Real & k- space imaging of electronic states in Na-doped $Ca_{2-x}Na_xCuO_2Cl_2$

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F.Ronning, K.Shen &Z.X.Shen (Stanford)

M.Azuma & M.Takano (Kyoto)

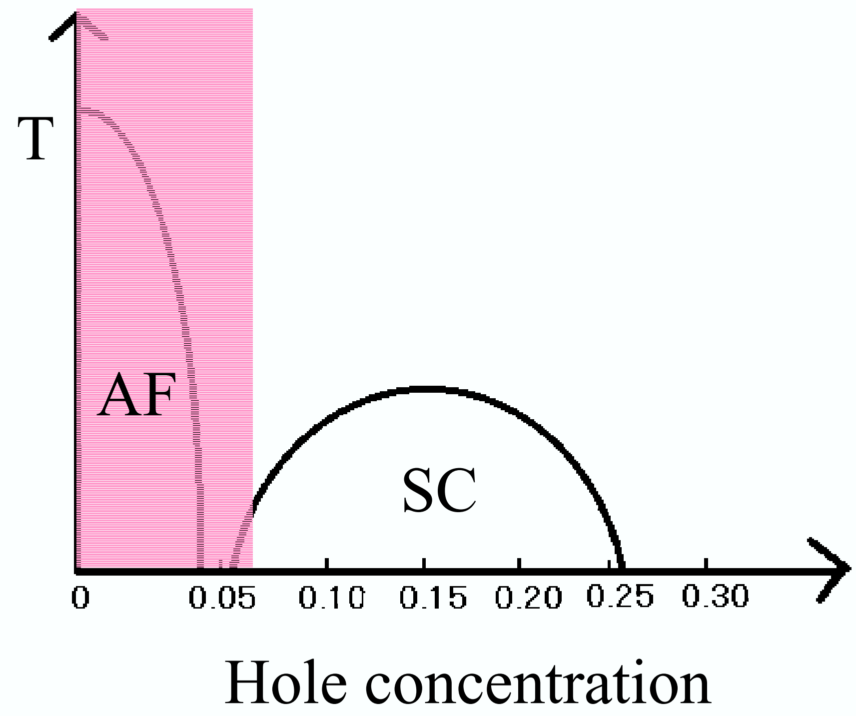
OUTLINE

1. *Motivation & Why* $Ca_{2-x}Na_xCuO_2Cl_2$
2. *Crystal Growth*
3. *Basic Properties - transport, optics & ARPES*
4. *ARPES observation of the chemical potential shift from Mott Insulator to lightly doped inuslator*
5. *STM/STS observation of nano-scale electronic inhomogeneity in lightly doped* CuO_2 *plane*

   organized structure ～*5a width river "Kishimen"*
6. *discussion*

Motivation
– Physics of lightly doped Cuprate

evolution of magnetic insulator into high-T_c SC upon carrier doping



- How FS developes?

- link between d-wave Mott gap, pseudo gap and SC gap?

- Intrinsic Electronic inhomogeneity? (electronic phase separation, poorly screened impurity) **Stripe?**

⋮

Real space/k-space imaging of electronic structure by STM/STS & ARPES (in the lightly doped region)

Surface sensitive technique & require high quality of surface

BSCCO chemically unstable near Ins.
- Need for New System

Bi cuprates:

favorites of STM/ARPES people, because of the easy cleavage

but not stable when heavily underdoped

M^2S 2000 Conference summary

Materials & Properties

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surfaces. We should pay more attention to developing materials suitable for such surface sensitive experiments. This is particularly true for the heavily underdoped region, where high-quality Bi single crystals are hard to come by. The exploration of the heavily underdoped region becomes increasing important to establish the connection between the parent Mott insulator and the key features outlined above.

Why $(Ca,Na)_2CuO_2Cl_2$?

- ***Excellent cleave***

only Bi and oxychloride

- ***No modulation, tetragonal down to low-T***

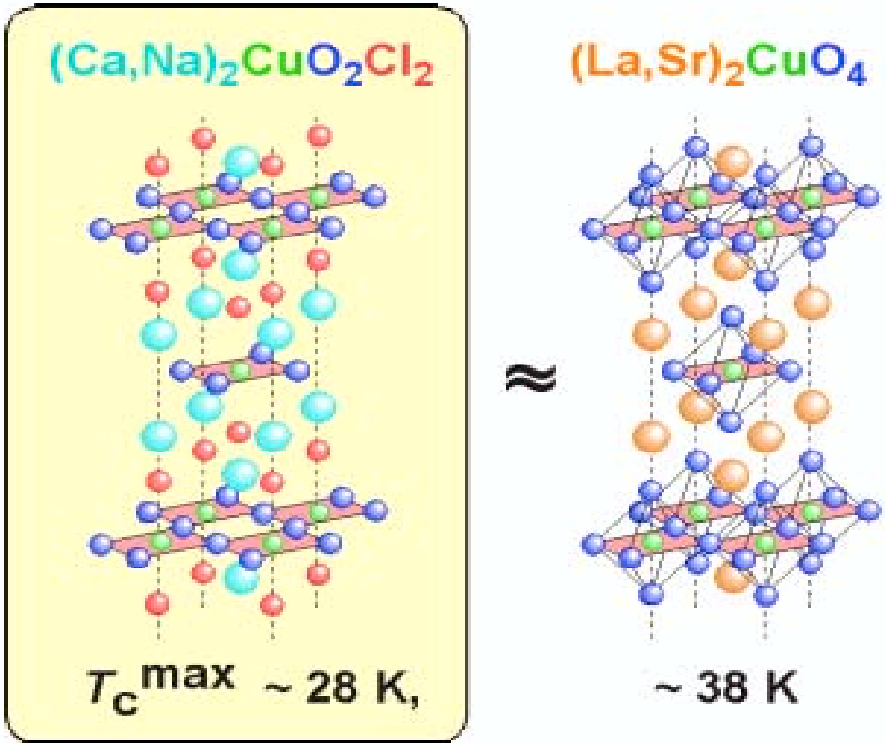
Undistorted CuO_2 monolayer

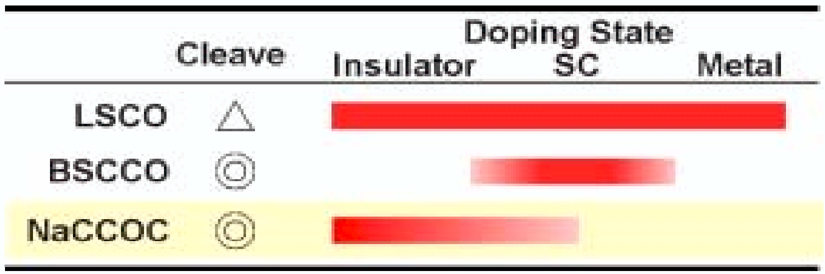
ideal candidate for STM &ARPES studies

- ***Phase exists from Ins. to UD SC***

Hole-doping achieved by Na^+ substitution for Ca^{2+}

Z. Hiroi *et al*., Nature **37**1, 139 (1994).





Parent compound $Ca_2CuO_2Cl_2$ ARPES Ins. standard

F.Ronning, Z.X.Shen *et al.* Science 282, 2067 (98)

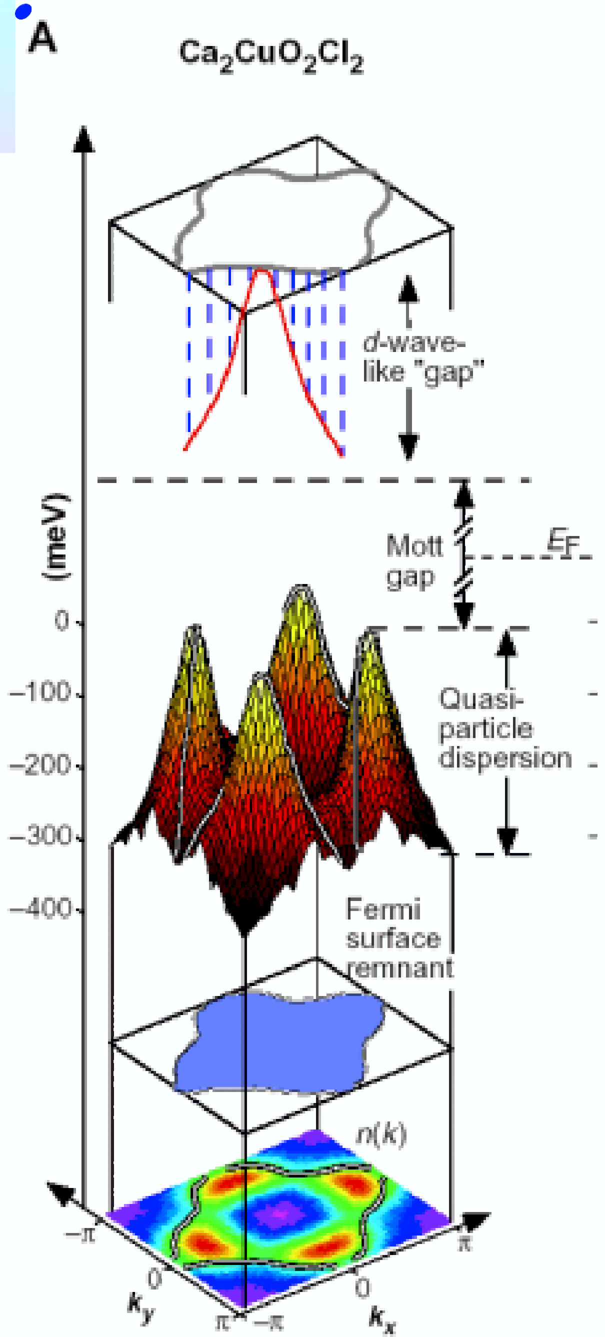
Mott gap with d-wave like dispersion

→

Evolution of d-wave Mott Ins into SC?

Bad news:Na-doped phase formed only under High Pressure

Na-doping requires high pressure synthesis under several GPa & No doped single crystal available



Single Crystal Growth under High Pressure

with Azuma & Takano

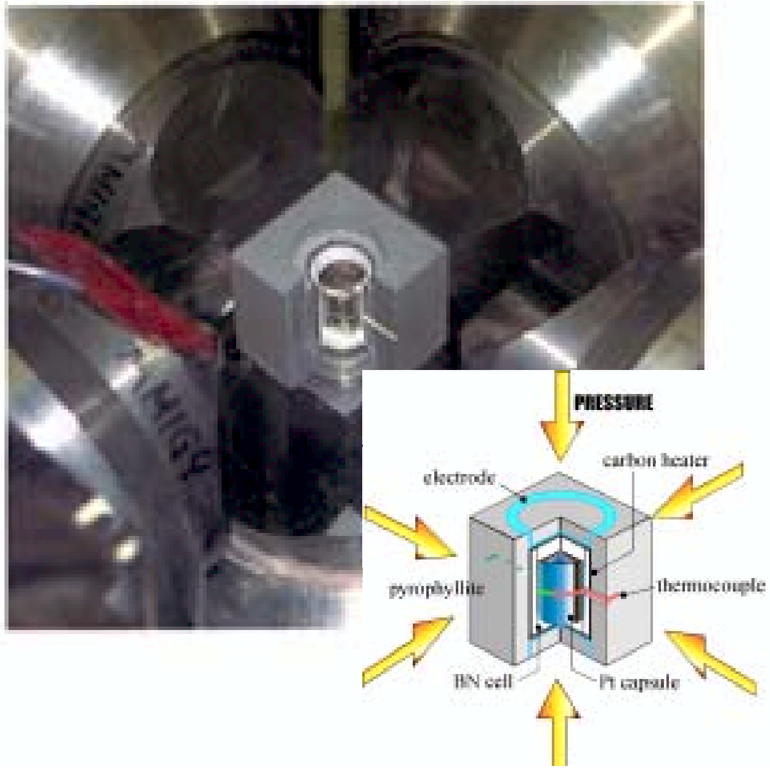
Specially designed
Cubic-Anvil type HP apparatus

☆ Pt capsule { Diameter: 9.6 mm
height: 15 mm

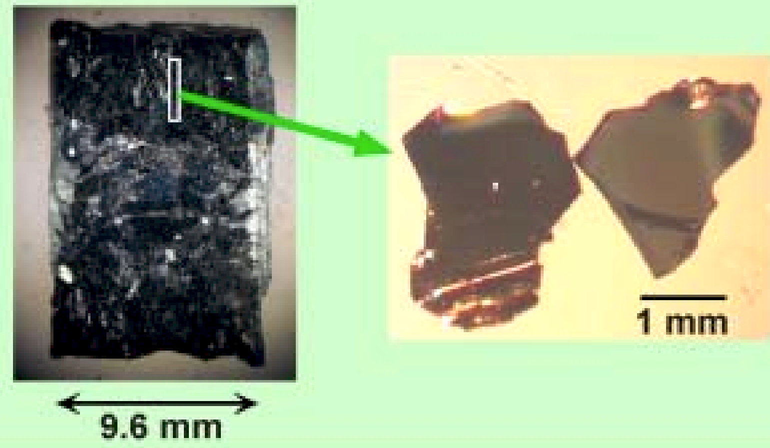
5.5 GPa in volume ~ 1 cm^3

$Ca_2CuO_2Cl_2$ Powder
NaCl (flux, Na source)
$NaClO_4$ (O_2 & Na source)

2 ~ 5.5 GPa
1230 ~ 970℃ / 30 hrs



$(Ca,Na)_2CuO_2Cl_2$ Crystals



recent success includes *$PrNiO_3$* a high valence compound

Chemistry - control of Na content

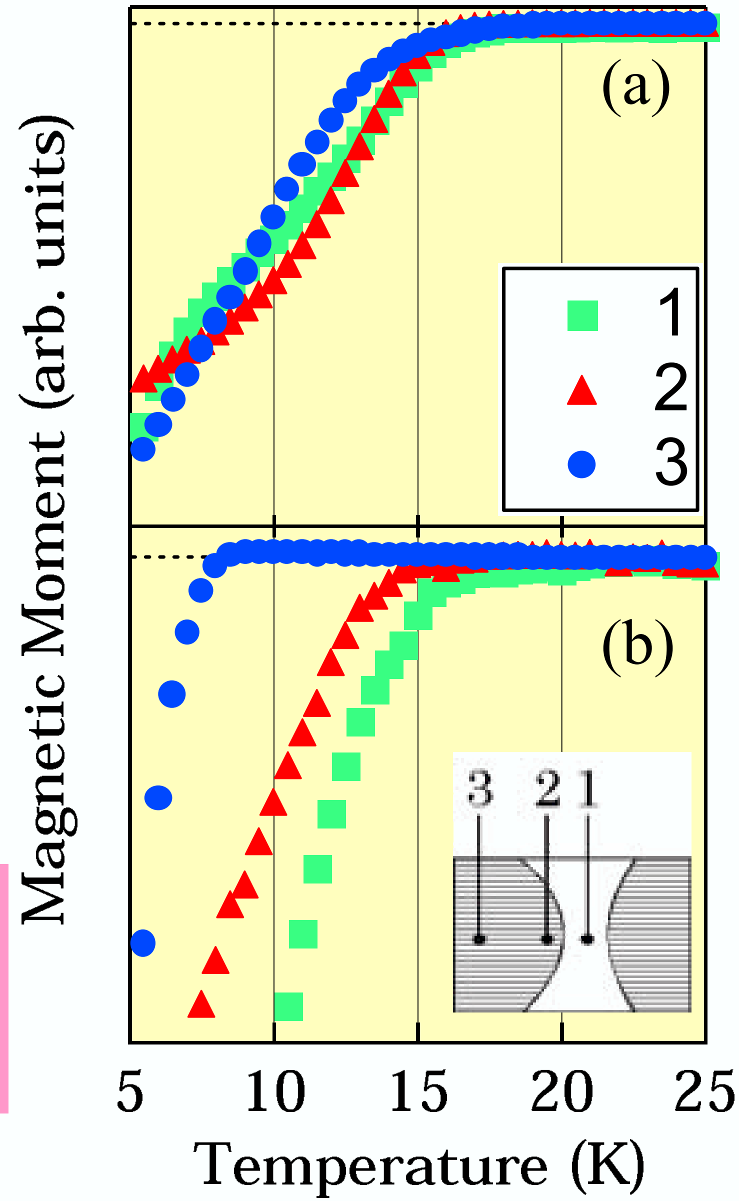
(a) $Ca_2CuO_2Cl_2$+0.2$NaClO_4$+0.2NaCl

(b) $Ca_2CuO_2Cl_2$+0.2$NaClO_4$

4GPa, 1230-1050℃ / 30hrs

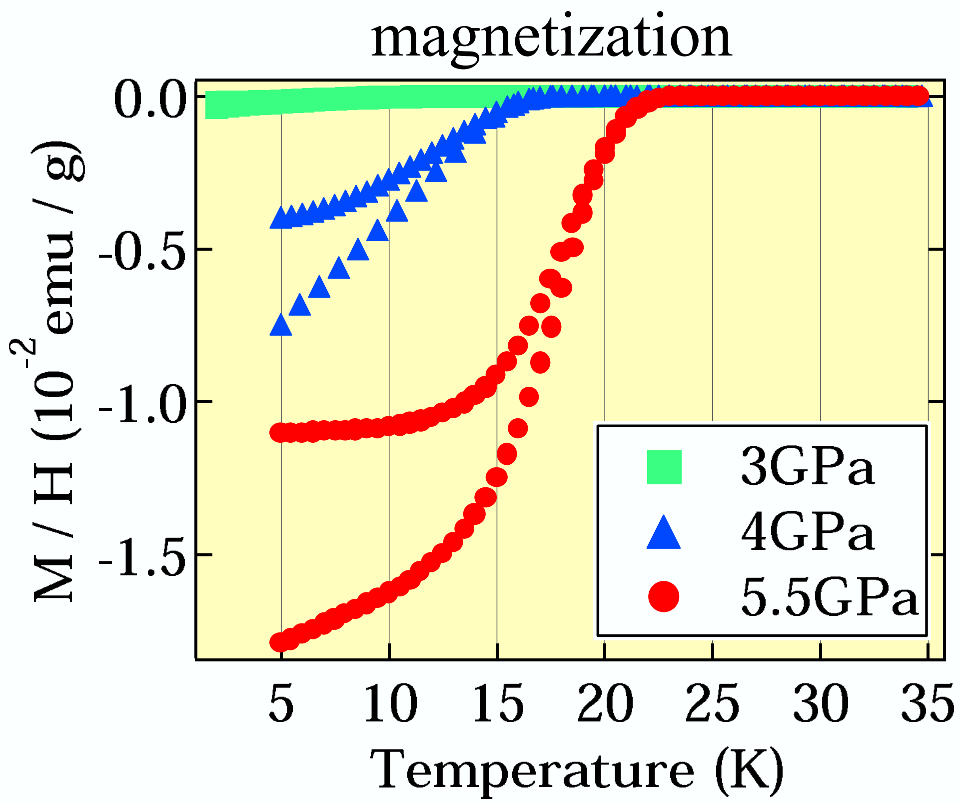
(b) Na content x changes from place to place

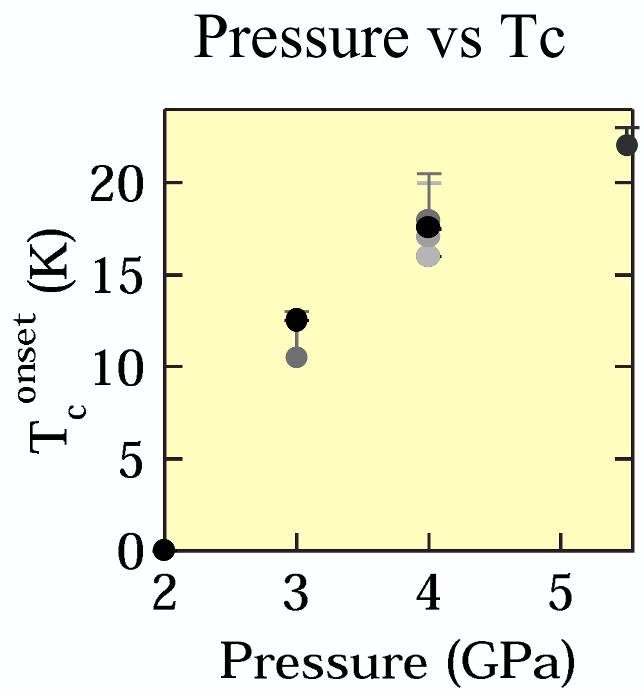
(a) ***substantially excess Na***
more homogeneous
because the solubility limit determines x



Pressure control of Na content

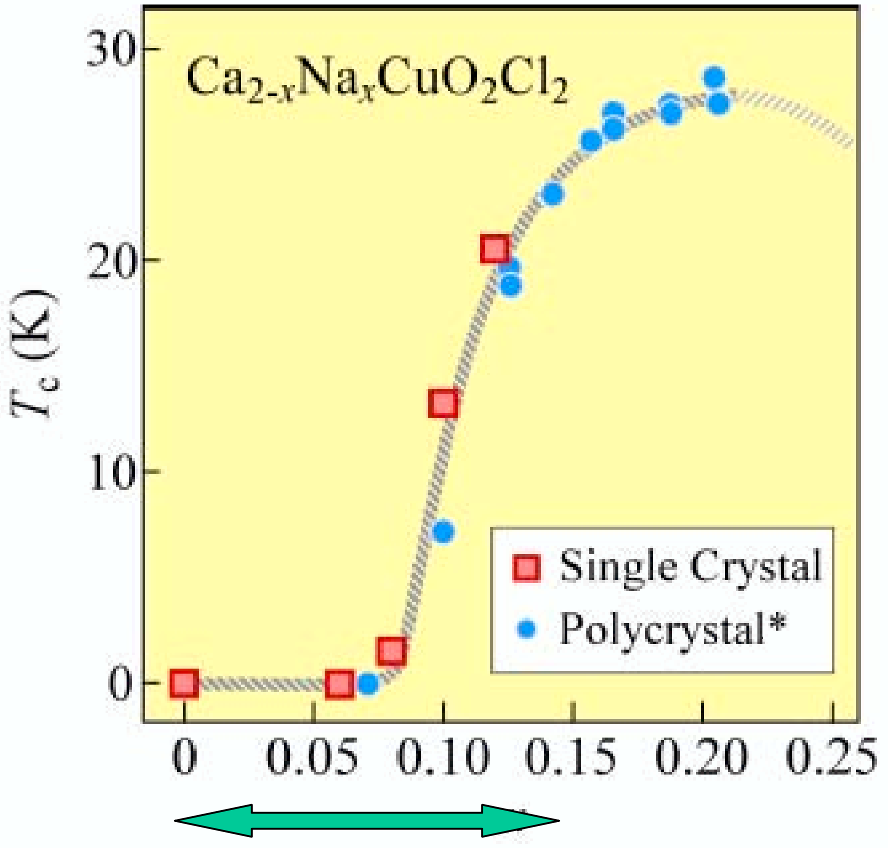
$Ca_2CuO_2Cl_2$+0.2$NaClO_4$+0.2NaCl, fixed





Na content can be controlled by P through solubility limit
→ by far more homogeneous

Phase Diagram of $Ca_{2-x}Na_xCuO_2Cl_2$ Single Crystals



Single crystal available from x=0 to 0.14

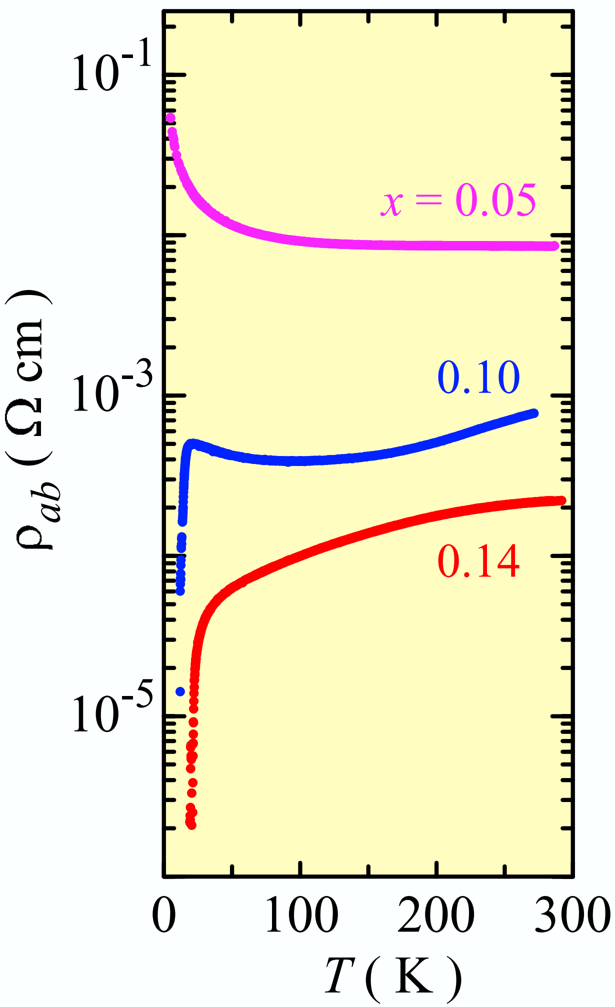
-Evolution of d-wave Mott gap

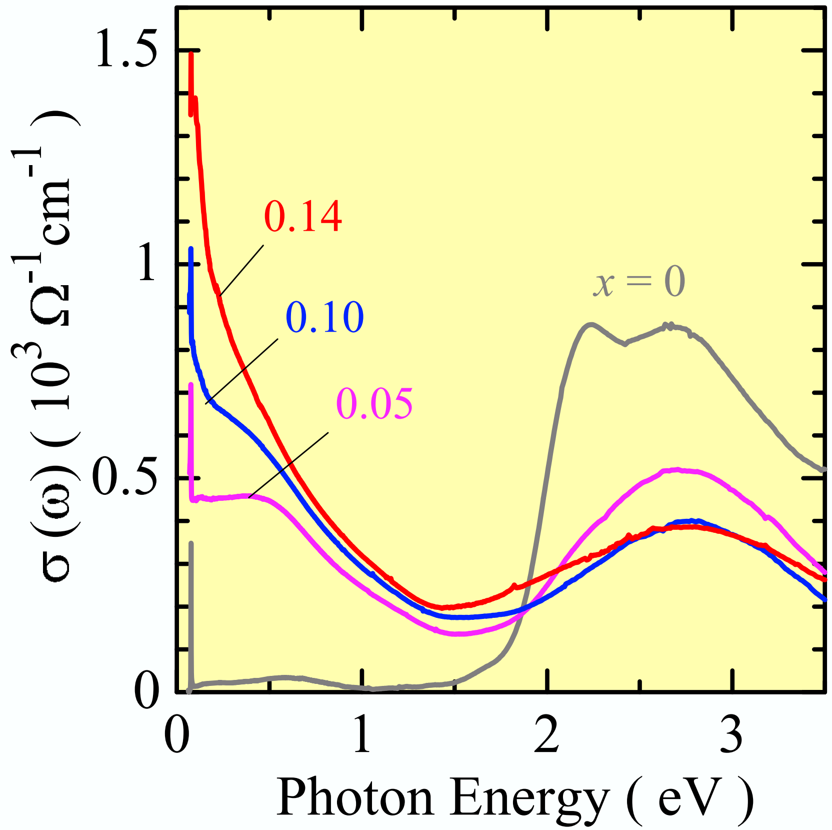
ARPES with Shen G

- Real space imaging of possible electronic phase separation

STM

Resistivity& Optical conductivity





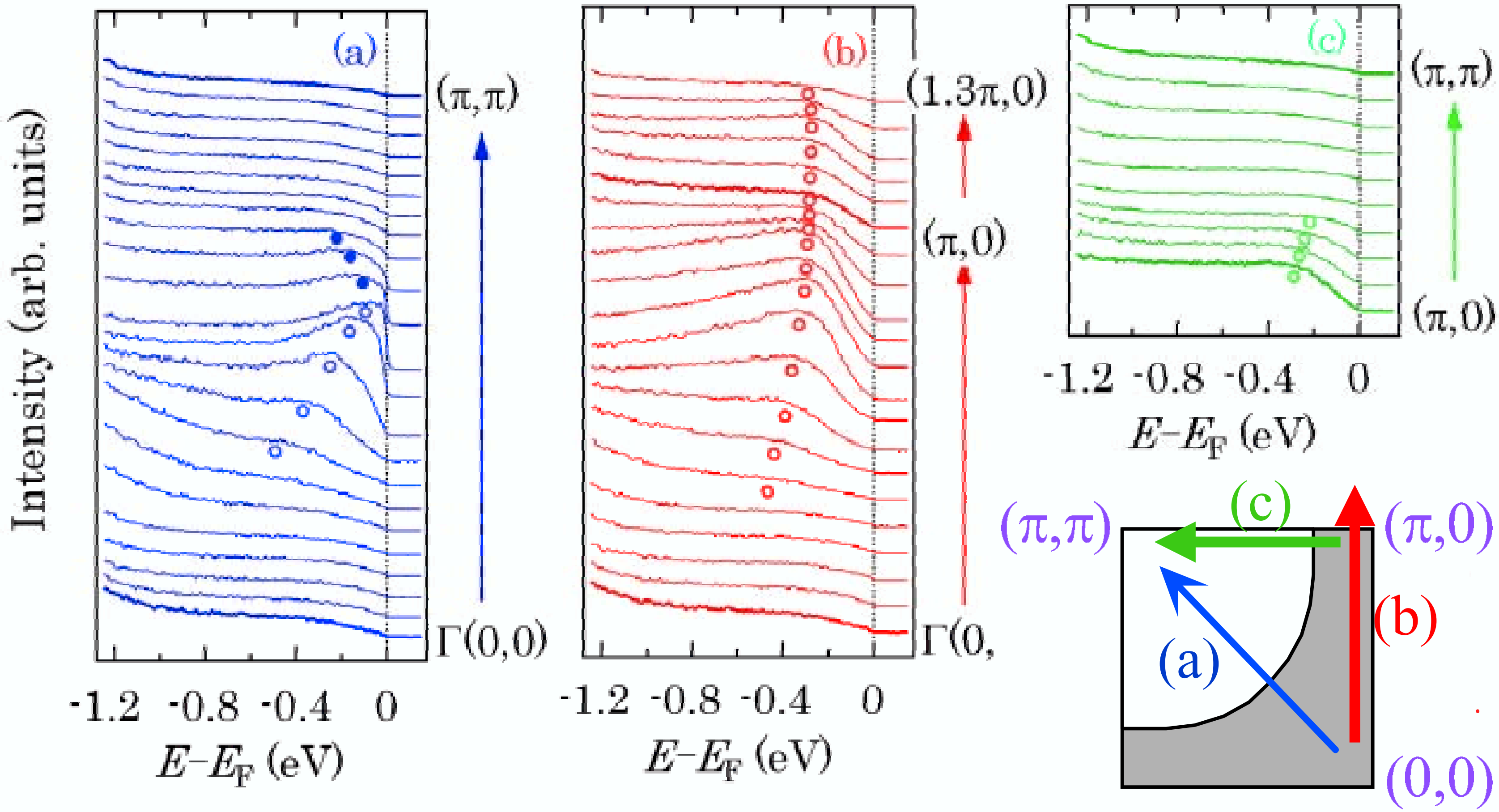
M-I (likely S-I) transition at x=0.05-0.1

ARPES on $Ca_{1.9}Na_{0.1}CuO_2Cl_2$ single crystal

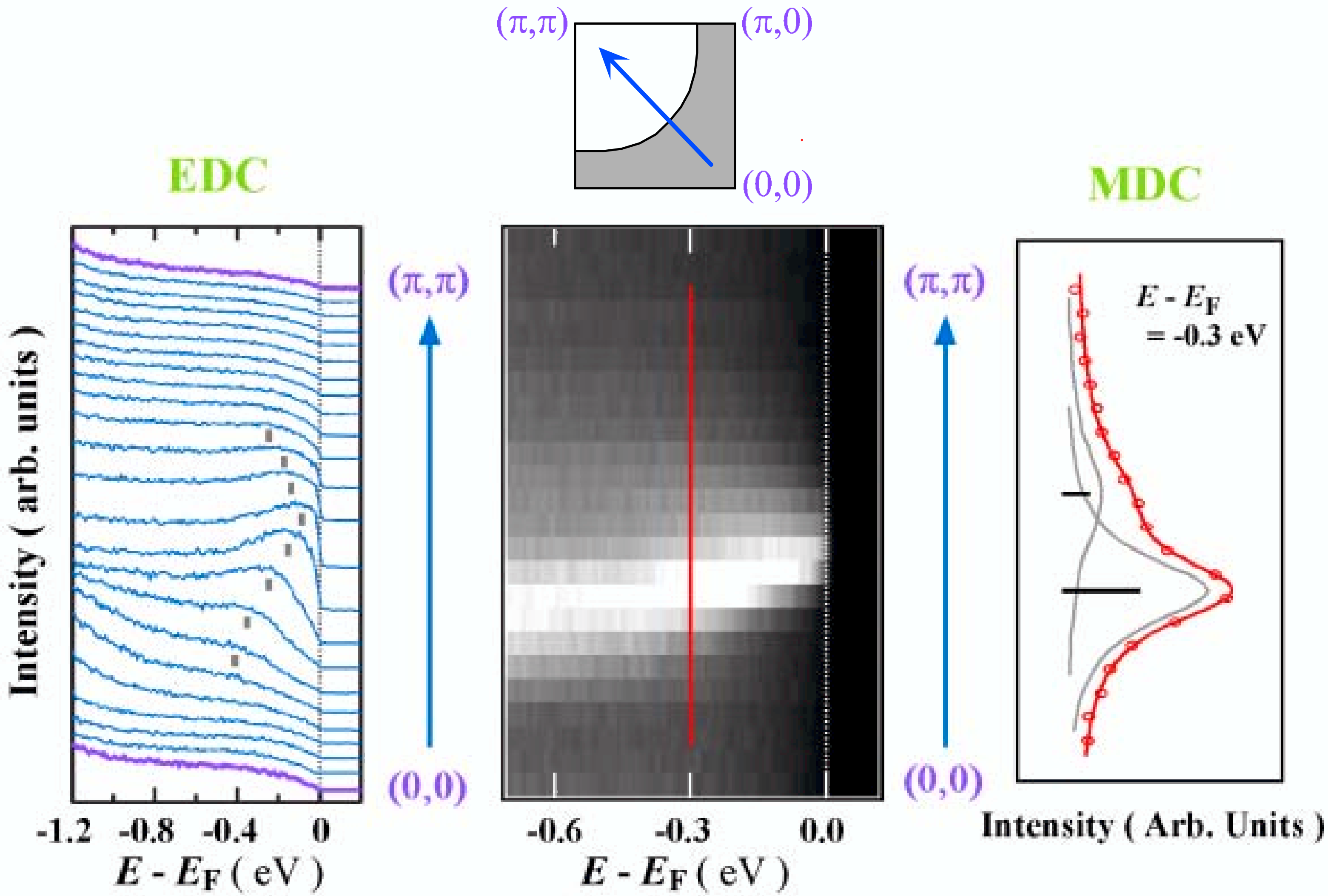
shadow band around (π/2,π/2)

Suppression of weight around (π, 0)

extremely large pseudogap 0.1-0.2 eV!



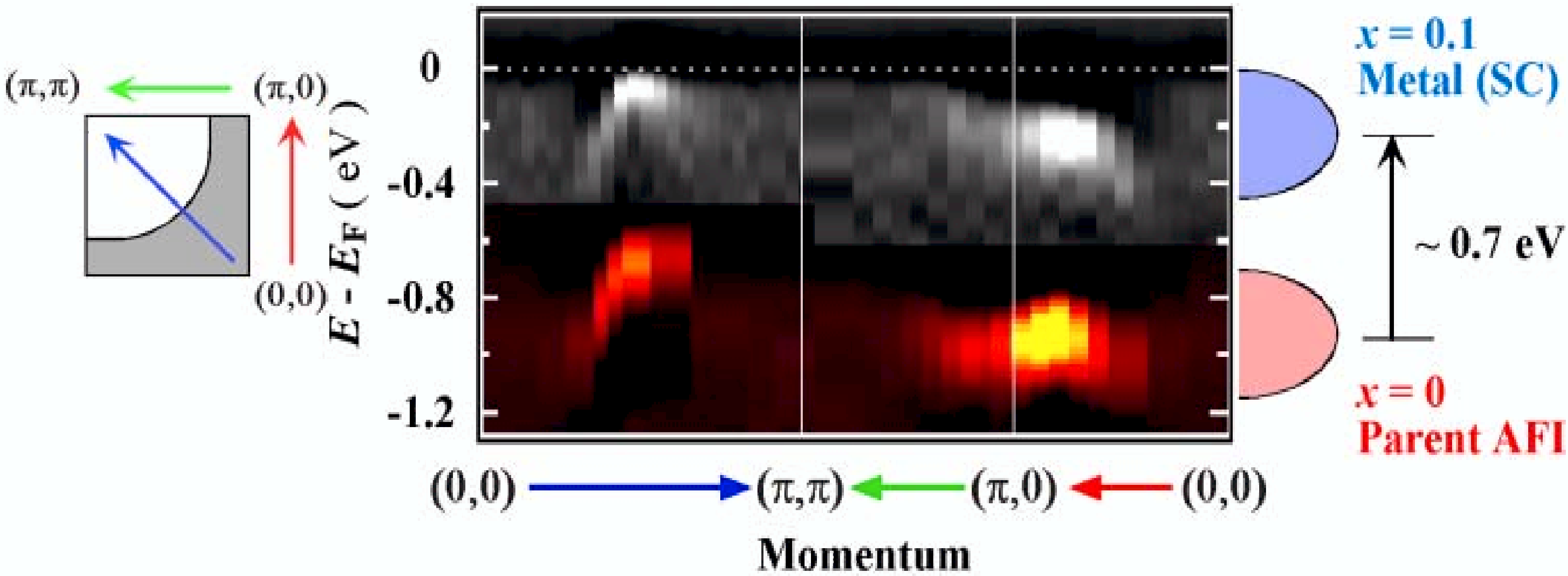
ARPES Spectra along (0,0) to (π,π)



Fermi Surface Crossing around (p/2,p/2)
Dispersion Pulling Back after FS-Crossing -- "Shadow Band"

Electronic evolution from AFI to SC in $Ca_{2-x}Na_xCuO_2Cl_2$ *"Chemical Potential Shift"*

ARPES With Z.X.Shen (Stanford)

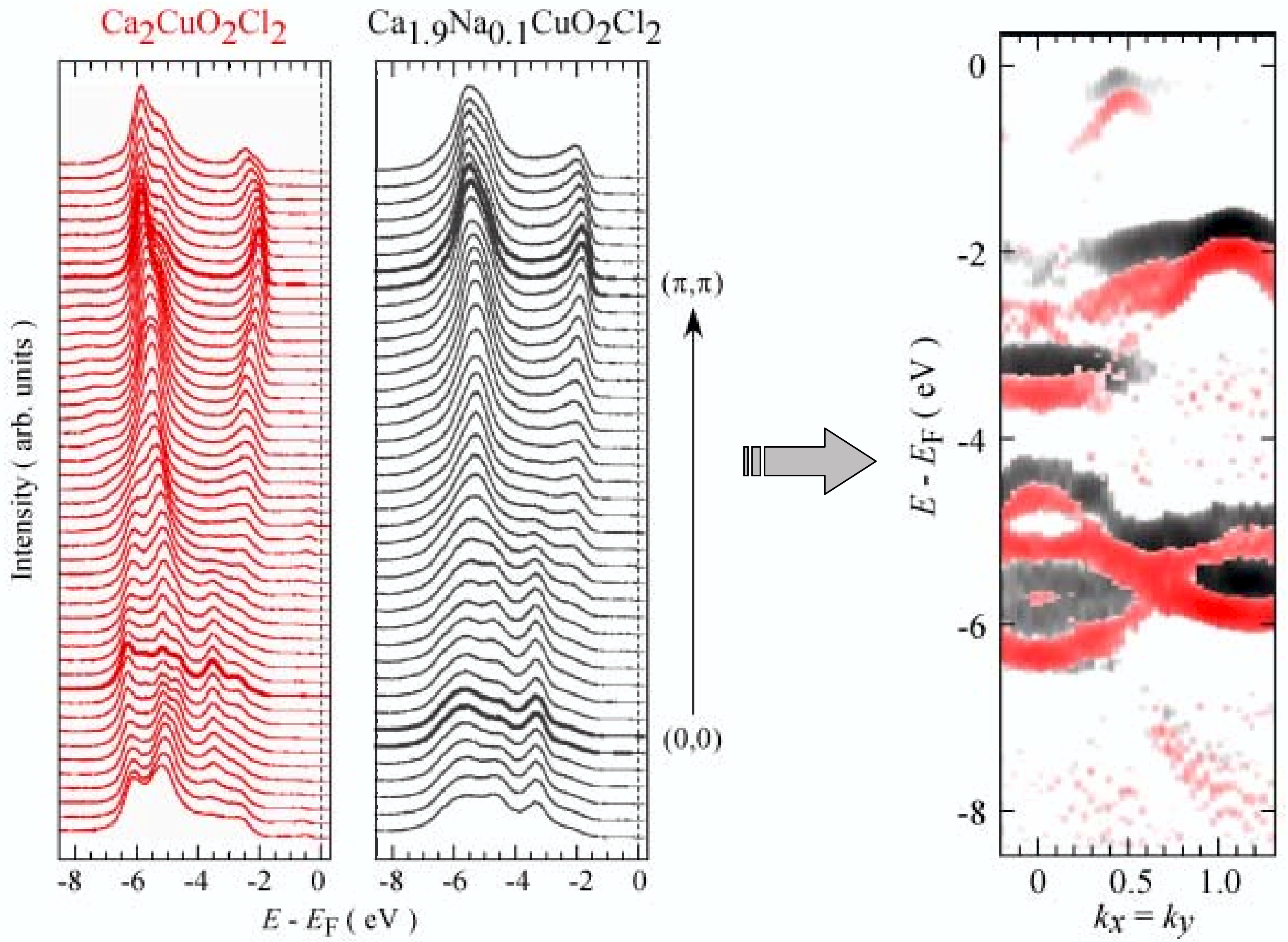


Fingerprints of the parent AFI

(1) Shadow Band near (π/2,π/2)

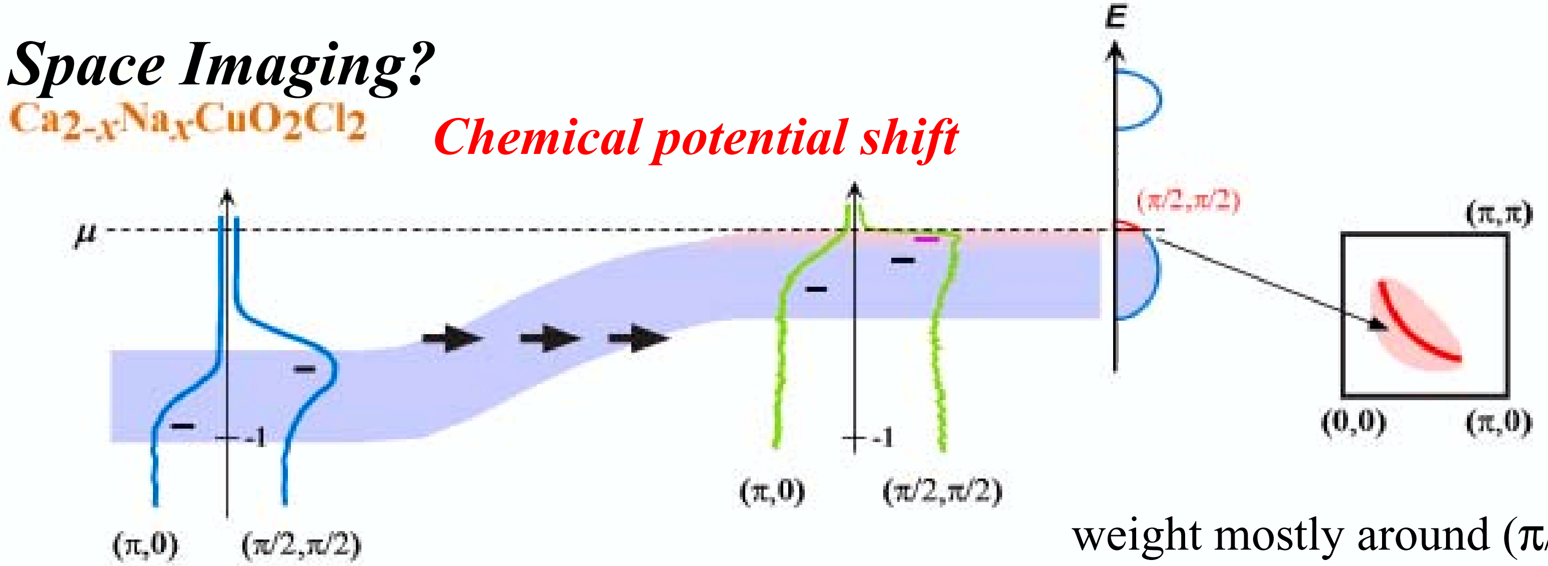
(2) Large Pseudo Gap around (π,0)

Valence Band Dispersion

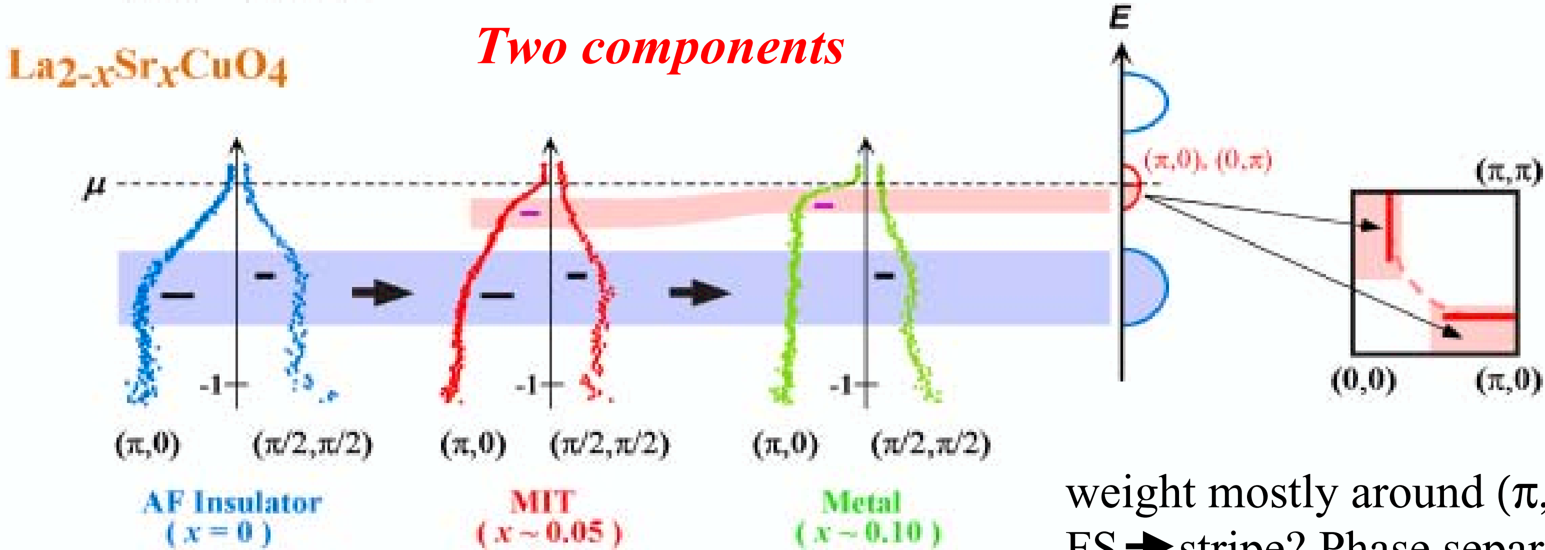


Electronic Evolution from AFI to SC
– contrast between $Ca_{2-x}Na_xCuO_2Cl_2$ & $La_{2-x}Sr_xCuO_4$

Real Space Imaging?



weight mostly around (π/2,π/2)



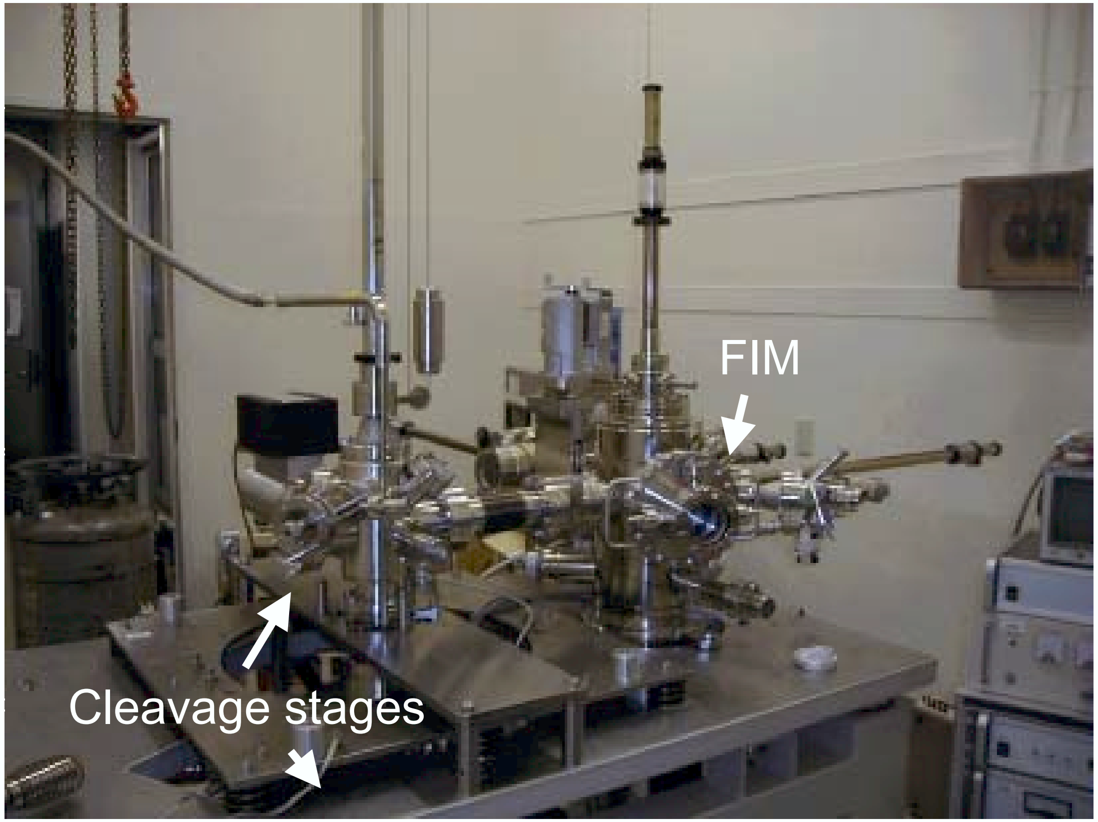
weight mostly around (π,0) 1D FS➔stripe? Phase separation?

New STM installed at Tokyo

Ultra high vacuum
(P ~ 10^{-11} Torr)

Low temperature
(T ~ 0.3 K)

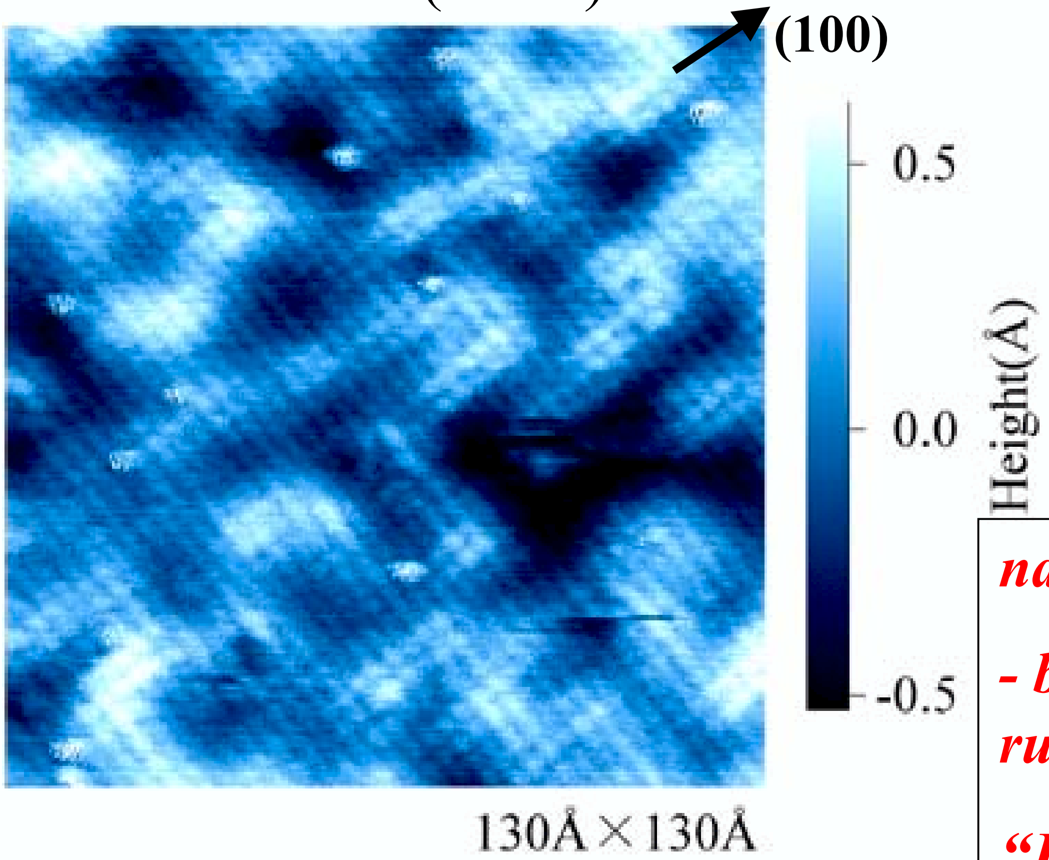
High magnetic field
(H ~ 11 T)



- *Low-temperature cleavage stages*
- *In-situ tip preparation using a field-ion microscope*

The first STM image of $Ca_{1.9}Na_{0.1}CuO_2Cl_2$

x~0.10 (4GPa)



P ~ 10^{-11} torr

T = 14K Sample bias : -100mV

I_t ~ 0.05nA constant current

-low temperature cleave, the same as ARPES , should have surface of similar quality

-atomic image observed from the first attempt

-square lattice with 3.9A spacing, ionic C a Cl layer

nano-scale (organized) structure

- bright river with 5a width are running along (100)

"Kishimen" (Japanese fettuccine)

not a terrace but electronic

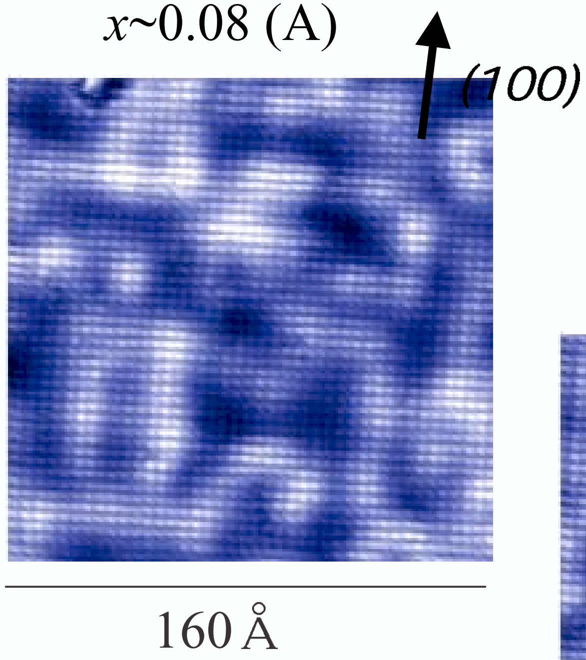
"Kishimen" like segments running along (100) with ～5 a (2nm) width

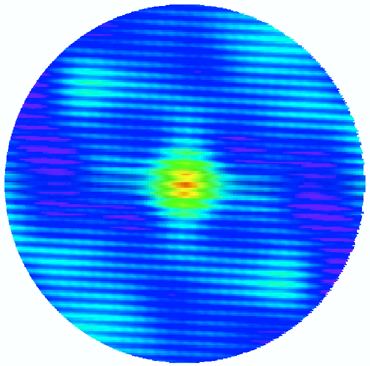
STM Images of $Ca_{1.92}Na_{0.08}CuO_2Cl_2$ (not SC)

$P \sim 10^{-11}$Torr, $T = 7$K

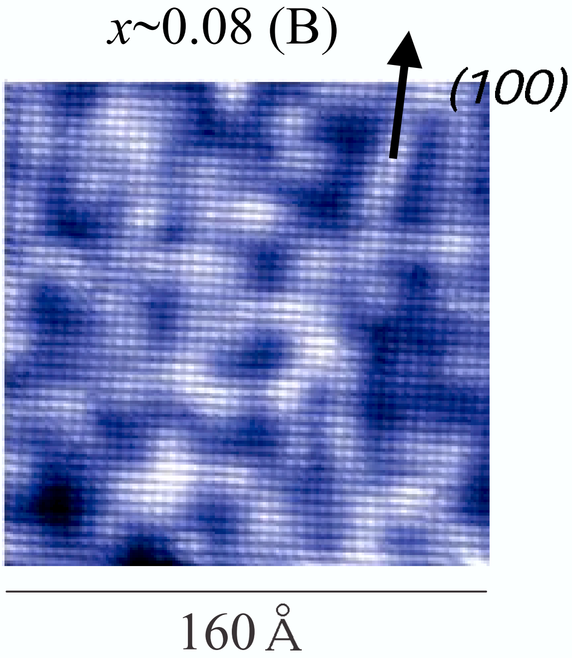
Sample bias voltage: V_s = -250mV

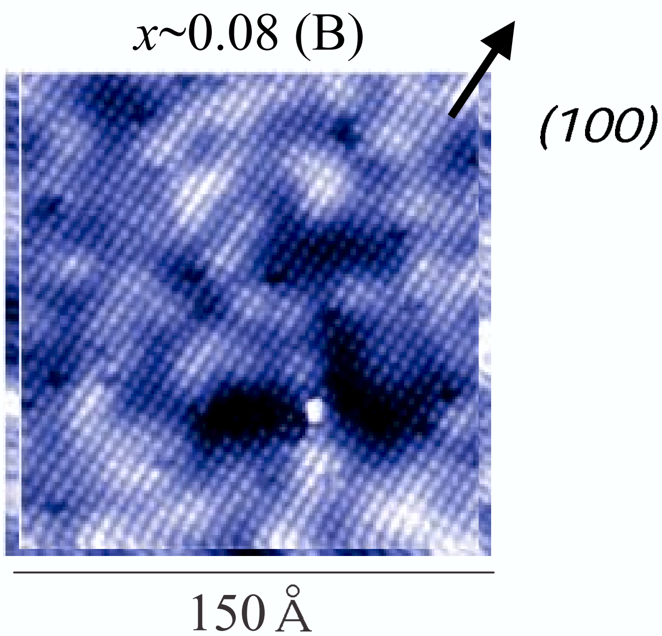
Tunneling current: $I_t \sim$ 0.01nA





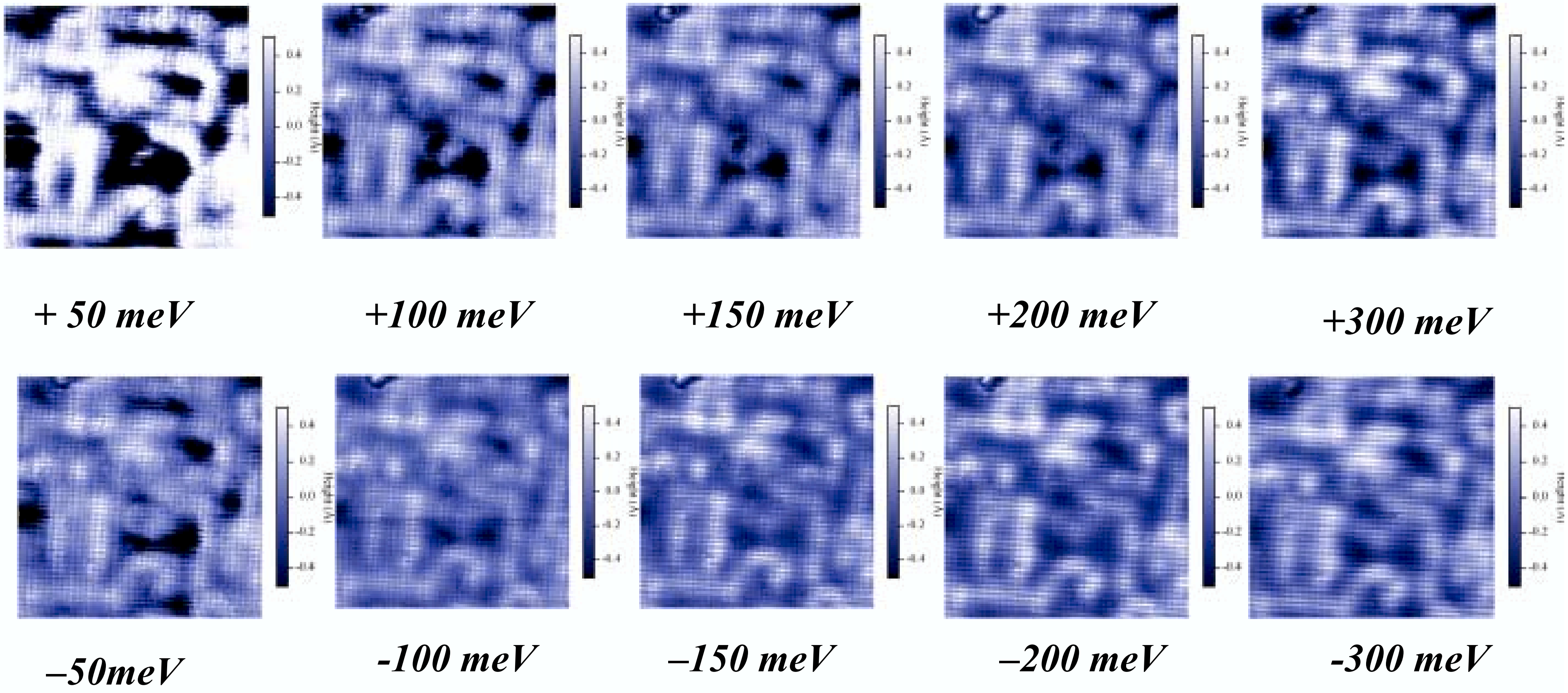
Auto-Correlation





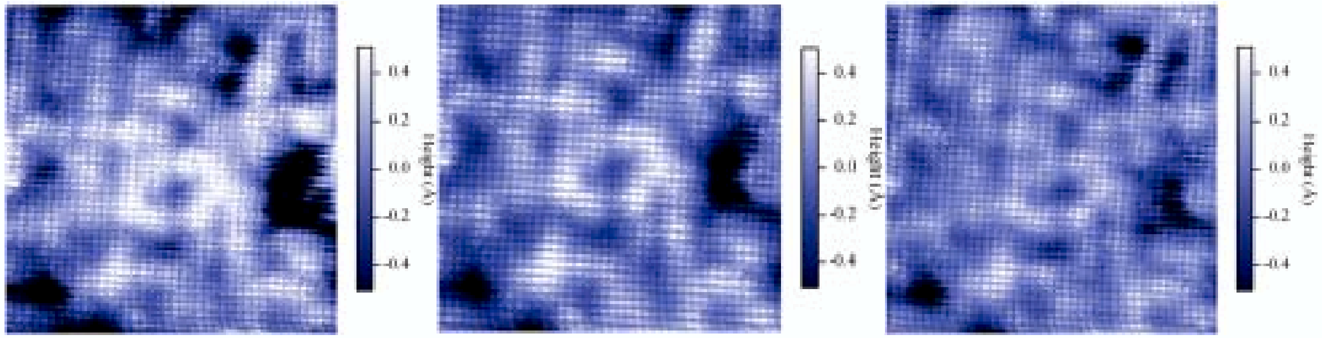
The nano-scale structure well defined & distinct

The position & shape of bright and dark segments does not depend on the bias voltage

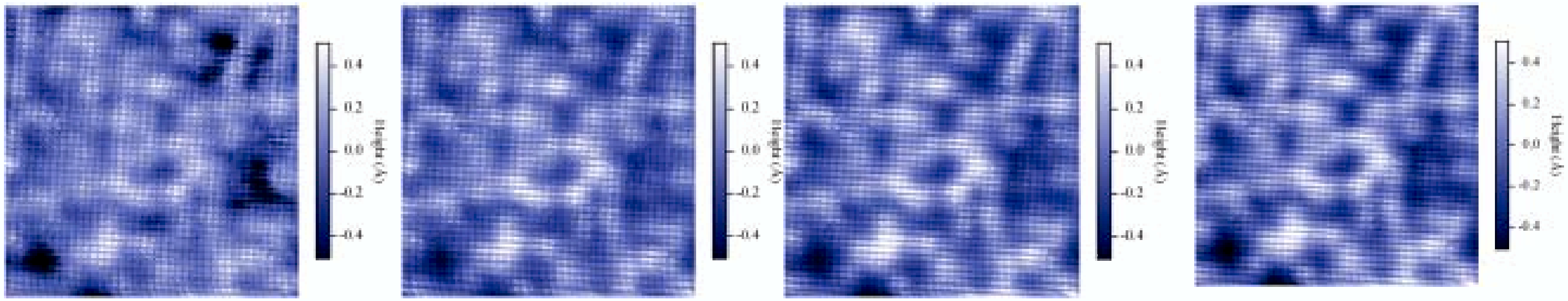


Bias voltage dependence of STM image on $Ca_{1.92}Na_{0.08}CuO_2Cl_2$

"Enhanced" Contrast at "positive" and "low" bias voltages



+ 50 meV ***+100 meV*** ***+150 meV*** ***+200 meV***



–50meV ***-100 meV*** ***–150 meV*** ***–200 meV***

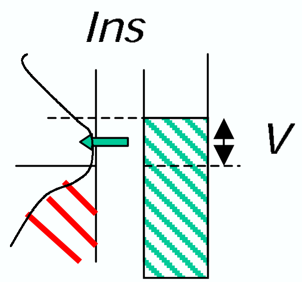
Bias voltage dependence of STM image on $Ca_{1.92}Na_{0.08}CuO_2Cl_2$

Two regions – different in low energy (100 meV) empty states (dark region gapped)

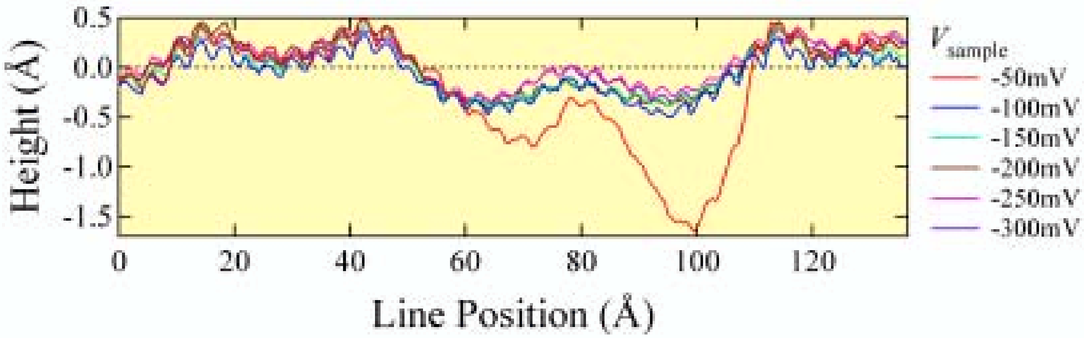
Empty state

The contrast represents the difference in integrated DOS up to the bias voltage

$$I_t \propto \int N(E)dE$$



Filled state



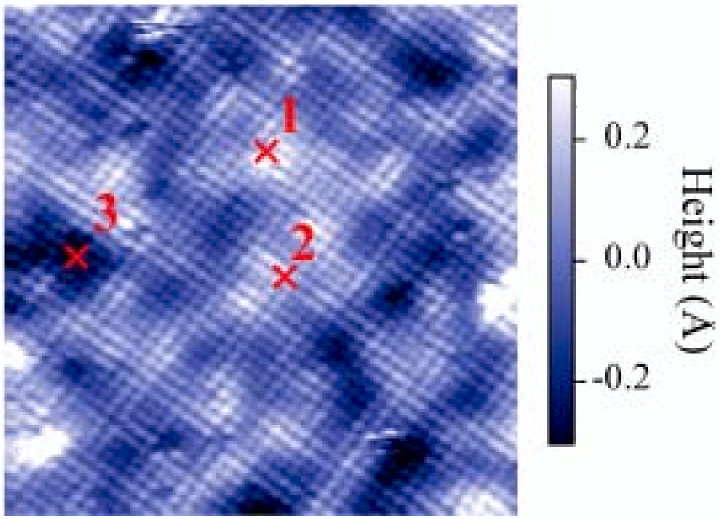
positive bias

↔

empty sates

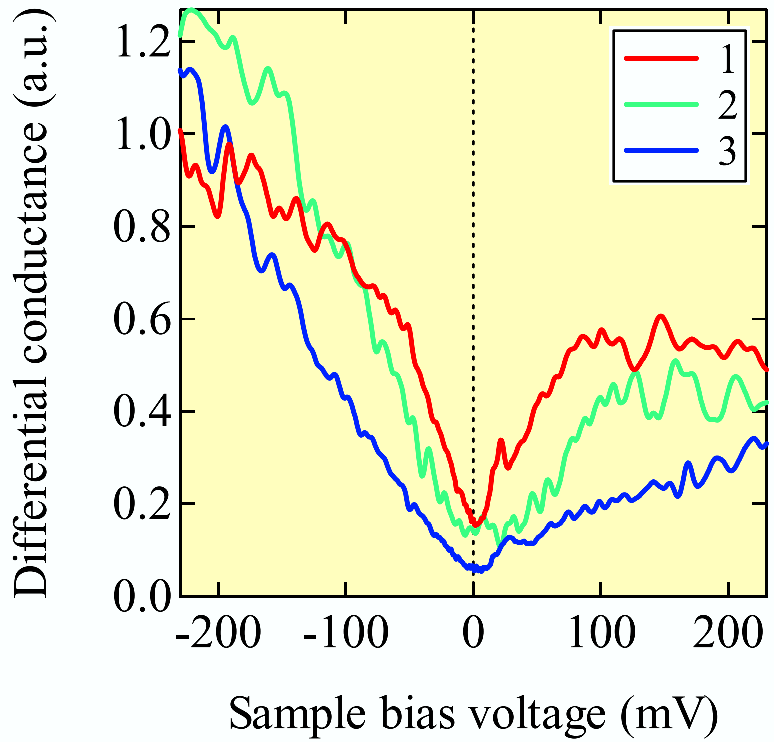
Contrast in Differential Tunneling Conductance

$Ca_{1.88}Na_{0.12}CuO_2Cl_2$



T = 7K
V_{sample} = -150mV
I_t ~ 50pA

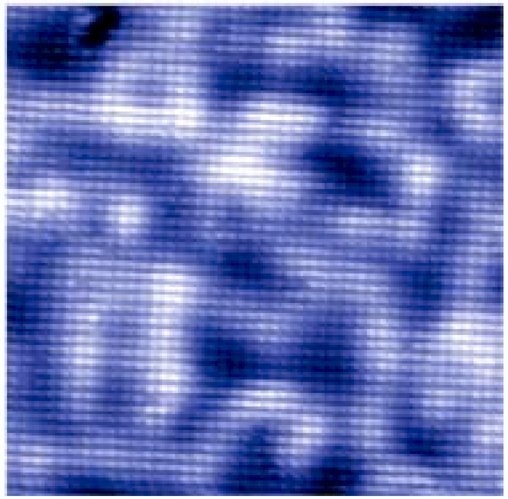
Normalized spectra



Bright segment more metallic with larger low energy DOS

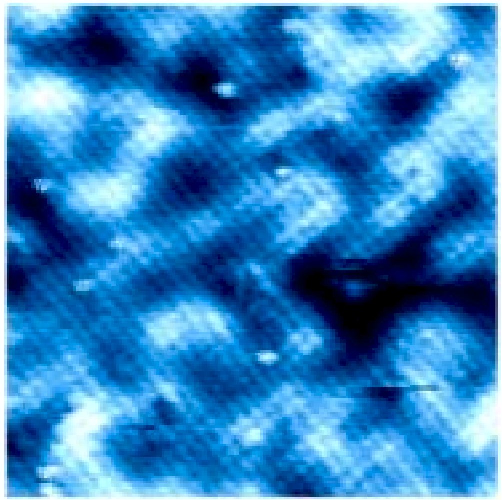
STM image of $Ca_{2-x}Na_xCuO_2Cl_2$ – evolution upon doping

x~0.08 (3GPa, Tc=0K)



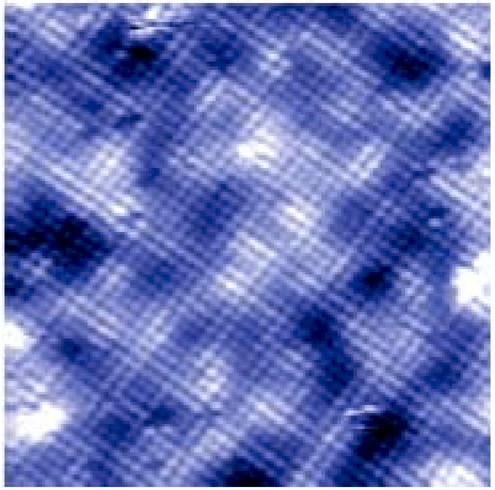
T = 7K
Sample bias : -250mV
I_t ~ 0.01nA

x~0.10 (4GPa, Tc=12K)



T = 14K
Sample bias : -100mV
I_t ~ 0.05nA

x~0.12 (5.5GPa, Tc=21 K)



T = 7K
Sample bias : -300mV
I_t ~ 0.4nA

STM image of Lightly doped oxychloride $(Ca,Na)_2CuO_2Cl_2$

Definite two regions with different electronic states : metallic Kishimen-like region (bright) & the remaining less metallic region (dark)

- 5*a* (2 nm) in width
- in many cases running along (100) [10-20 *a* (5nm) in length]
- Two phases different in 0.05-0.1 eV scale electronic structure

-different from much discussed "stripe"

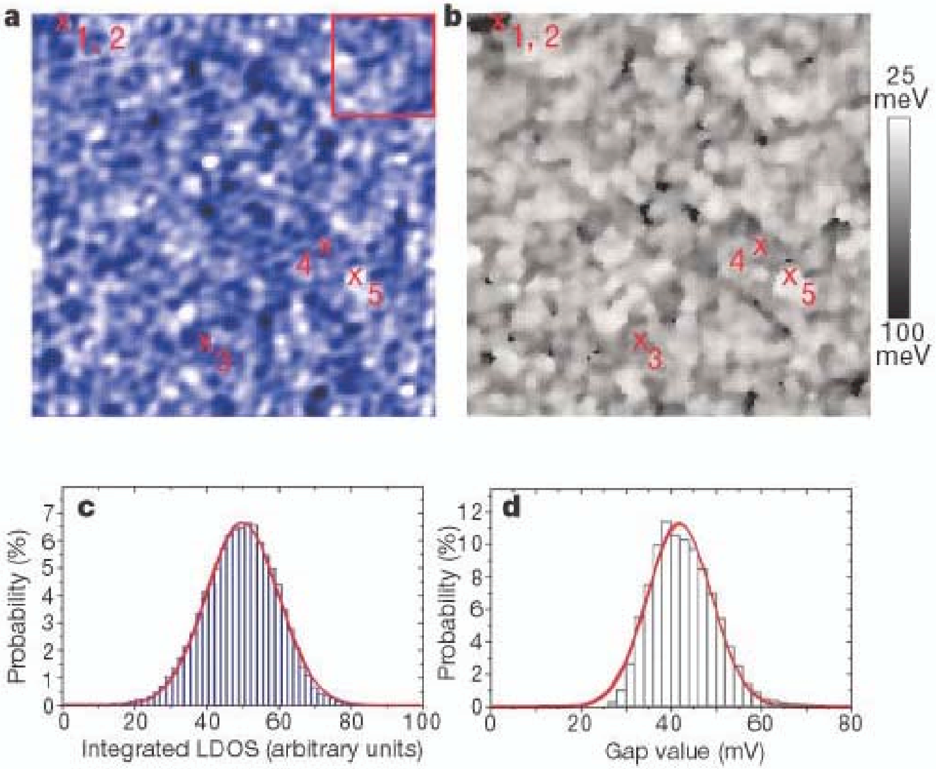
Metallic region much wider (1a width metallic river for every 4a)

- Any link with SC Inhomogeneity observed in BSCCO by Berkely G?

-Consistent with ARPES?

Microscopic electronic inhomogeneity in the high-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+x}$

S. H. PAN*, J. P. O'NEAL*, R. L. BADZEY*, C. CHAMON*, H. DING†,
J. R. ENGELBRECHT†, Z. WANG†, H. EISAKI‡ § , S. UCHIDA‡,
A. K. GUPTA , K.-W. NG , E. W. HUDSON ¶§ , K. M. LANG ¶&
J. C. DAVIS ¶



Oxychloride

- lightly doped close to Mott insulator

-Normal state "

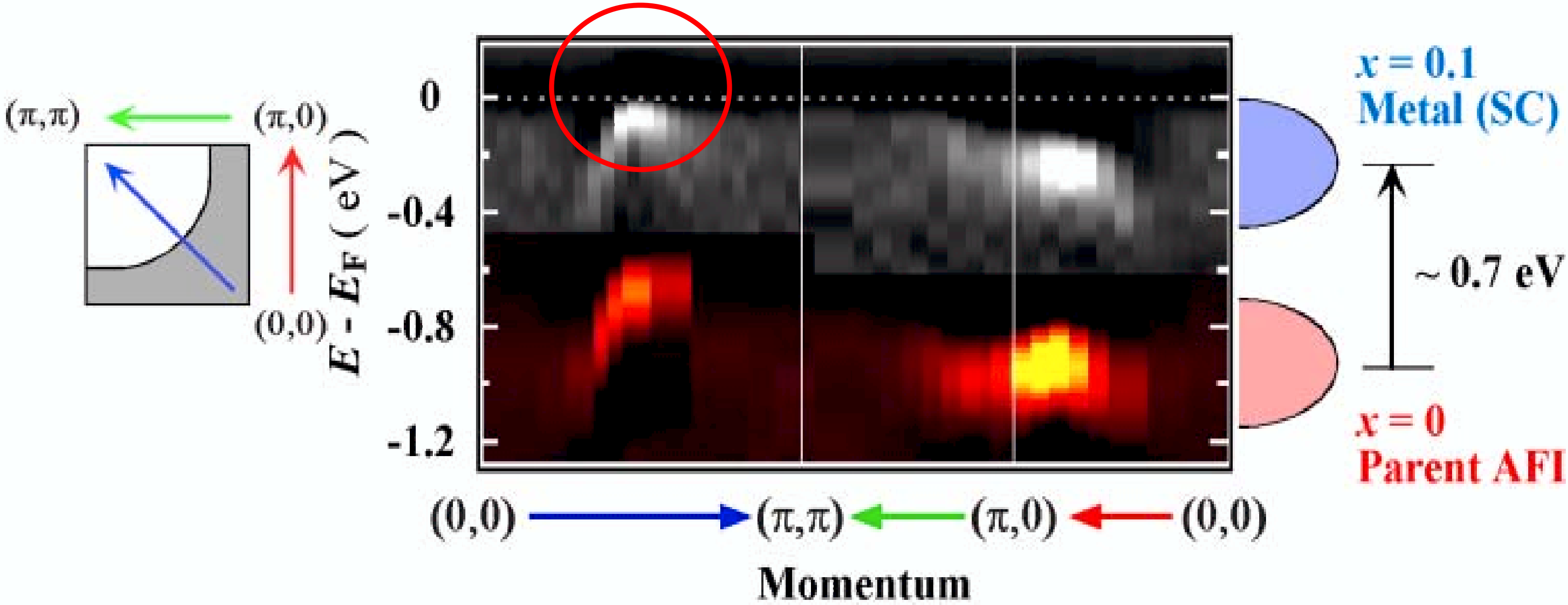
-***Distinct two regions*** rather than inhomogeneous distribution

-***Organized structure***

more like “phase separation”

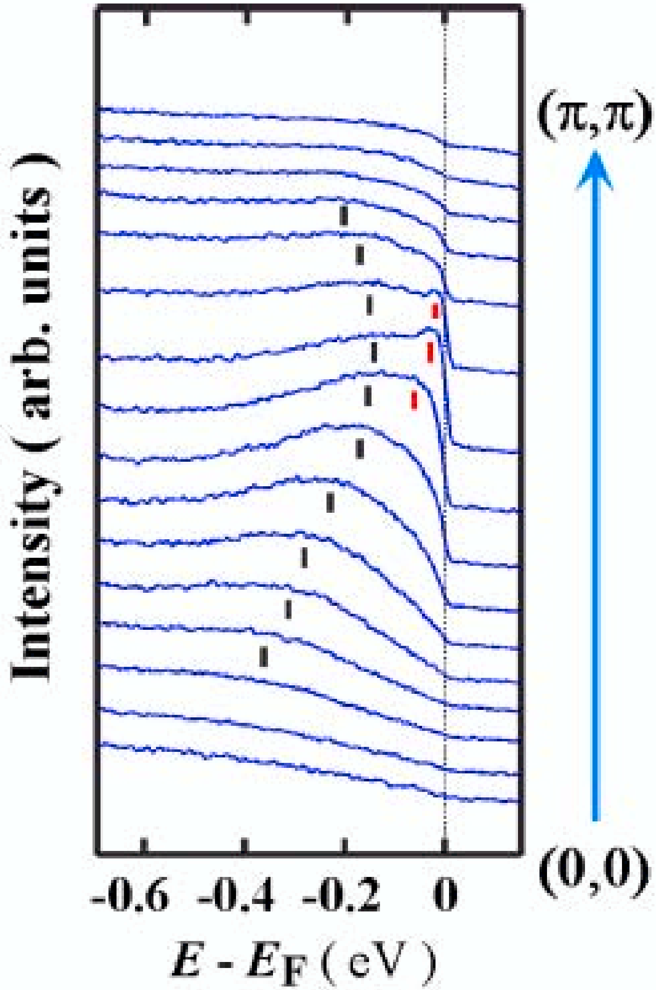
Signature of inhomogeneity seen in ARPES?

ARPES With Z.X.Shen (Stanford)

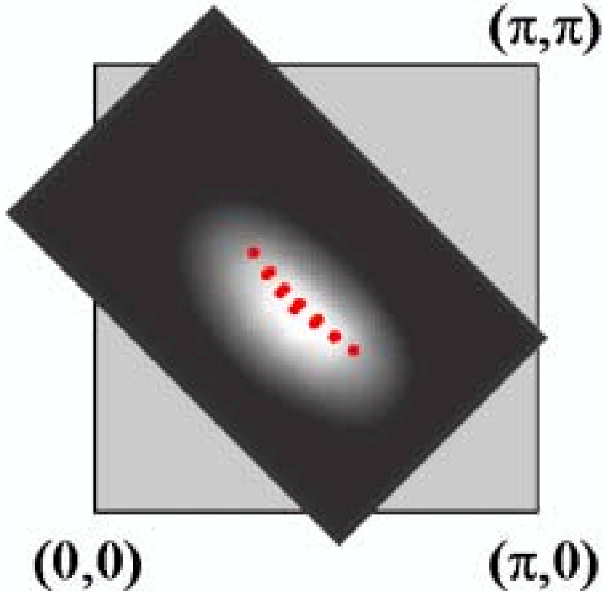


Energy scale too small ??

Low energy two component feature observed in ARPES around (π/2,π/2)



Intensity map (100 meV window)



- ***coherent peak observed***

  →Fermi surface arc

Broad (incoherent) bump
→shadow band

Origin of the electronic inhomogeneity?

Chemical inhomogeneity?

-Fluctuation of Na concentration inherent to the solid-solution.
each Kishimen segment contains a few to several Na ions.

- Why the structure is organized to a certain extent on such a microscopic level??

Length scale by far larger than conventianl λ_{TF}(~1 A) &
need to introduce very poor screening

Electronic phase separation?

(& the resultant self organization, charge ordering)

- Distinct two regions

-Static, pinned at defect and/or impurity?

- Enhanced by surface effect ?

Bulk phase separation? NMR, x-ray should be done

Summary of STM and Future Target

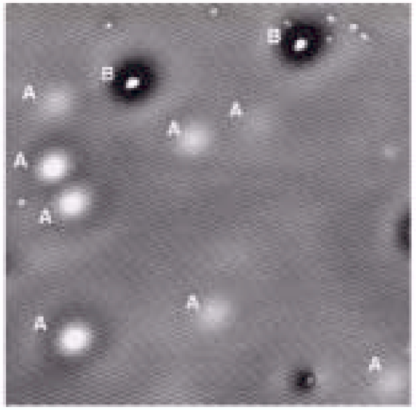
-Nano-scale electronic inhomogeneity observed in lightly doped $Ca_{2-x}Na_xCuO_2Cl_2$ single crystals in a form of organized structure

- Likely a kind of electronic phase separation
stabilized by impurities and surface?
universal feature of doped strongly correlated insulator

Mn oxide Renner&Aeppli

-Future target:
approach dilute and dense carrier concentration limit
likely switches to different physics

dilute limit - individual dopant?
Impurity States,
the same as conventional semiconductor?
how it evolves into the (uniform) dense limit ?



GaAs:Te

Depuidt, PRB 60 2919 (99)