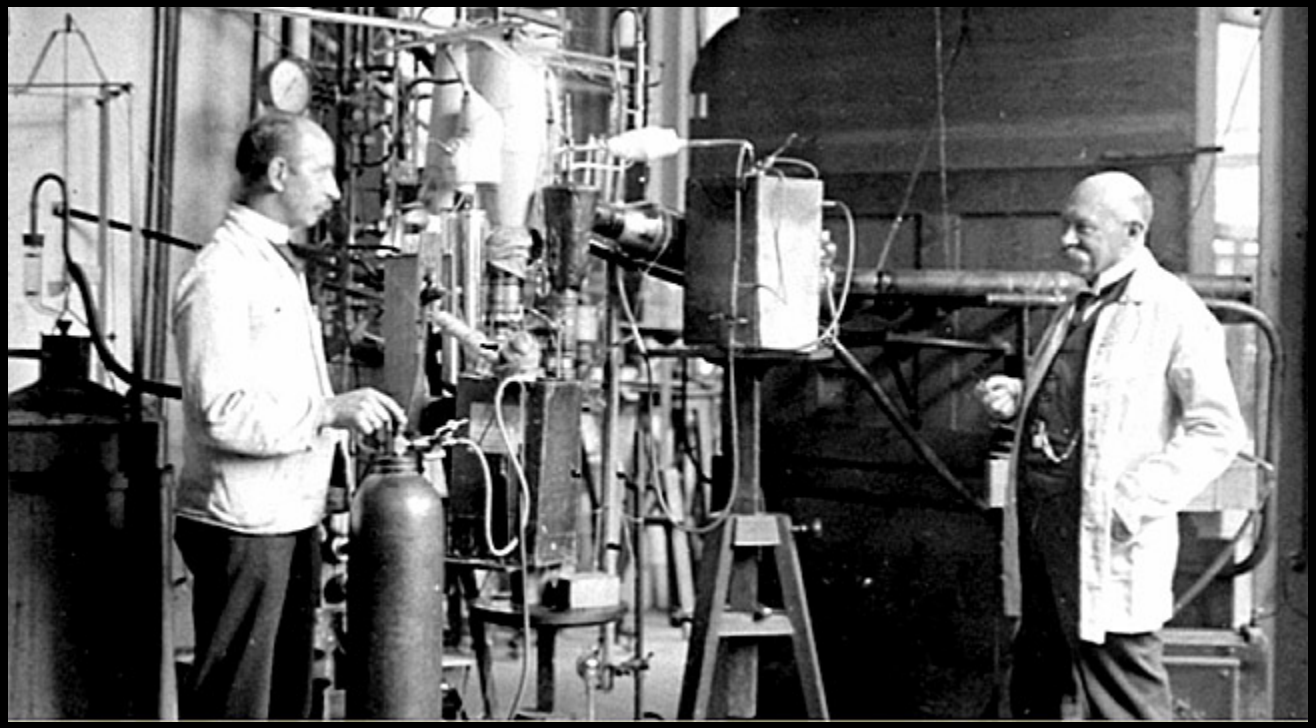
Part I: Pseudogap in cuprates:

- Competing or collaborating?
  (introduction to scanning tunneling microscopy)
- Nanoscale inhomogeneity: energy & charge modulation
  → what is the hidden variable??
- Previous studies of chemical disorder
  → hidden variable remains mysterious…
- STM imaging of oxygen dopants & vacancies
  → we found the hidden variable!!

Part II: Vortex pinning in iron-based superconductors:

- MFM imaging of $NdFeAsO_{1-x}F_x$, in-plane anisotropy
- Single atoms → collective pinning

101 Years Ago: Discovery of Superconductivity



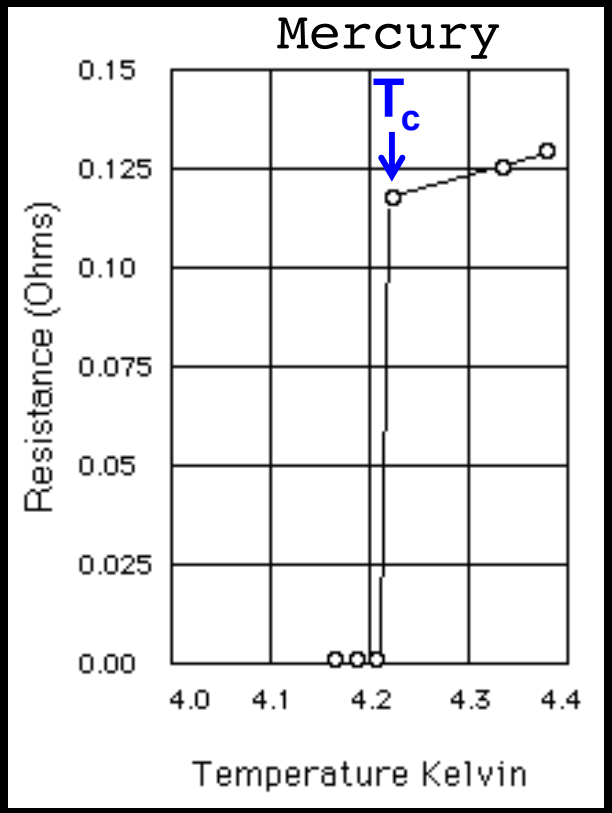
Heike Kamerlingh Onnes (right) and Gerrit Flim, his chief technician, at the helium liquefier in Kamerlingh Onnes's Leiden laboratory, circa 1911.

Physics Today, Sept 2010

(101 years later… funding for helium liquefier at Harvard!)

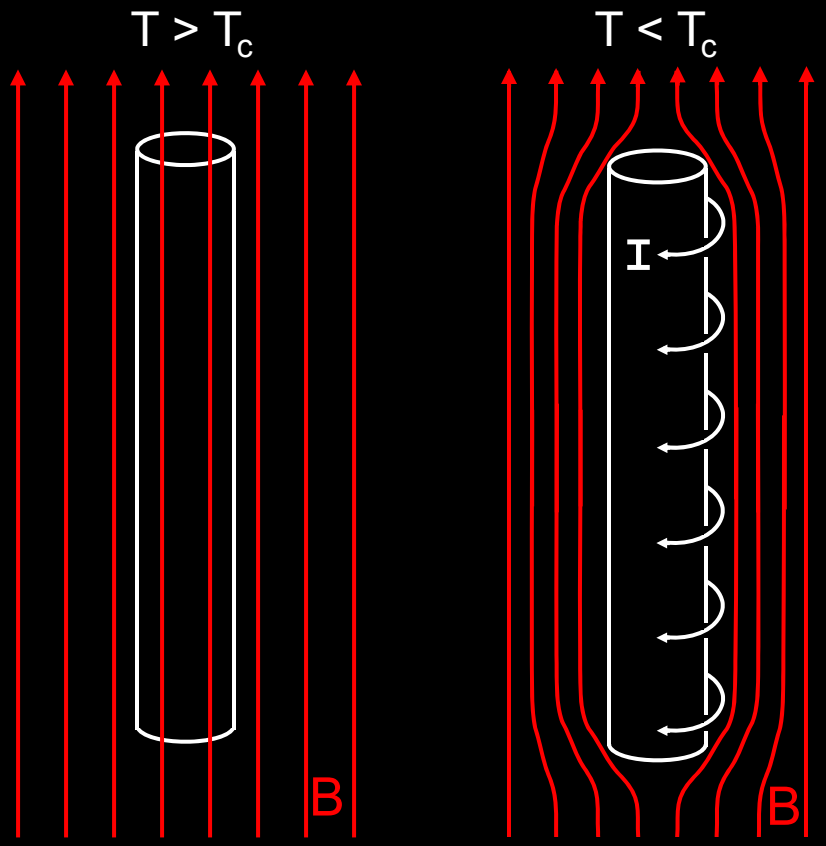
2 Properties of Superconductors

1. Vanishing of electrical resistivity (by Cooper pairing)



Kamerlingh-Onnes, 1911

2. Expulsion of magnetic field (by shielding currents)



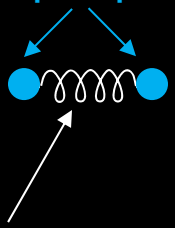
Meissner, 1933

Today's frontiers:

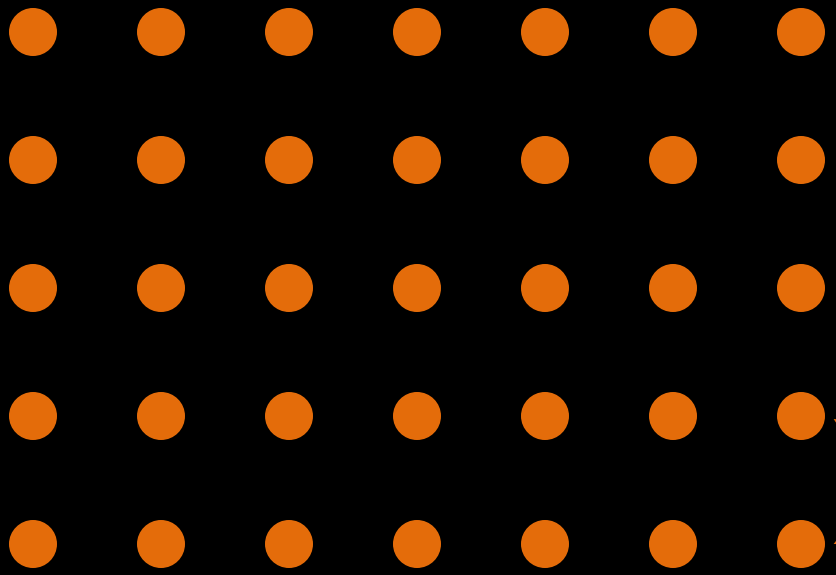
1. Understand pairing → increase T_c
2. Improve magnetic flux pinning

Cooper pairing

negative electrons form "Cooper pairs"



bound together by a "phonon"



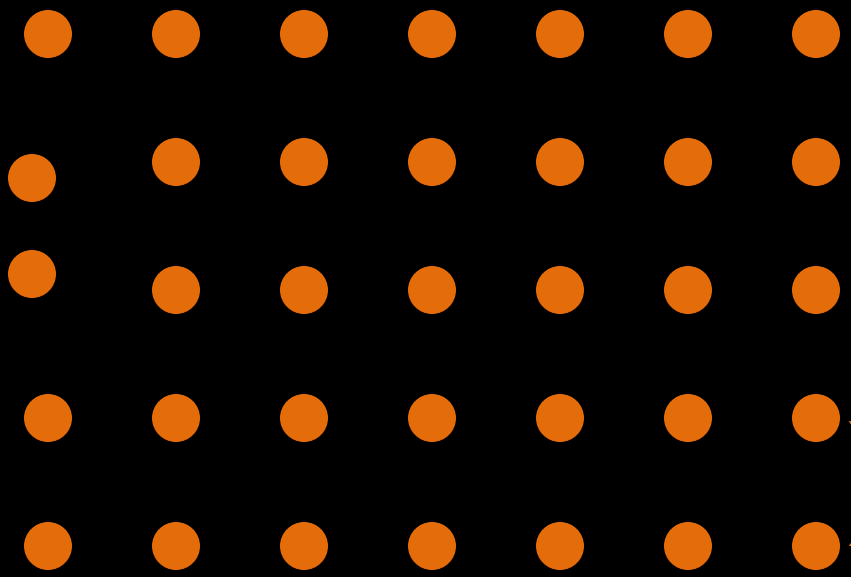
positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"

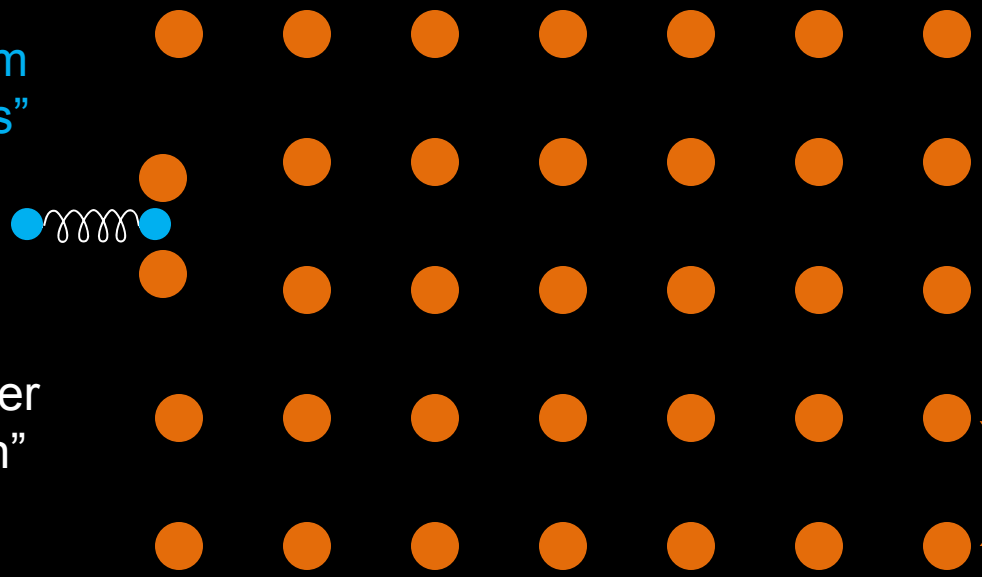
bound together by a "phonon"



Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"



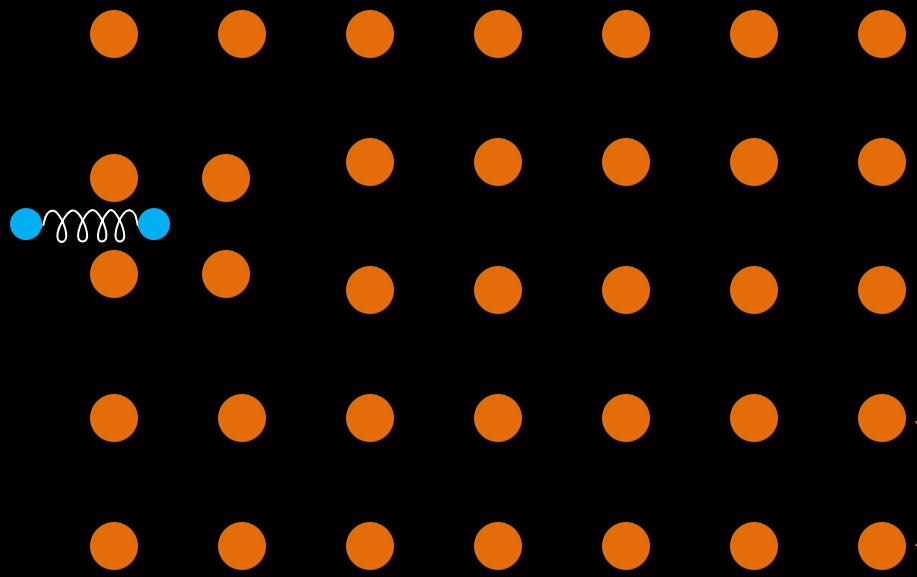
bound together by a "phonon"

positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"



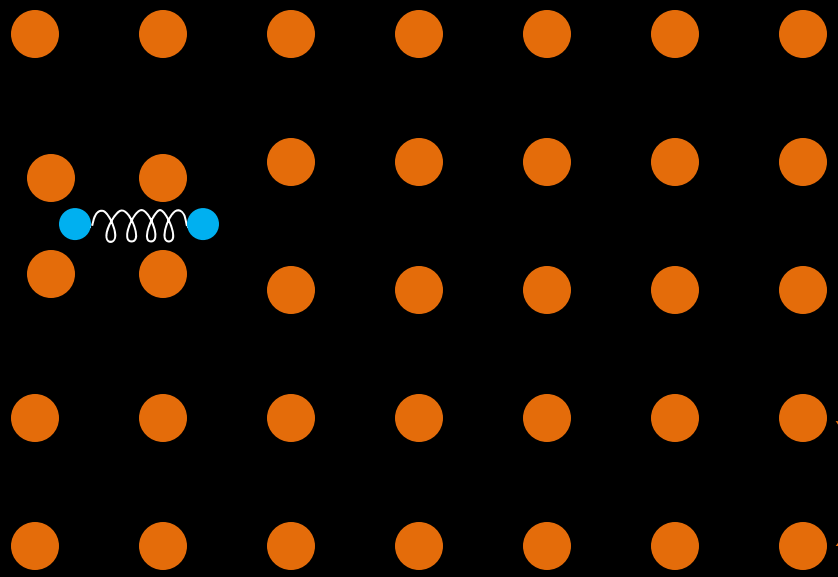
bound together by a "phonon"

positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"



bound together by a "phonon"

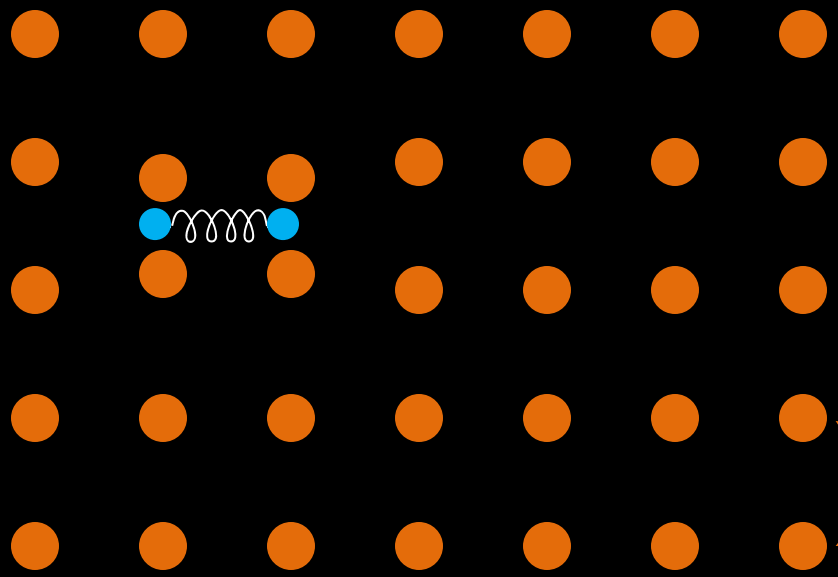
positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"

bound together by a "phonon"

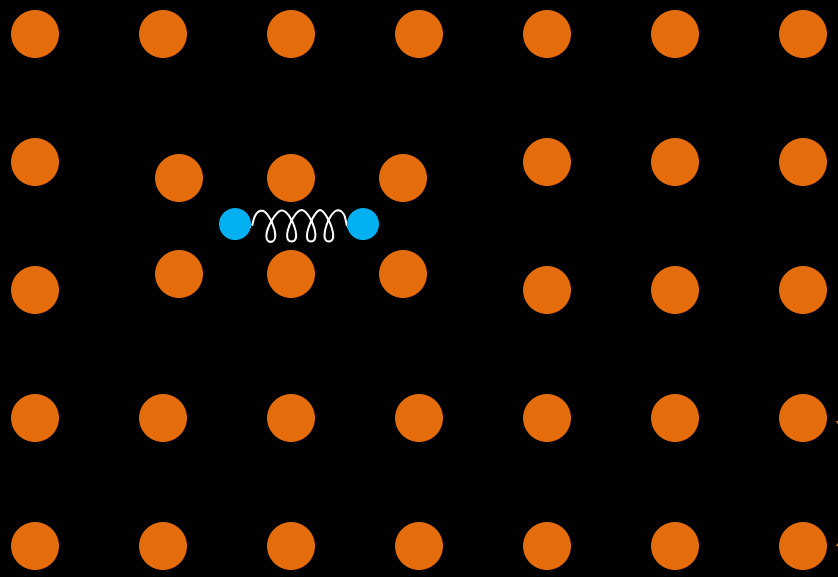


positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"



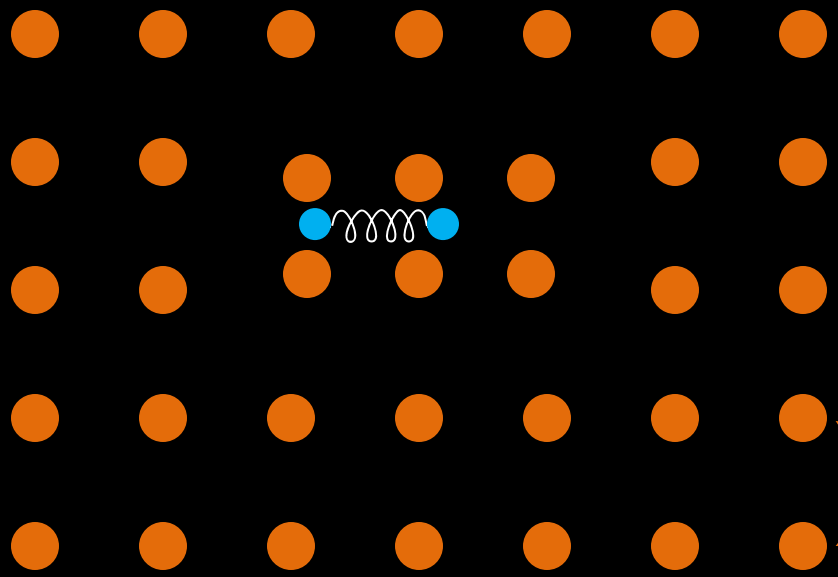
bound together by a "phonon"

positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"



bound together by a "phonon"

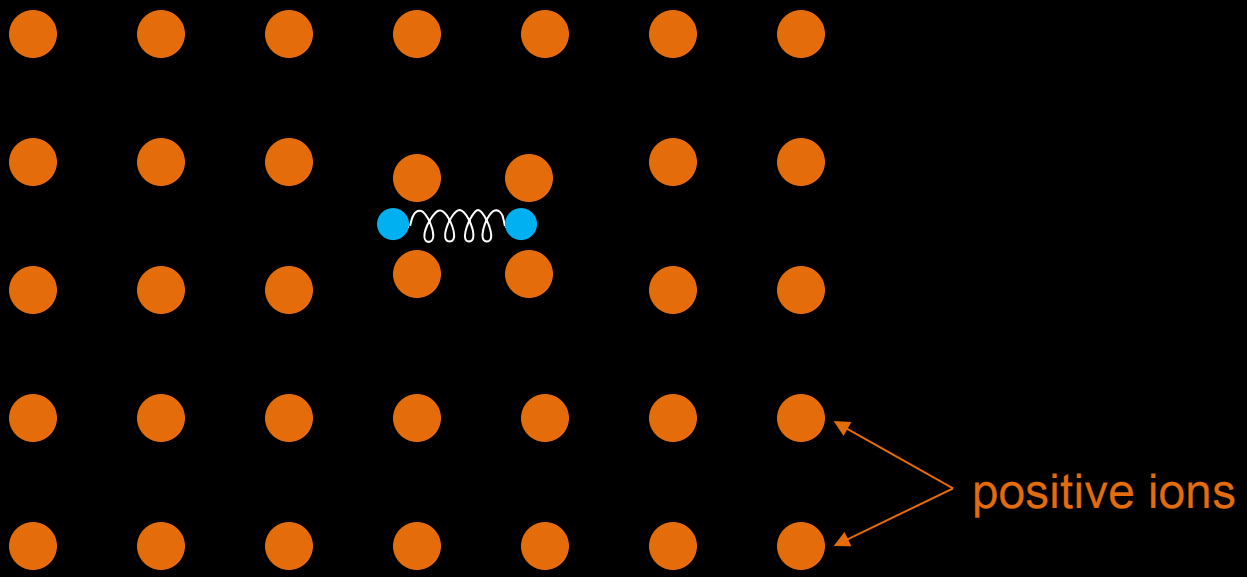
positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"

bound together by a "phonon"

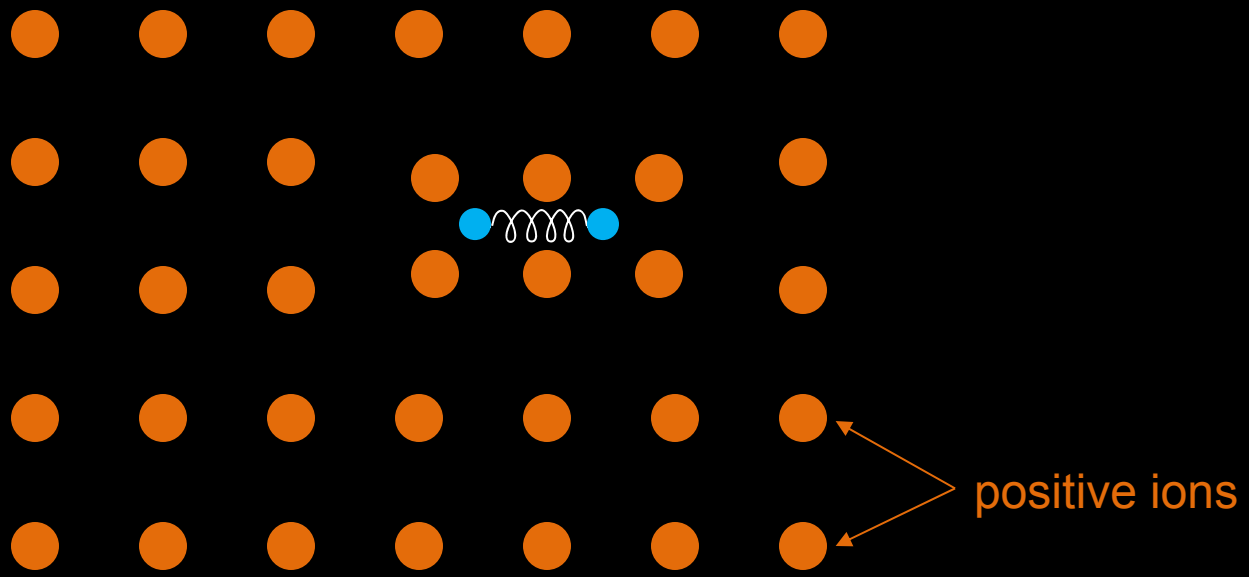


Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"

bound together by a "phonon"

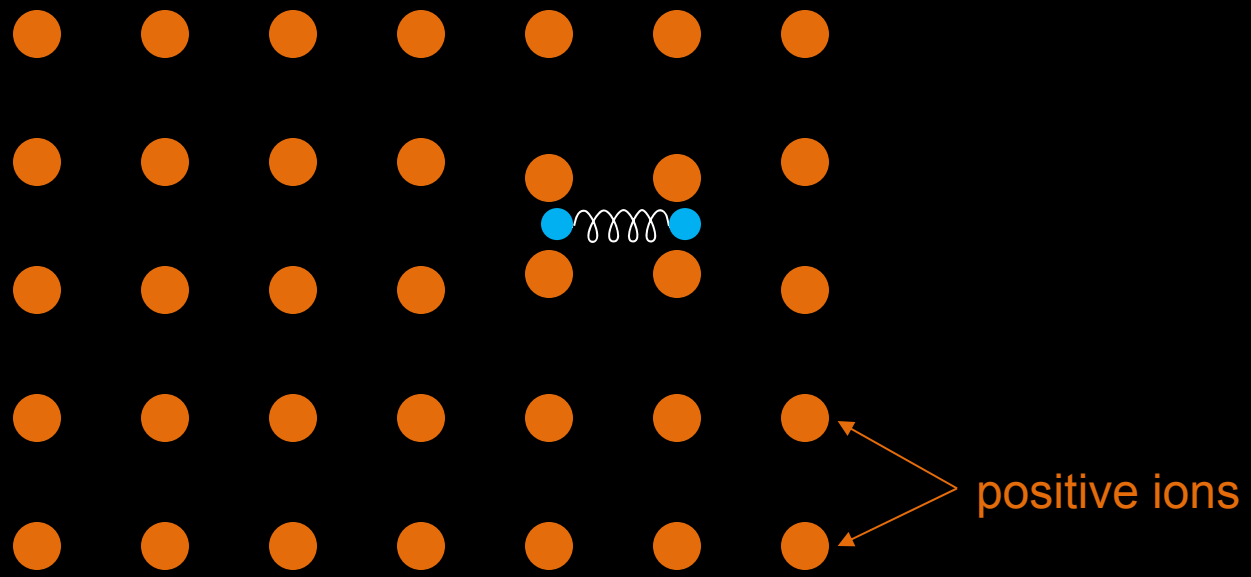


Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"

bound together by a "phonon"

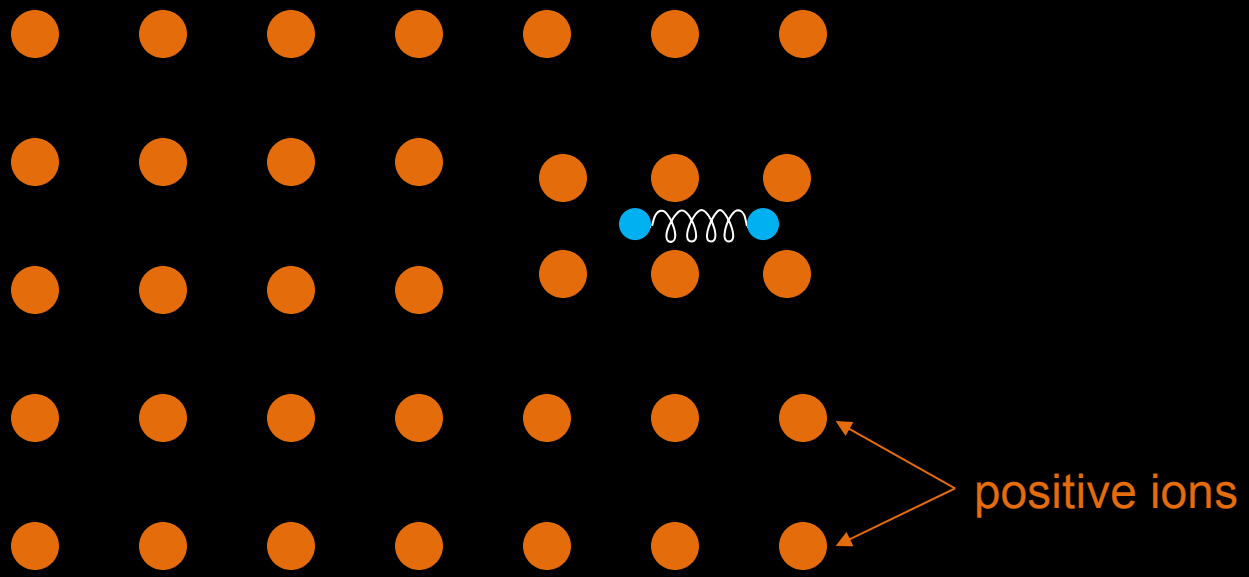


Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"

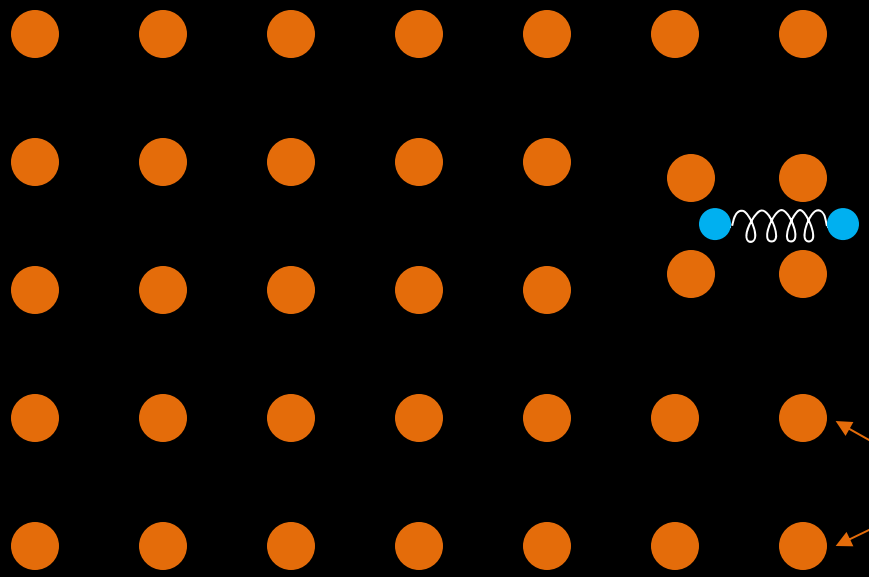
bound together by a "phonon"



Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"



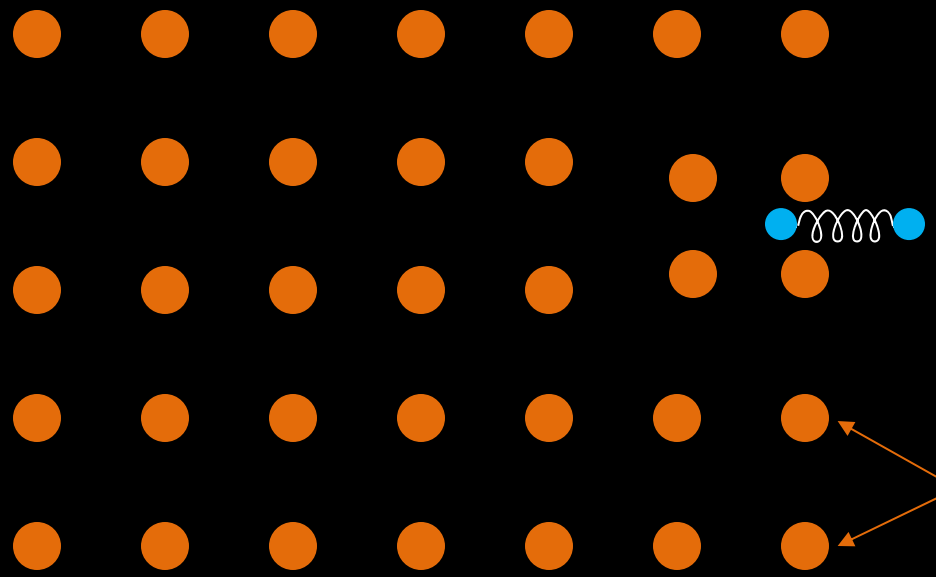
bound together by a "phonon"

positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"



bound together by a "phonon"

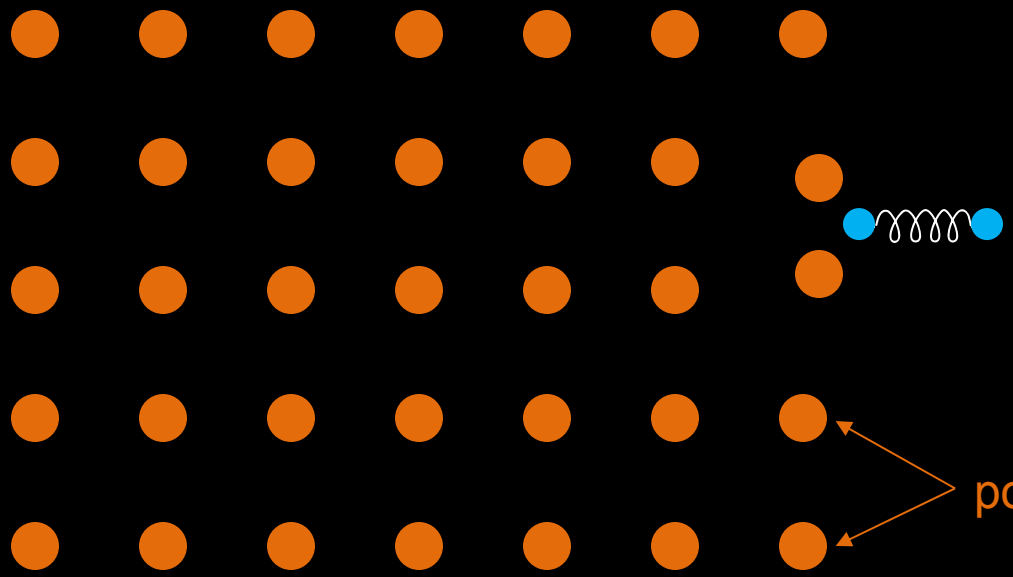
positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"

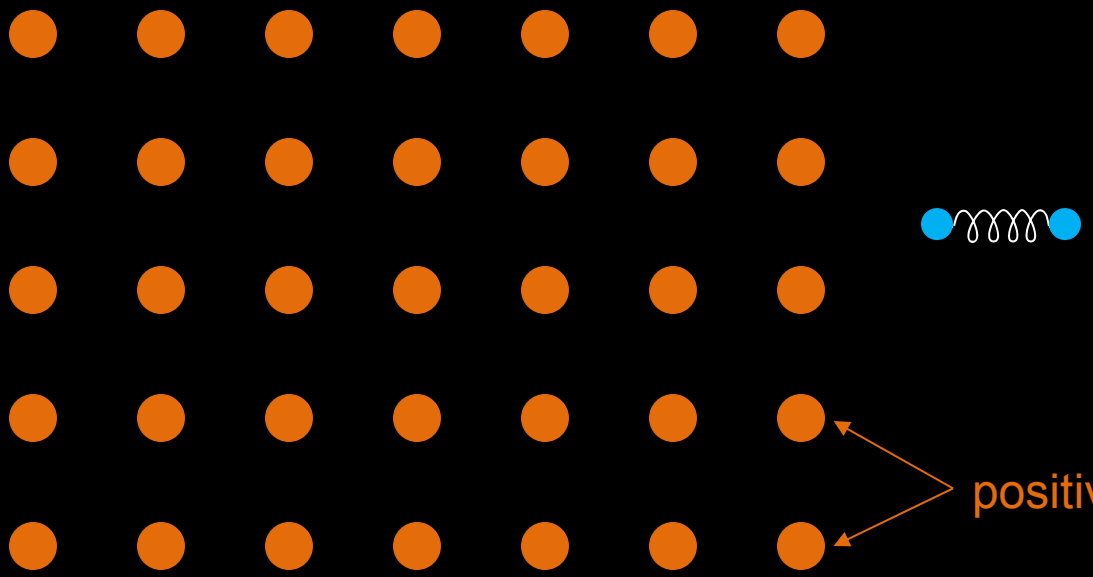
bound together by a "phonon"



Cooper, Phys. Rev. 104, 1189 (1956)

Cooper pairing

negative electrons form "Cooper pairs"



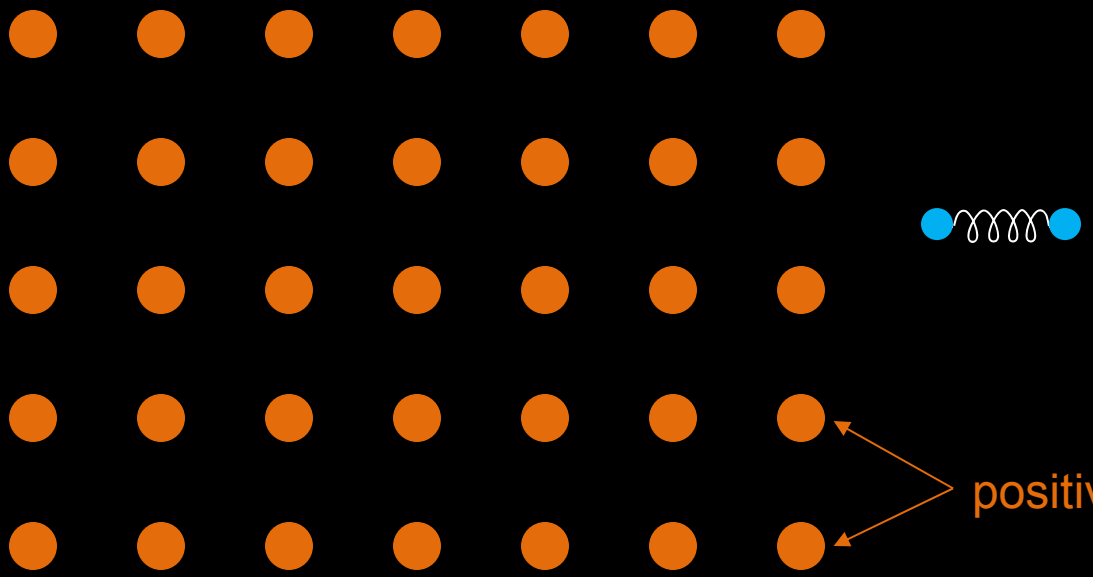
bound together by a "phonon"

positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

Bardeen-Cooper-Schrieffer Theory

negative electrons form "Cooper pairs"



bound together by a "phonon"

positive ions

Cooper, Phys. Rev. 104, 1189 (1956)

BCS formula: $k_B T_c = 1.13 \hbar \omega_D e^{\frac{-1}{N(\varepsilon_F)V}}$

ω_D ~ Debye frequency = highest energy phonon

V ~ electron-phonon coupling

$N(\varepsilon_F)$ = density of states at the Fermi level
= electrons available for pairing

Bardeen, Cooper, Schrieffer, Phys. Rev. 108, 1175 (1957)

Discovery of cuprate high-T_c superconductors

BCS formula: $k_B T_c = 1.13 \hbar \omega_D e^{\frac{-1}{N(\varepsilon_F)V}}$

ω_D ~ Debye frequency = highest energy phonon

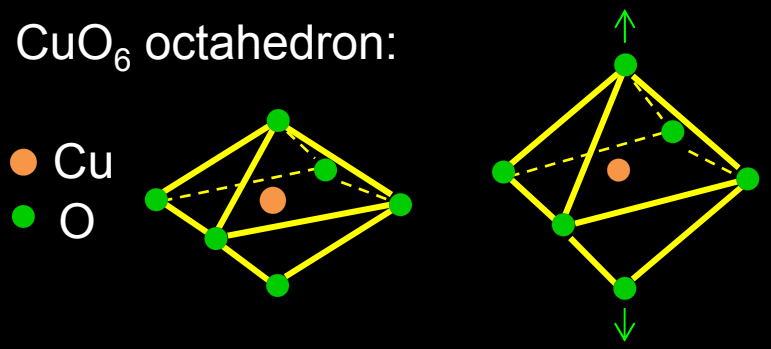
V ~ electron-phonon coupling

$N(\varepsilon_F)$ = density of states at the Fermi level
= electrons available for pairing

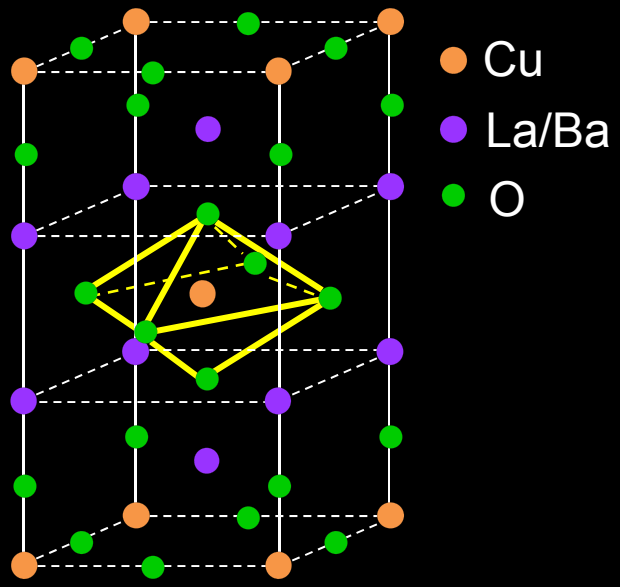
Bardeen, Cooper, Schrieffer, Phys. Rev. 108, 1175 (1957)

Müller's good idea: increase V by the Jahn-Teller effect

CuO_6 octahedron:



$T_c = 35\ K$



Cu d^9 has 3 e^- in 2 degenerate e_g orbitals
→ distorts to lift degeneracy
→ strong electron-phonon coupling via polaron formation

Bednorz & Müller, Zeitschrift für Physik B 64, 189 (1986)

Isotope effect in cuprates?

BCS formula: $k_B T_c = 1.13 \hbar \omega_D e^{\frac{-1}{N(\varepsilon_F)V}}$

ω_D ~ Debye frequency = highest energy phonon

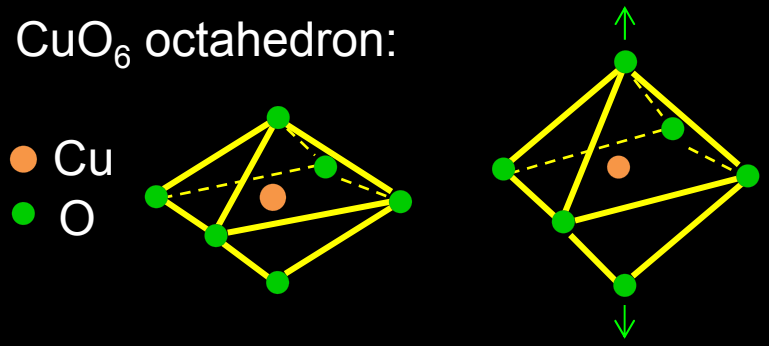
V ~ electron-phonon coupling

$N(\varepsilon_F)$ = density of states at the Fermi level
= electrons available for pairing

Bardeen, Cooper, Schrieffer, Phys. Rev. 108, 1175 (1957)

Test phonon idea: try to modify ω_D by $^{16}O \rightarrow {}^{18}O$ substitution

CuO_6 octahedron:



ideally $\rightarrow T_c \propto \omega_D \propto \sqrt{\frac{k}{m_O}}$

- experiment: apical O isotope effect is negligible [*Zech, Nature 371, 681 (1994)*]
- phonon mechanism falls out of favor for high-T_c
- apical oxygens mostly forgotten… *(stay tuned)*

Outline

Superconductors: 100 Year History

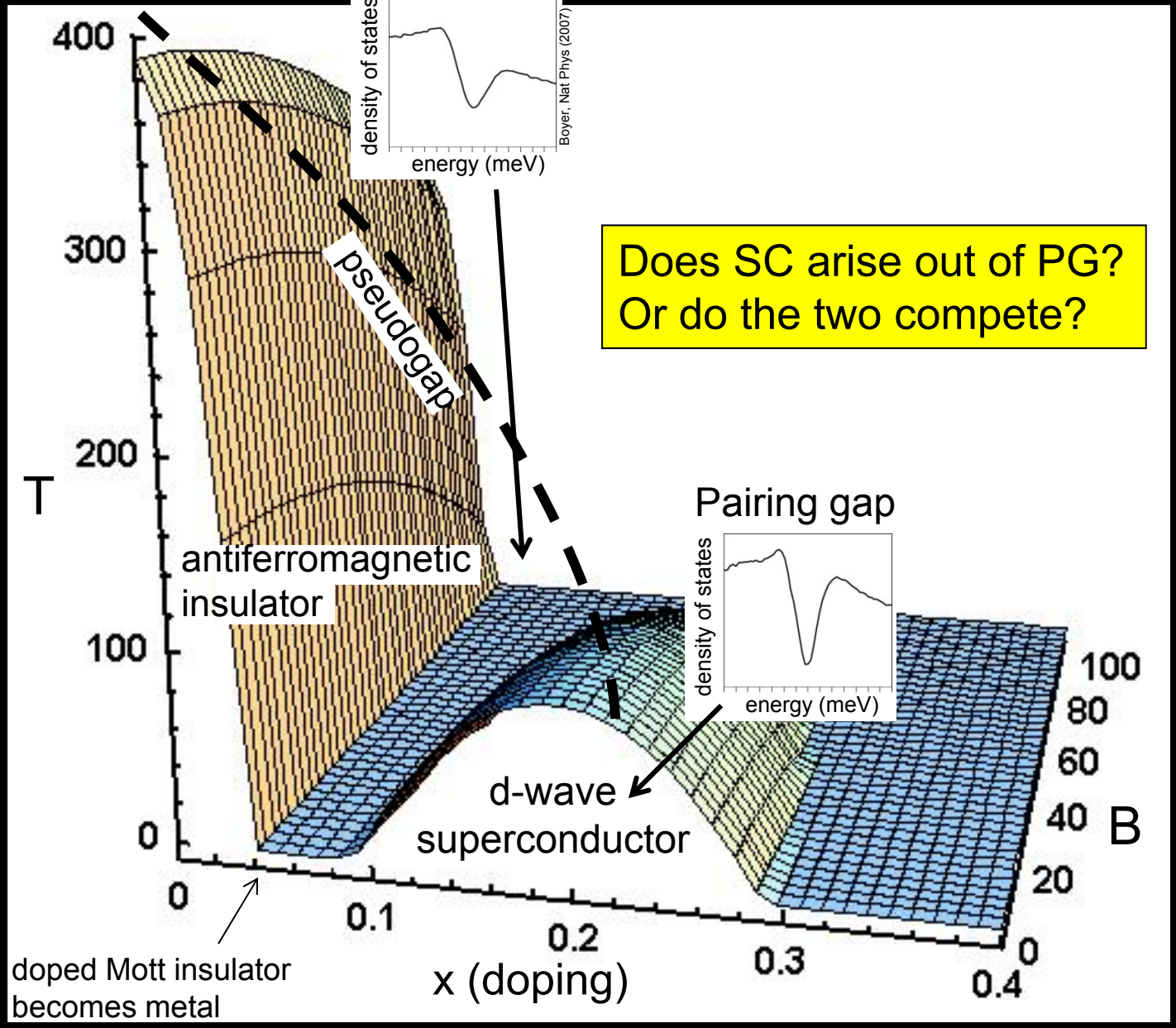
Part I: Pseudogap in cuprates:

- Competing or collaborating?
  (introduction to scanning tunneling microscopy)
- Nanoscale inhomogeneity: energy & charge modulation
  → what is the hidden variable??
- Previous studies of chemical disorder
  → hidden variable remains mysterious…
- STM imaging of oxygen dopants & vacancies
  → we found the hidden variable!!

Part II: Vortex pinning in pnictides:

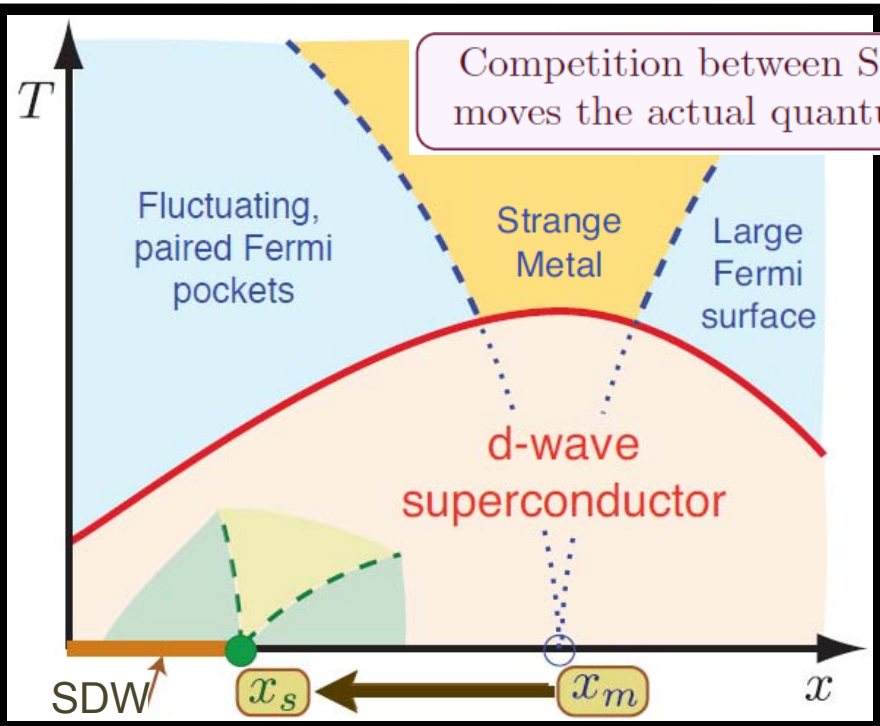
- Discovery of iron-based superconductors
- MFM imaging of NdFeAsO, in-plane anisotropy

Cuprate Phase Diagram



Much evidence: PG competes with SC

Theory:



Moon, Sachdev, PRB 80, 035117 (2009)

Experiment:

Other work (global PG competition):

Pushp, *Science* 324, 1689 (2009)

Kondo, *Nature* 457, 296 (2009)

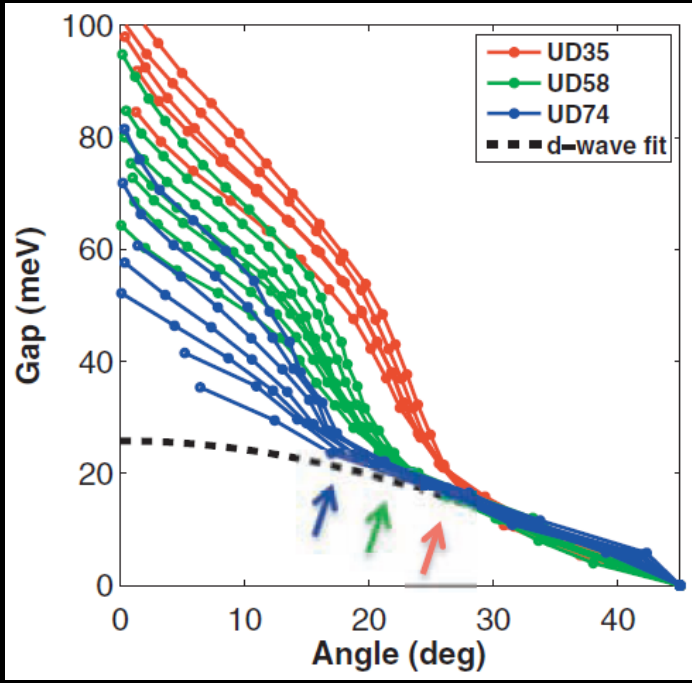
Our preliminary work (local PG competition):

Strong PG regions (Δ_{PG} > 10meV): no d-wave coherence

Weak PG regions (Δ_{PG} < 10meV): d-wave coherence

Yang He

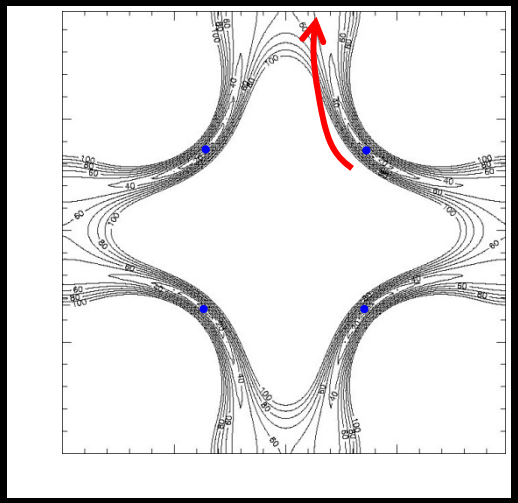
Relationship Between PG and SC ?

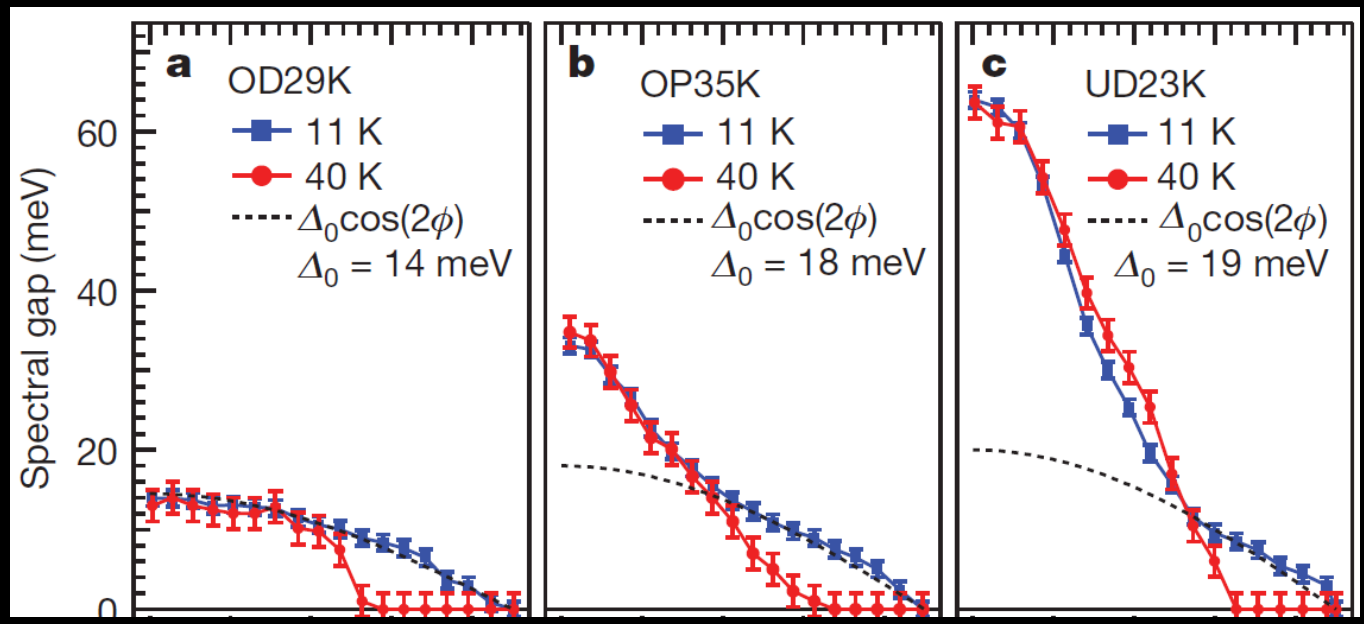


← STM
Pushp, Science 324, 1689 (2009)

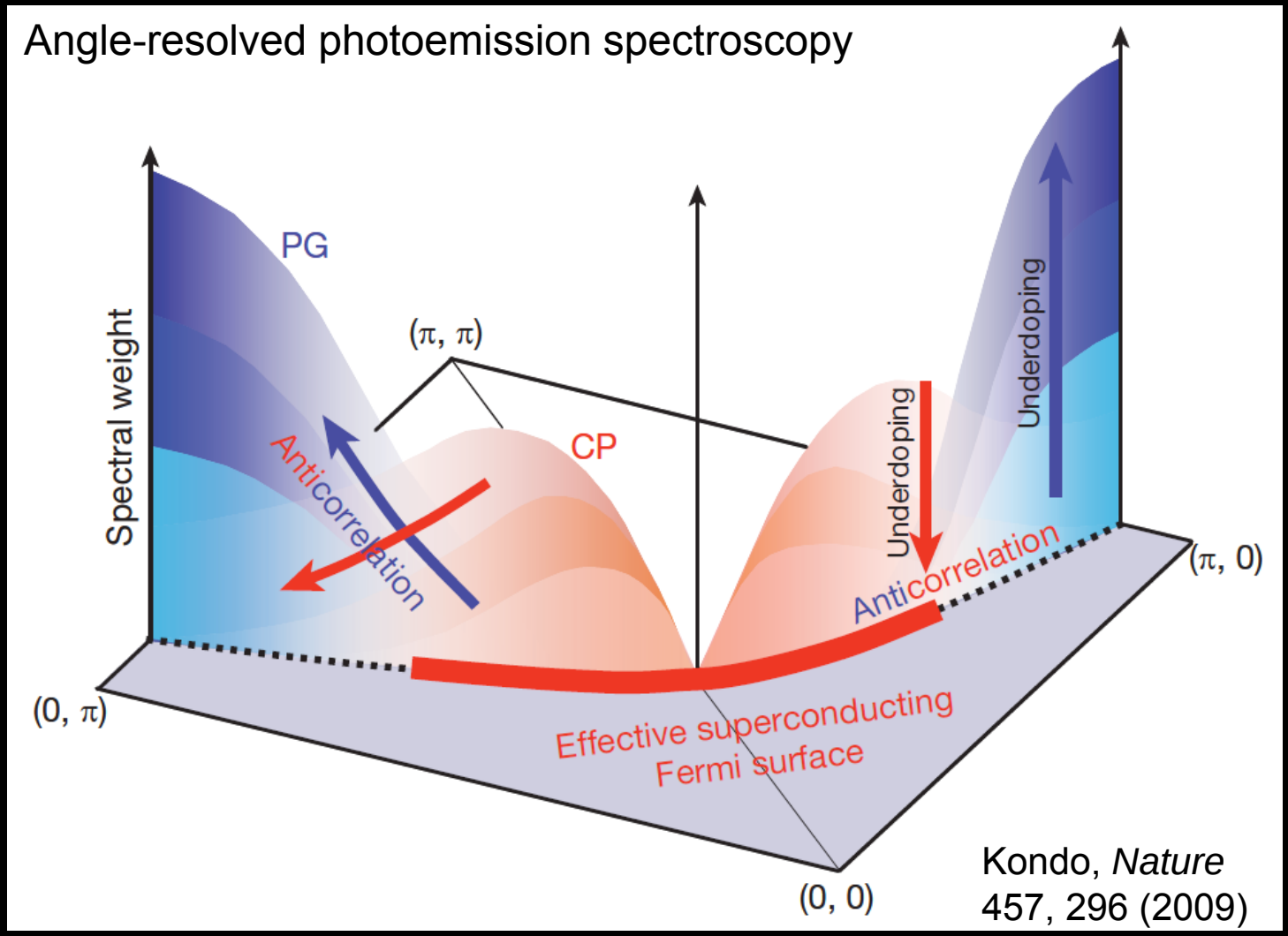
STM and ARPES both show competition between superconductivity (wins in nodal region) & pseudogap (wins in antinodal region)

↓ ARPES
Kondo, *Nature* 457, 296 (2009)





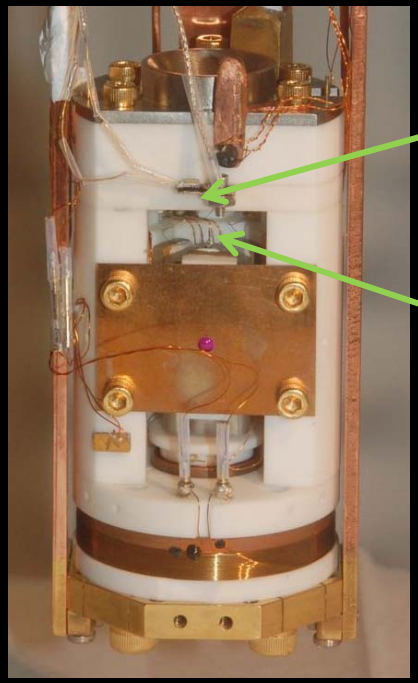
Competition Between PG and SC

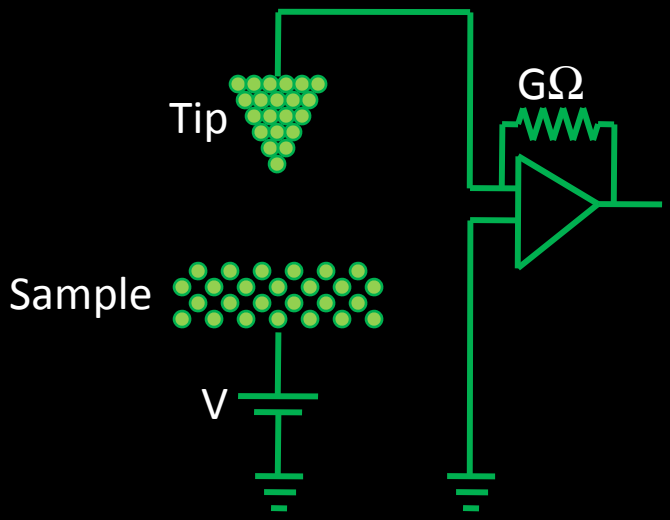


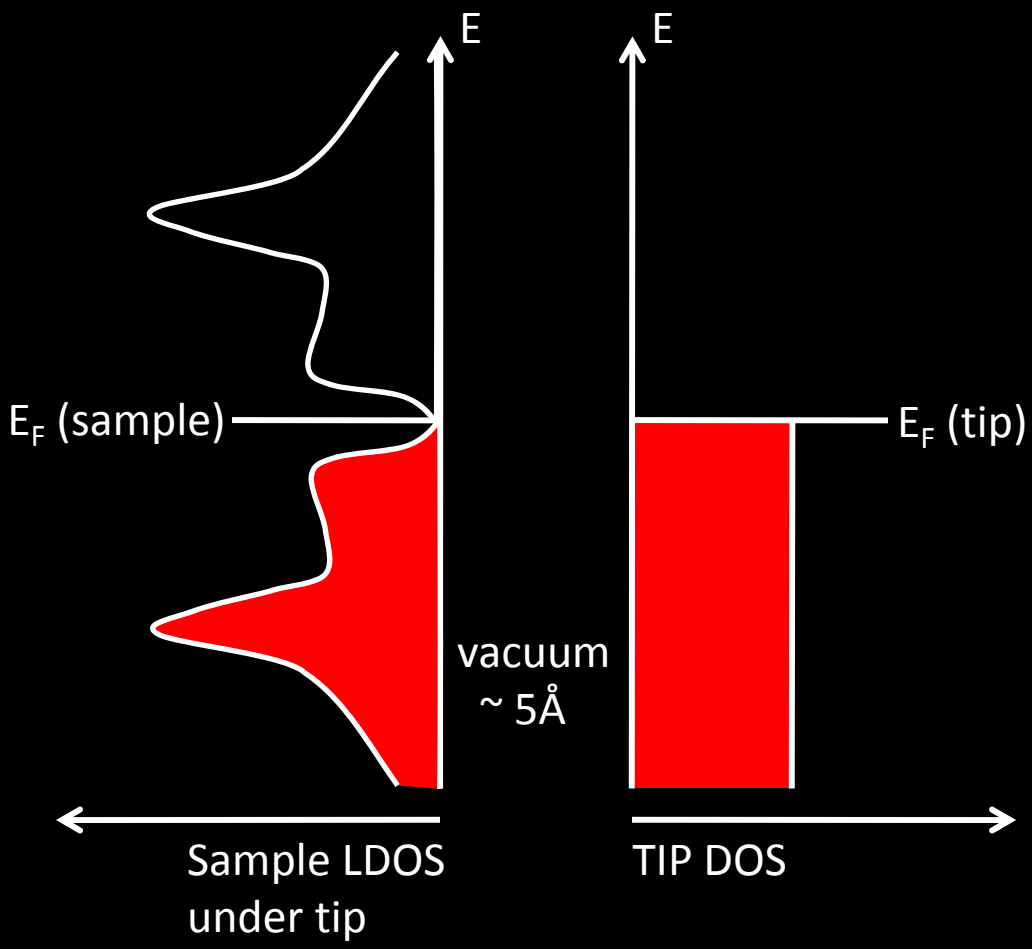
→ We want to know more about the PG
so we can control it & mitigate the competition!!

No obvious long-range order → use real space probe → STM

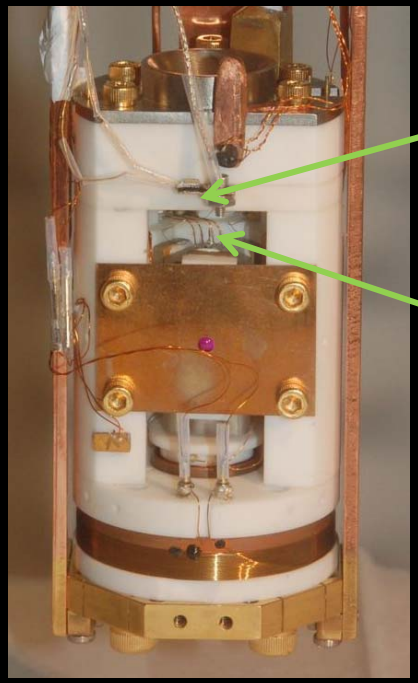
Introduction to STM



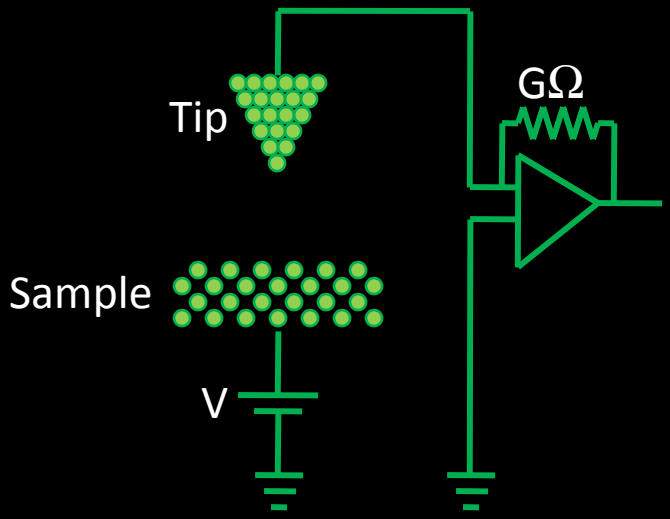


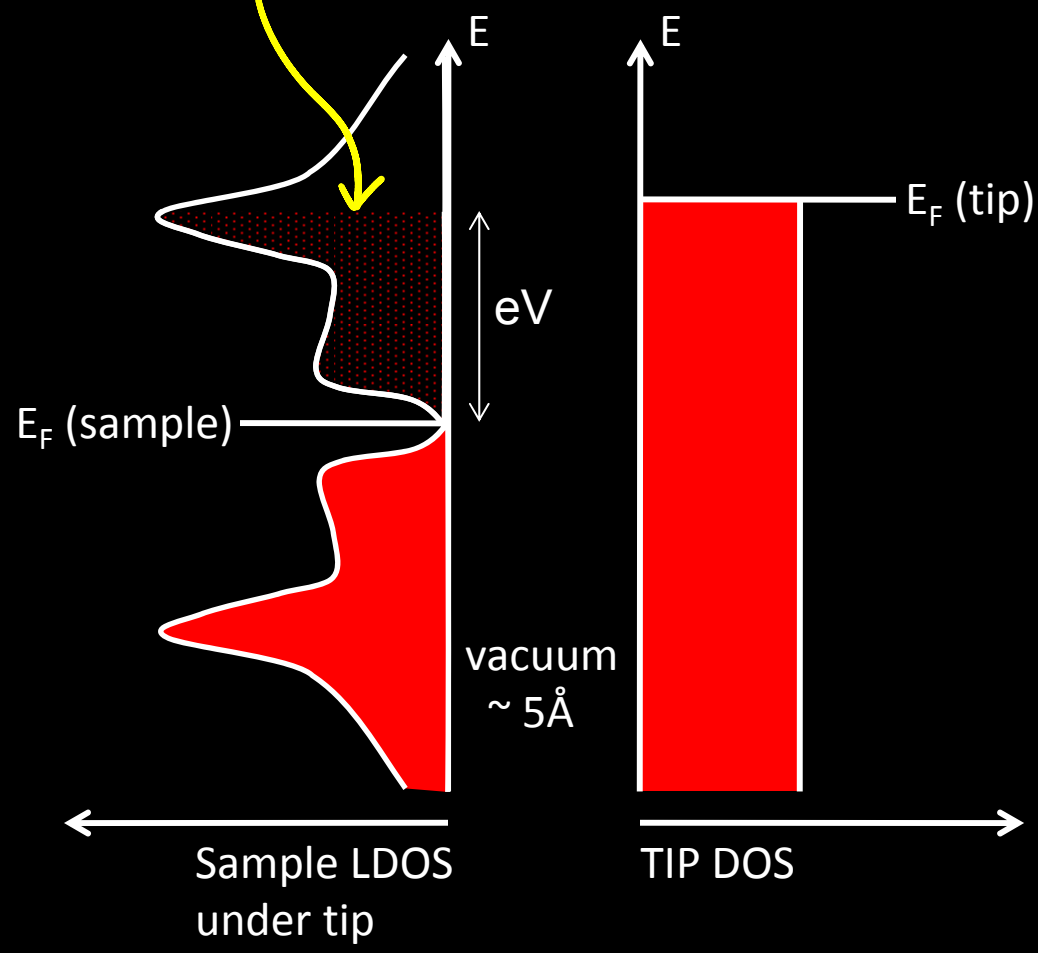


Introduction to STM

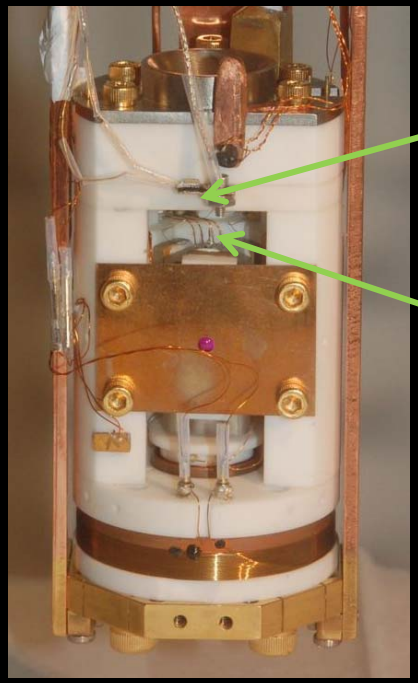


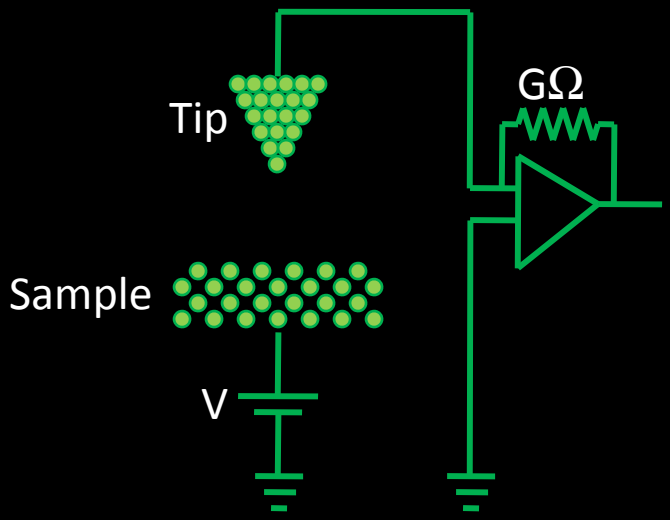
$$I(V) \propto \int_{E_F}^{eV} LDOS(E)dE$$





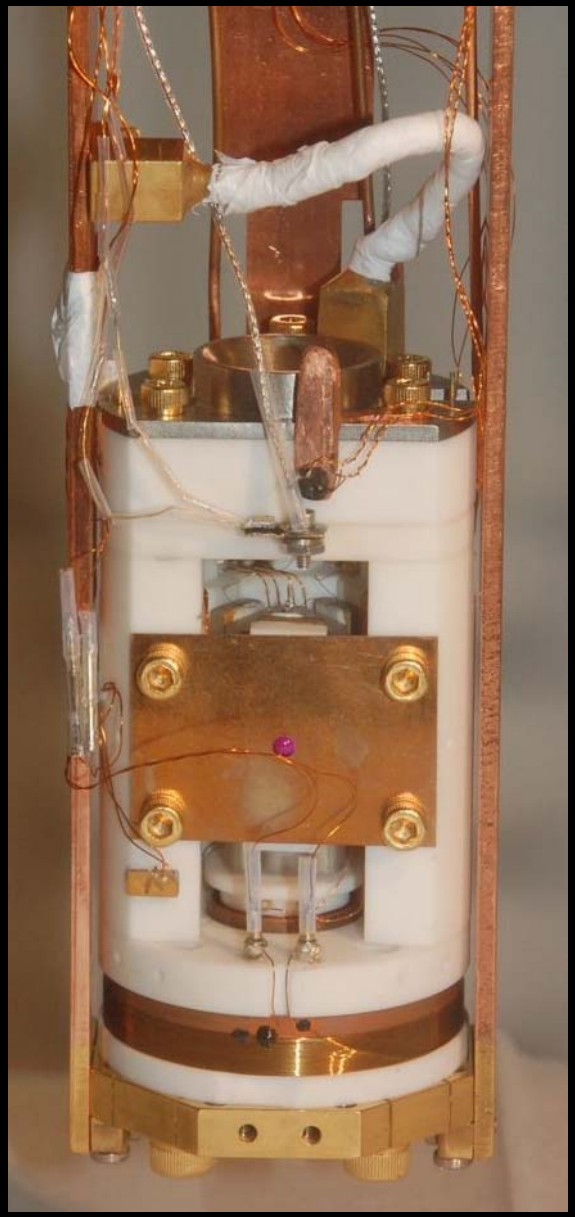
Introduction to STM



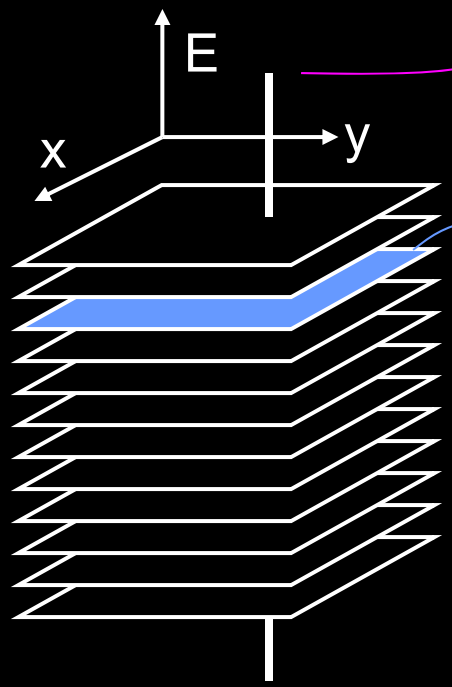


$\frac{dI}{dV} \propto LDOS(eV)$

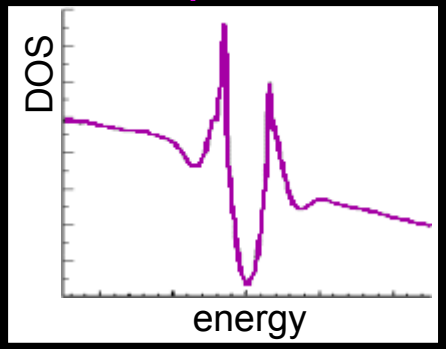
Types of STM Measurements



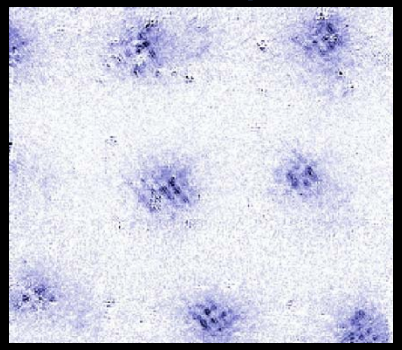
Local Density of States (x, y, E)



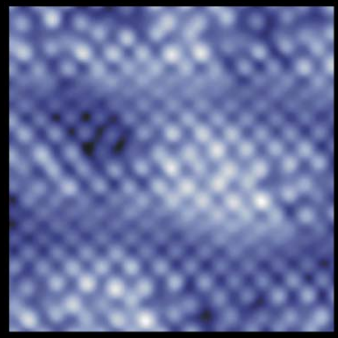
dI/dV Spectrum



dI/dV Map



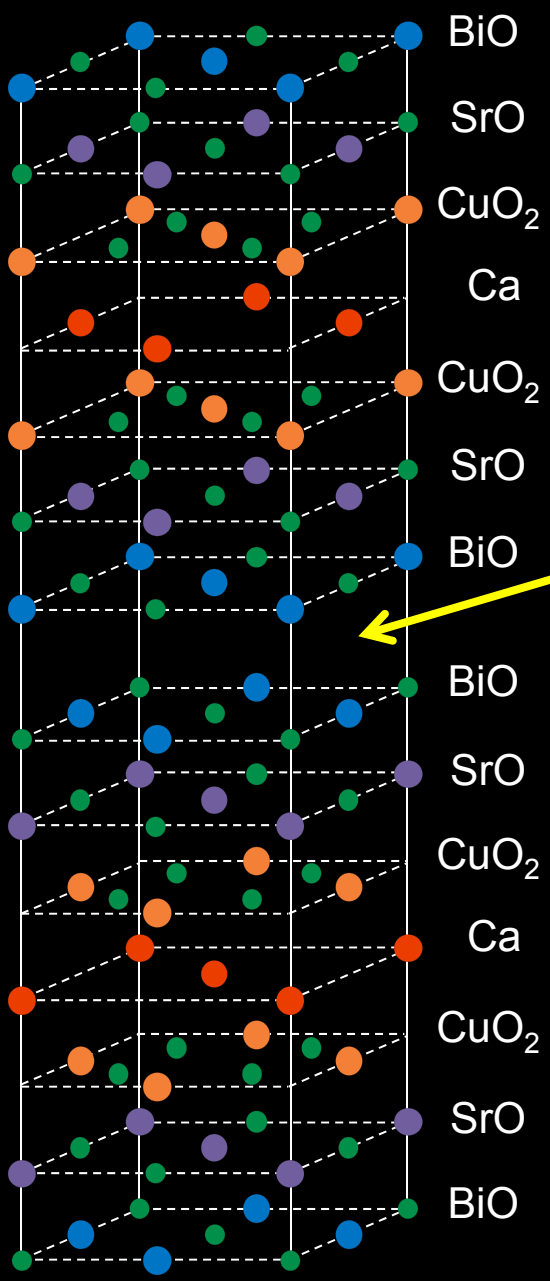
Topography

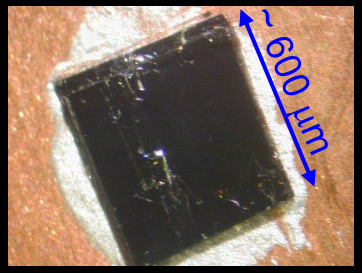


Constant current mode:

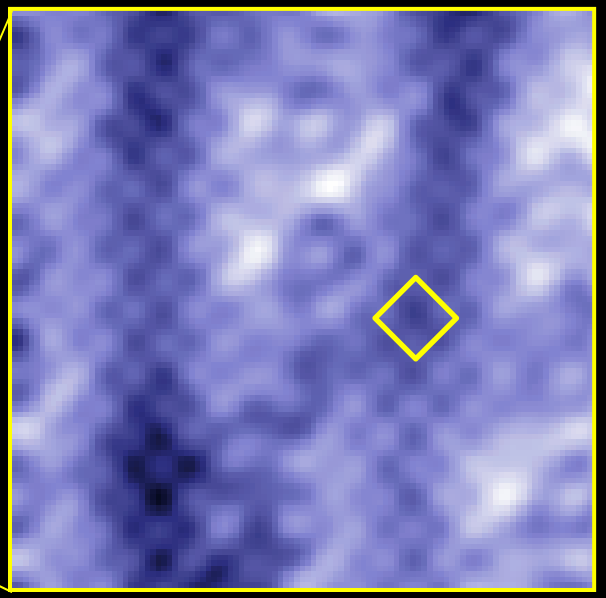
$$\int \frac{dI}{dV}$$

Structure of $Bi_2Sr_2CaCu_2O_{8+\delta}$

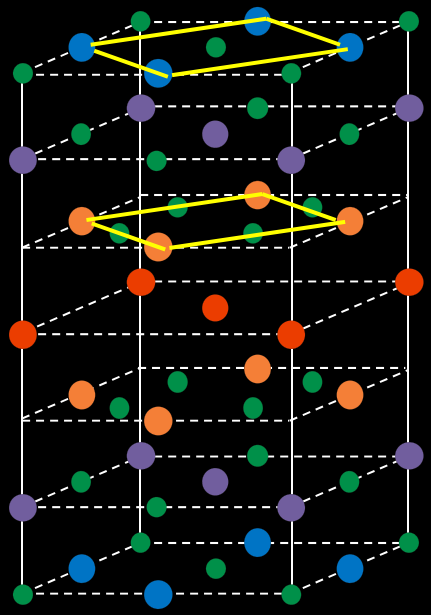




Cleave Here
Reveals
BiO Surface



BiO plaquette



CuO_2 plaquette

Outline

Superconductors: 100 Year History

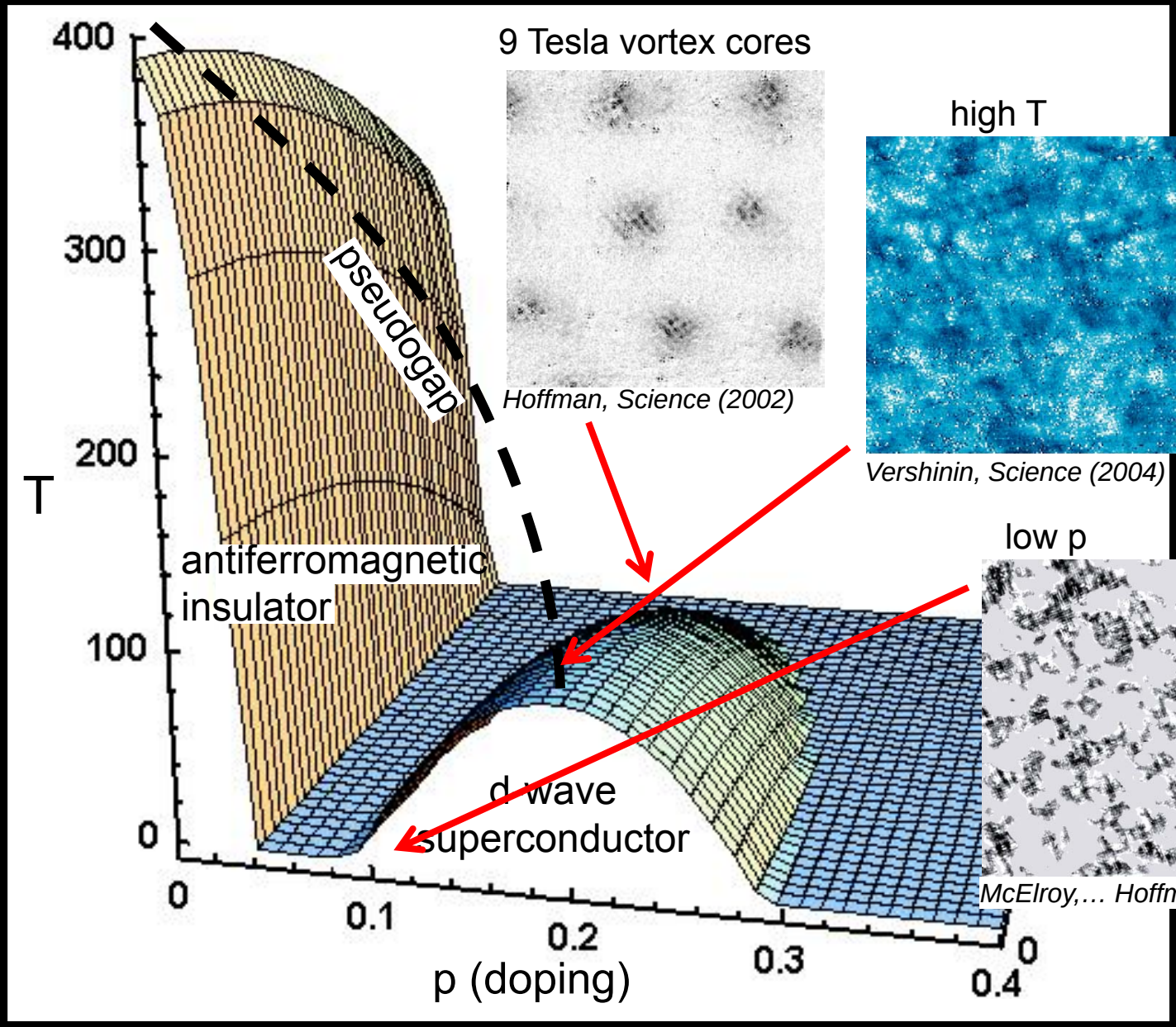
Part I: Pseudogap in cuprates:

- Competing or collaborating?
  (crash course in solid state physics)
- Nanoscale inhomogeneity: energy & charge modulation
  → what is the hidden variable??
- Previous studies of chemical disorder
  → hidden variable remains mysterious…
- STM imaging of oxygen dopants & vacancies
  → we found the hidden variable!!

Part II: Vortex pinning in pnictides:

- Discovery of iron-based superconductors
- MFM imaging of NdFeAsO, in-plane anisotropy

“Checkerboard”



“Checkerboard”

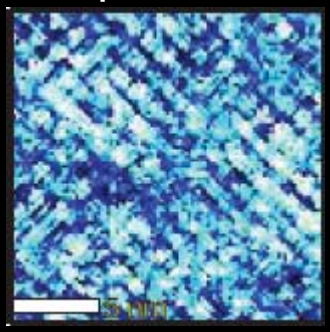
“Static Striped DOS”

Howald, PNAS (2003)

CDW

Wise, Nat Phys (2008)

“Fluctuating Stripes”



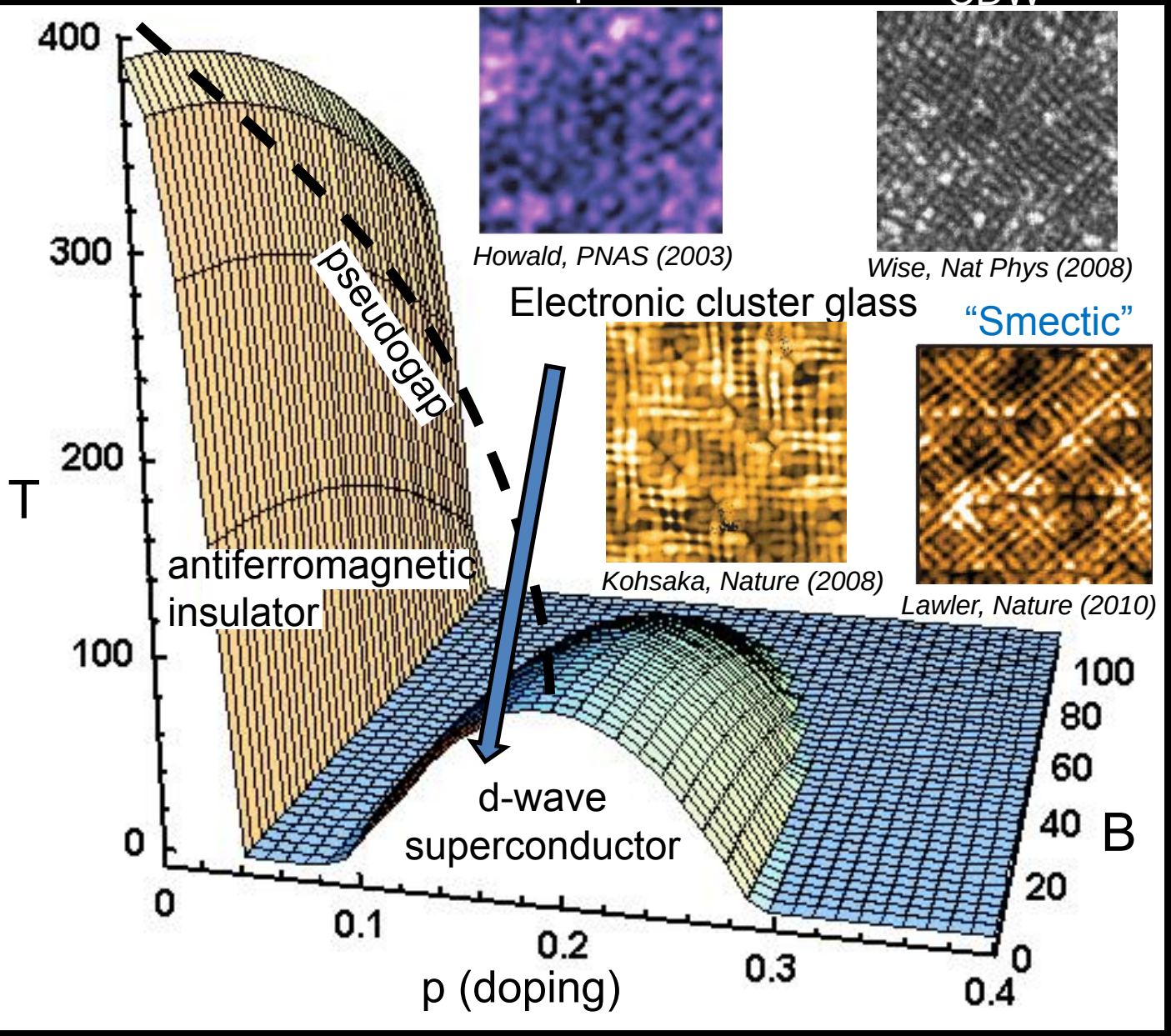
Parker, Nature (2010)

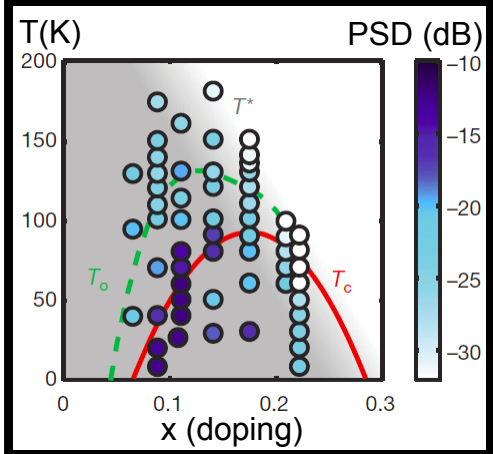
Electronic cluster glass

Kohsaka, Nature (2008)

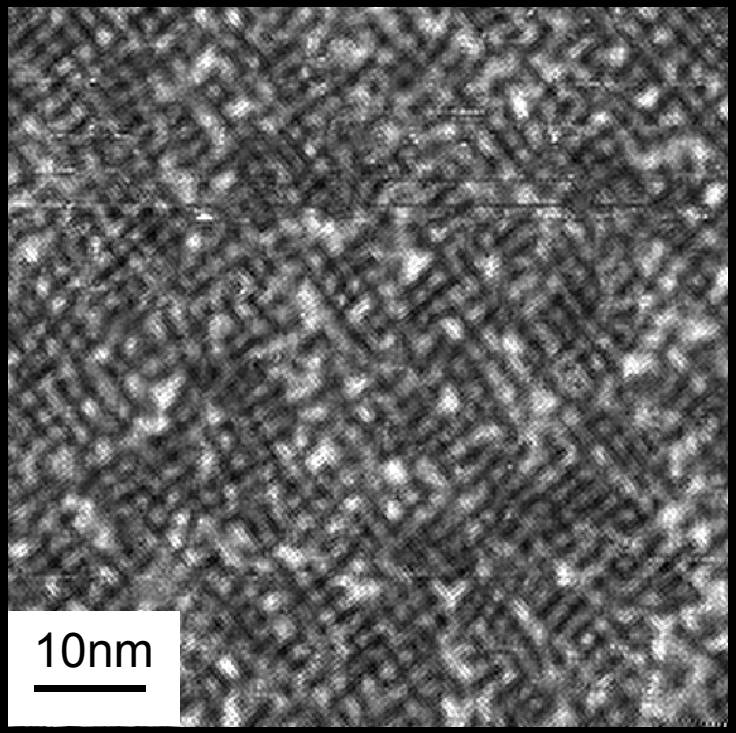
“Smectic”

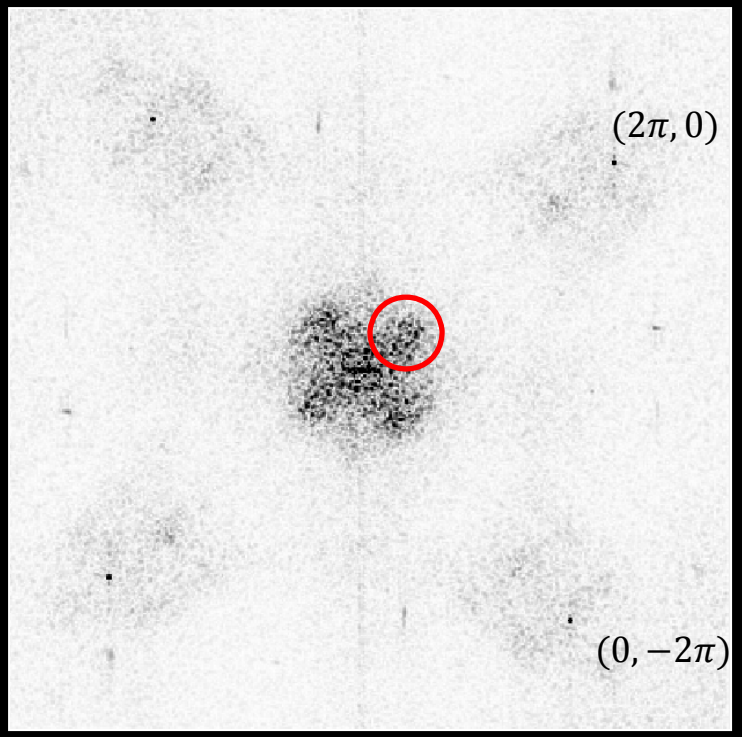
Lawler, Nature (2010)





“Checkers” are disordered

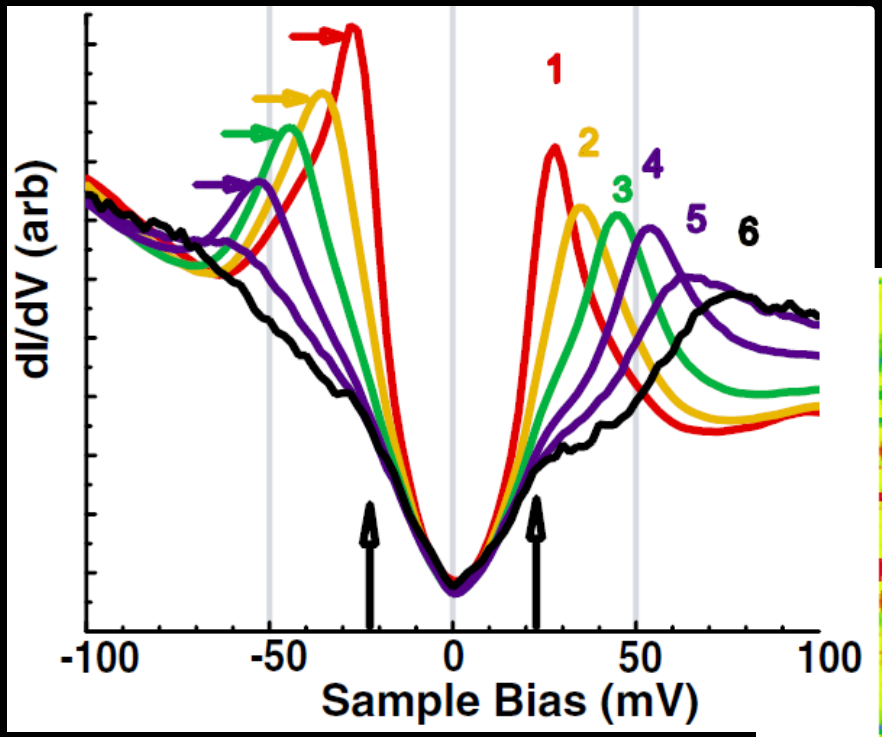


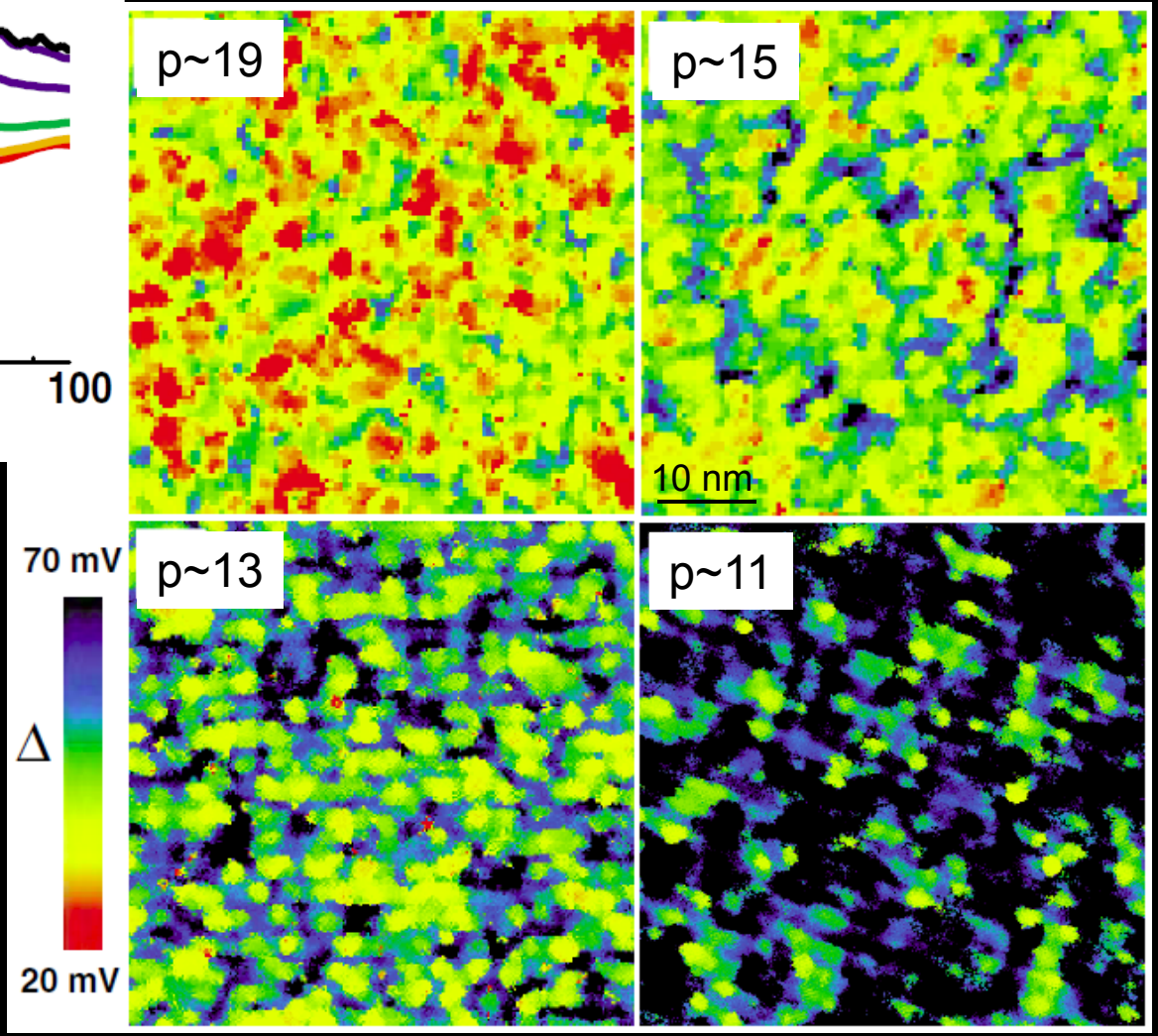


FT peaks are broad

→ Need to understand what disorders the “checkers”
in order to get a handle on their intrinsic nature

Gap is inhomogeneous





McElroy, … Hoffman, … Davis,
PRL 94, 197005 (2005)

Outline

Superconductors: 100 Year History

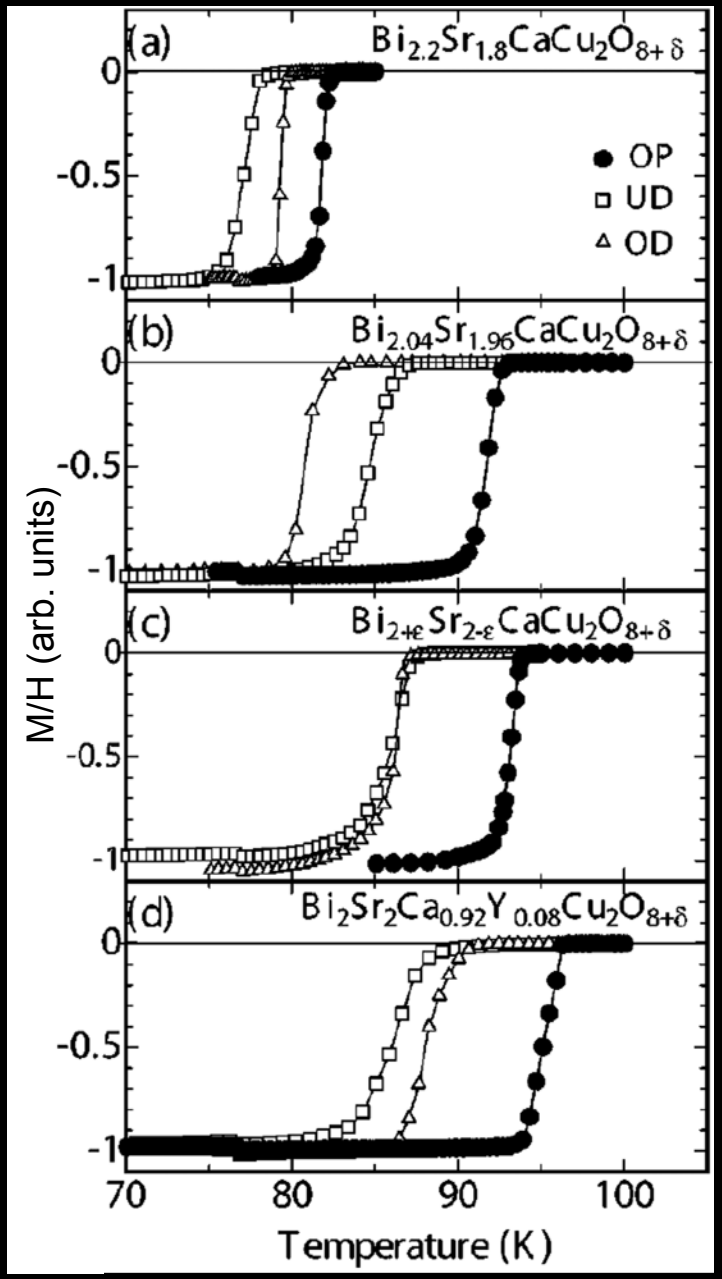
Part I: Pseudogap in cuprates:

- Competing or collaborating?
  (crash course in solid state physics)
- Nanoscale inhomogeneity: energy & charge modulation
  → what is the hidden variable??
- Previous studies of chemical disorder
  → hidden variable remains mysterious…
- STM imaging of oxygen dopants & vacancies
  → we found the hidden variable!!

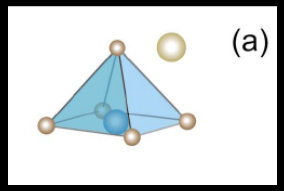
Part II: Vortex pinning in pnictides:

- Discovery of iron-based superconductors
- MFM imaging of NdFeAsO, in-plane anisotropy

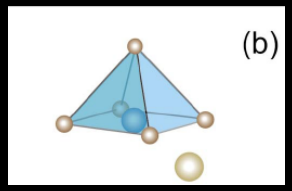
Chemical disorder is crucial to Tc



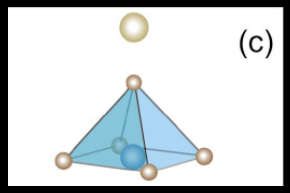
A-site disorder:
(Bi^{3+} on Sr^{2+} site)
strongly couples
to apical oxygen



B-site disorder:
(Y^{3+} on Ca^{2+} site)
does not couple
to apical oxygen



interstitial O in BiO plane
weakly couples to CuO_2
provides charge carriers
but little disorder
→ "type-B oxygen"



Eisaki, PRB 69, 064512 (2004)

Chemical disorder: location matters

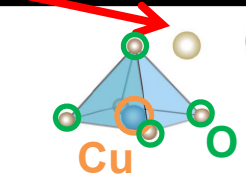
A-site disorder

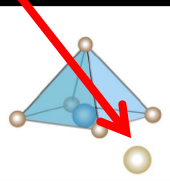
B-site disorder

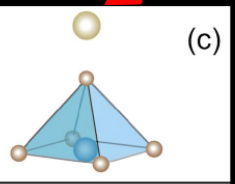
interstitial O near B-site

Inference from transport:

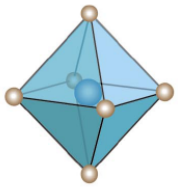
Halogen Family	Bi Family
Pb Family	1L Tl Family
La Family	2L Family
YBCO Family	Hg Family







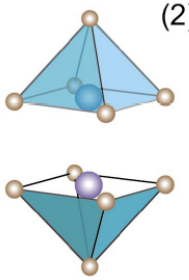
single layer

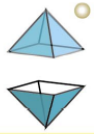


	T_c
$Ca_{2-x}Na_xCuO_2Cl_2$	26
$Pb_2Sr_{2-x}La_xCu_2O_z$	33
$La_{2-x}M_xCuO_4$	39
$Bi_2Sr_{1-x}Ln_xCuO_{6+\delta}$	38
$TlBa_{1+x}La_{1-x}CuO_5$	45

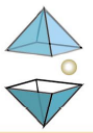
	T_c
$Sr_2CuO_2F_{2+x}$	46
$La_2CuO_{4+\delta}$	45
$Tl_2Ba_2CuO_{6+\delta}$	93
$HgBa_2CuO_{4+\delta}$	98

double layer

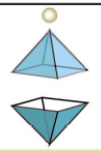




	T_c
$La_{2-x}Sr_xCaCu_2O_6$	60
$(La_{1-x}Ca_x)(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$	80
$Bi_{2+x}Sr_{2-x}CaCu_2O_{8+\delta}$	90

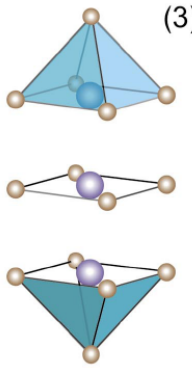


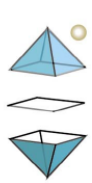
	T_c
$Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$	80
$Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$	90
$Bi_2Sr_2Ca_{1-x}Y_xCu_3O_{8+\delta}$	96



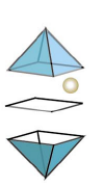
	T_c
$YBa_2Cu_3O_{7-\delta}$	93
$TlBa_2CaCu_2O_{7+\delta}$	110
$Tl_2Ba_2CaCu_2O_{8+\delta}$	110
$HgBa_2CaCu_2O_{6+\delta}$	120

triple layer

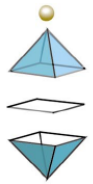




	T_c
$Bi_{2+x}Sr_{2-x}Ca_2Cu_3O_{10+\delta}$	110
$TlBa_{2-\varepsilon}Ca_2Cu_3O_{9+\delta}$	123



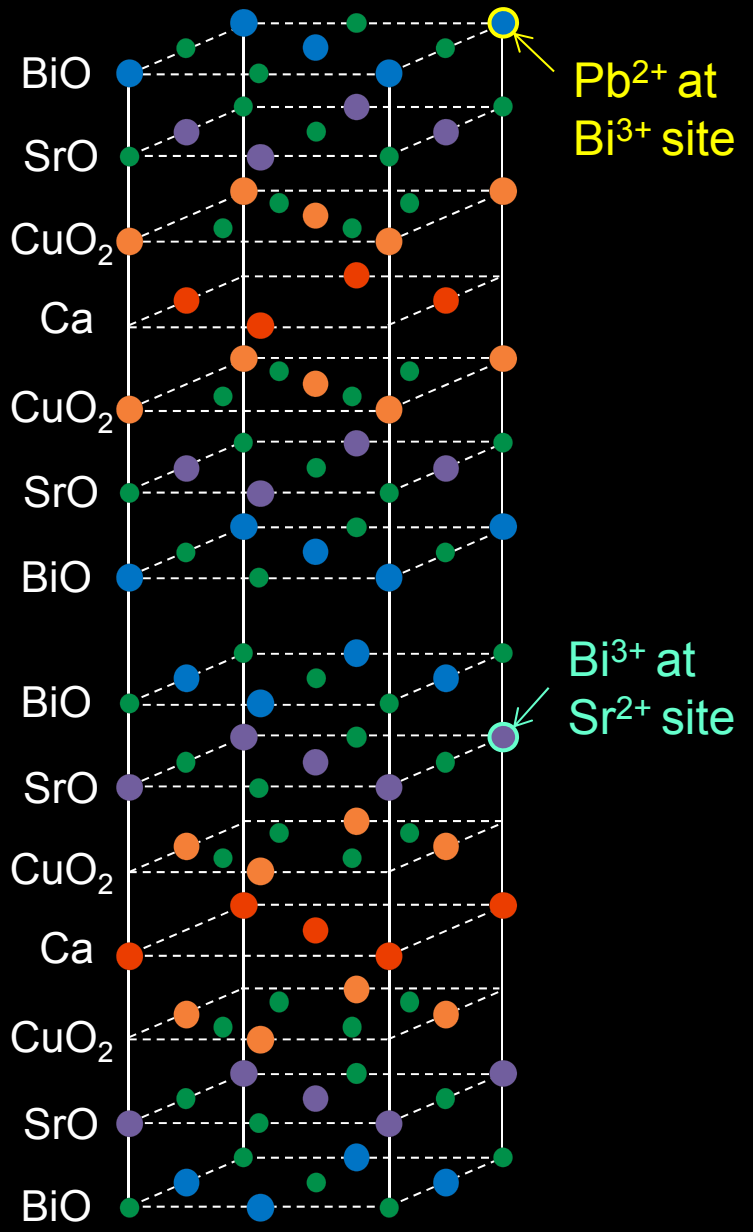
	T_c
$TlBa_2Ca_{2-\varepsilon}Cu_3O_{9+\delta}$	131

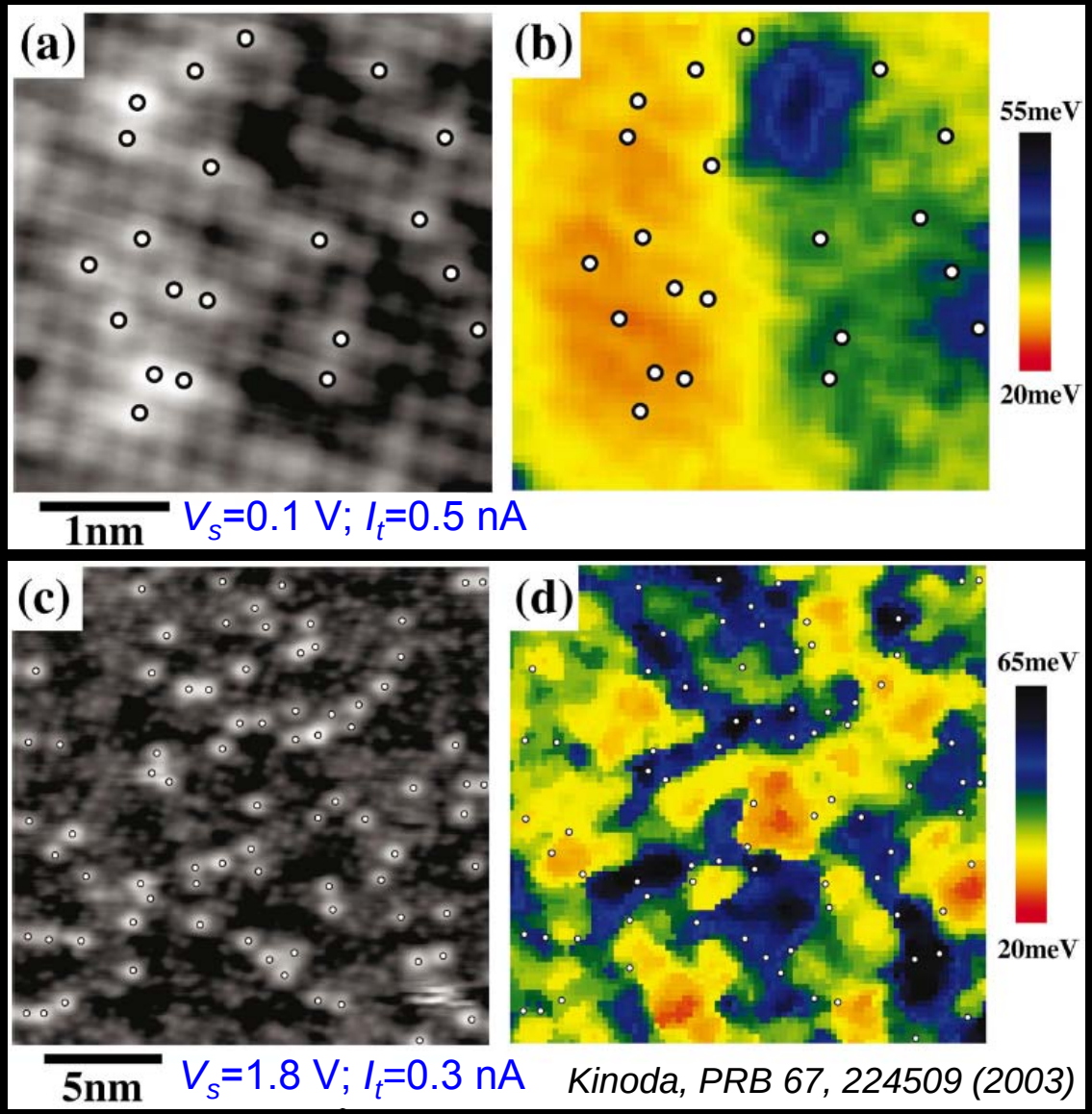


	T_c
$TlBa_2Ca_2Cu_3O_{9+\delta}$	133
$Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$	125
$HgBa_2Ca_2Cu_3O_{10+\delta}$	135

Eisaki, PRB 69, 064512 (2004)

Is cation chemistry causing inhomogeneity?





→ Conclude: no correlation between Pb/Bi/Sr substitutions & local Δ

Are oxygen dopants causing inhomogeneity?

Conclusions about interstitial oxygen:

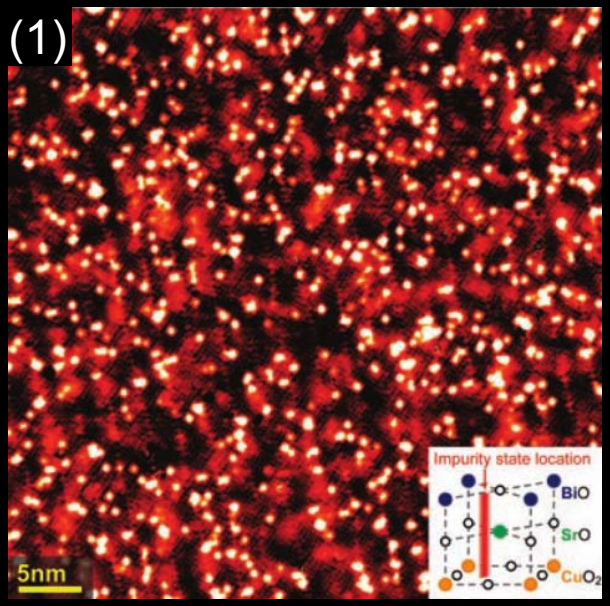
(1) Observed at -0.96 V in dI/dV

(2) “Strong correlations” exist between these oxygen dopants and “the gap”

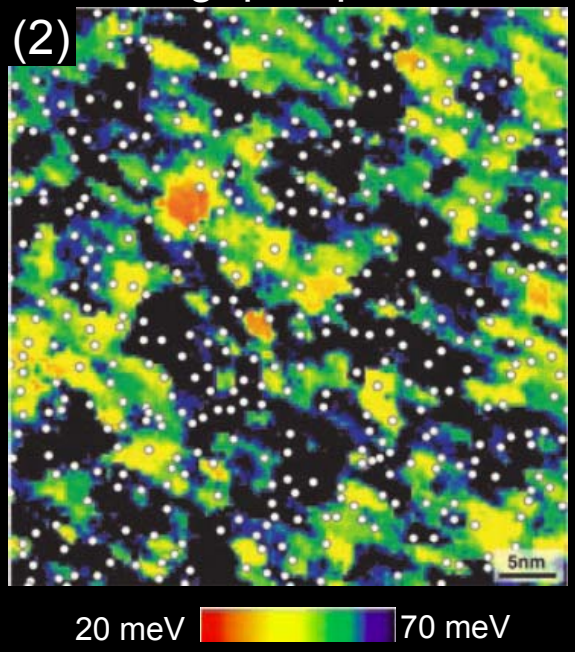
(3) These oxygen dopants are primarily positioned in the minima of the “QPI”

McElroy, Science 309, 1048 (2005)

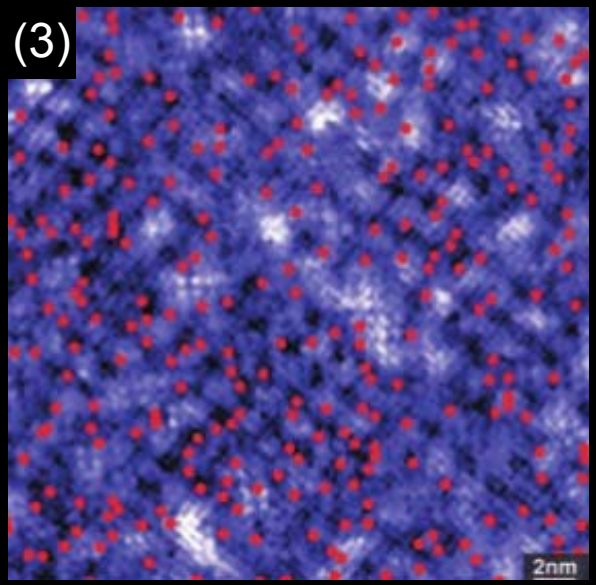
dI/dV at -1V



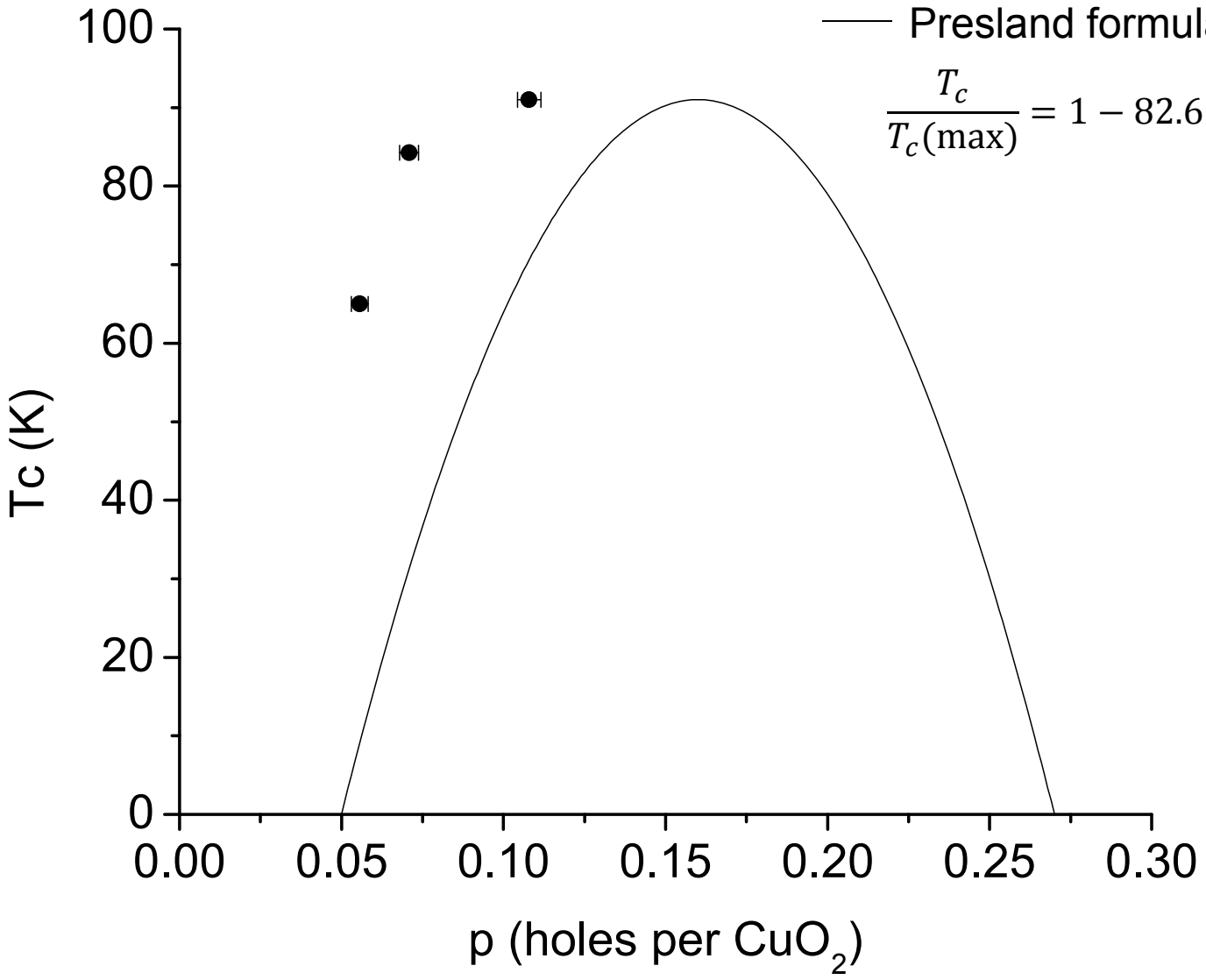
gapmap



dI/dV at -24 mV

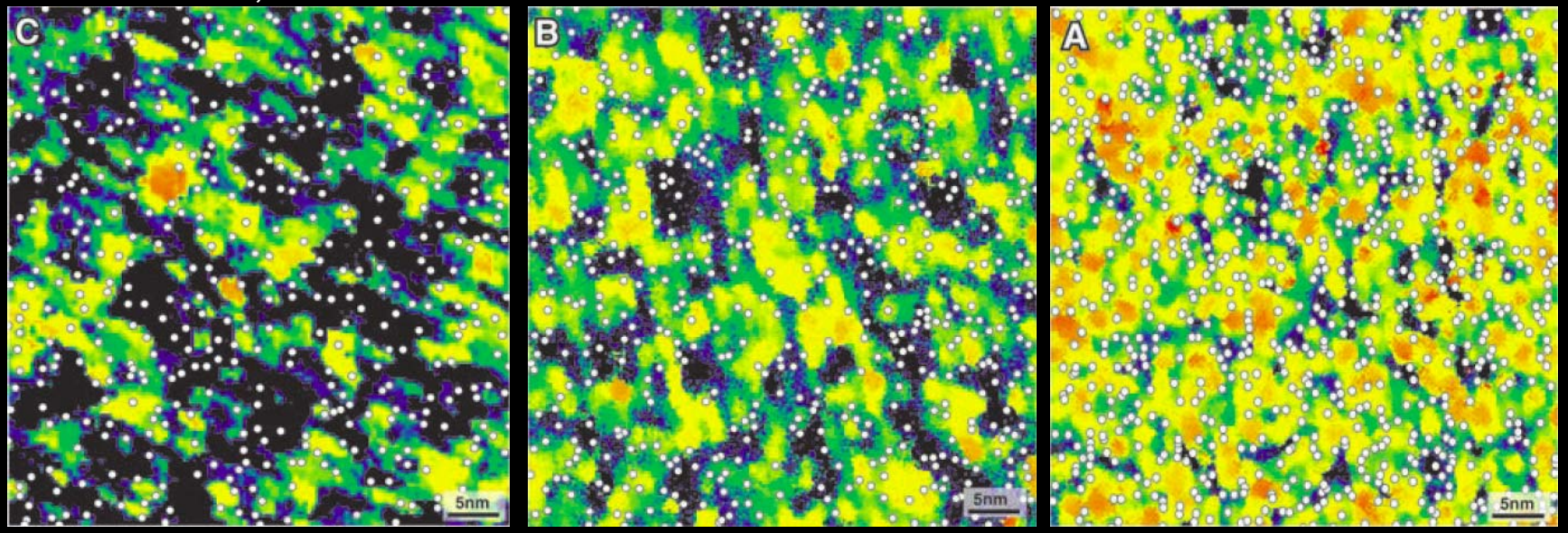


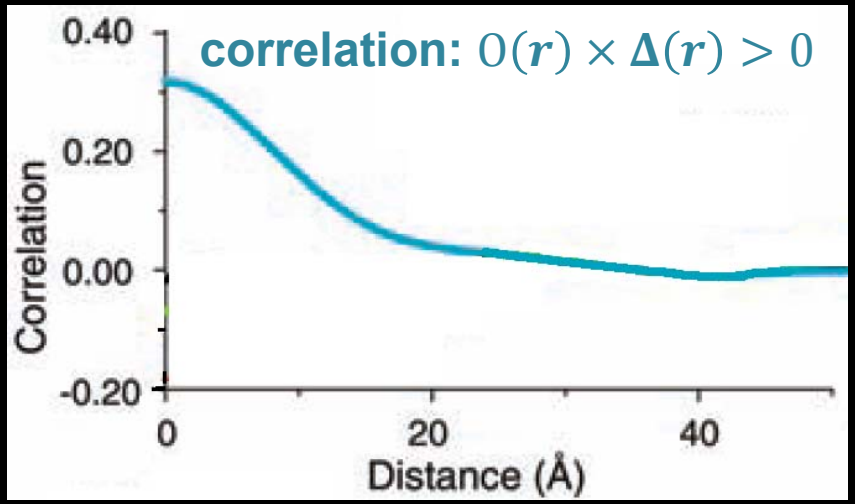
Puzzle 1: too few O dopants



Puzzle 2: local trend opposes global trend

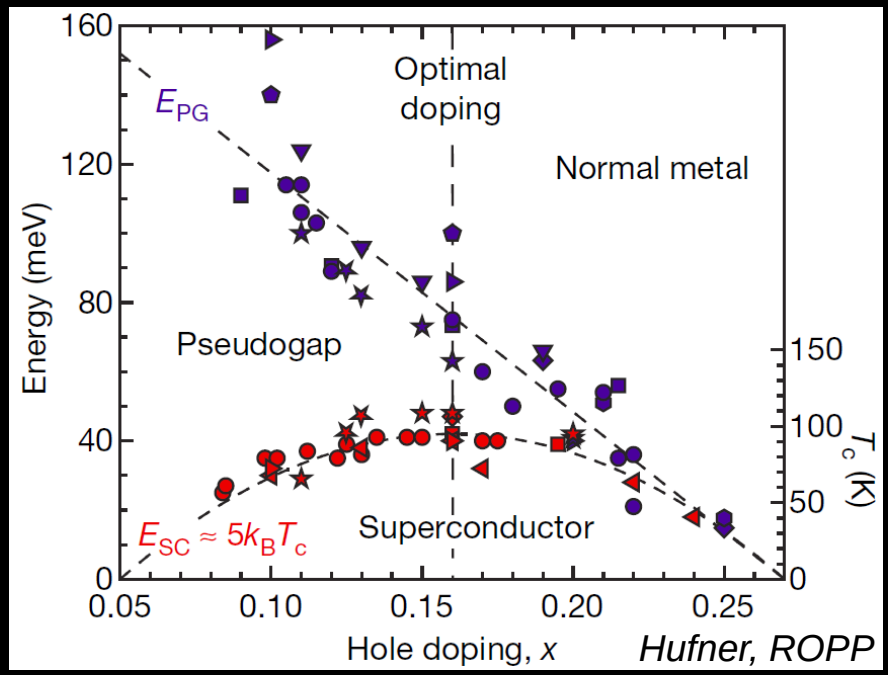
$\overline{\Delta}$ = 65 meV; N=455 | $\overline{\Delta}$ = 55 meV; N=580 | $\overline{\Delta}$ = 45 meV; N=883



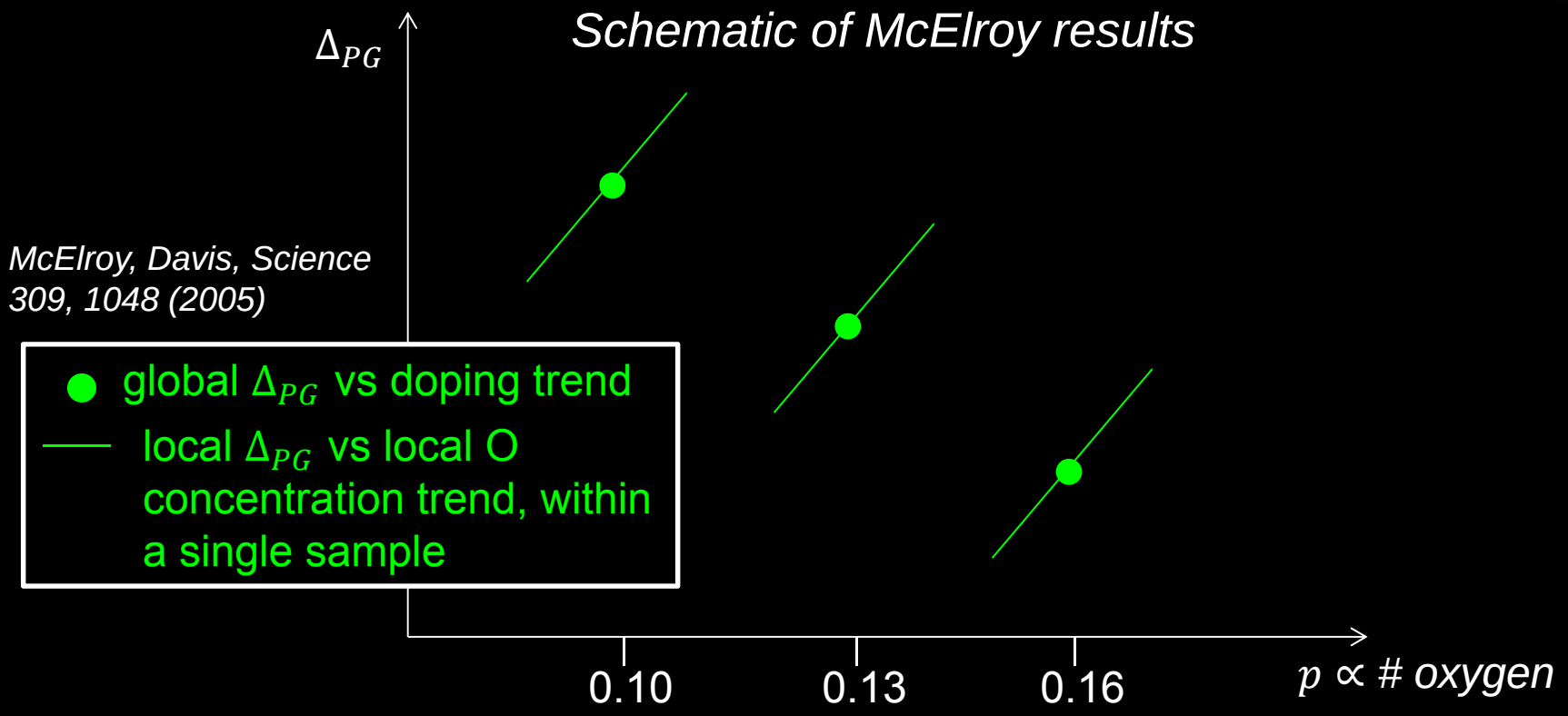


McElroy, Science 309, 1048 (2005)

→ Assumption: oxygen dopants ***cause*** local regions of large Δ



Puzzle 2: local trend opposes global trend



Many attempts to explain ***causality***, focusing on local strain:

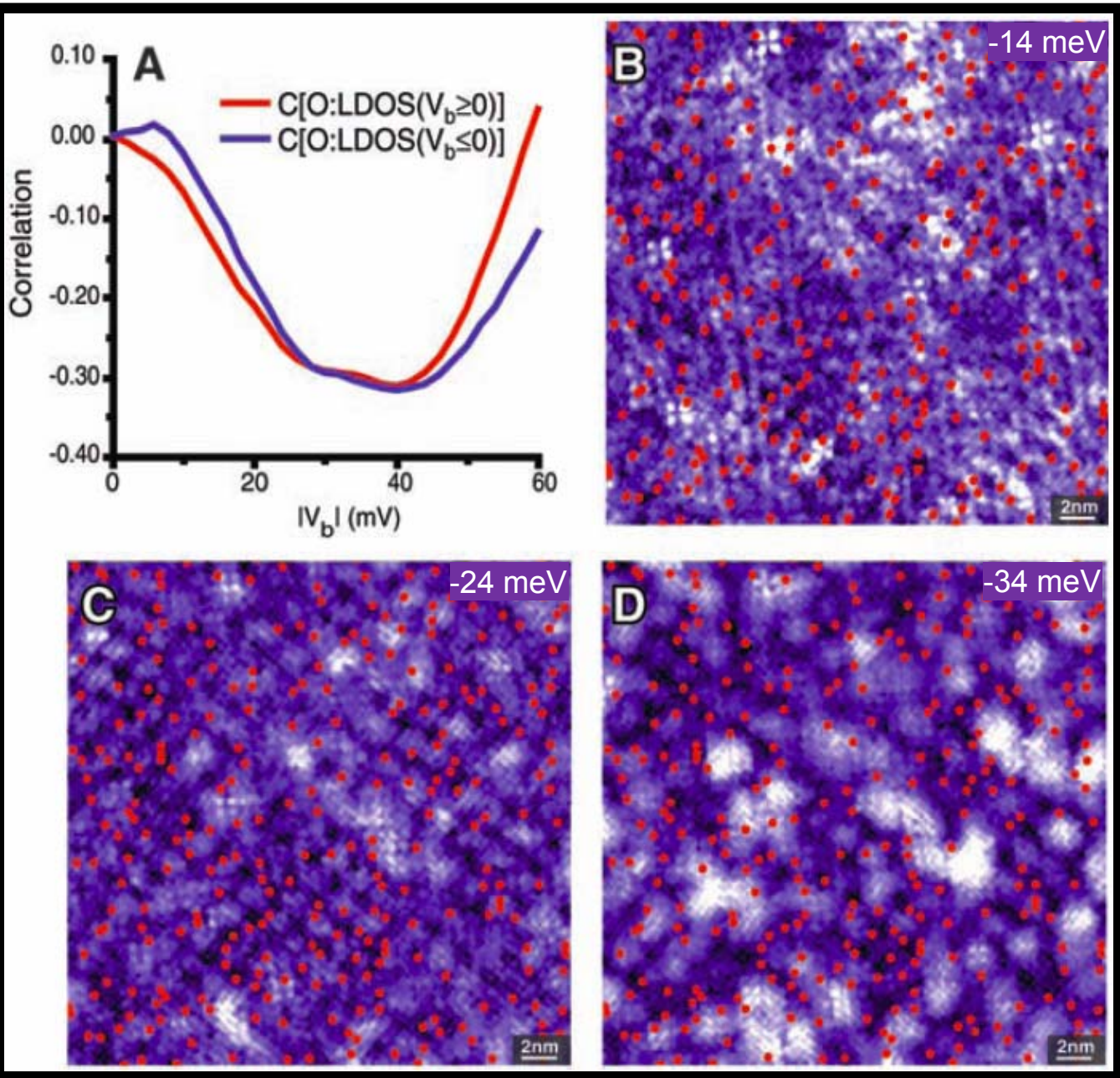
- O → local strain, increases local superexchange $J(\vec{r})$, locally strengthens pairing

  Nunner, Hirschfeld, PRL 95, 177003 (2005)
- experiment: local strain of supermodulation controls the pseudogap

  Slezak, Davis, PNAS 105, 3203 (2008)
- O → accumulates local holes, must include phenomenological increase of pairing strength near the dopants, with specific length scale $0.5a_0$, to match the data

  Chen, Hirschfeld, NJP 14, 033004 (2012)

Problem 3: relation to QPI



Dopants seem to chase away the low energy states.

Both filled & empty!

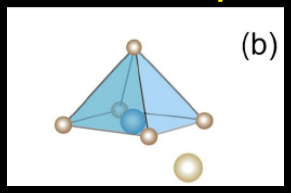
But QPI has spatial phase flip across E_F

→ this anticorrelation must concern the static checkerboard, not the dispersion QPI

McElroy, Science 309, 1048 (2005)

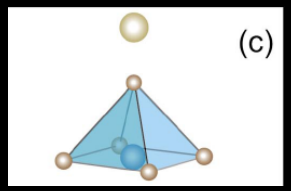
Zhou prediction: type-A oxygen

B-site disorder:
(e.g. Pb^{2+} on Bi^{3+} site
or Y^{3+} on Ca^{2+} site)
does not couple to CuO_2



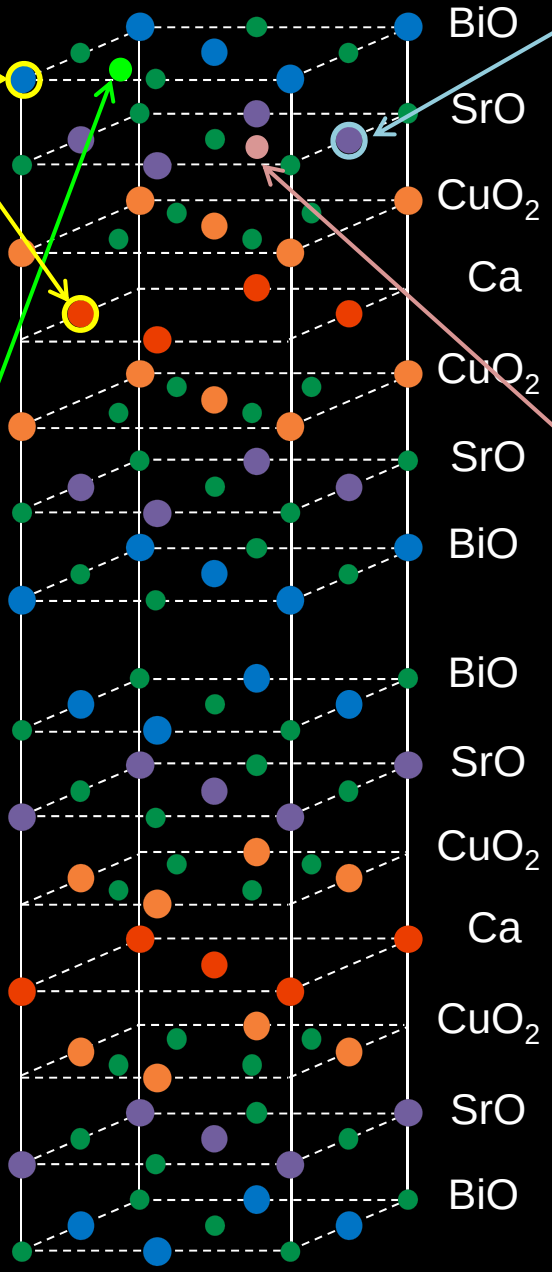
Eisaki, PRB 69, 064512 (2004)

interstitial O in BiO plane
weakly couples to CuO_2
provides charge carriers
but little local effect
→ "type-B oxygen"

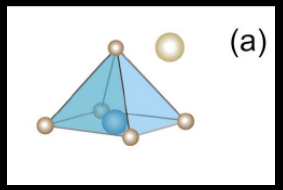


seen at -0.96V

McElroy, Science 309, 1048 (2005)



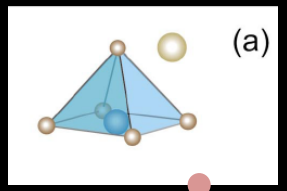
A-site disorder:
(Bi^{3+} on Sr^{2+} site)
strongly couples to apical O



claim: seen at +1.8V

Kinoda, PRB 67, 224509 (2003)

interstitial O in SrO plane
strongly couples to CuO_2
provides charge carriers
and disorder
→ "type-A oxygen"



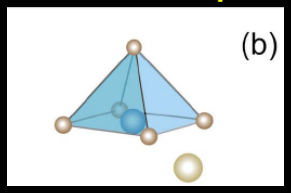
Zhou, PRL 98, 076401 (2007)

expected << -1V

Why is this a problem?

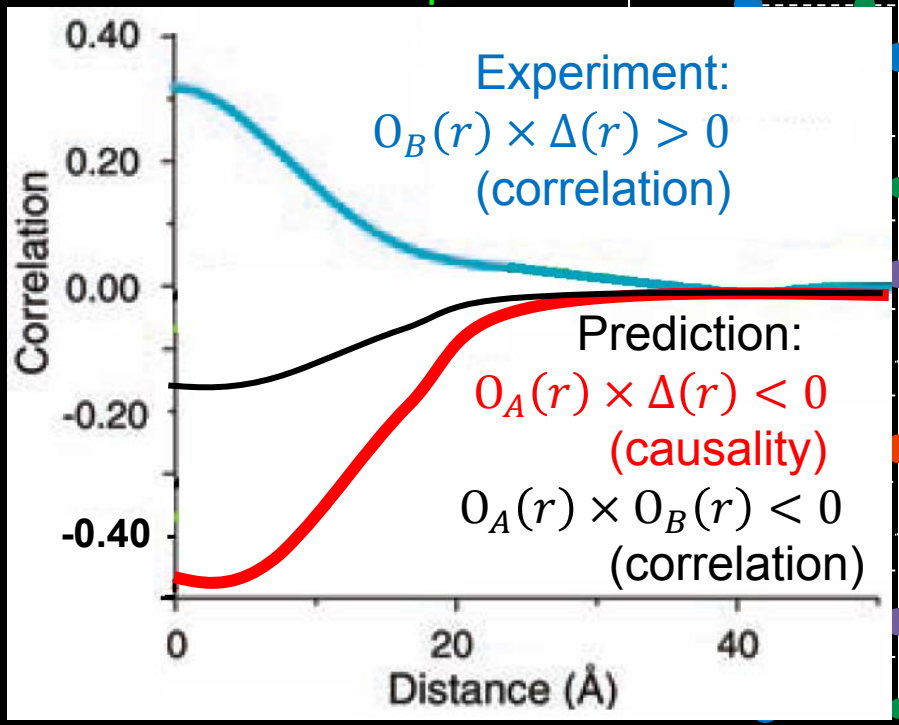
Zhou prediction: type-A oxygen

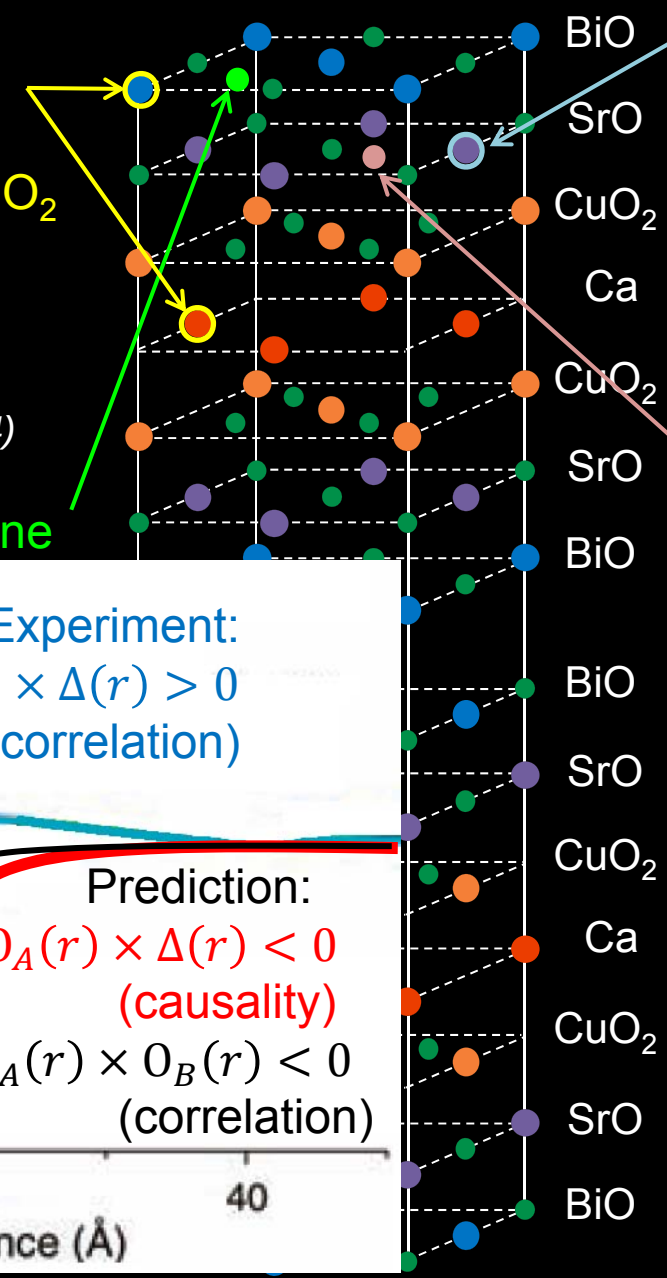
B-site disorder:
(e.g. Pb^{2+} on Bi^{3+} site
or Y^{3+} on Ca^{2+} site)
does not couple to CuO_2



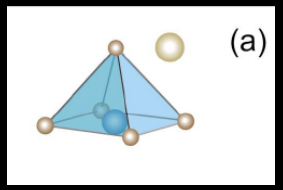
Eisaki, PRB 69, 064512 (2004)

interstitial O in BiO plane





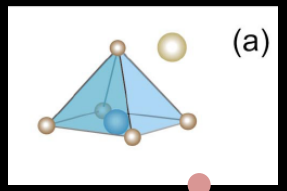
A-site disorder:
(Bi^{3+} on Sr^{2+} site)
strongly couples to apical O



claim: seen at +1.8V

Kinoda, PRB 67, 224509 (2003)

interstitial O in SrO plane
strongly couples to CuO_2
provides charge carriers
and disorder
→ "type-A oxygen"



Zhou, PRL 98, 076401 (2007)

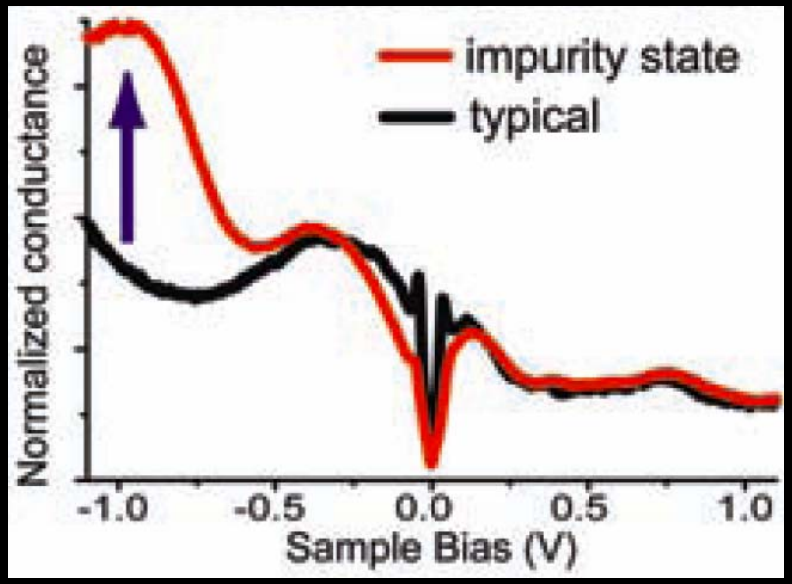
expected << -1V

Why is this a problem?

“High” tip-sample bias

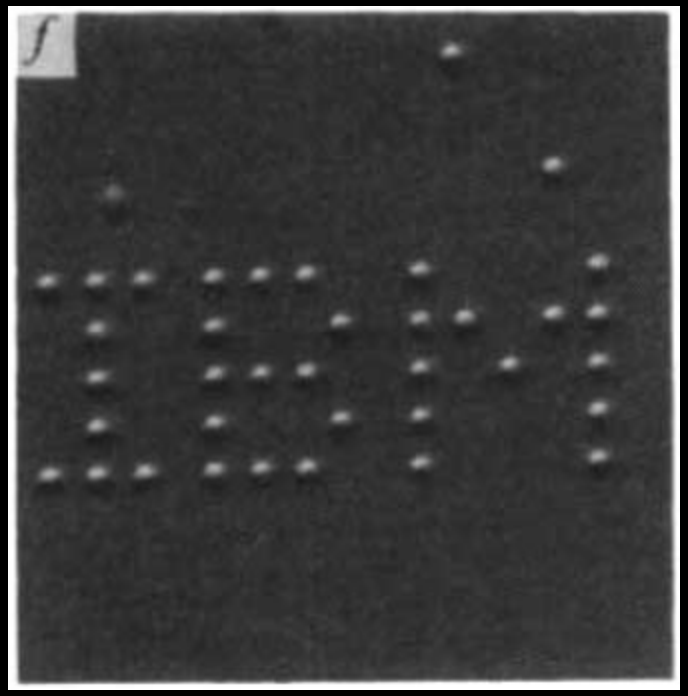
Need to access energies > 1V → Why is this hard?

Highest bias spectroscopy to date on BSCCO



McElroy, Science 309, 1048 (2005)

What kinds of things happen if one applies higher tip-sample bias?



D. M. Eigler & E. K. Schweizer
Nature 344, 524 (1990)

- move Xe atoms on Ni(110) surface
- using tip-sample bias as low as 0.01 V

Outline

Superconductors: 100 Year History

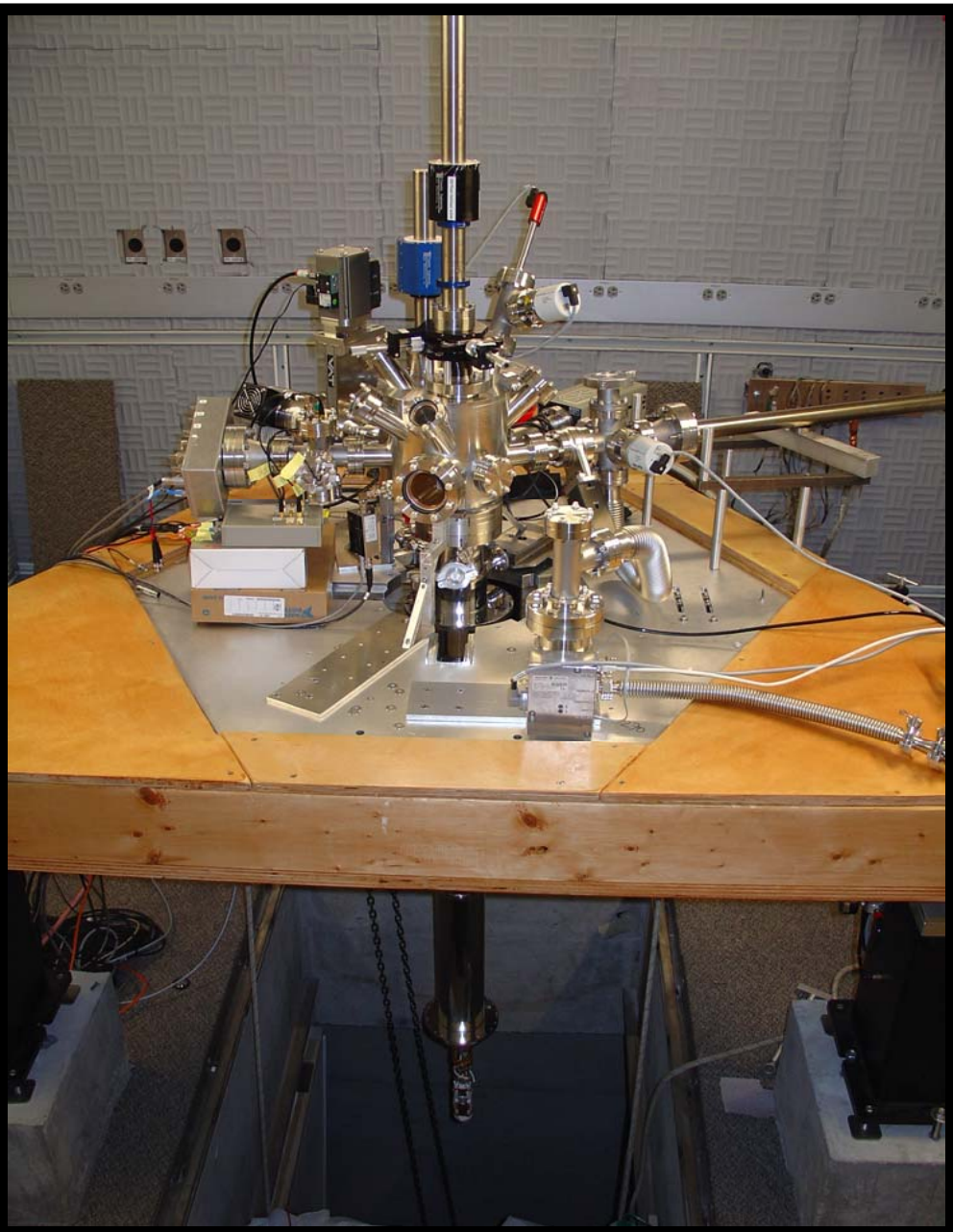
Part I: Pseudogap in cuprates:

- Competing or collaborating?
  (crash course in solid state physics)
- Nanoscale inhomogeneity: energy & charge modulation
  → what is the hidden variable??
- Previous studies of chemical disorder
  → hidden variable remains mysterious…
- STM imaging of oxygen dopants & vacancies
  → we found the hidden variable!!

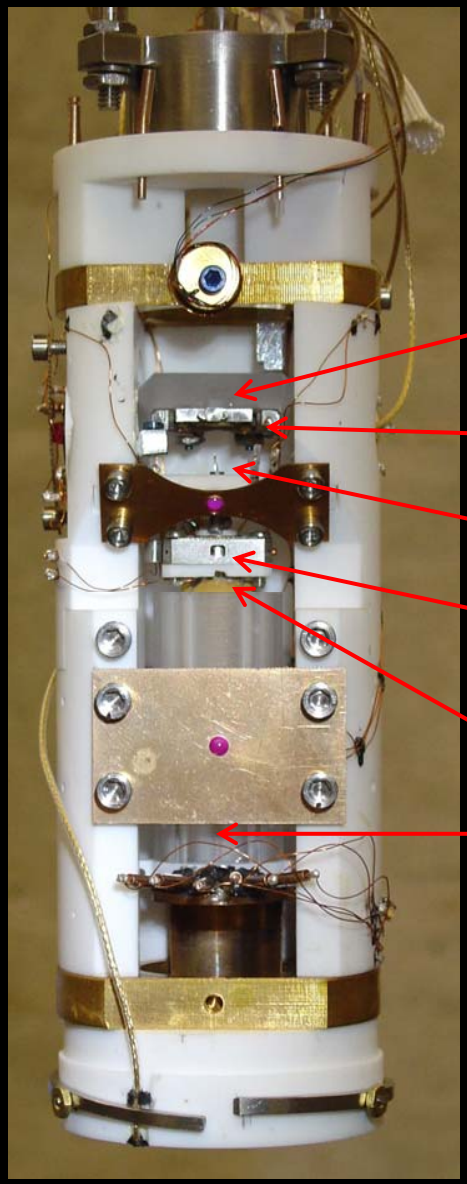
Part II: Vortex pinning in pnictides:

- Discovery of iron-based superconductors
- MFM imaging of NdFeAsO, in-plane anisotropy

Our STM



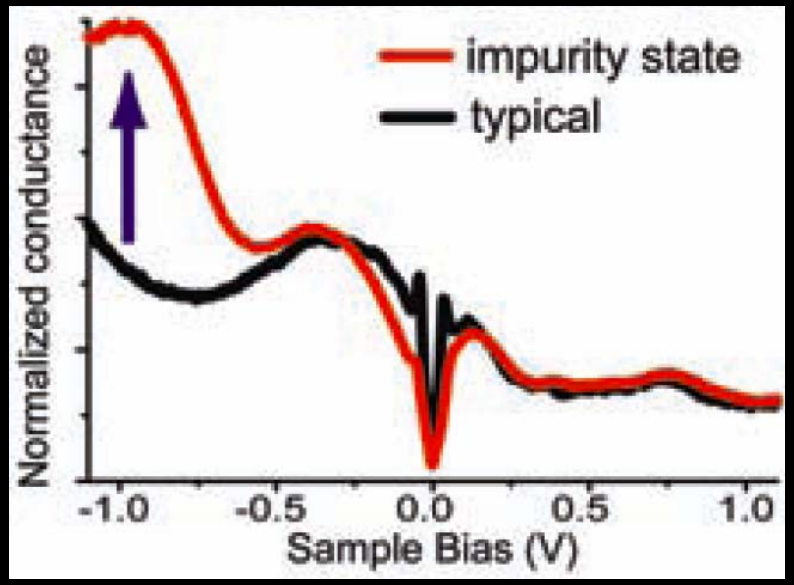
built by: Liz Main, Adam Pivonka, Ilija Zeljkovic



Parameters:

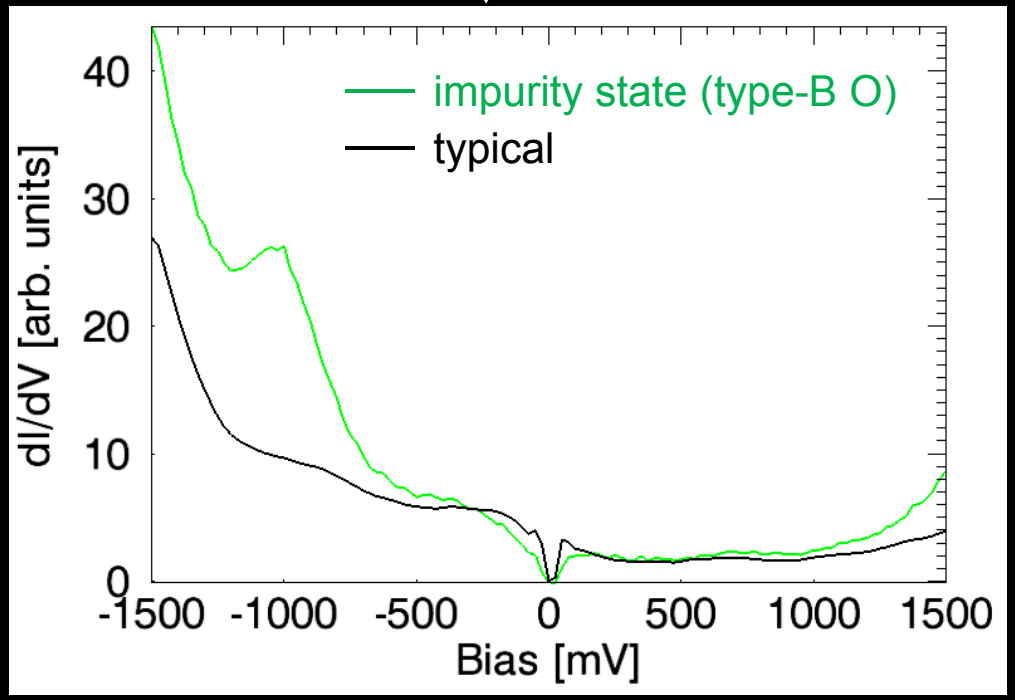
- UHV
- 2 – 80K
- 9 T vertical
- 3 T horizontal

Extending the energy range

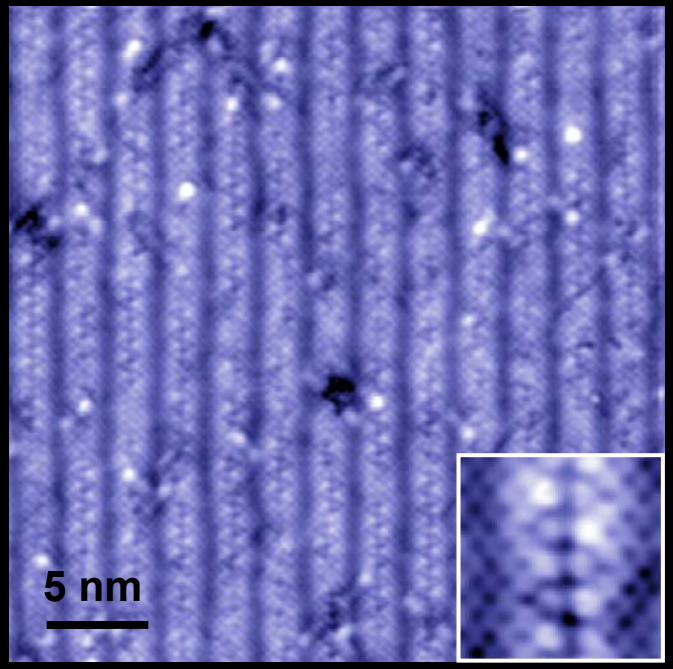


McElroy, Science 309, 1048 (2005)

Ilija Zeljkovic

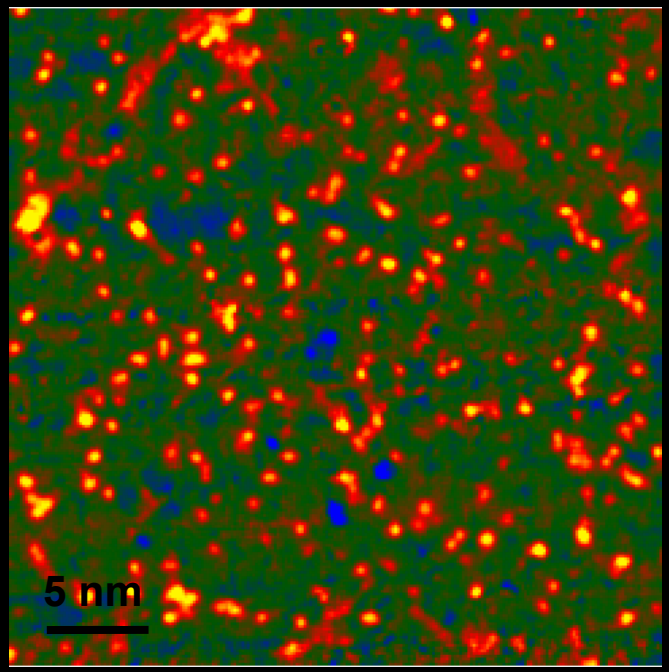


Mapping type-B oxygen



Low High

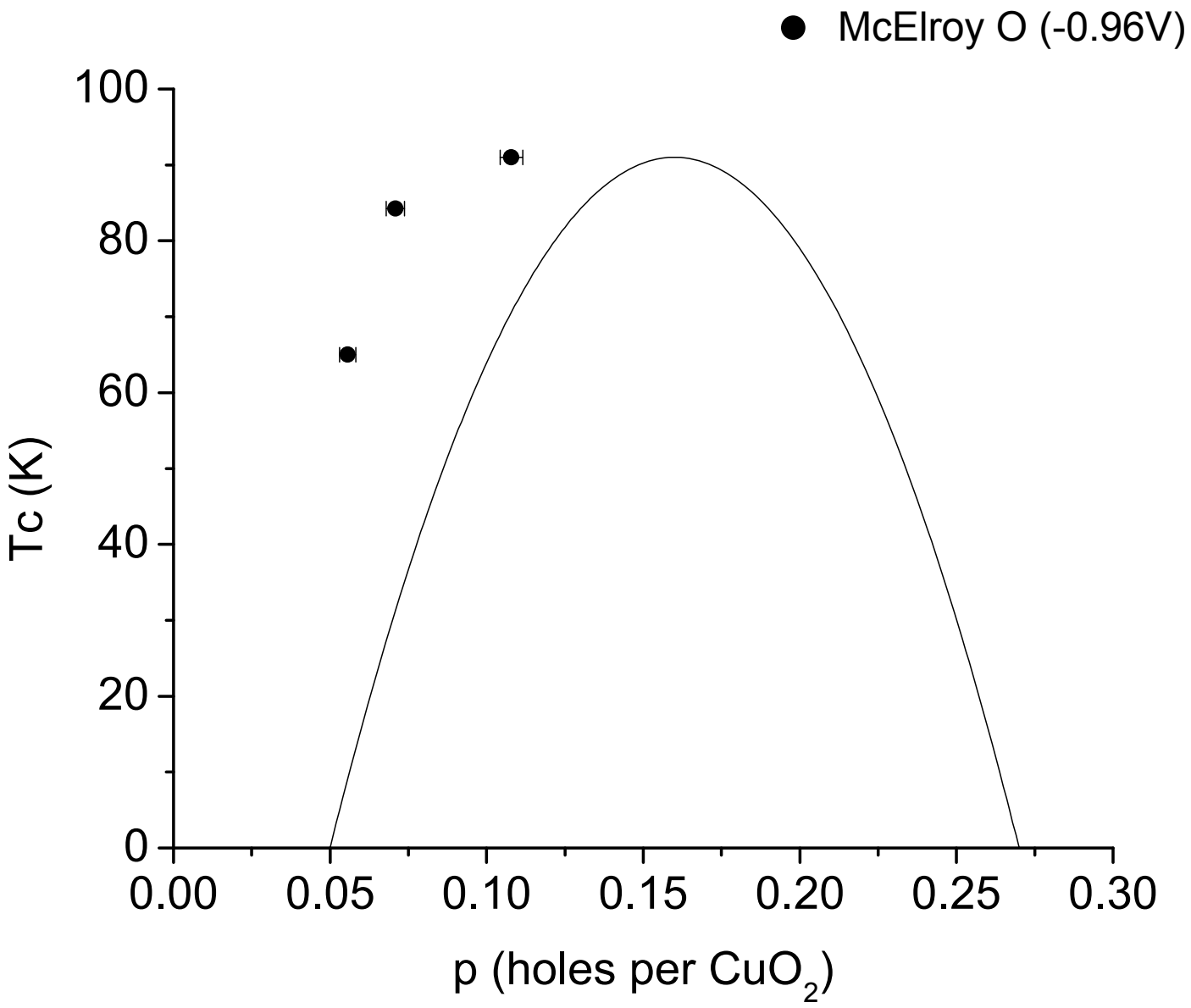
T_c = 55K



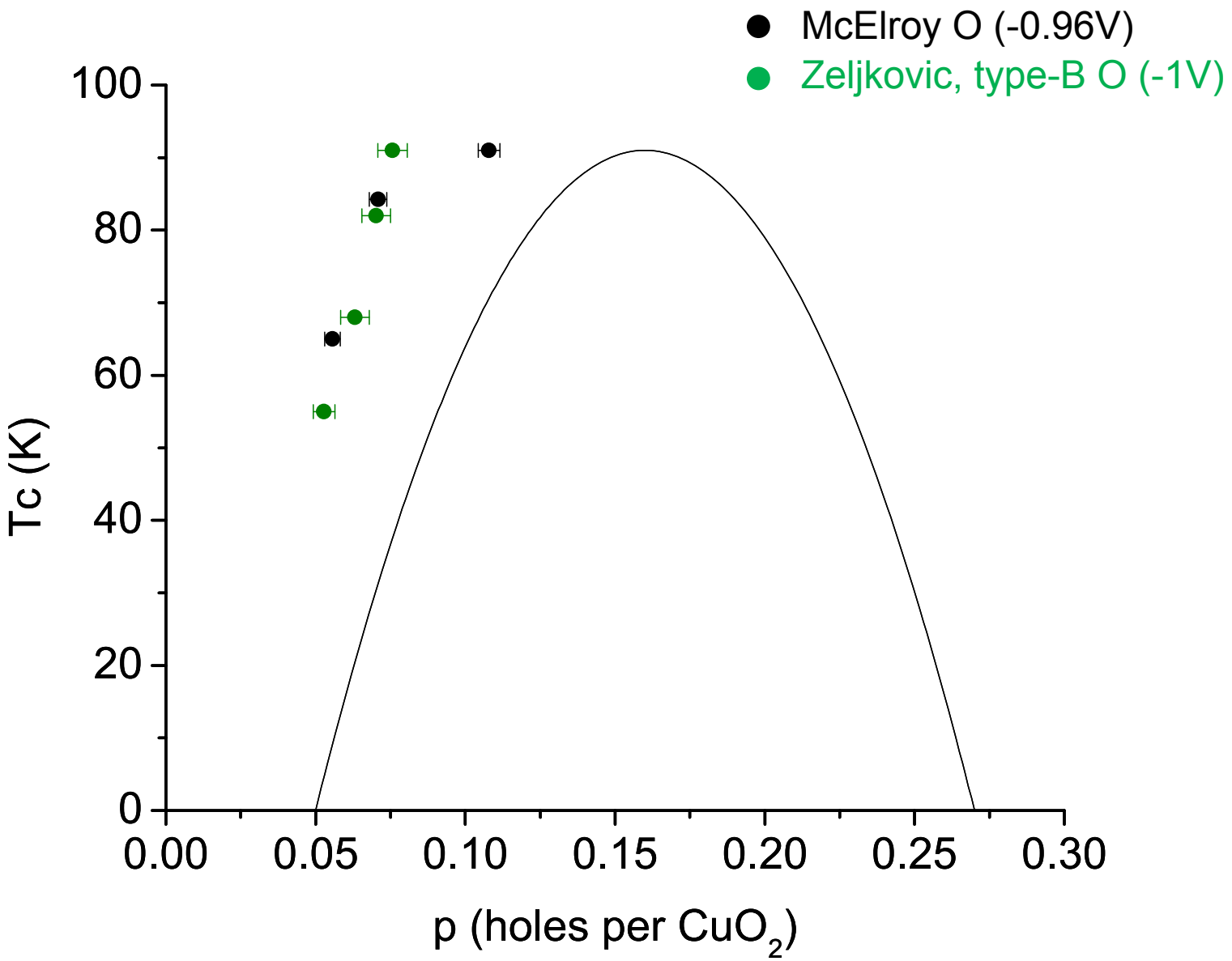
Low High

V_s = -1 V; I_t = 150 pA

Dopants found by STM

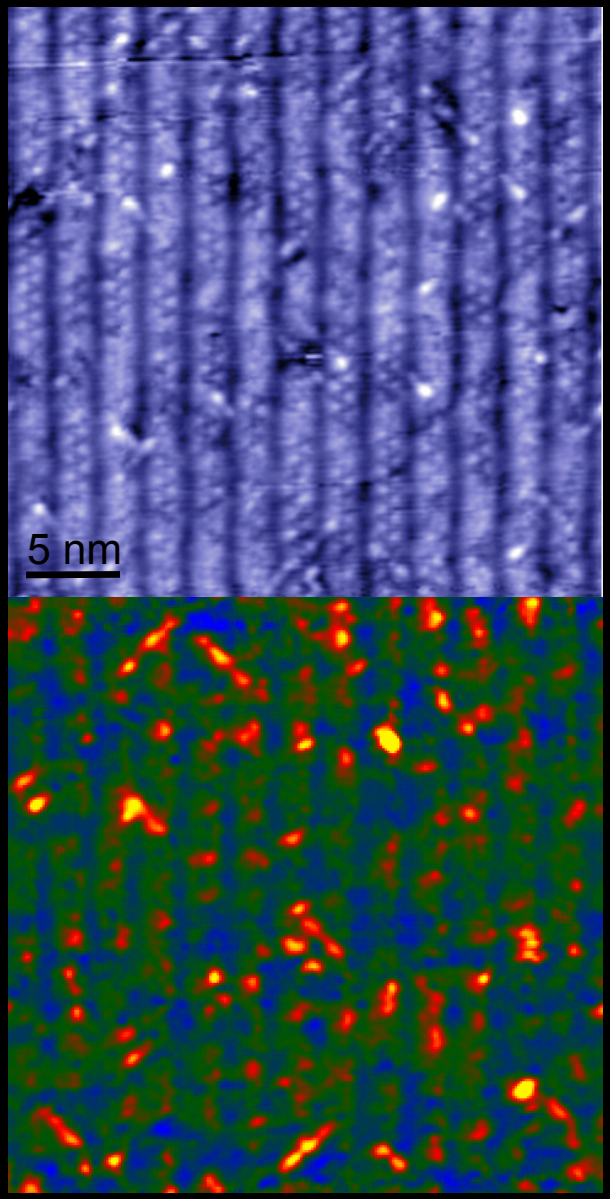


Dopants found by STM

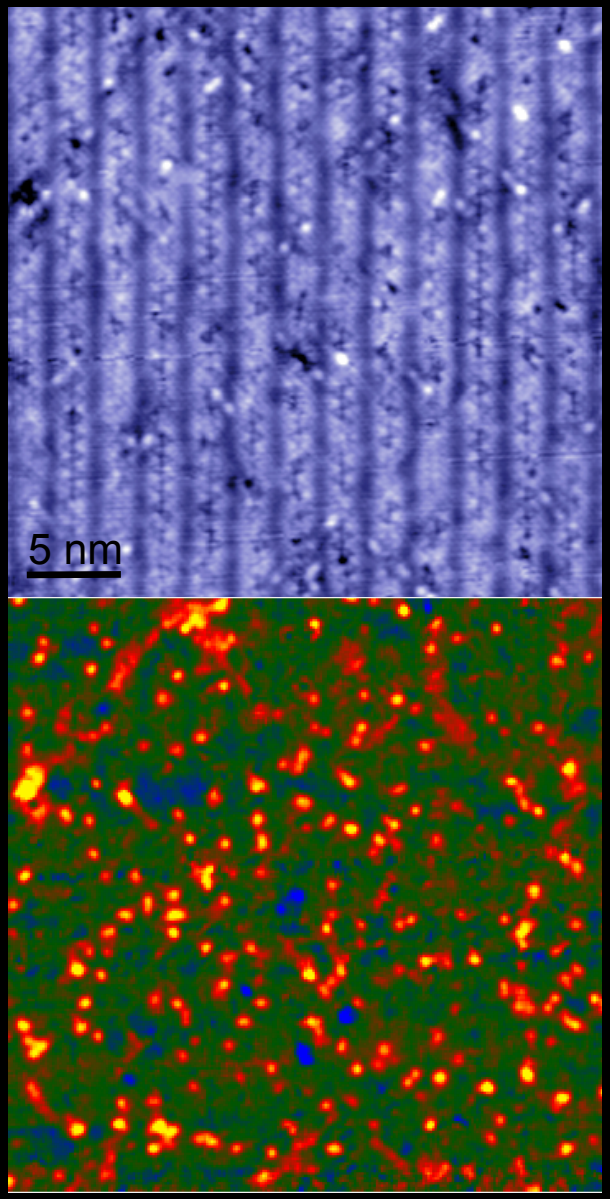


Mapping additional dopants (T_c=55K)

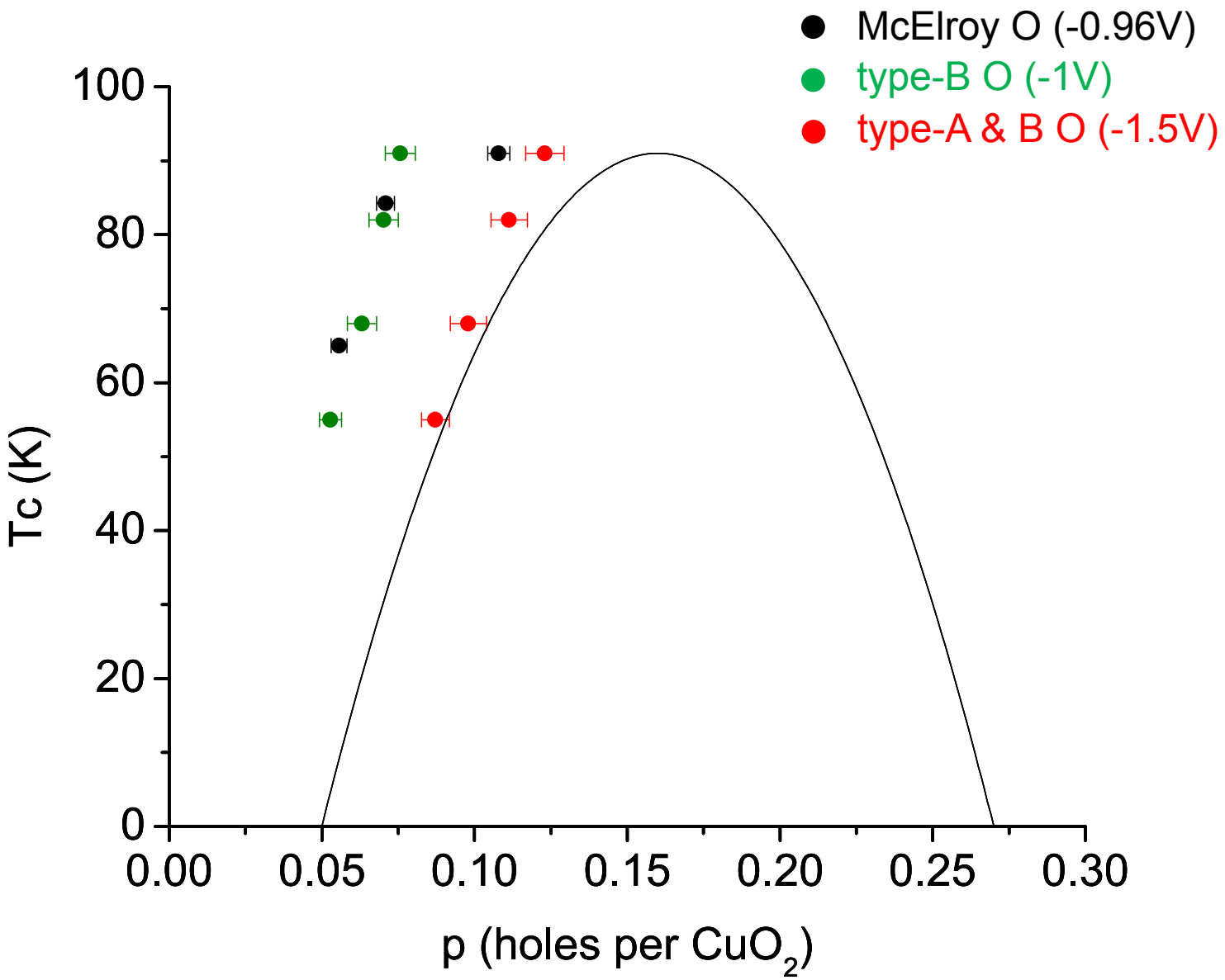
-1.5V, type-A Oxygen



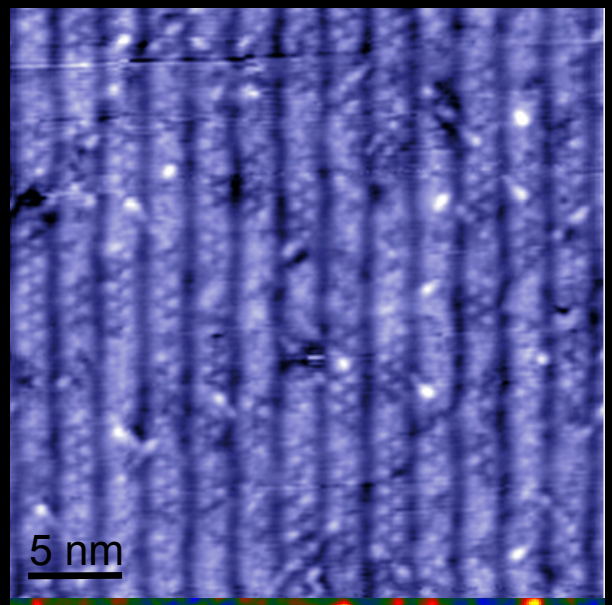
-1V, type-B Oxygen

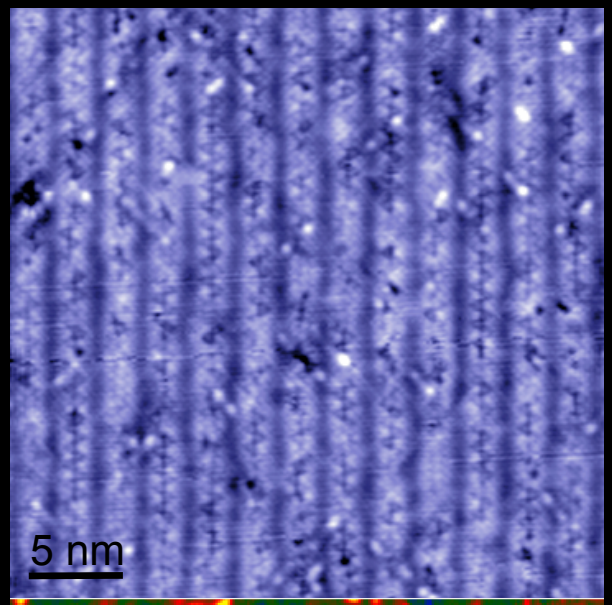


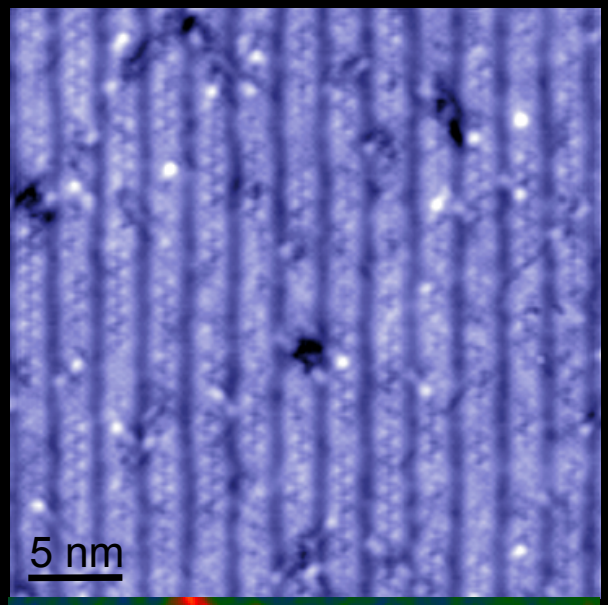
Dopants found by STM

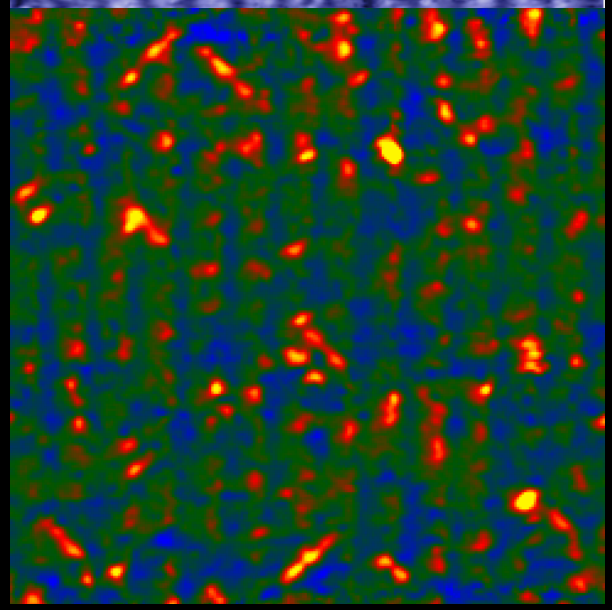


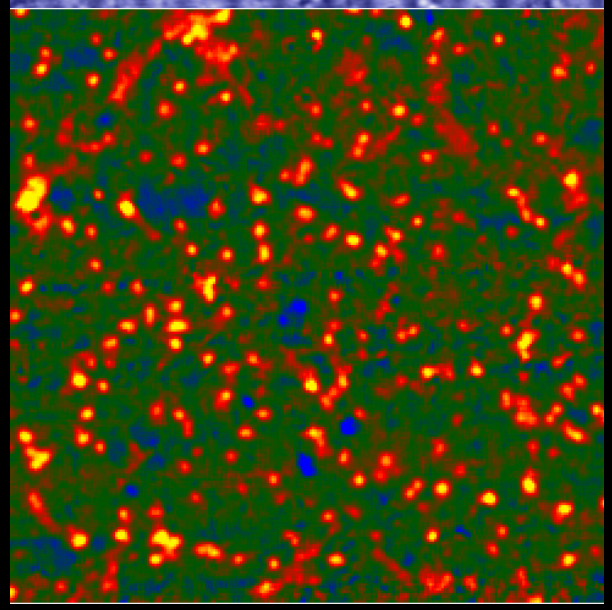
Mapping additional dopants (T_c=55K)

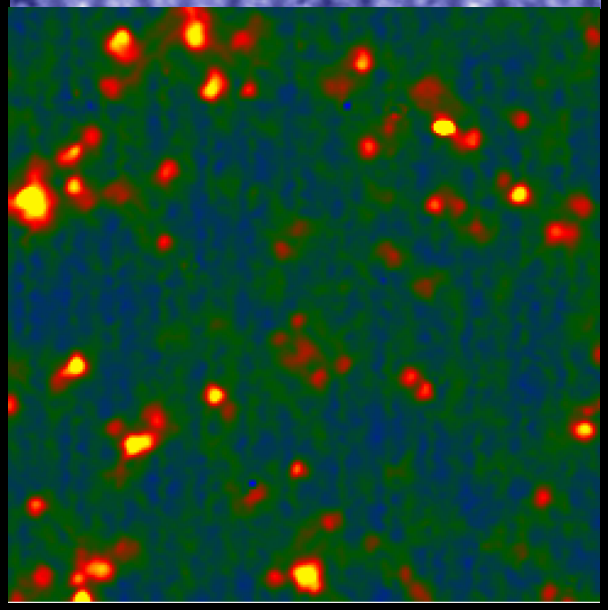




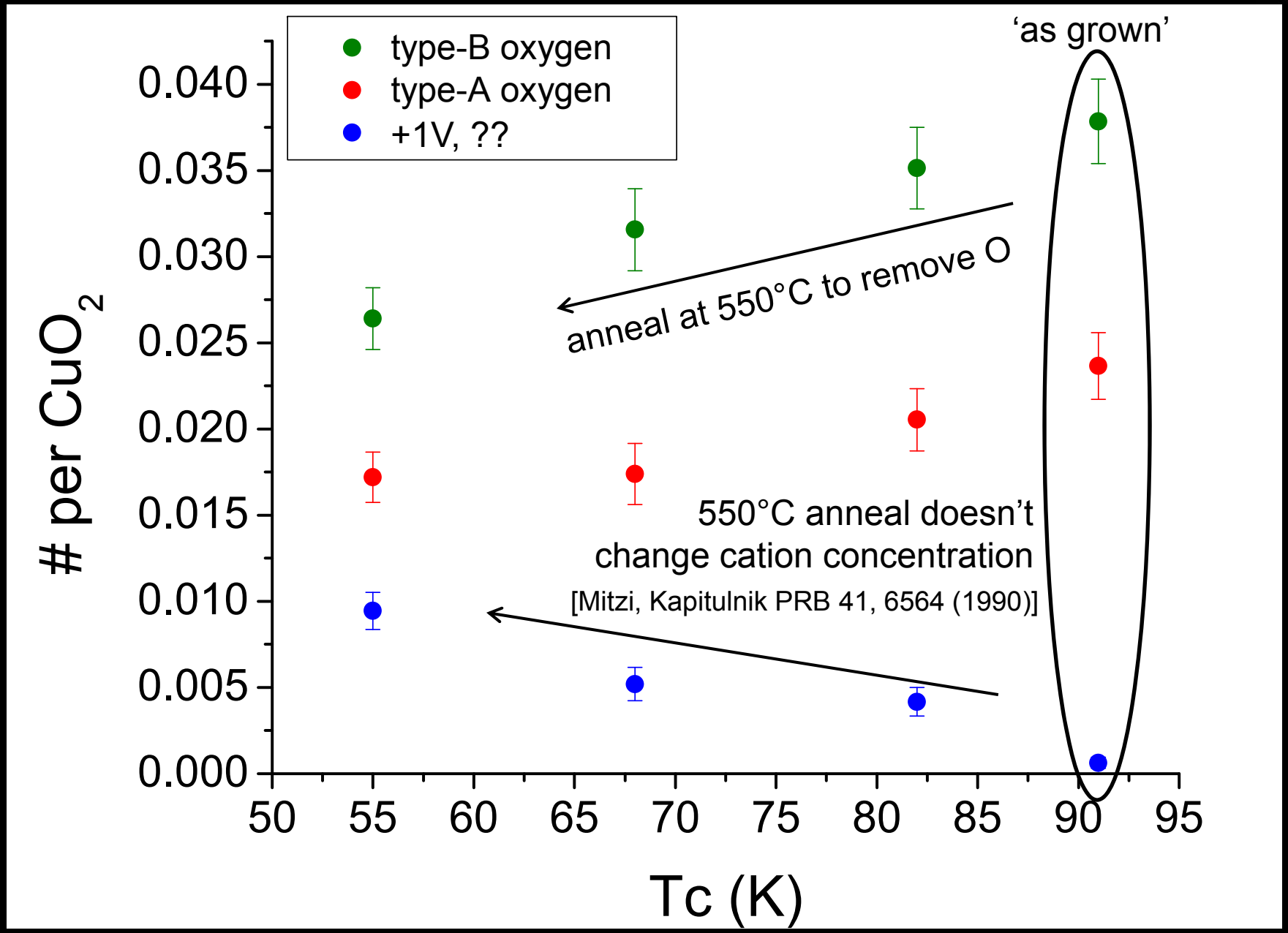




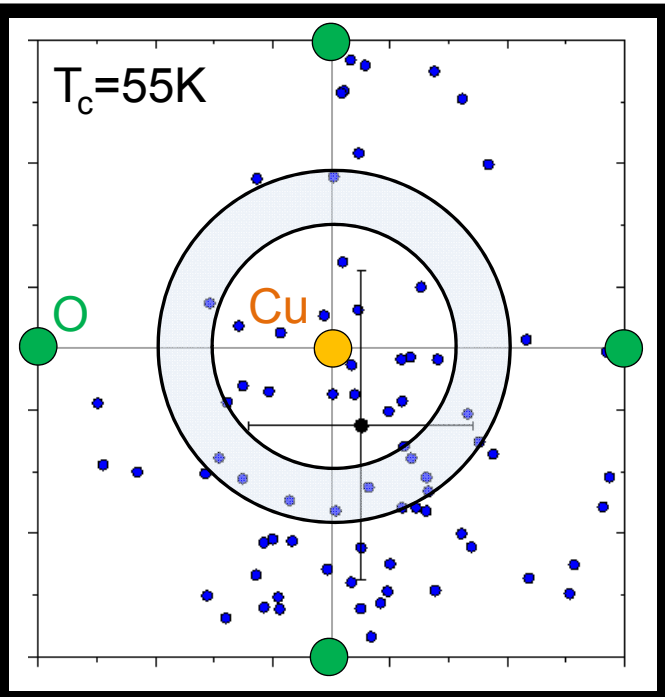


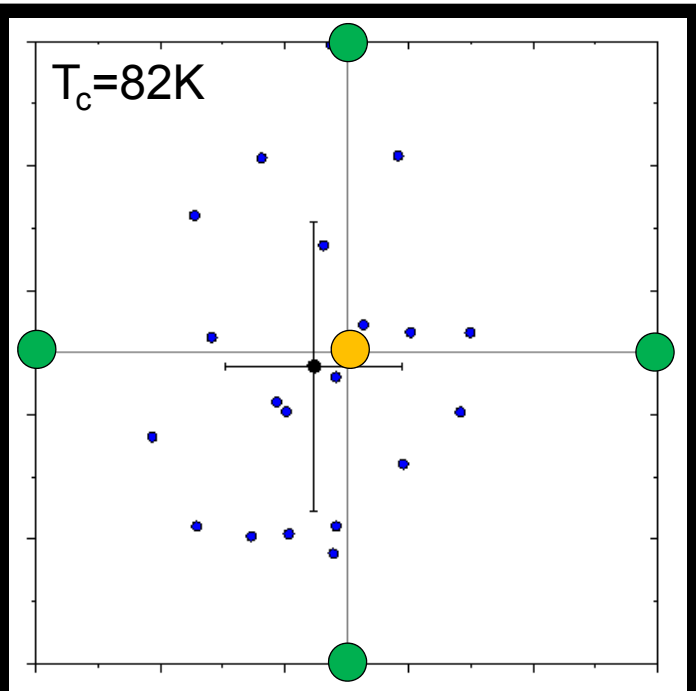


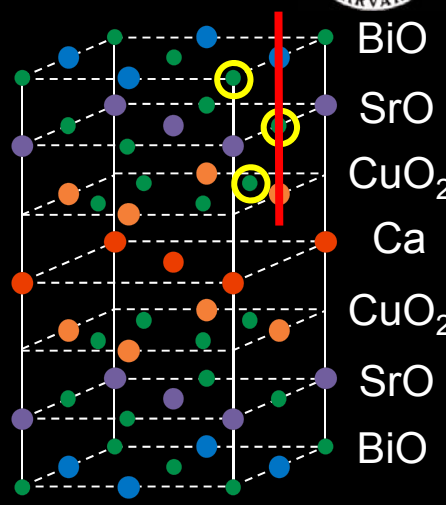
Concentration vs. Tc



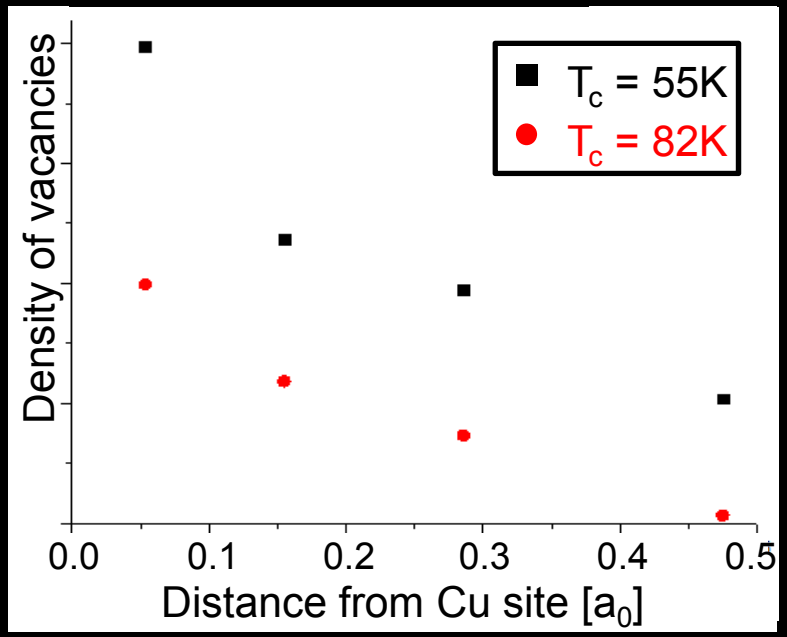
Intra-unit-cell location of +1V features





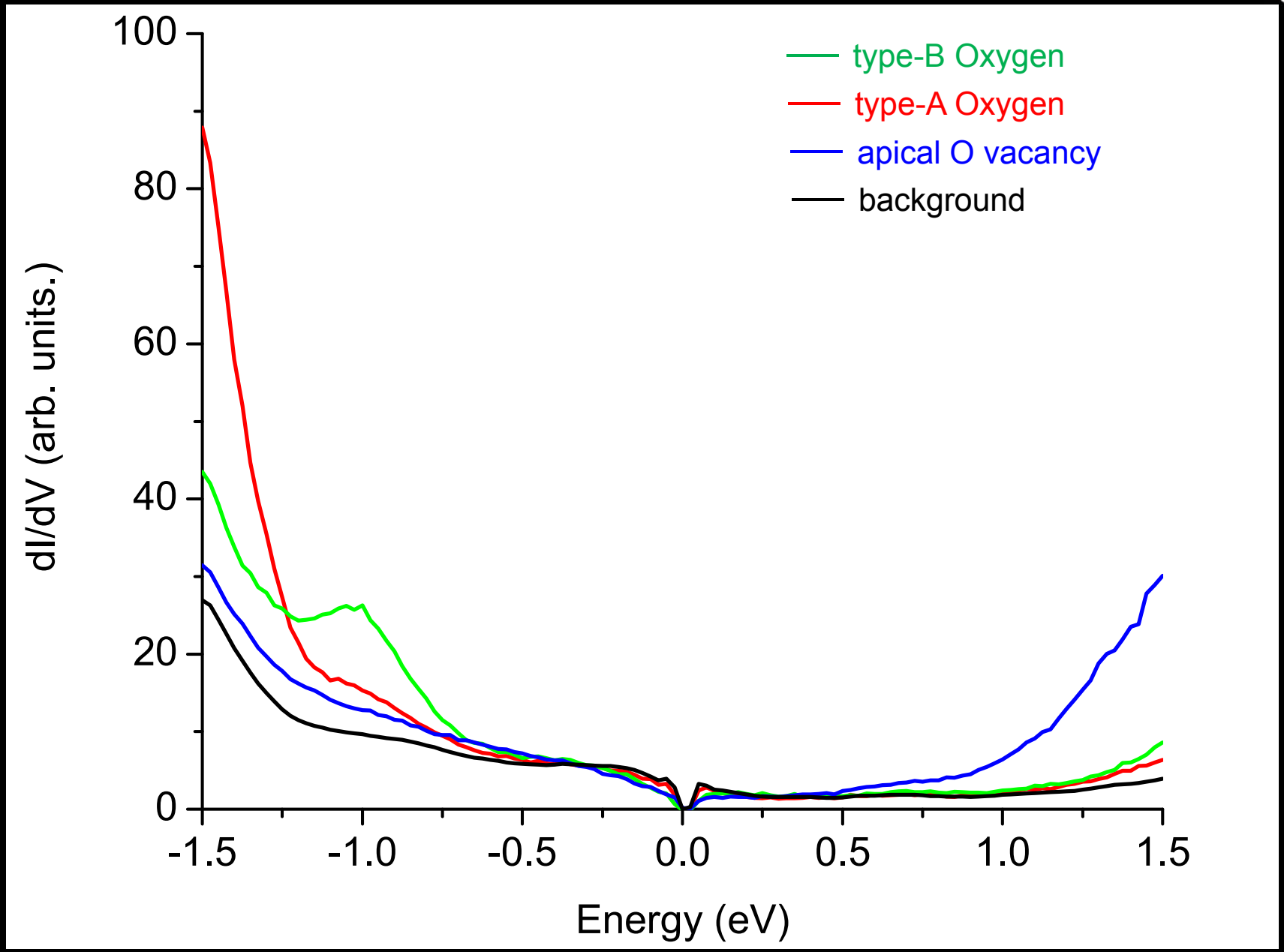


3 distinct O lattice sites

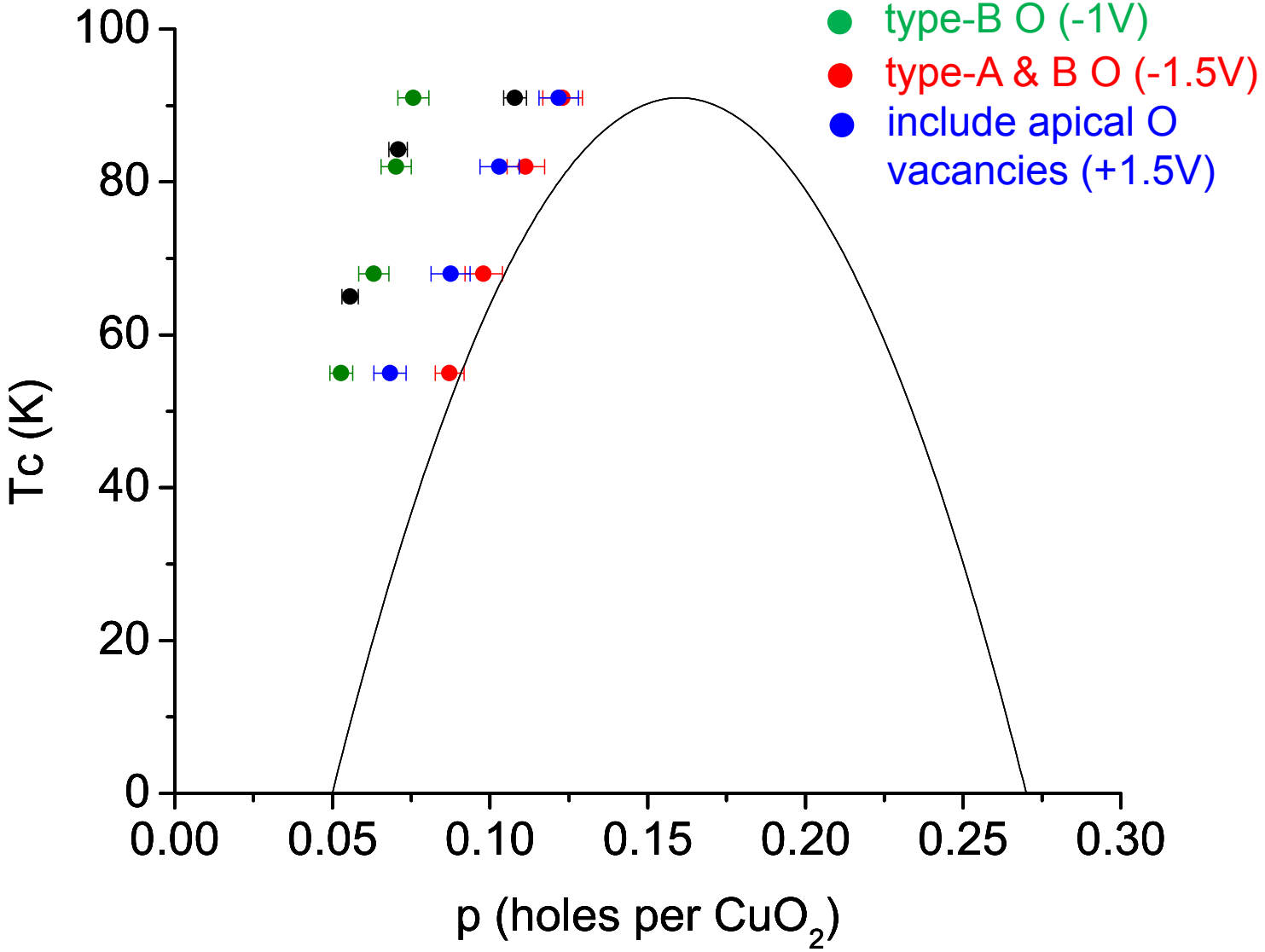


Conclusion:
apical oxygen vacancy

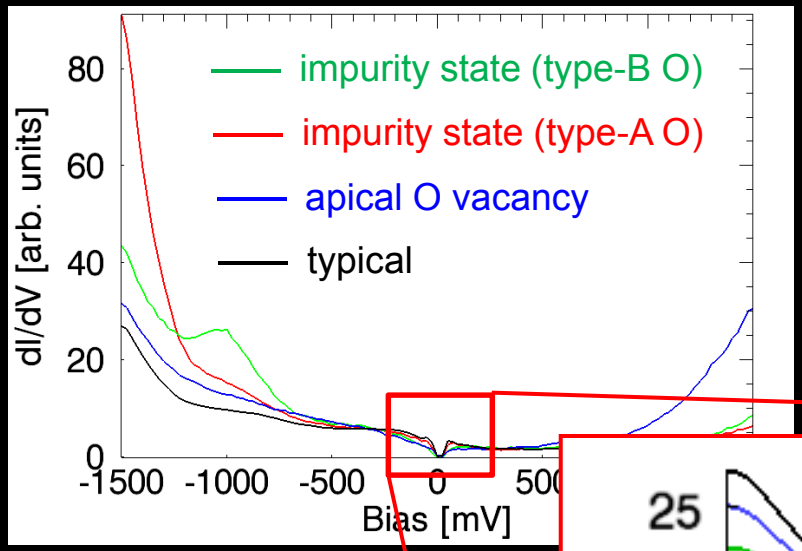
Spectral signatures (T_c=82K)



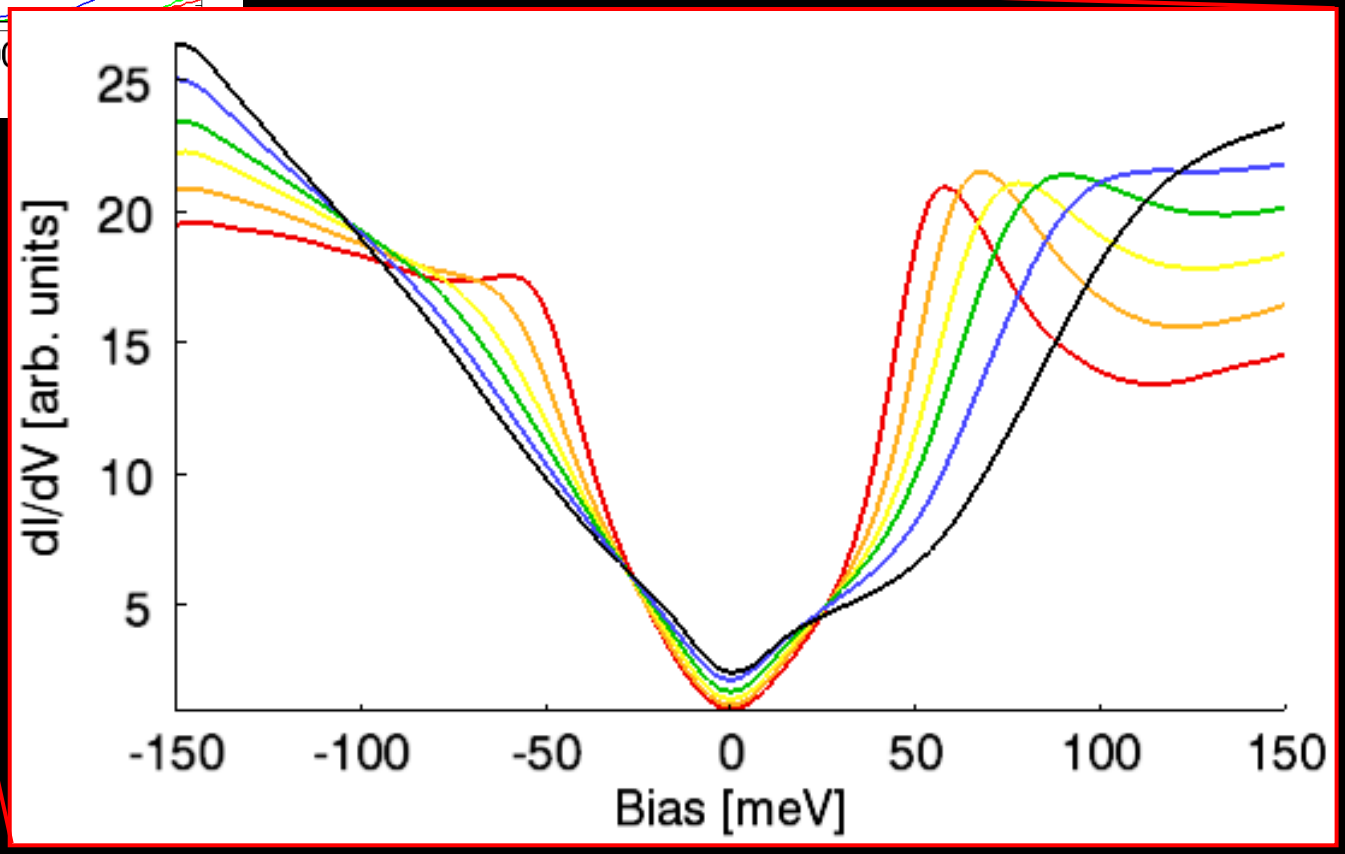
Dopants found by STM



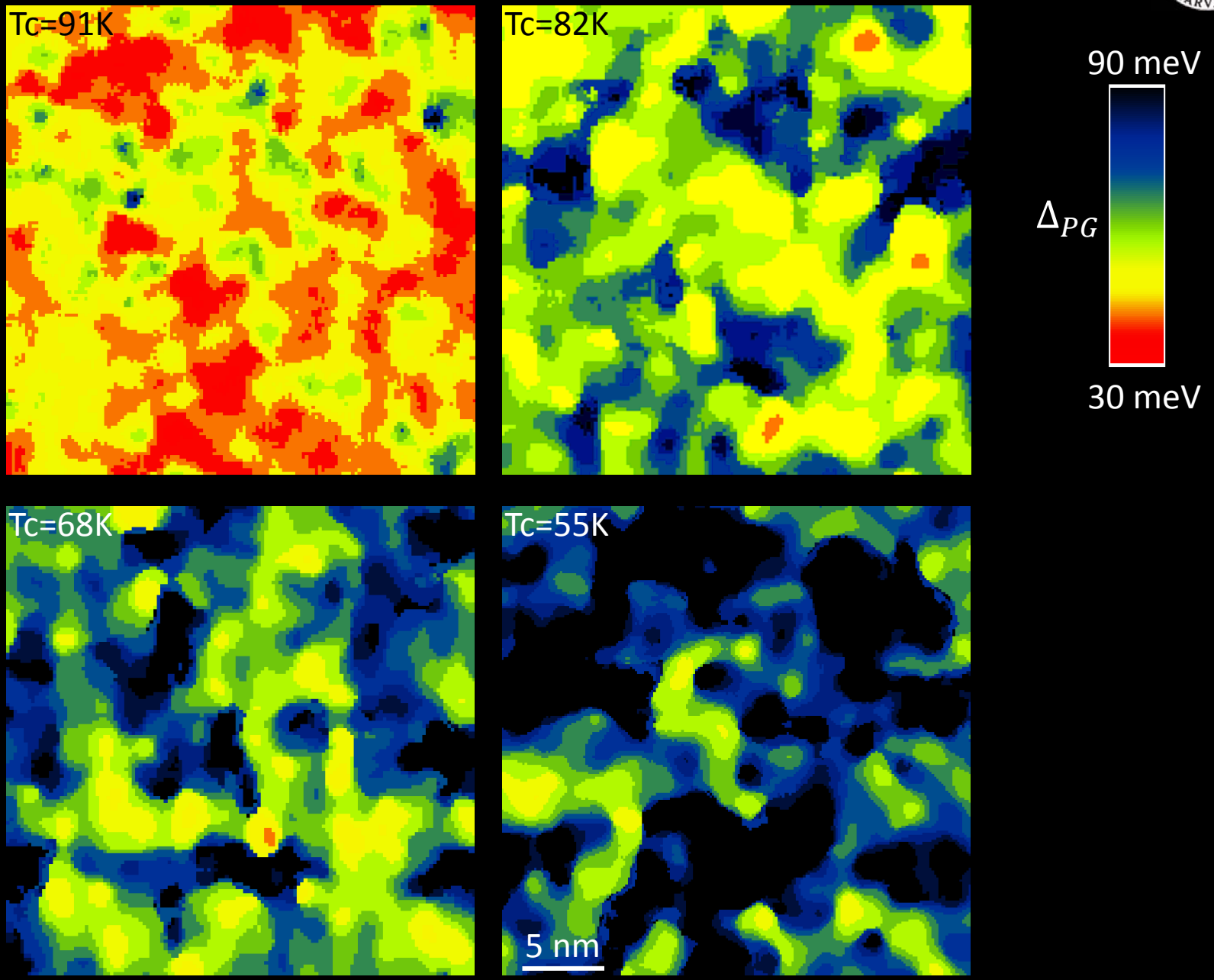
Zoom on Pseudogap



Bin spectra by local pseudogap energy Δ_{PG}



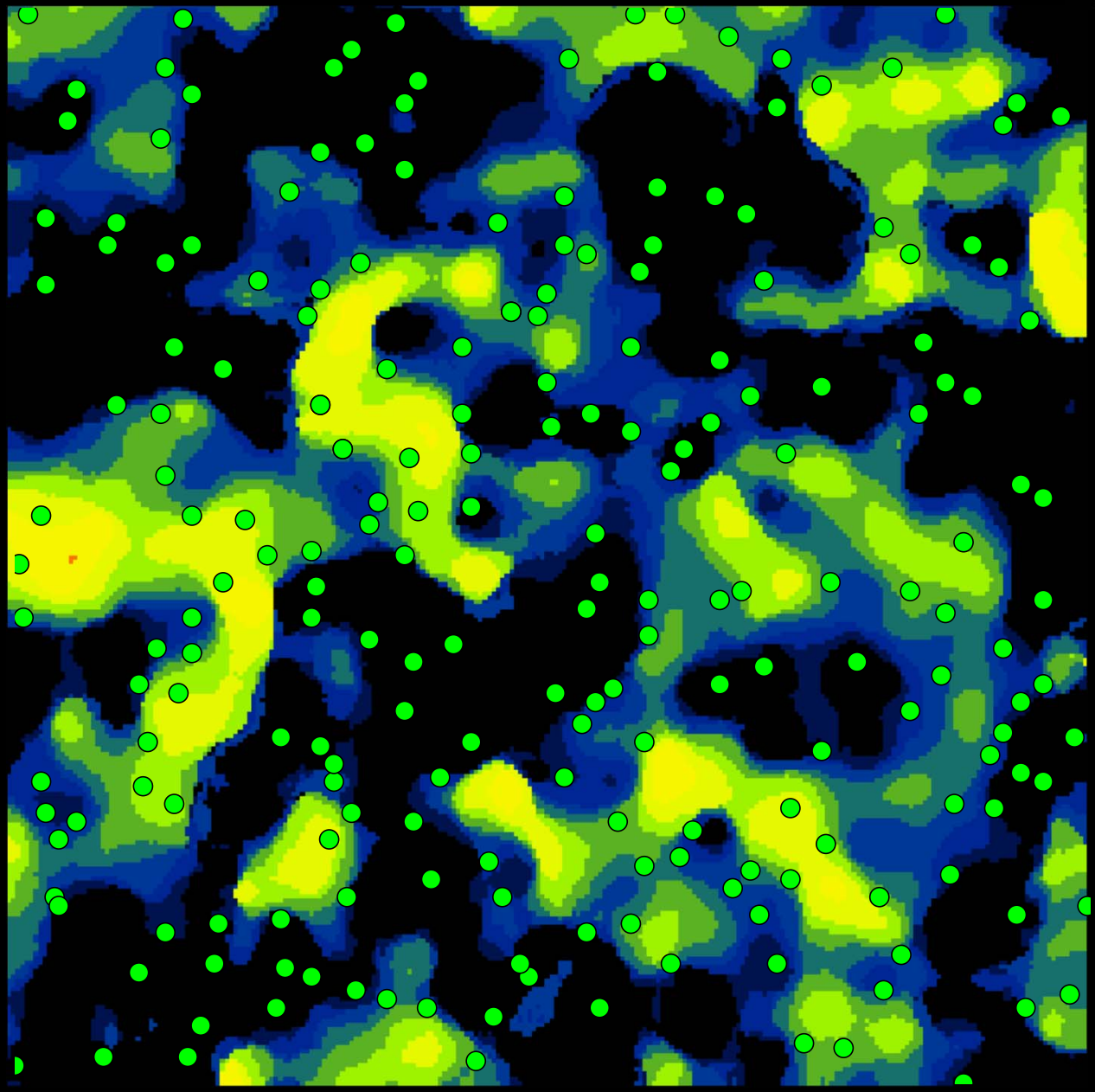
Gapmap: map of Δ as a function of location



Tc = 55K

- O, type-B

expect $O_B(r) \times \Delta(r) > 0$ (correlation)

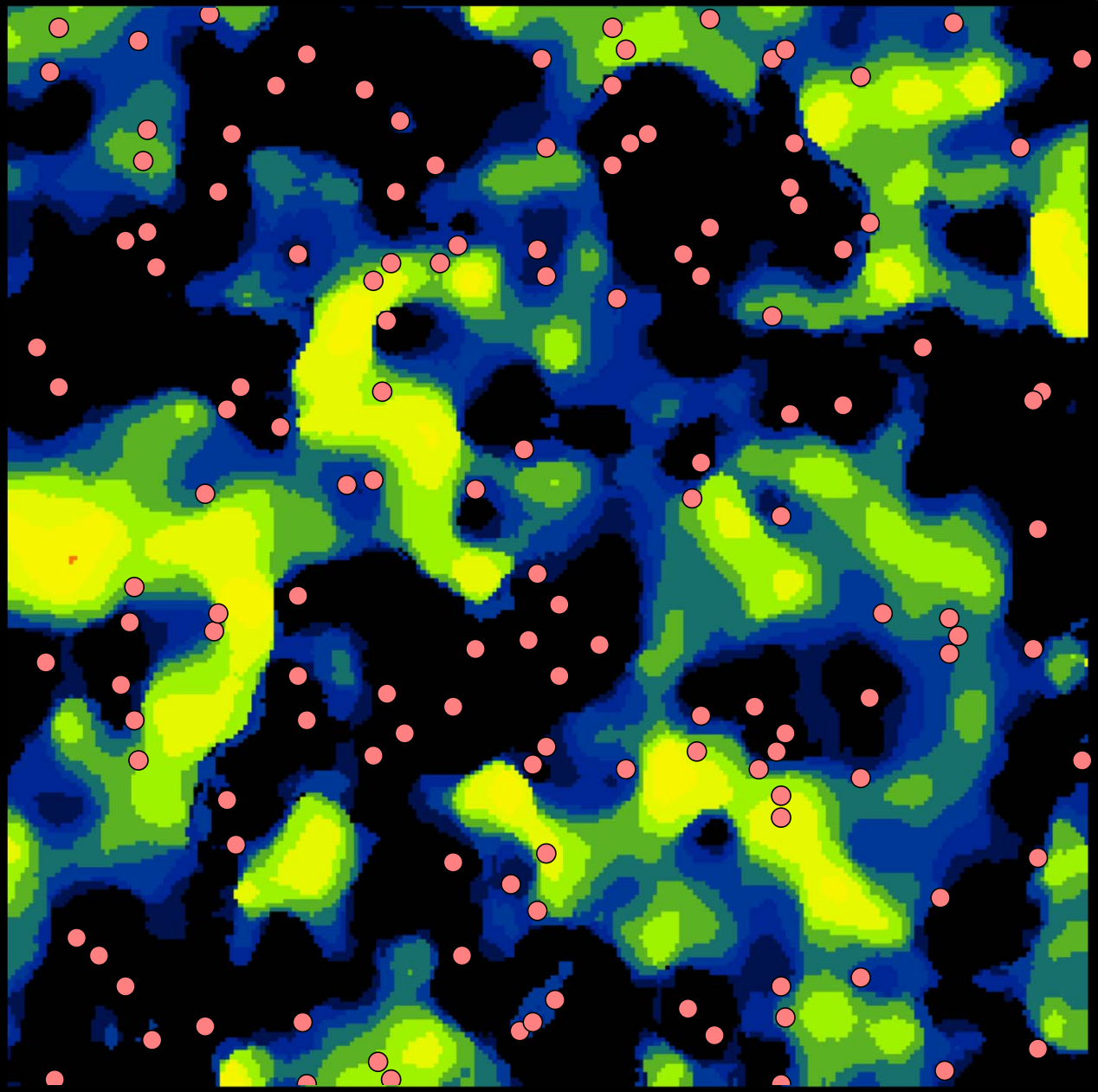


Tc = 55K

- O, type-A

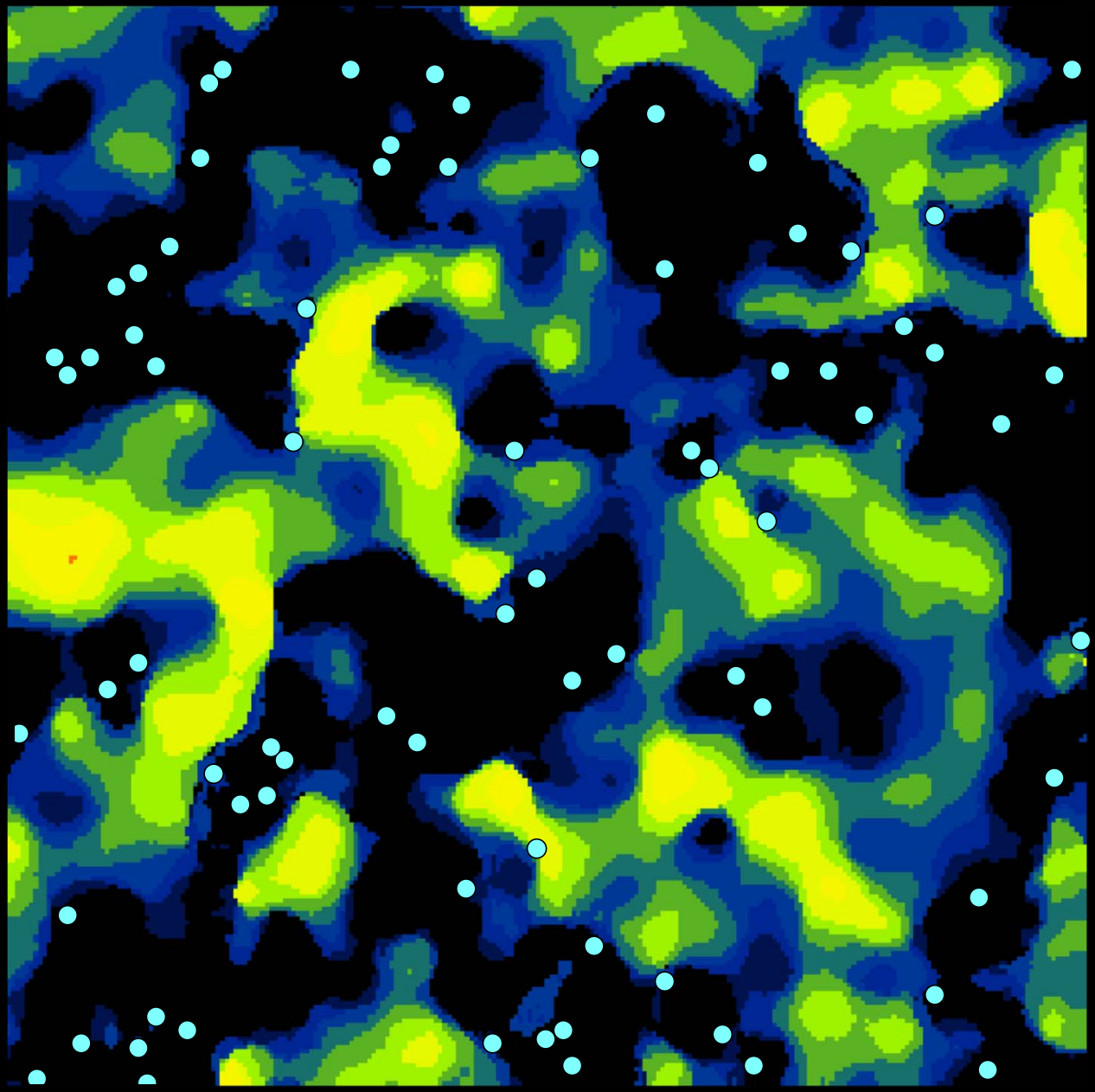
expect $O_A(r) \times \Delta(r) < 0$ (causality)

→ **NOT OBSERVED**



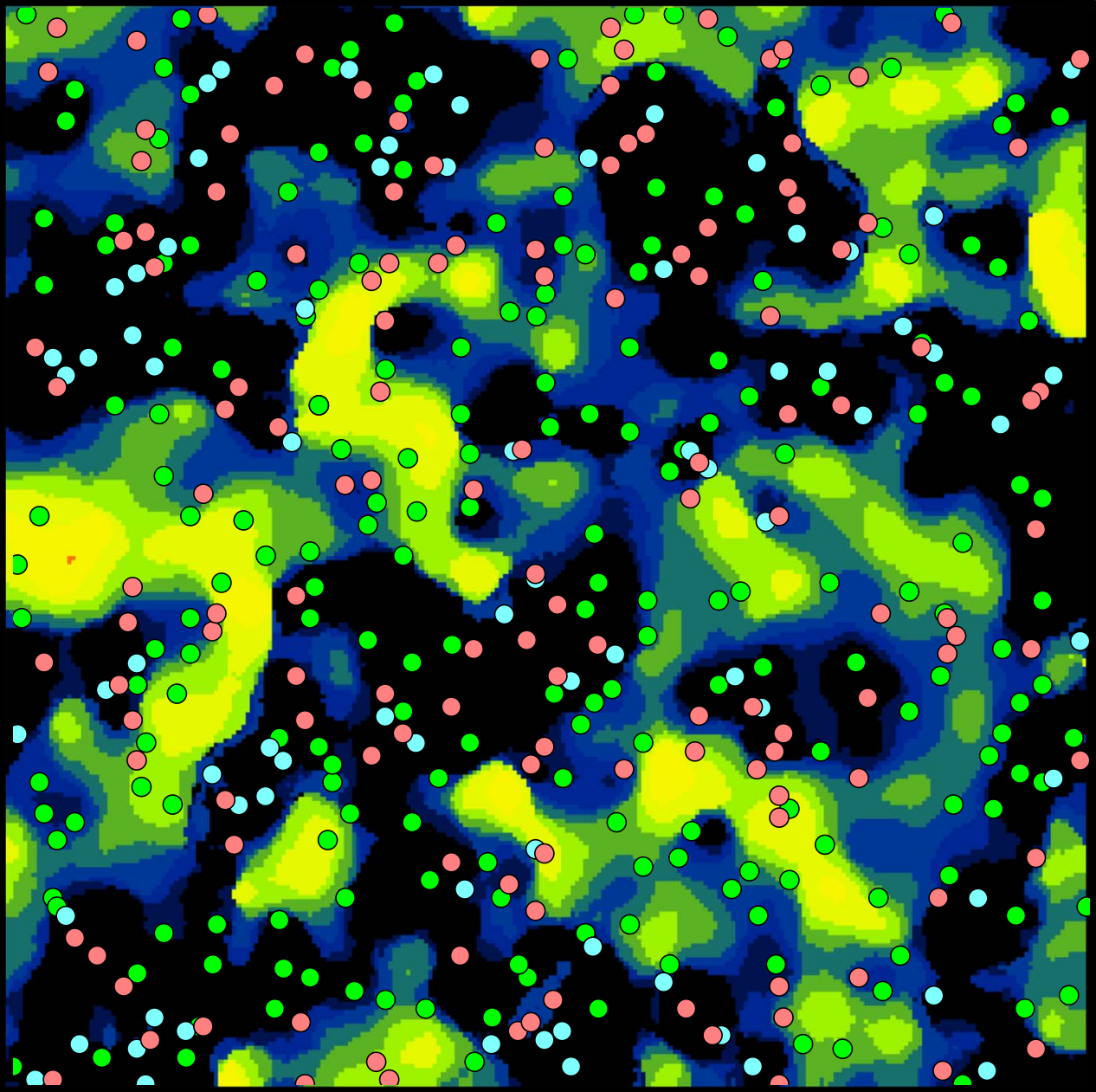
Tc = 55K

- apical O vacancy



Tc = 55K

- apical O vacancy
- O, type-A
- O, type-B



90 meV

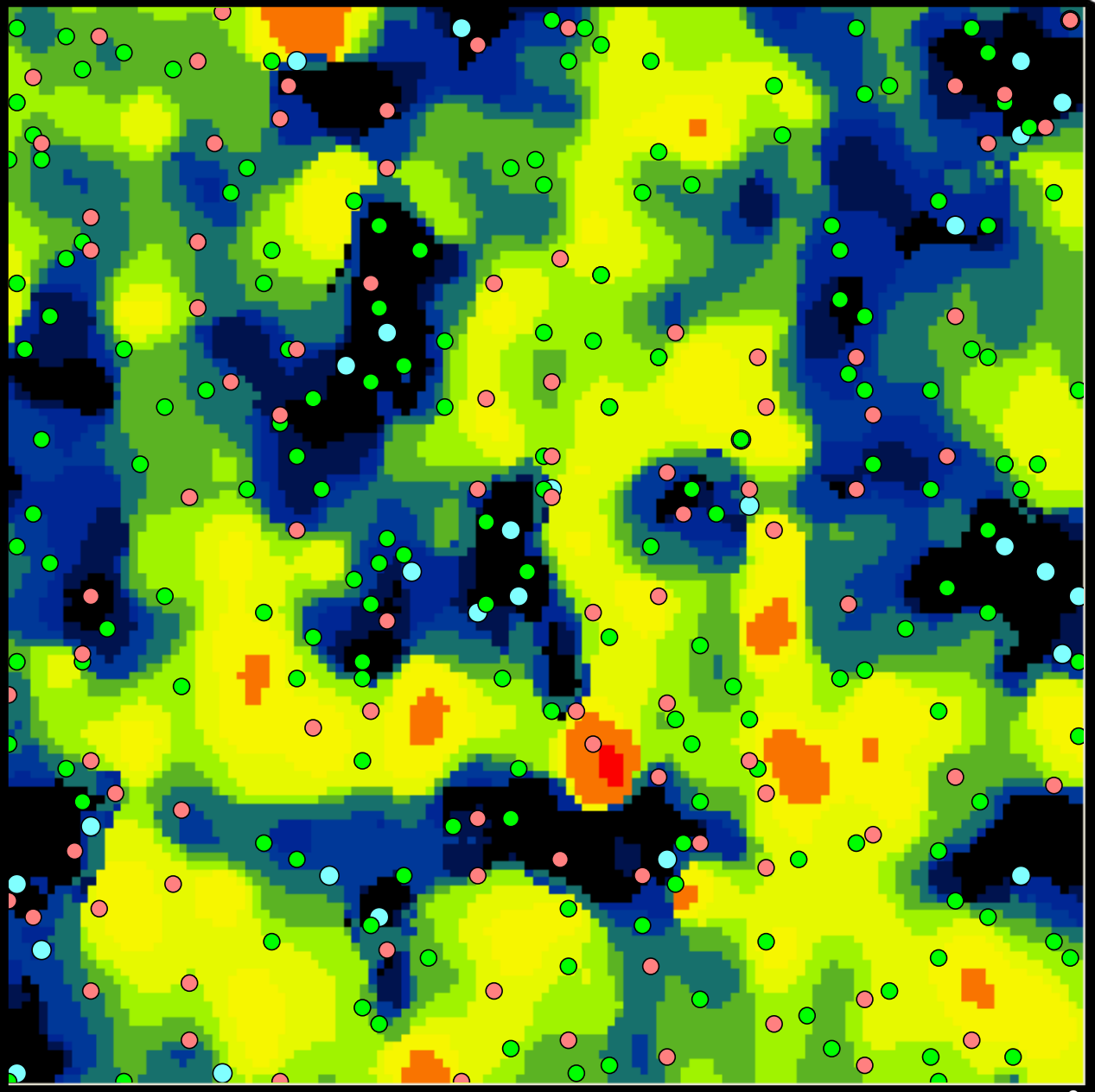
Δ_{PG}

35 meV

29 x 29 nm^2

Tc = 68K

- apical O vacancy
- O, type-A
- O, type-B



90 meV

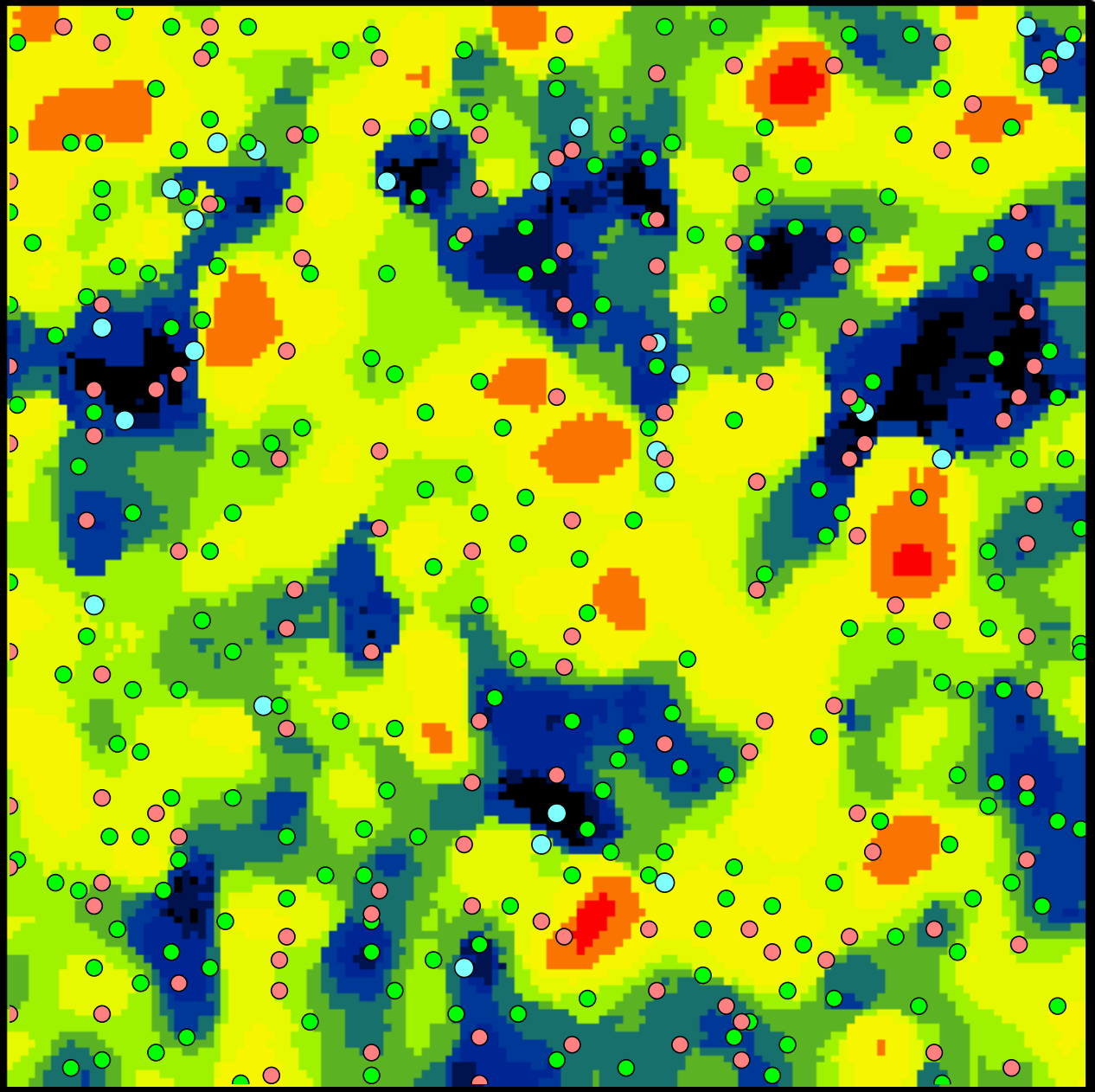
Δ_{PG}

35 meV

29 x 29 nm^2

Tc = 82K

- apical O vacancy
- O, type-A
- O, type-B



90 meV

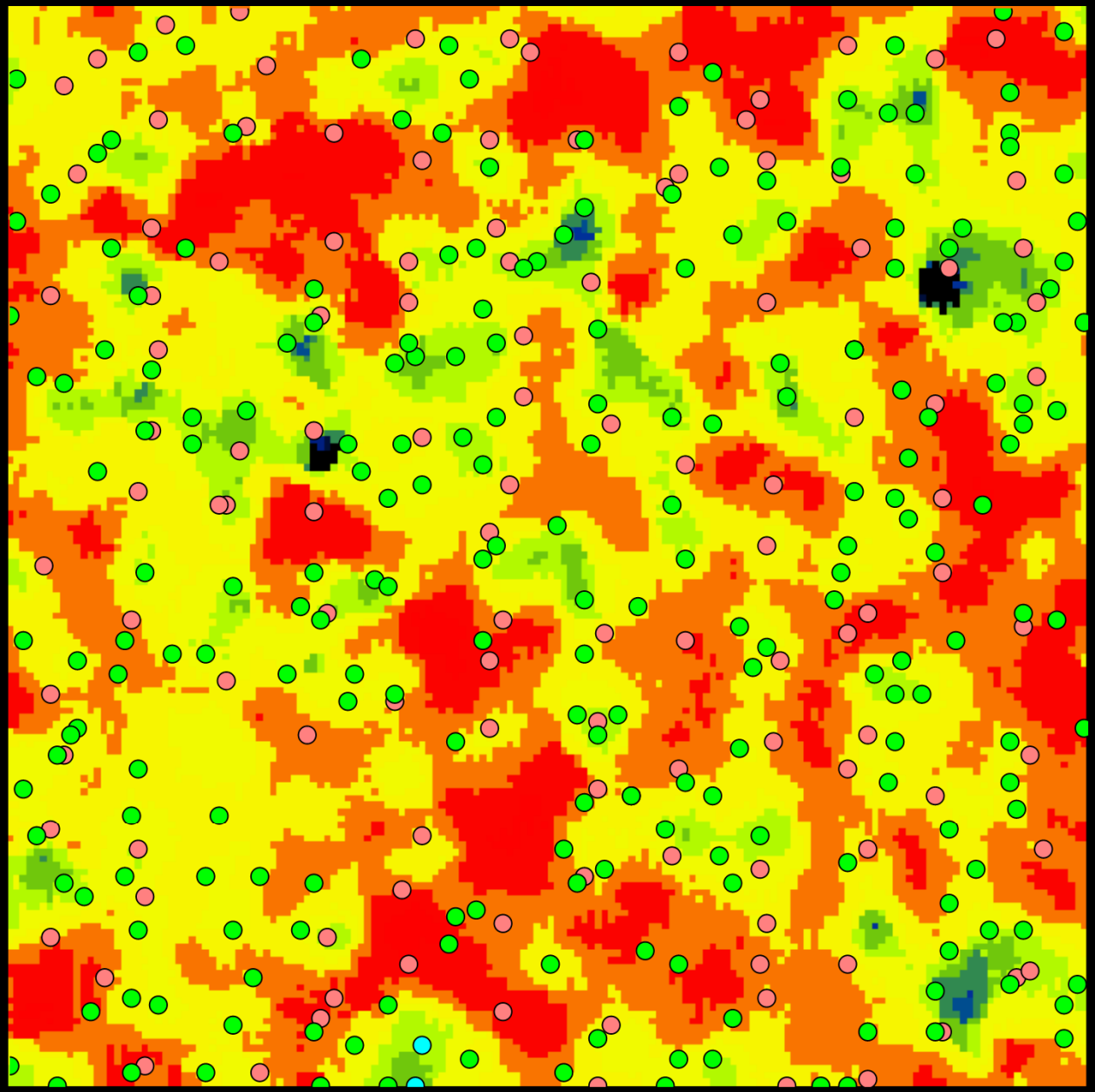
Δ_{PG}

35 meV

29 x 29 nm^2

Tc = 91K

- apical O vacancy
- O, type-A
- O, type-B



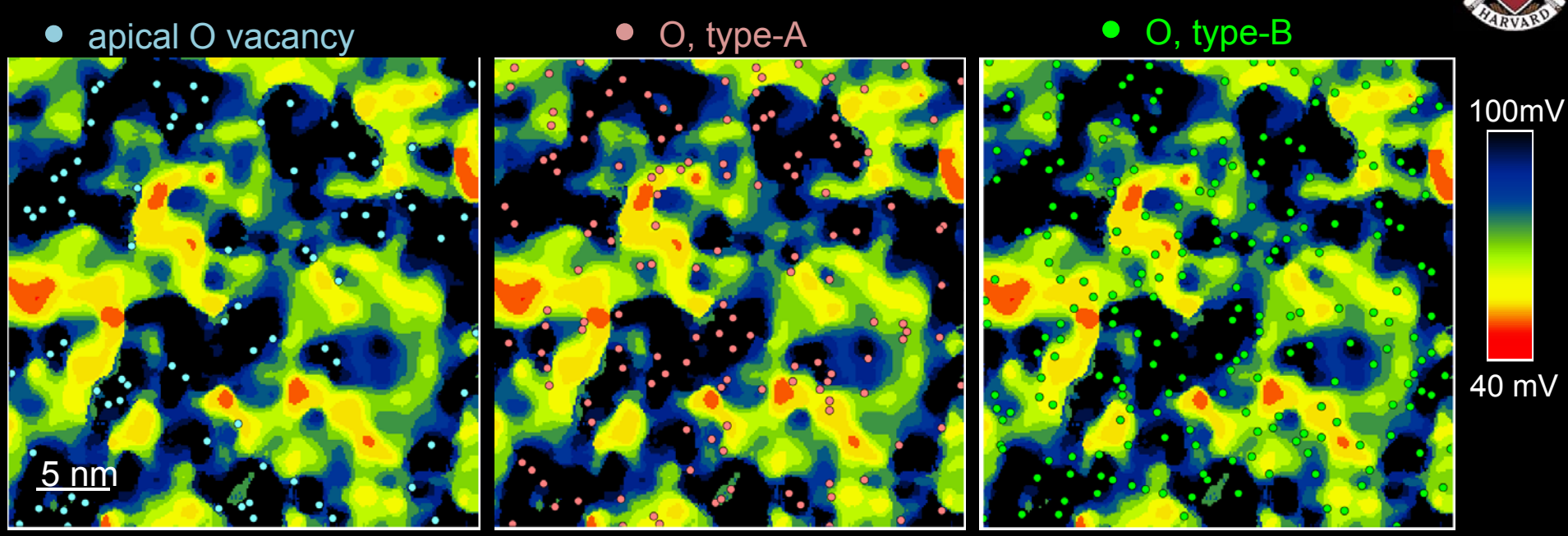
89 meV

Δ_{PG}

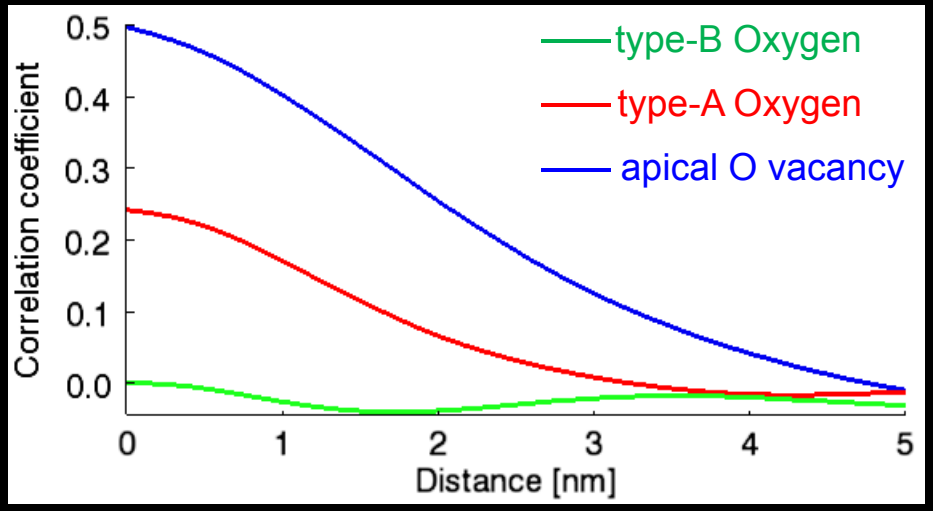
31 meV

29 x 29 nm^2

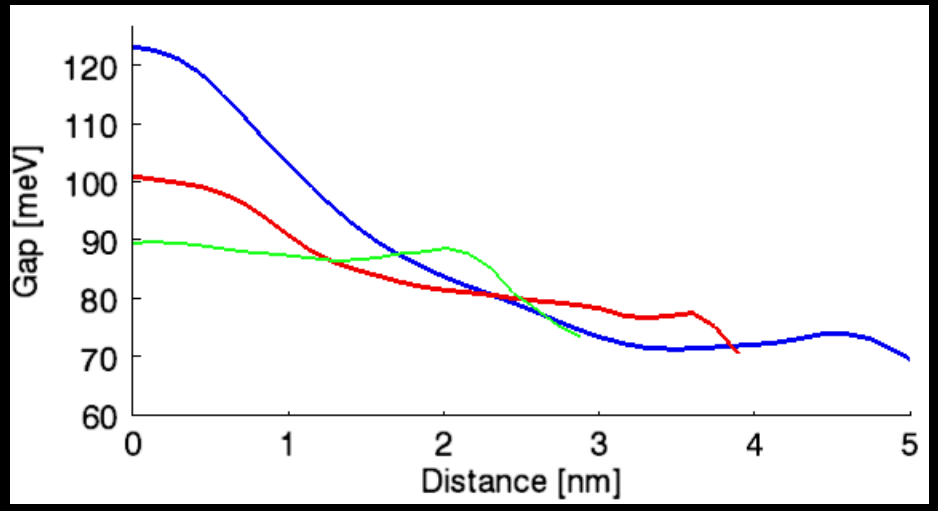
Correlation to Pseudogap (T_c=55K)



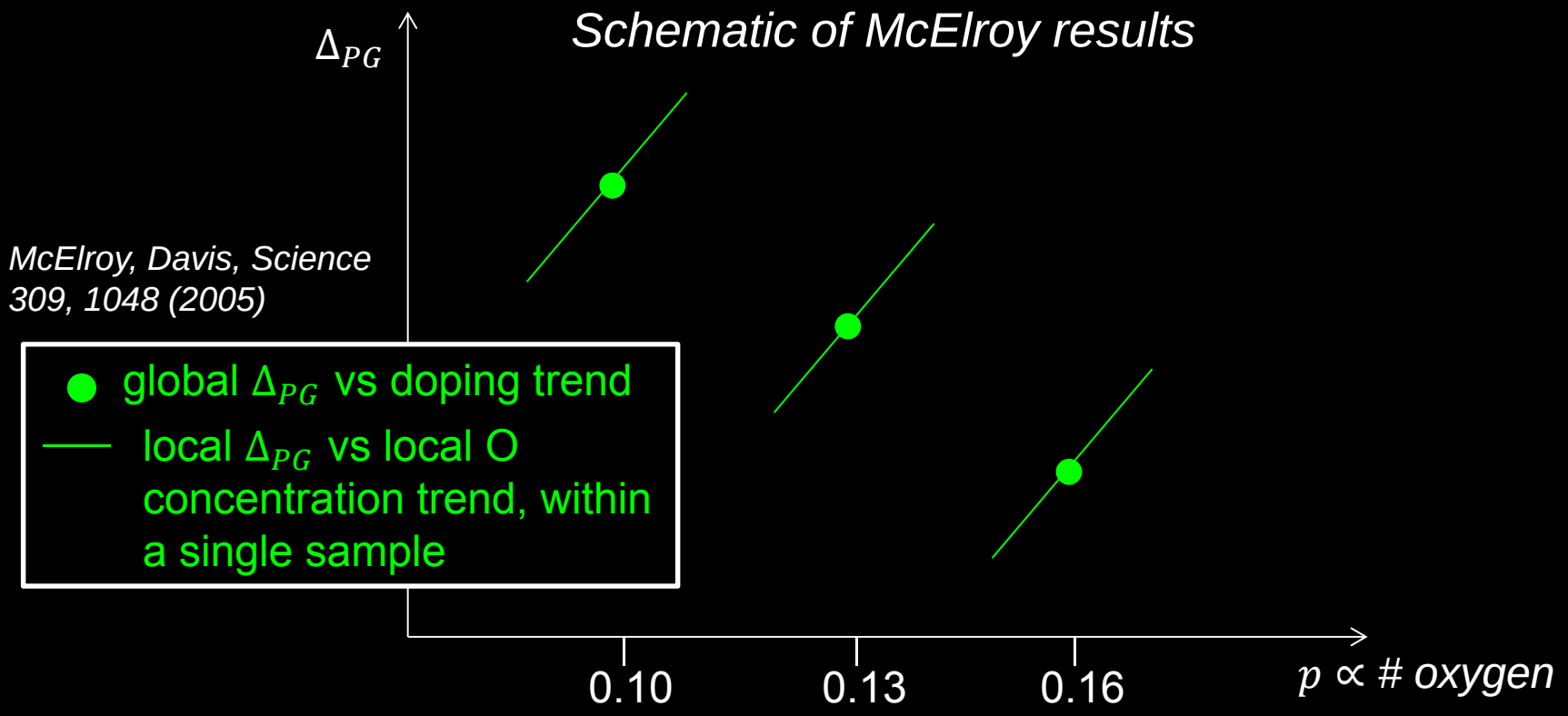
Cross-correlation



Δ vs. distance from nearest impurity



What about that weird local vs. global dependence?



Many explanation attempts, focusing on local strain:

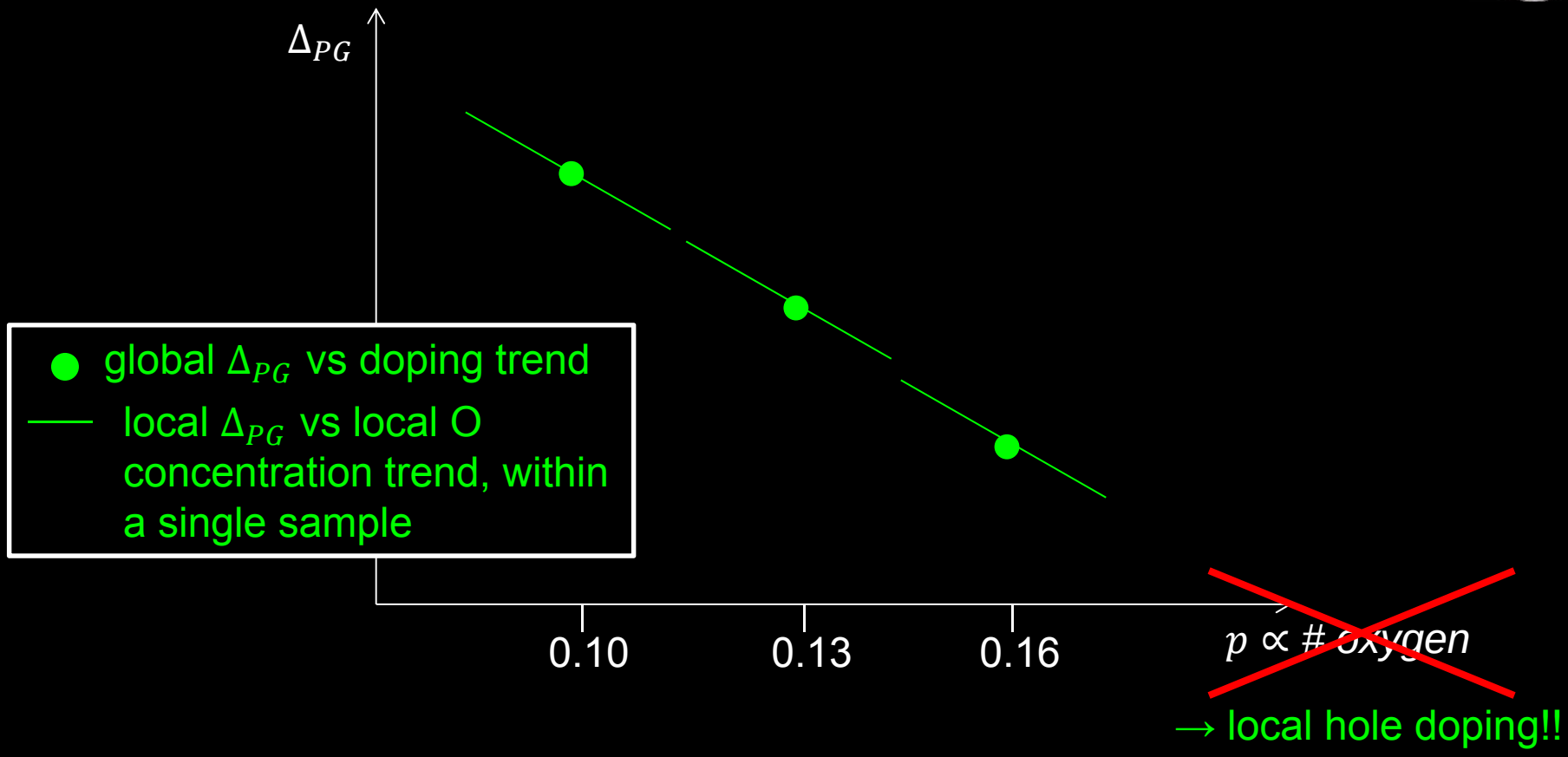
- O → local strain, increases local superexchange $J(\vec{r})$, locally strengthens pairing

  Nunner, Hirschfeld, PRL 95, 177003 (2005)
- local strain of supermodulation controls the pseudogap

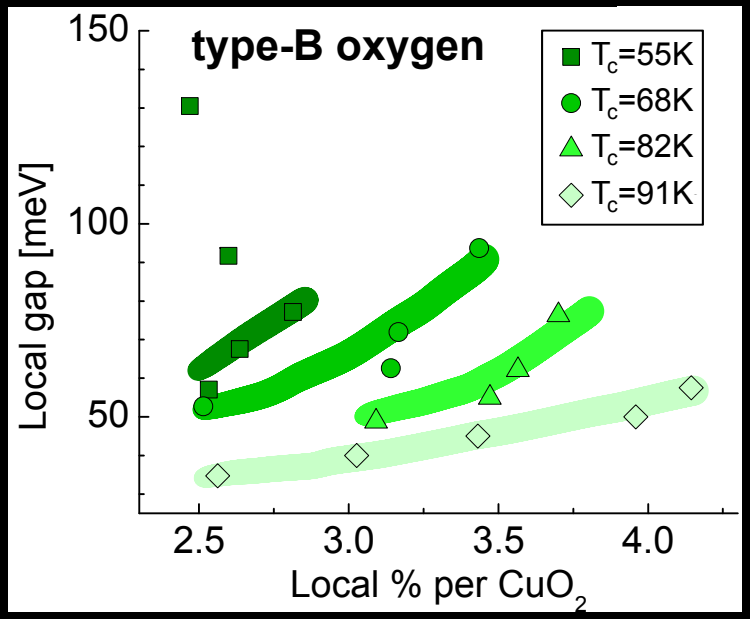
  Slezak, Davis, PNAS 105, 3203 (2008)
- O → accumulates local holes, must include phenomenological increase of pairing strength near the dopants, with specific length scale $0.5a_0$, to match the data

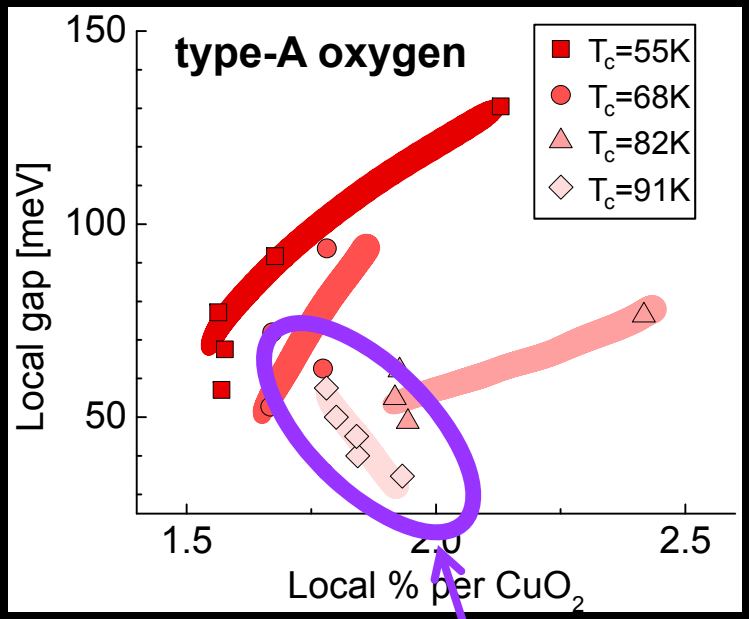
  Chen, Hirschfeld, NJP 14, 033004 (2012)

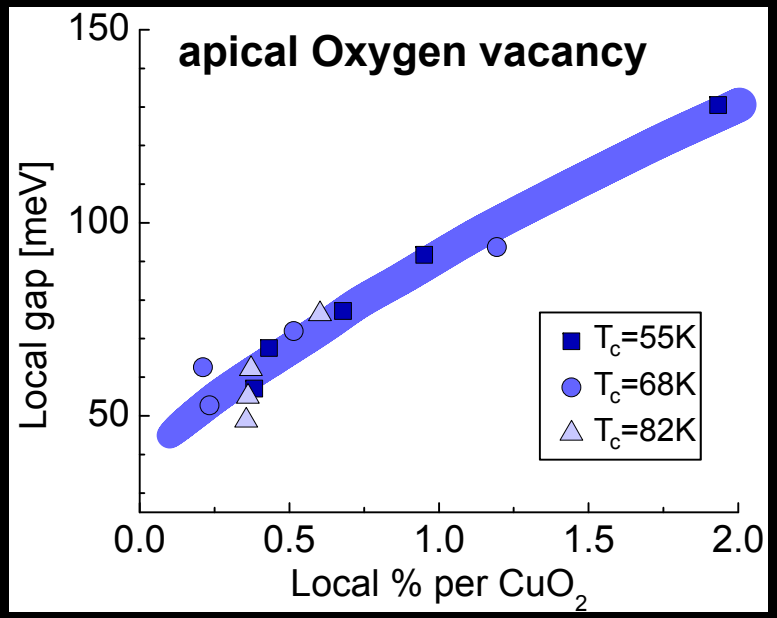
What about that weird local vs. global dependence?



Resolved! local vs. global dependence





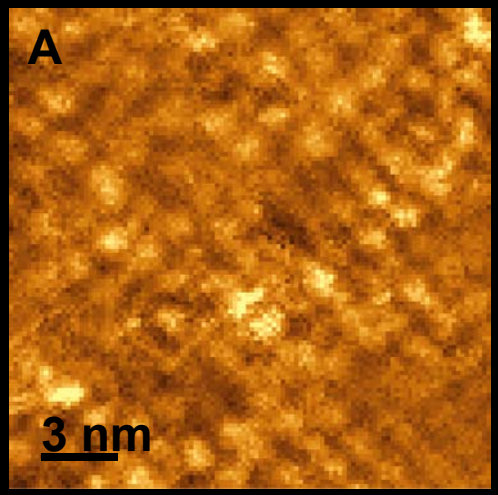


Optimal doping:
no apical O vacancies

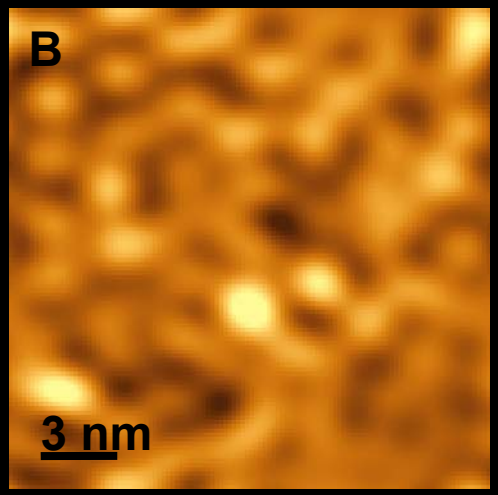
→ local charge controlled by type-A interstitial O

Determining the relationship to “checkers”

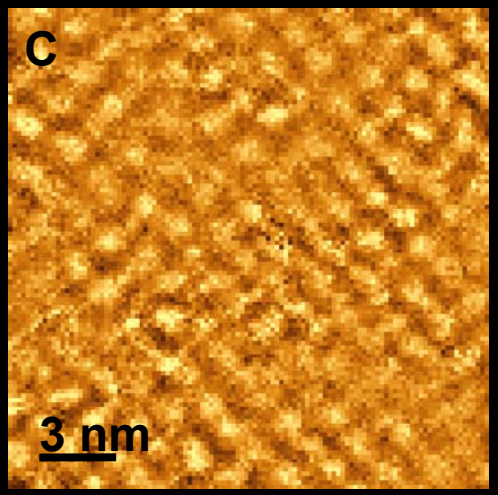
(1) raw data: dI/dV at +21mV



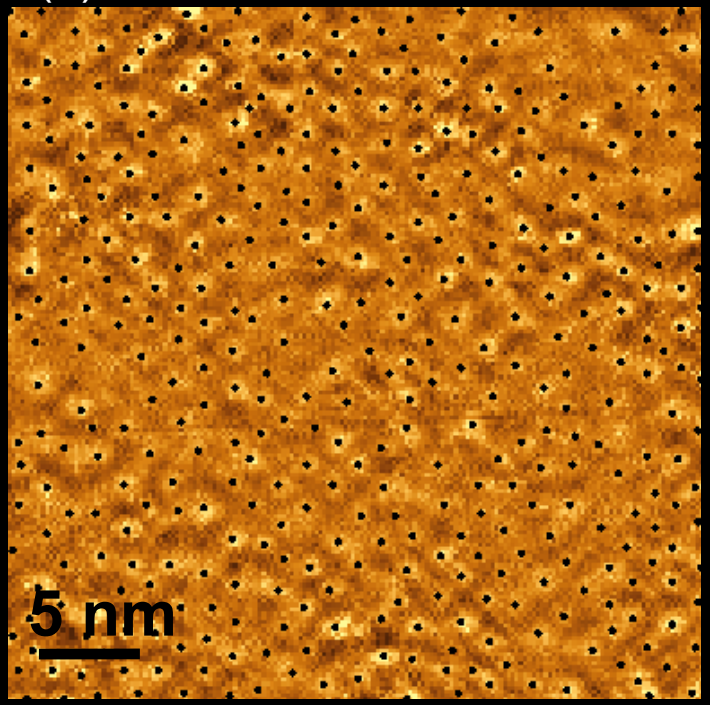
(2) wavelength > $10a_0$



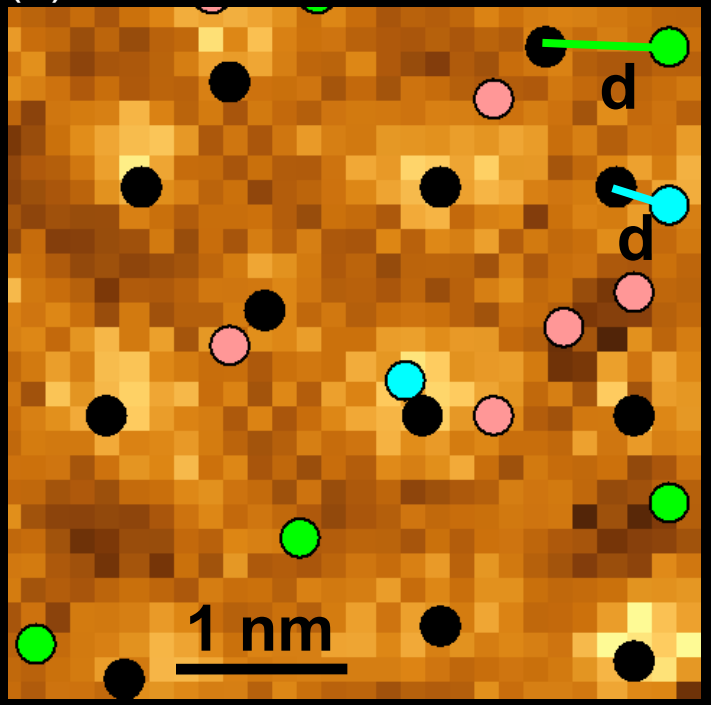
(3) divide: C = A/B



(4) locate all checker maxima



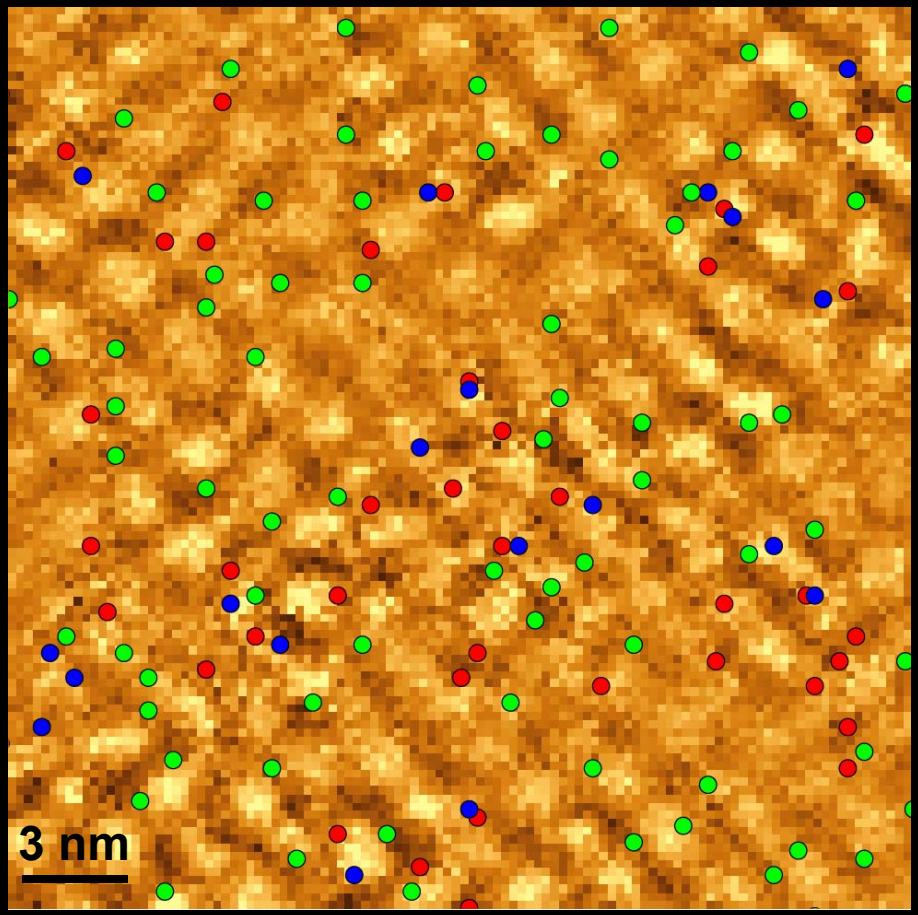
(5) distance to nearest maximum



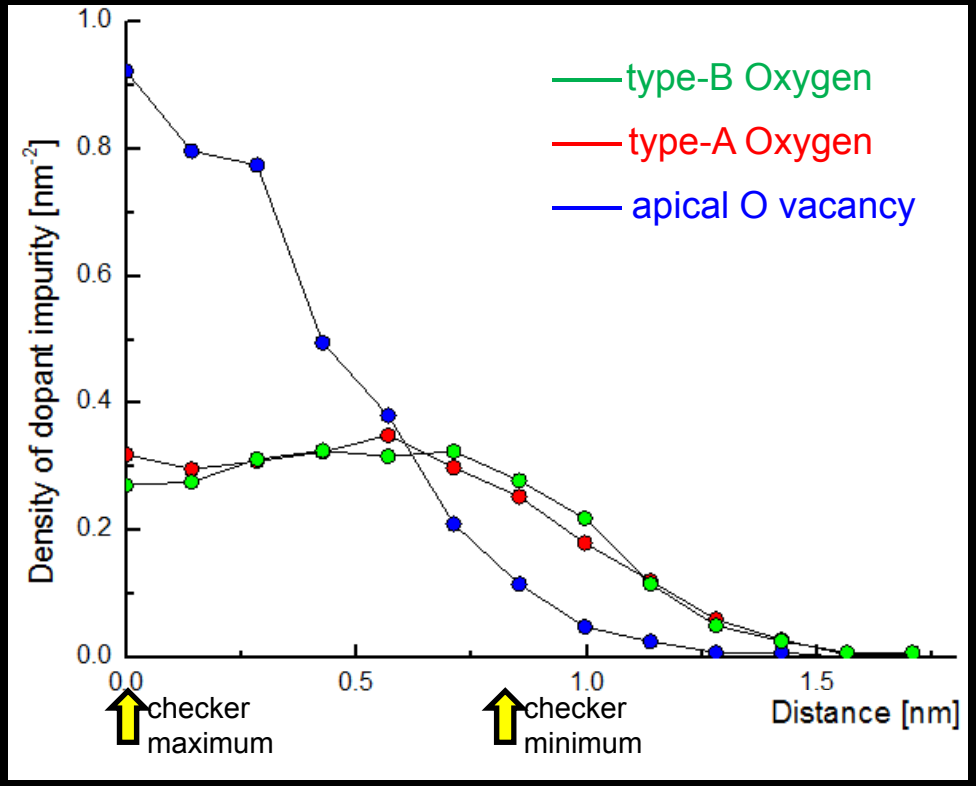
- O, type-A
- O, type-B
- apical O vacancy

“Checkers” are pinned by dopants

V = +24 mV



Low High



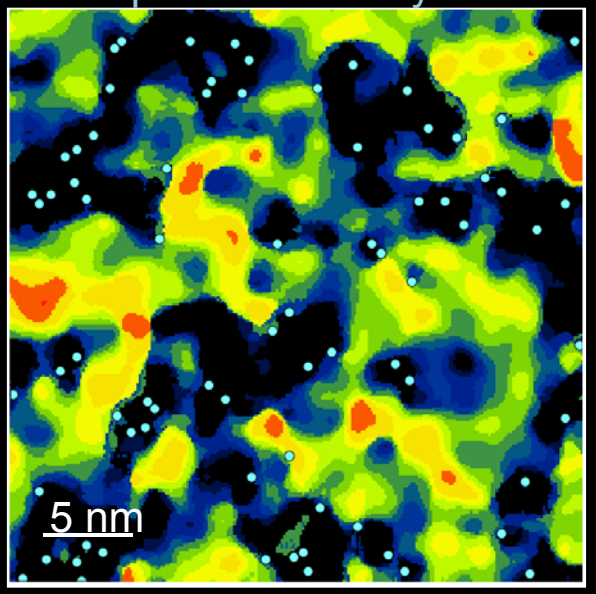
Part I: Conclusions

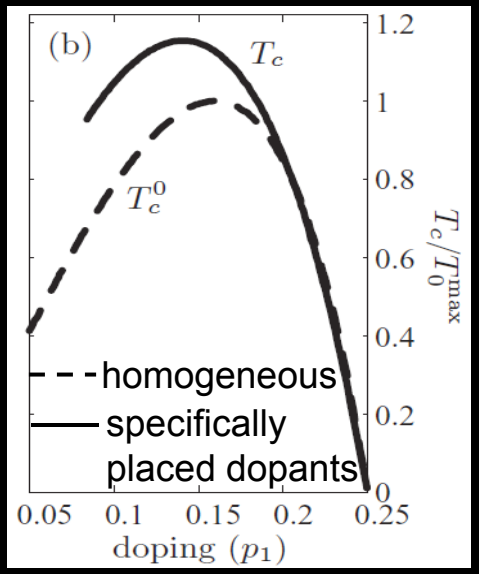
- Doubled the energy range for local spectroscopy on BSCCO
- Found all oxygen dopants: type-A & B oxygen, apical O vacancies
- apical O vacancies
  - strongly enhance the pseudogap energy
  - pin the “checkers” charge order

$$k_B T_c = 1.13 \hbar \omega_D e^{\frac{-1}{N(\varepsilon_F)V}}$$

- type-A oxygens
  - attracted to apical O vacancies in UD
  - control local charge in OPT
- type-B oxygens
  - weakly correlate, secondary effect

To appear in Science (2012)





Next steps:

- control dopants to raise T_c ??
- fit to find effective charge & radius of dopants
- understand how dopants affect stripes vs. checkers

Theory: *Goren, Altman, PRB 84, 094508 (2011)*