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SMR.1572 - 13

**Workshop on  
Novel States and Phase Transitions in Highly Correlated Matter**

**12 - 23 July 2004**

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**Physics of lightly doped cuprate revealed from  
 $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$**

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JAPAN**

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These are preliminary lecture notes, intended only for distribution to participants

# Physics of lightly doped cuprate revealed from $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$

Hide TAKAGI (University of Tokyo & RIKEN)

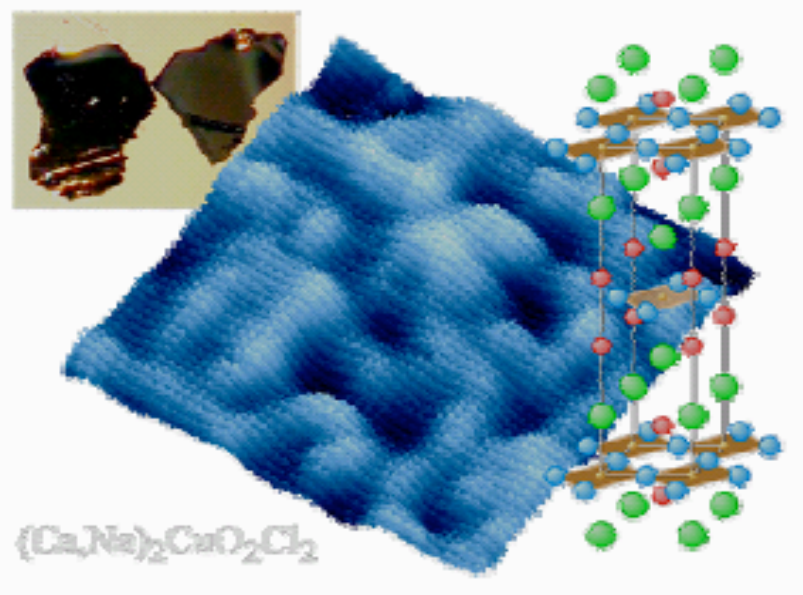
With Y.Kohsaka, K.Waku and T. Sasagawa (Tokyo )

T.Hanaguri &K.Iwaya (RIKEN)

C. Lupien & J.C.S Davis (Cornell)

K. Shen & Z.X.Shen (Stanford )

M.Azuma & M Takano (Kyoto)



Supported by **CREST-JST**

# OUTLINE

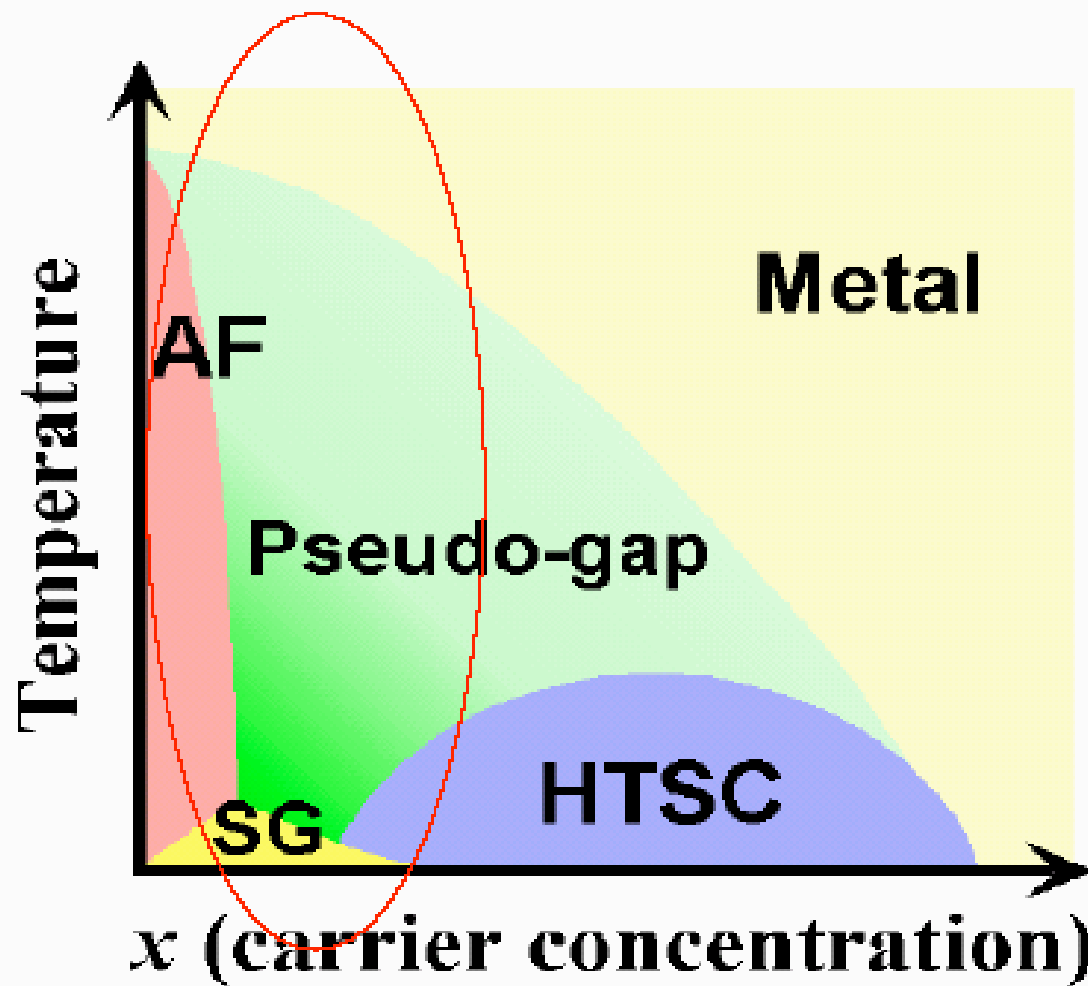
1. Introduction – why oxychlorides?
2. Phase diagram and transport of  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$
3. Pseudogap observed by optics and ARPES
3. STM/STS observation of nano-scale heterogeneity  
“Kishimen”
4.  $4a \times 4a$  checkerboard LDOS modulation
5. Implication to pseudogap physics
6. Remarks on FAQs

Friday morning

Geometrical frustration in spinel oxides

(+ electron-phonon interaction in cuprates)

## Need for real/ $k$ -space spectroscopy (STM/STS, ARPES) on "lightly doped" cuprates



electronic evolution from Mott ins. to d-wave SC?

- Fermi Surface evolution
- Pseudogap

Mottness vs. Cooperiness?

*Hidden order?*

- charge ordering (stripe, checkerboard)

- DDW

Electronic phase separation

real space physics important

***BSCCO, favorite of STM/ARPES community,  
chemically unstable near Ins.***

M<sup>2</sup>S 2000 (Houston), conference summary

Materials & Properties

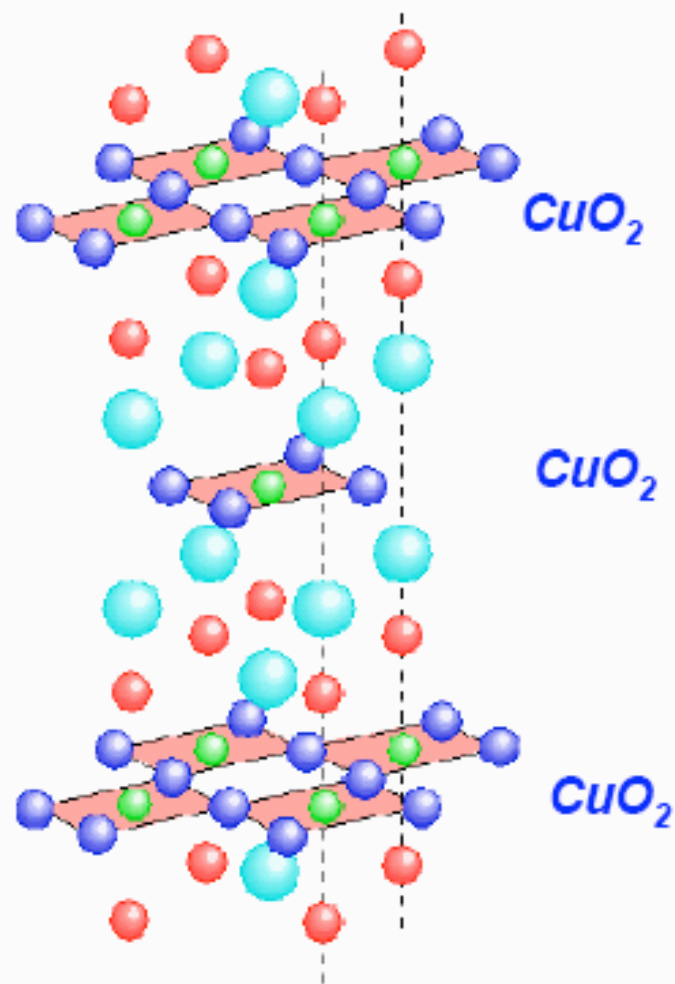
Hidenori TAKAGI

Department of Advanced Materials Science, University of Tokyo, 7-3-1 Hongo, Tokyo 1

mainly because of the difficulty in obtaining clean 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 increasingly important to establish the connection between the parent Mott insulator and the key features outlined above.

# $(\text{Ca,Na})_2\text{CuO}_2\text{Cl}_2$ - ideal system for STM & ARPES

- **Excellent cleave**  
only Bi and oxychloride
- **Undistorted  $\text{CuO}_2$  monolayer**  
remains tetragonal down to low T
- **Phase exists from Ins. to UD SC**  
Z. Hiroi *et al.*, Nature 371, 139 (1994).



|        | Cleave   | Doping State |    |       |
|--------|----------|--------------|----|-------|
|        |          | Insulator    | SC | Metal |
| LSCO   | $\wedge$ | [Red bar]    |    |       |
| BSCCO  | $\odot$  | [Red bar]    |    |       |
| NaCCOC | $\odot$  | [Red bar]    |    |       |

# Parent compound $\text{Ca}_2\text{CuO}_2\text{Cl}_2$

## ARPES Ins. standard

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

Mott gap with d-wave like dispersion

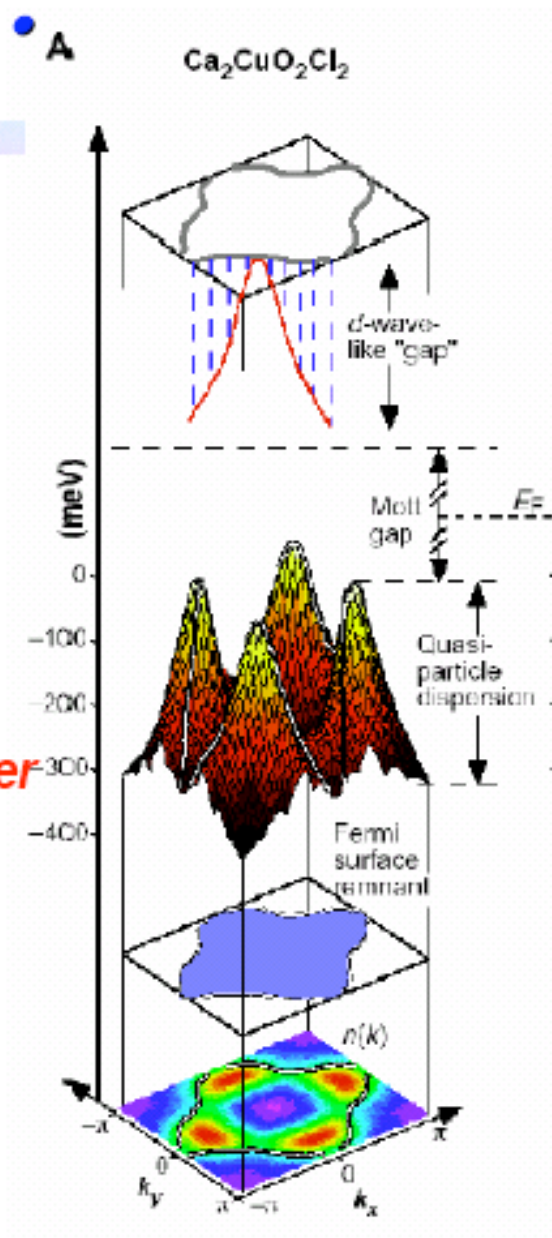
High quality surface due to easy cleavage

→  
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

Y. Kohsaka *et al.*, J. Am. Chem. Soc., 124, 12275 (2002).

Cubic-Anvil type HP apparatus  
“Elephant”

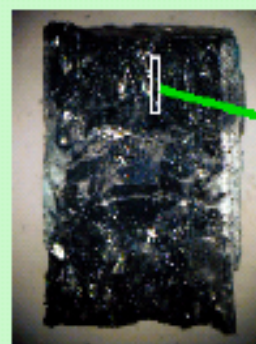
5.5 GPa in a volume of 1cm<sup>3</sup>



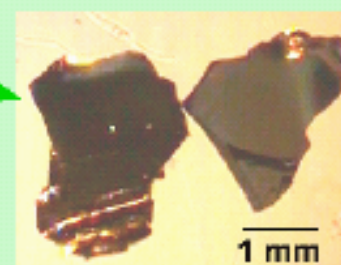
$\text{Ca}_2\text{CuO}_2\text{Cl}_2$  Powder  
NaCl (flux, Na source)  
NaClO<sub>4</sub> (O<sub>2</sub> & Na source)

2 ~ 5.5 GPa  
1230 ~ 970 °C / 30 hrs

$(\text{Ca,Na})_2\text{CuO}_2\text{Cl}_2$  Crystals



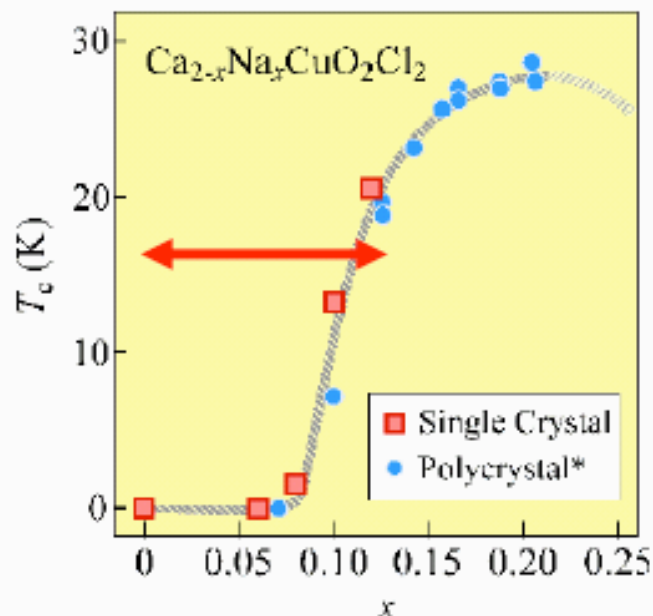
9.6 mm



1 mm



# Phase Diagram and transport properties of $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ Single Crystals

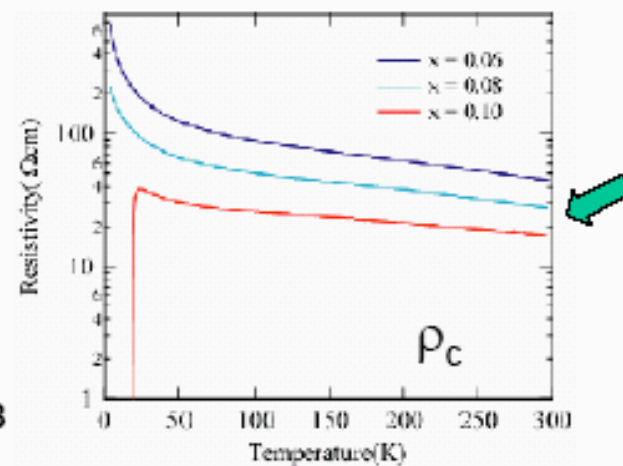
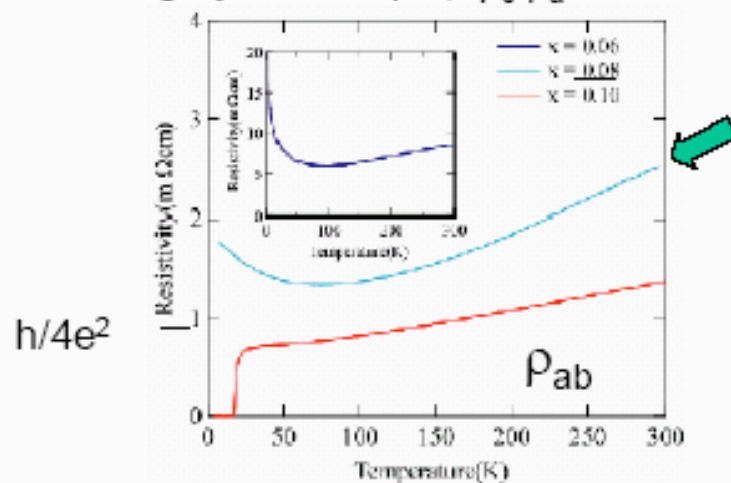


single crystals from  $x=0$  to  $x=0.12$

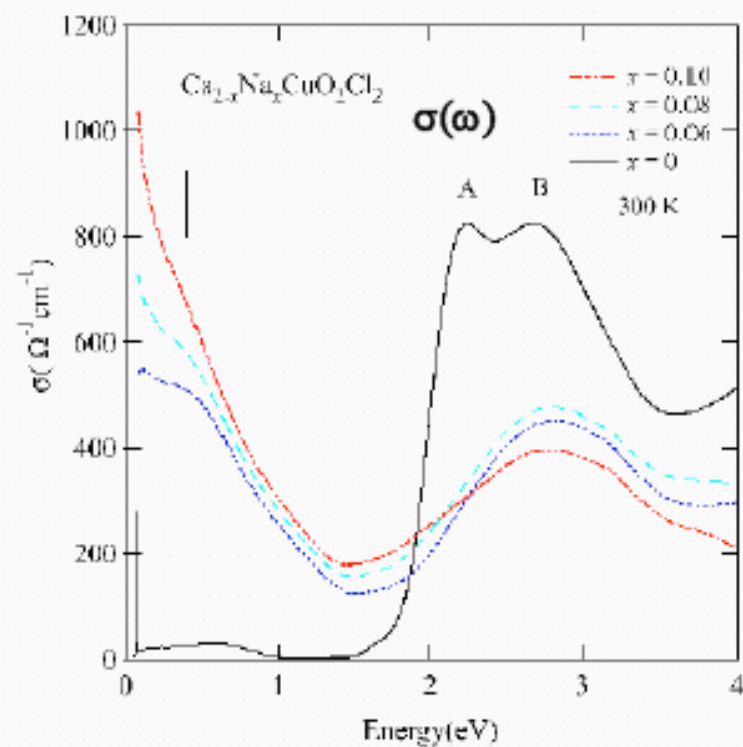
*M-I (likely S-I) transition around  $x=0.08$*

K.Waku et al., submitted to PRB

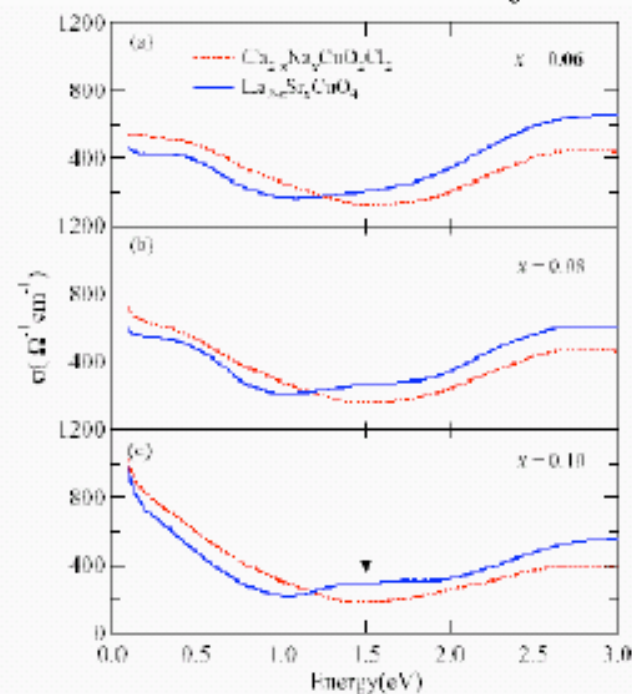
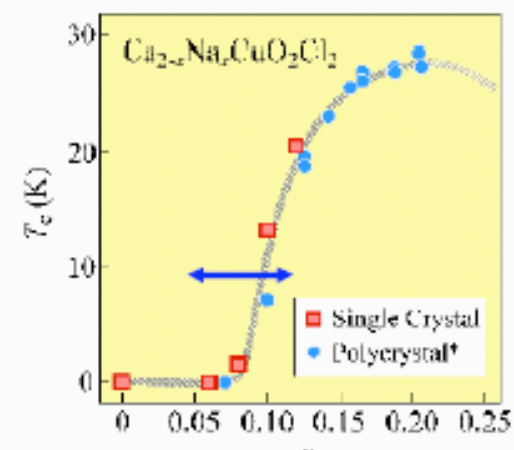
highly anisotropic,  $\rho_c/\rho_a \gg 10^4$



## Evolution of optical conductivity in $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$



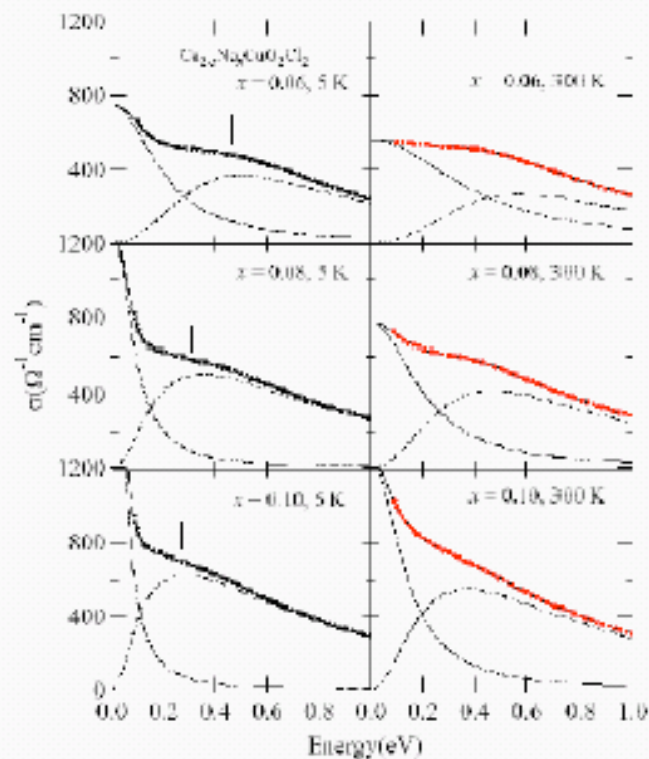
K. Waku et al. PRB  
submitted



# Pseudogap signature in optical conductivity

Two component

Drude + Mid IR absorption

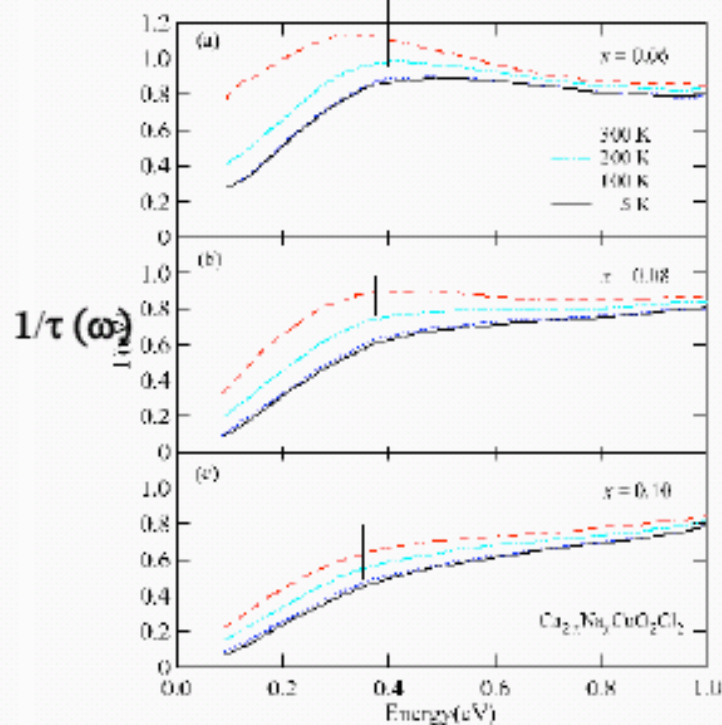


Drude-like nodal + (pseudo)gapped antinodal?

Softening of Mid-IR

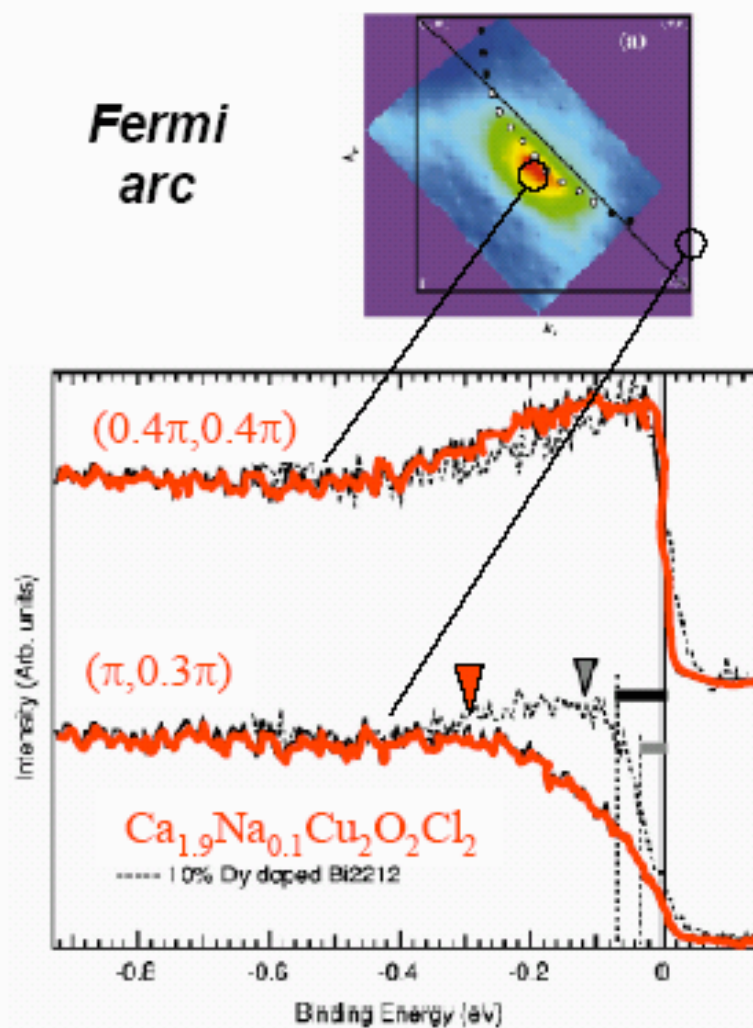
One component "Generalized Drude"

"knee" = pseudogap signature



*all doped single crystals have pseudogap signature 0.2-0.3 eV in optical conductivity*

## Large Pseudogap at antinodal region observed by APPES



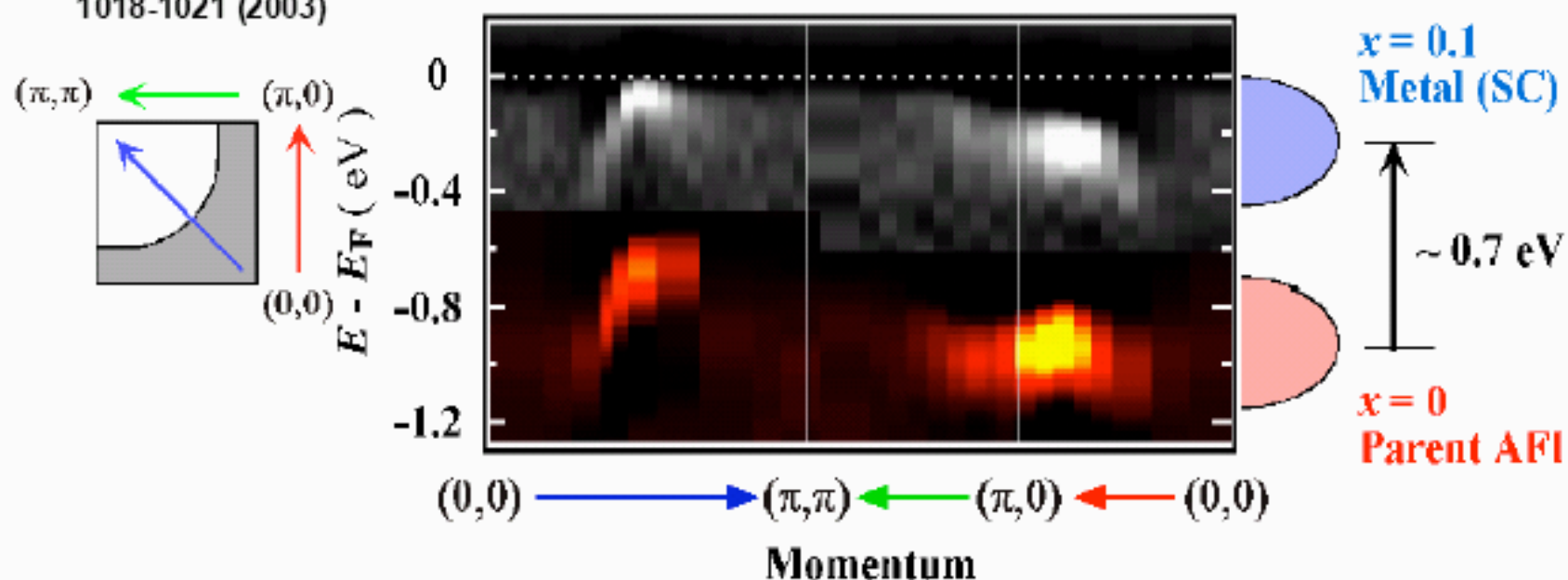
0.1-0.2 eV gap at antinodal region

Y.Kohsaka *et al.* JPSJ  
(2003); F. Ronning, *et al.*,  
Phys. Rev. B 67, 165101  
(2003).

## Fingerprint of Mott insulator in metallic phase -Chemical Potential Shift

Y.Kohsaka et al. J. Phys. Soc. Jpn. 72, 1018-1021 (2003)

ARPES With Z.X.Shen (Stanford)



*Fingerprints of the parent AFI*

(1) *Shadow Band near  $(\pi/2, \pi/2)$*

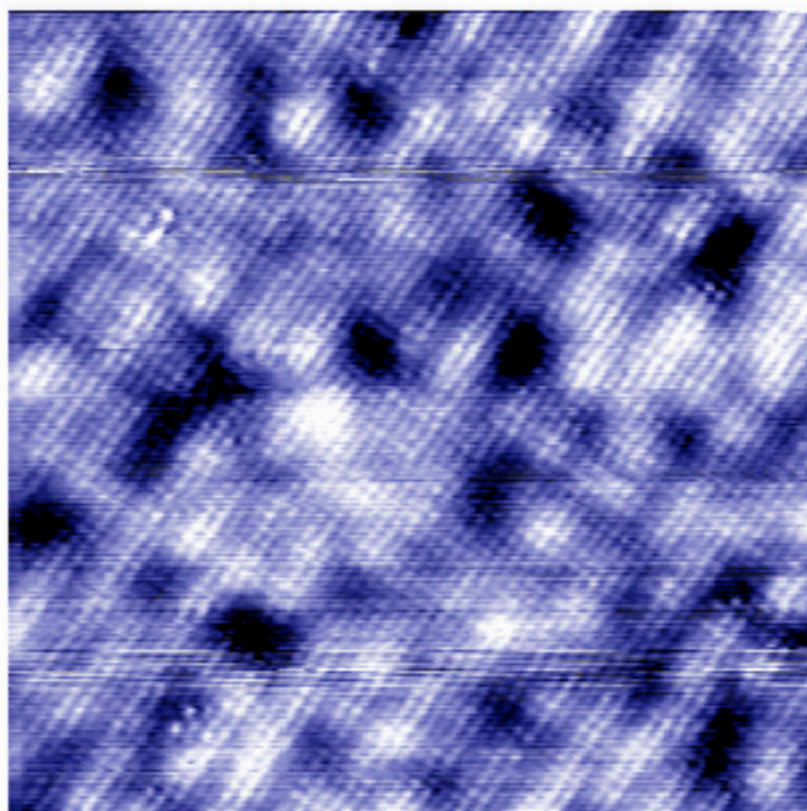
(2) *Large Pseudo Gap around  $(\pi, 0)$*

*gap originates from d-wave dispersion of Mott gap*

## Real space image of “pseudo-gapped” $\text{Ca}_{1.90}\text{Na}_{0.10}\text{CuO}_2\text{Cl}_2$

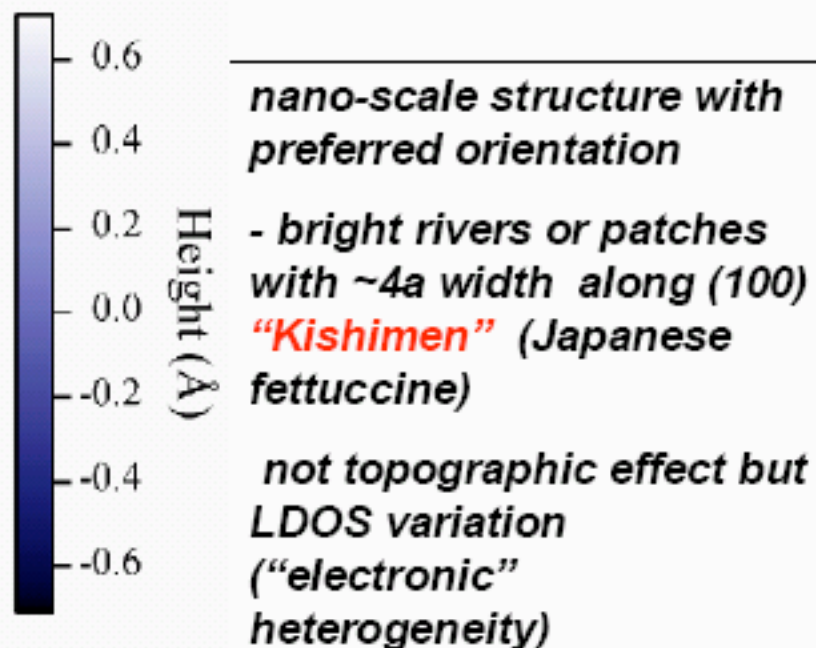
Y. Kohsaka et al., PRL in press

(100) square lattice with 3.9Å spacing, cleaved surface: ionic CaCl layer  
(010)  $P \sim 10^{-11}$  Torr,  $T = 7$  K  
 $x \sim 0.10$



Sample bias voltage:  $V_s = -250$  mV

Tunneling current:  $I_t \sim 0.01$  nA

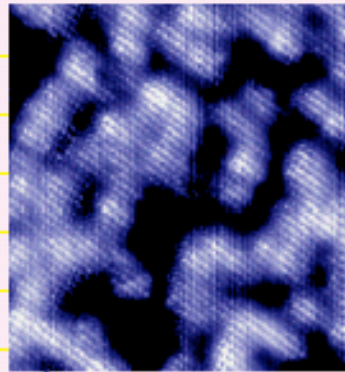


# Doping dependence of real space images

Why organized?

Why screening so poor?

$x = 0.06$  (insulator)



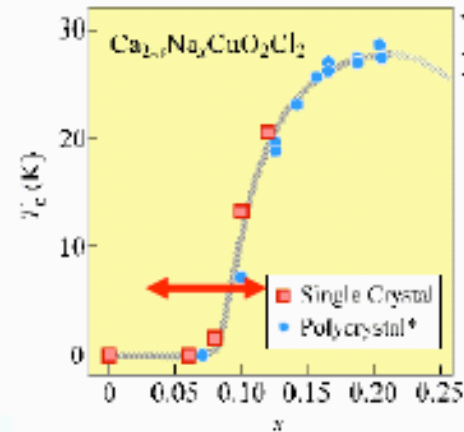
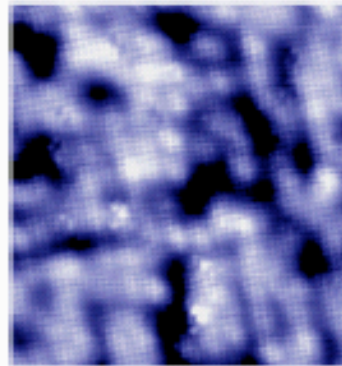
100 Å

*Kishimen robust*

*but contrast becomes less pronounced with  $x$*

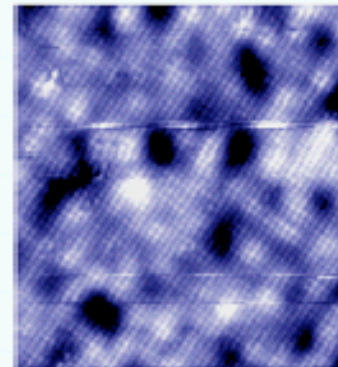
Real space physics Important for M-I

$x = 0.08$   
(S-I transition)

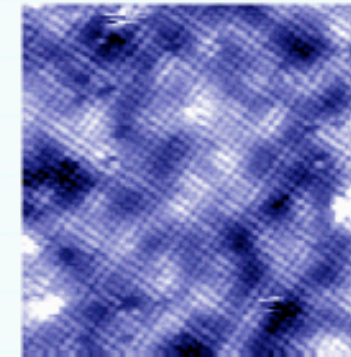


Y. Kohsaka et al.,  
PRL in press

$x = 0.10$   
( $T_c = 13$  K)



$x = 0.12$   
( $T_c = 21$  K)



## Checkerboard LDOS modulation in $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ ( $x=0.1$ )

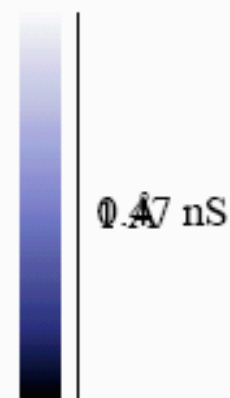
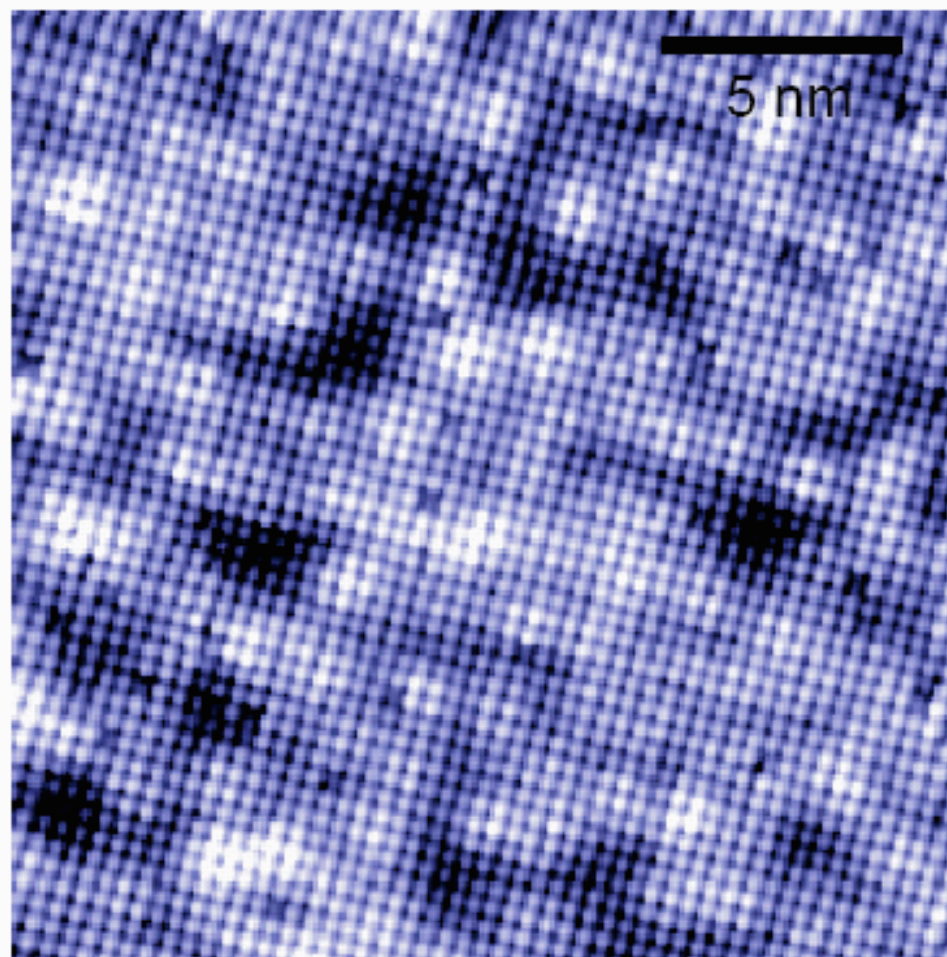
Hanaguri et al., Nature in press

Topograph

$T < 250$  mK

$V_{\text{sample}} = 200$  mV

$I_t = 10$  pA

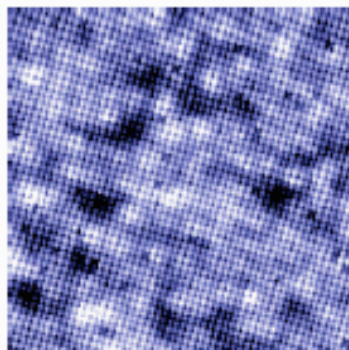




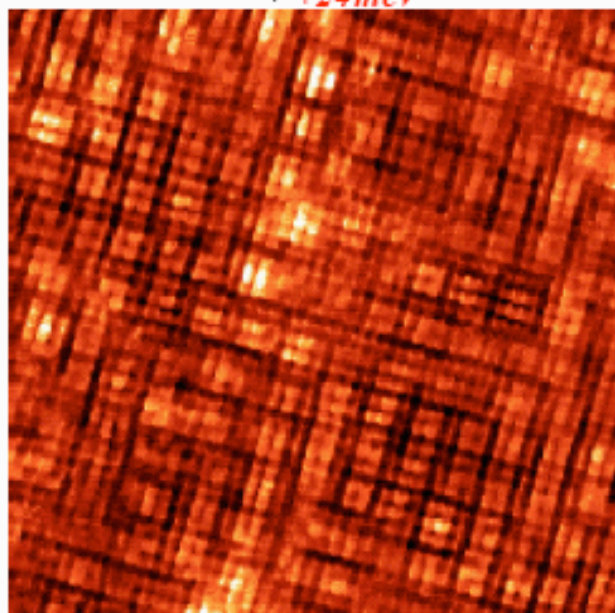
# "4a x 4a" checkerboards in $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ ( $x=0.1$ )

Hanaguri et al., Nature in press

Topograph

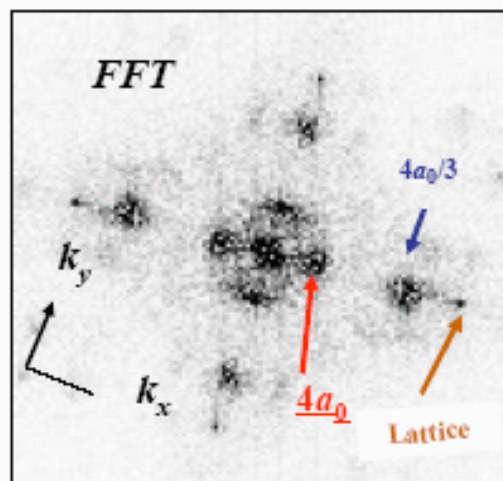


$dI/dV|_{+24\text{meV}}$



Relative change  
of normalized  
LDOS at a  
specific  $V$

periodicity: 4a x 4a



canceled by  
normalization in  $dI/dV$

Kishimen =  
"Checker board" + nano-scale variation of potential  
(likely impurity)

# "4a x 4a" checkerboards in $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ ( $x=0.1$ )

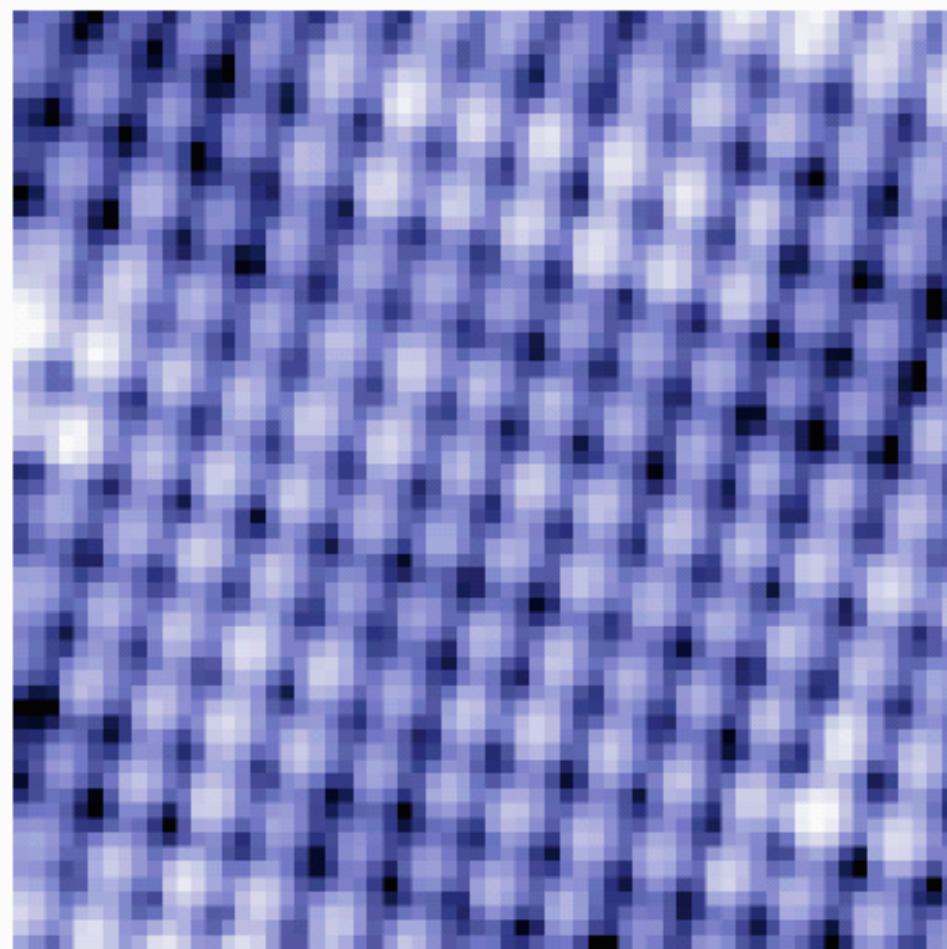
Hanaguri et al., Nature in press

Topograph

$T < 250$  mK

$V_{\text{sample}} = 200$  mV

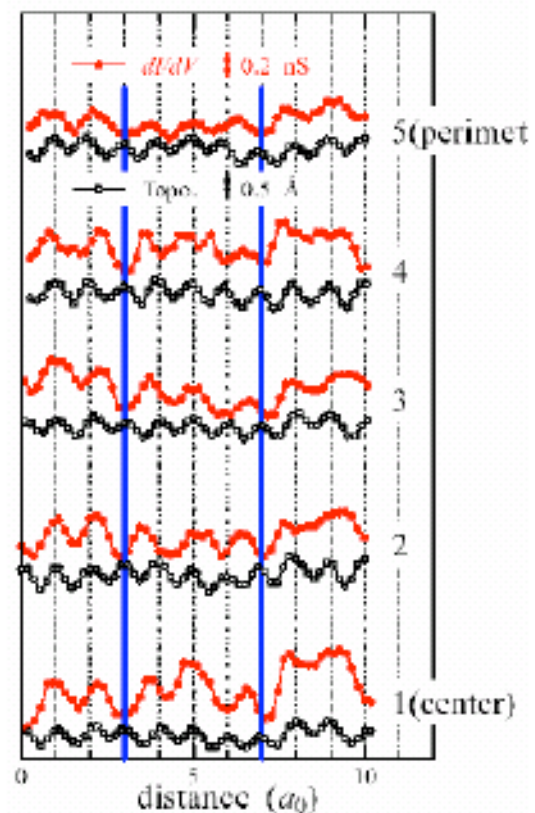
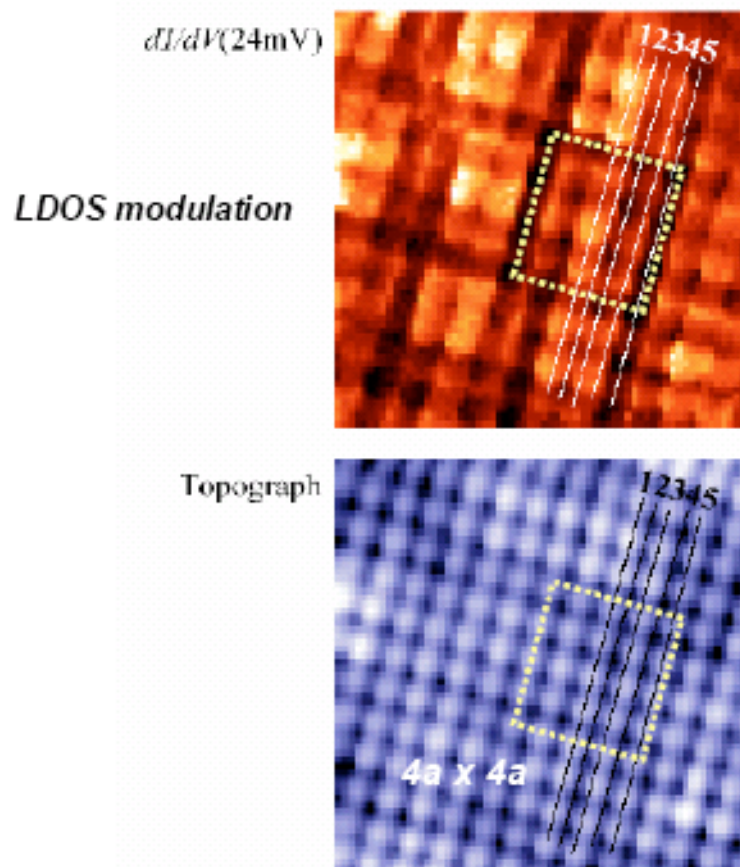
$I_t = 100$  pA



0.17 nS

# 4a x 4a checkerboard CDW formation in $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ ( $x=0.1$ )

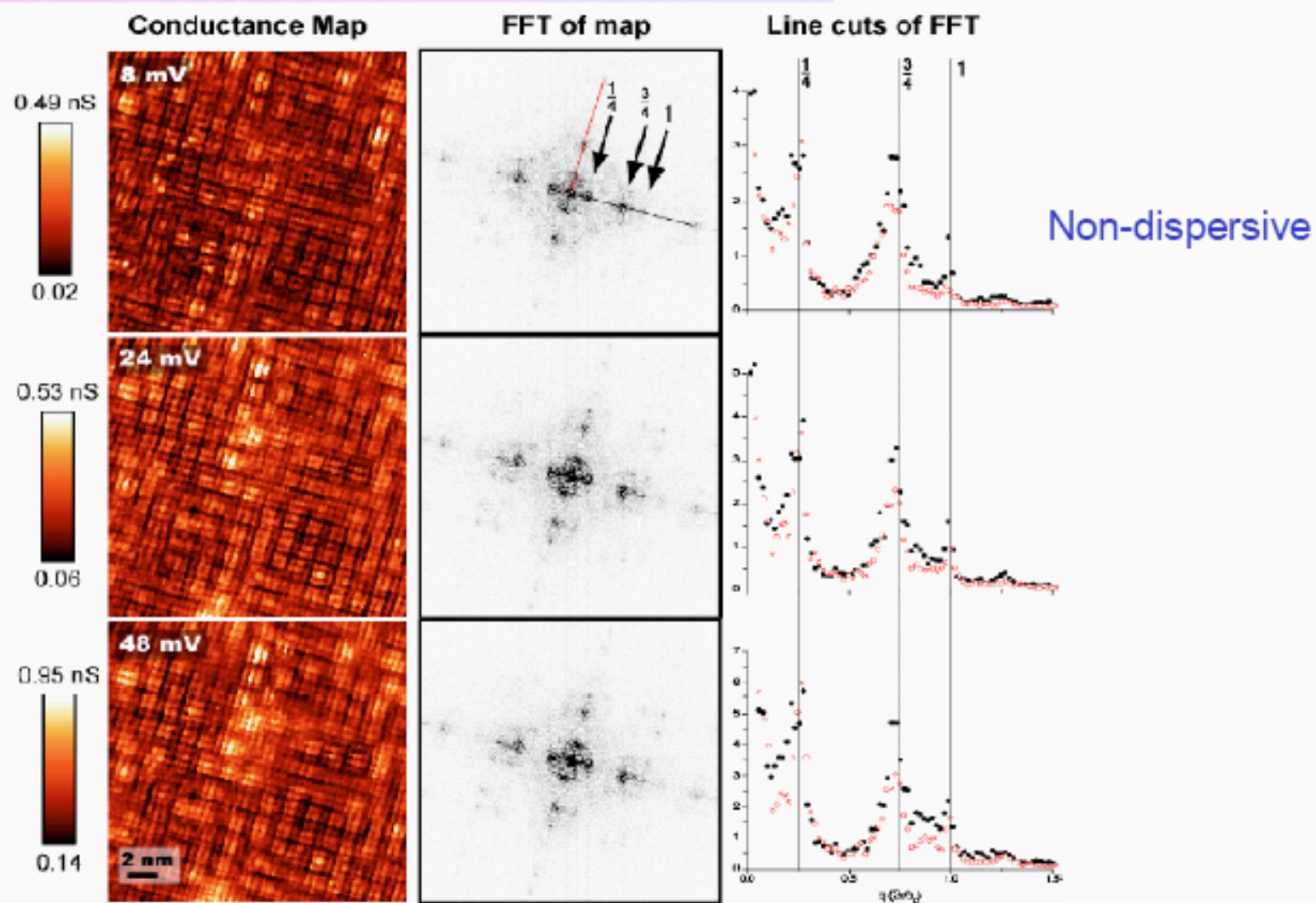
Hanaguri et al., Nature in press



3LDOS peaks for  $4 a_0$

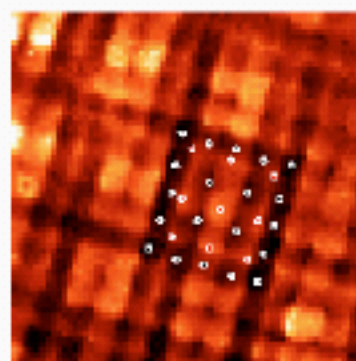
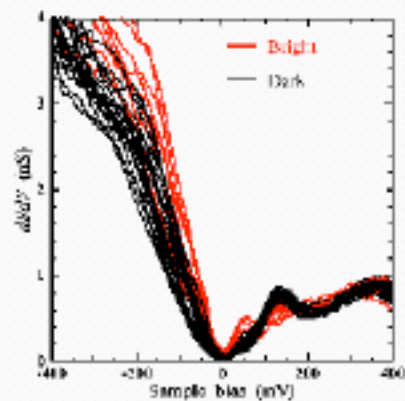
—  $4/3a_0$  in FFT

## Energy dependence of periodicity

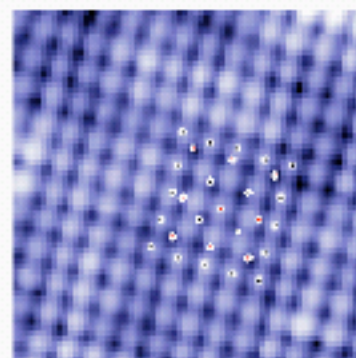


T. Hanaguri *et al.*, Submitted to *Nature*

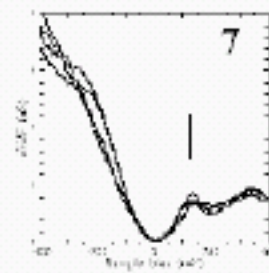
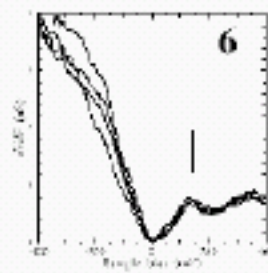
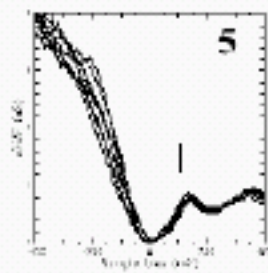
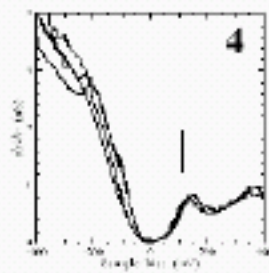
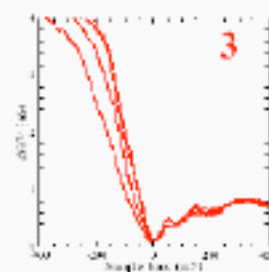
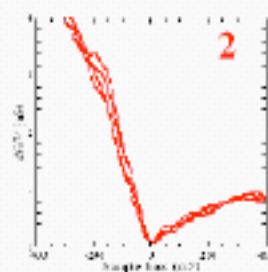
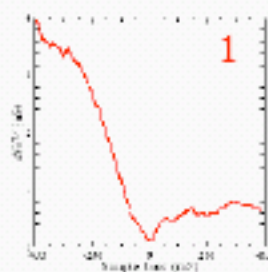
# Energy scale for 4a x 4a CDW – 100-200 meV



$dI/dV(30\text{mV})$



Topograph



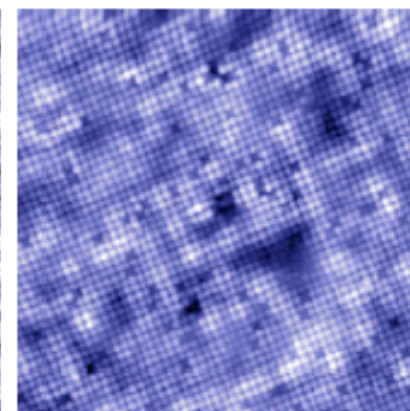
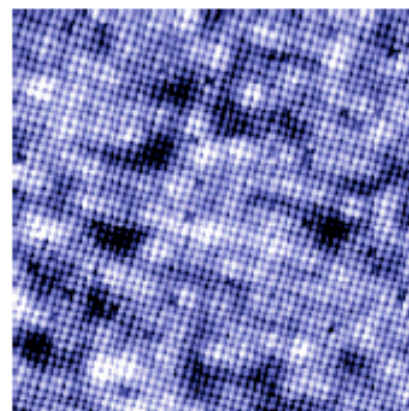
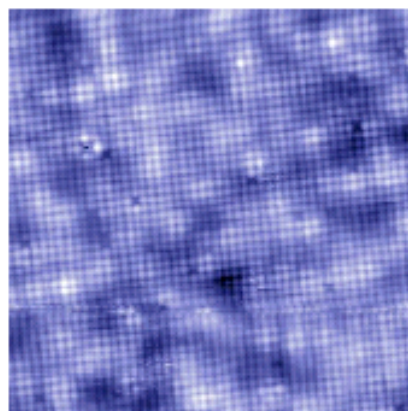
## Checkerboard robust against doping

$x \sim 0.08$  (MIT)

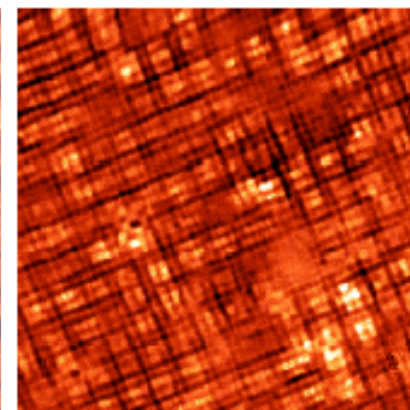
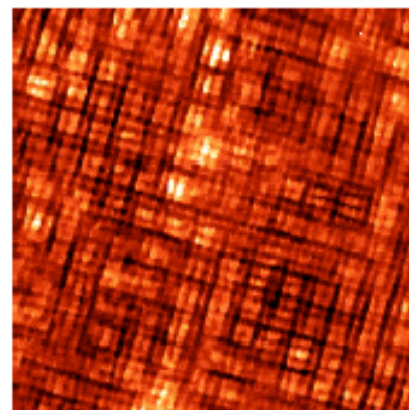
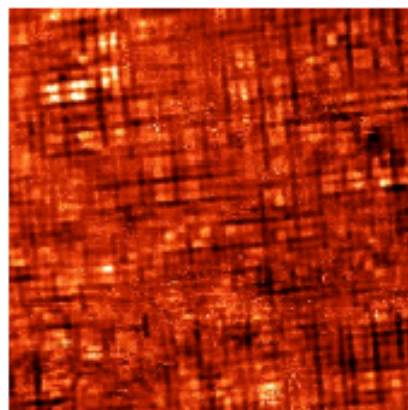
$x \sim 0.10$  (SC)

$x \sim 0.12$  (SC)

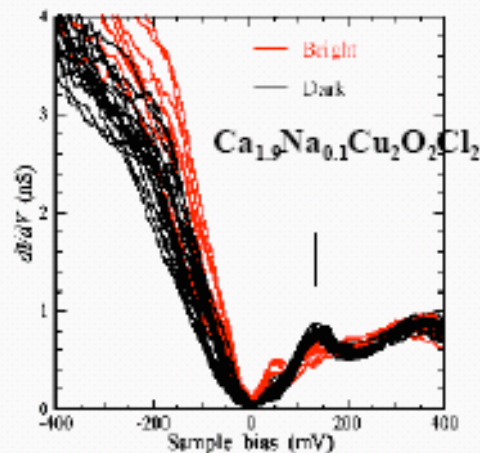
Topo.



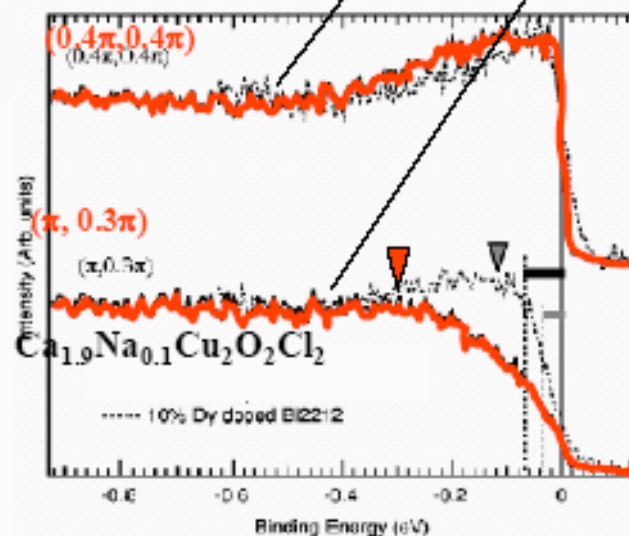
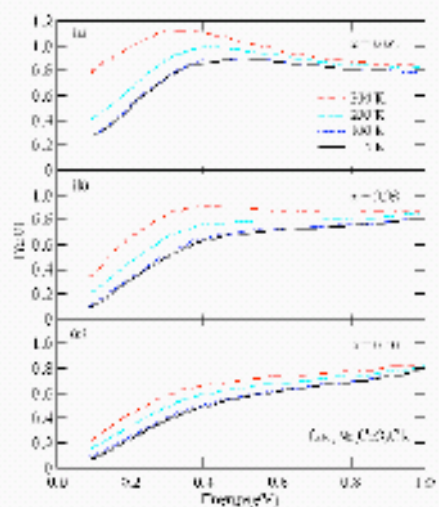
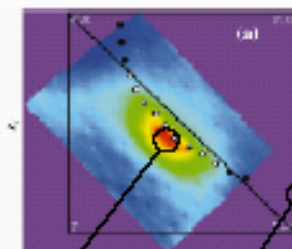
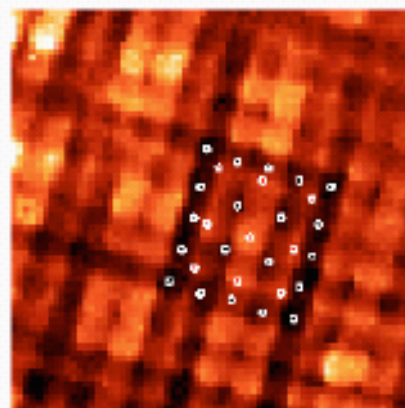
$dI/dV|_{24\text{mV}}$



# Checkerboard responsible for pseudogap ? - comparable $E$ - scale



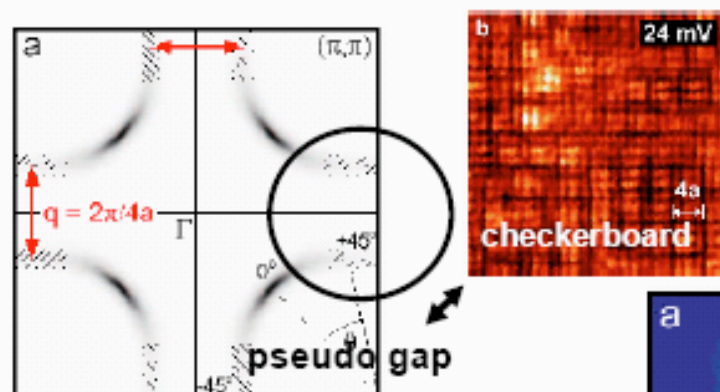
LDOS modulation on 100-200meV scale



F. Ronning, *et al.*, Phys. Rev. B 67, 165101 (2003).

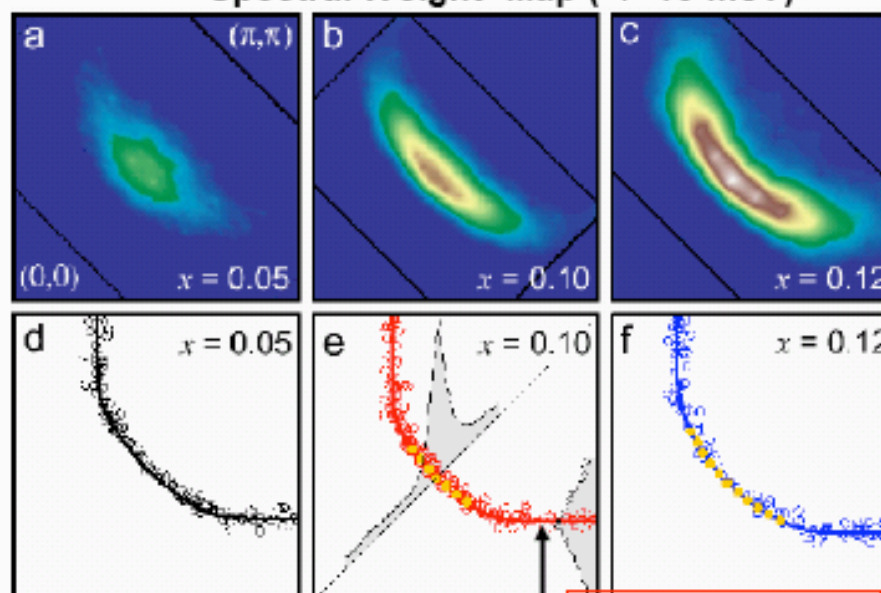
# FS nesting in anti-nodal region gives $4a$ periodicity

Kyle Shen & Z.X. Shen



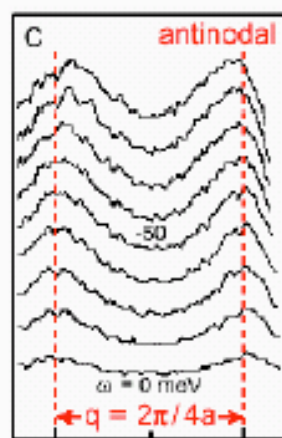
Support for the link between the checkerboard and antinodal pseudogap

Spectral Weight Map ( $\pm 10 \text{ meV}$ )



Extracted Fermi Surfaces (MDC Analysis)

$$q = \pi/2a = 2\pi/4a$$



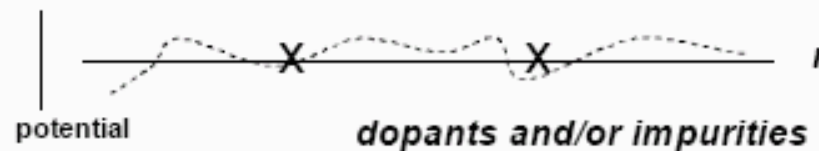
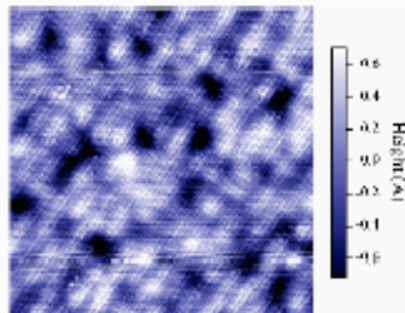
MDC Analysis

metallicity maintained by nodal QP



## Picture emerged: STM/STS + ARPES

- $4a \times 4a$  checkerboard likely (hidden) order  
behind pseudogap formed around  $(\pi, 0)$
- $4a$  periodicity originates from FS nesting around  $(\pi, 0)$
- Nodal FS arc appears to protect antinodal nesting checkerboard stable over a wide concentration range  
so homogeneous on inhomogeneous background - "Kishimen"



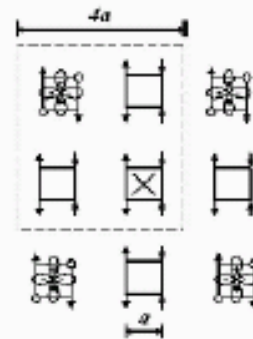
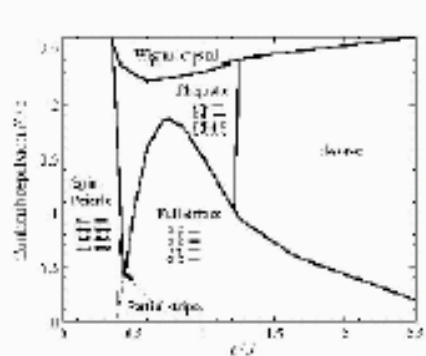
-Connection to SC gap? previous talk

## possible scenario for chaecerboard: charge ordering (Wigner crystallization)

- bulk compositions close to " $1/8$ " = 0.125

Charge ordering at " $X=1/8$ " = 2 holes / 16 ( $4 \times 4$ ) sites (possibly  $1/16$ ) ?

- Wigner crystallization of holes or hole pairs proposed



M. Vojta, PRB 66, 104505 (2002).

J. Zaanen & O. Gunnarsson PRB 40, 7391 (1989).

H.-D. Chen *et al.*, PRL 89 137004 (2002).

D.-H. Lee *et al.*, Preprint

.....

- link with FS nesting at antinodal region ??

Can these picture give stable  $4a$  nesting?

importance of  $k$ -space (FS) physics (nodal vs. antinodal)

real space and  $k$ -space pictures should be unified

## FAQs:

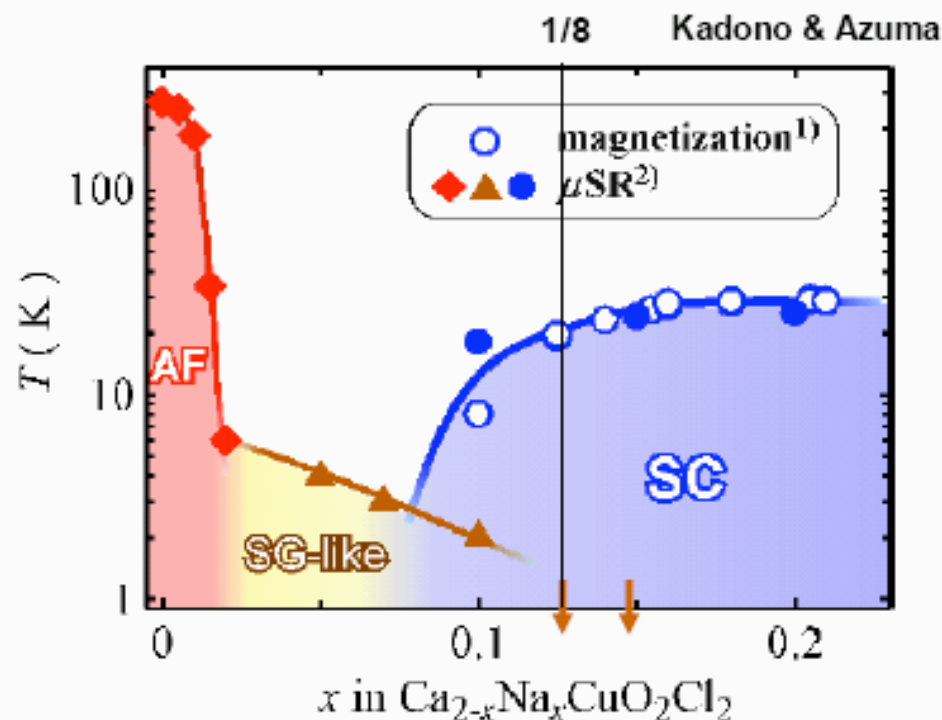
**Charge ordering at “ $X=1/8$ ” = 2 holes / 16 (4x4) sites (possibly 1/16) ??**

-Any singularity at 1/8? (real space ordering of “1/8” holes)

within the available data we have, no pronounced anomaly in  $T_c$  and  $T_{SG}$  observed.

“1/8” anomaly very weak in the other systems except for LBCO

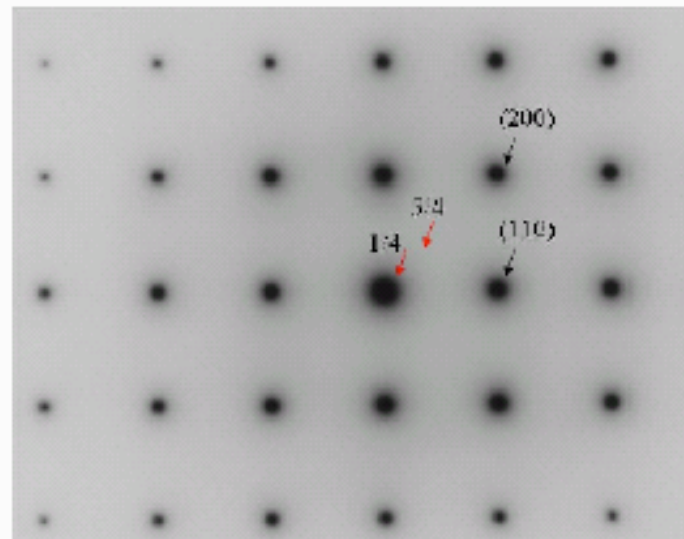
need detailed study



FAQs :

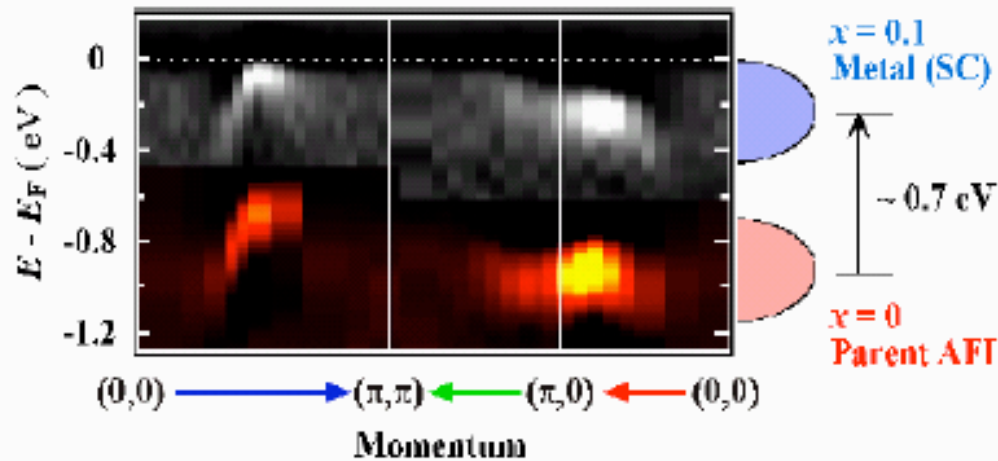
## ***Bulk evidence? - Search for diffraction evidence for charge ordering***

Electron Diffraction @ 30 K (with M. Uchida, NIMS)



- charge (lattice) modulation very weak
- x-ray diffraction using synchrotron source now in progress
  - ( La214 CO peak not in electron diffraction but in x-ray)
- NMR signal extremely broad around M-I and sharpens in SC phase  
(Zheng & Kitaoka, Osaka)

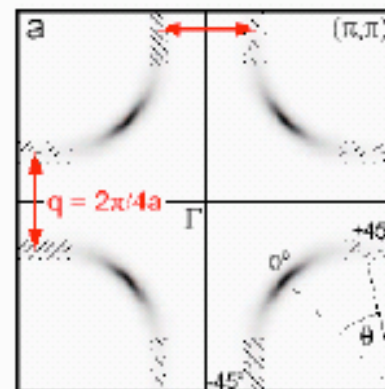
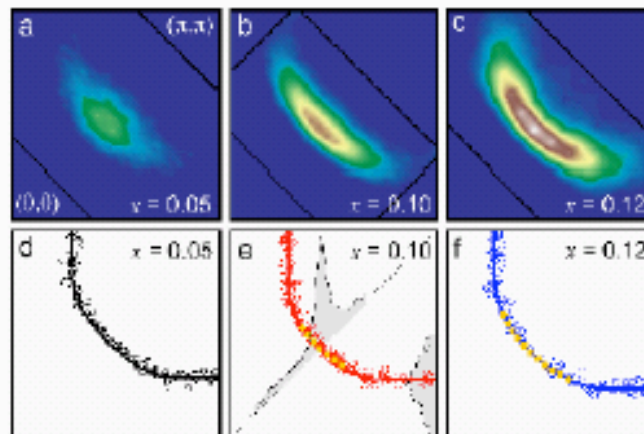
## FAQs: Mottness vs Charge orderness



Mottness irrelevant to pseudogap?

Chemical potential shift high energy phenomena??

Until last year  
Mott gap with d-wave like dispersion



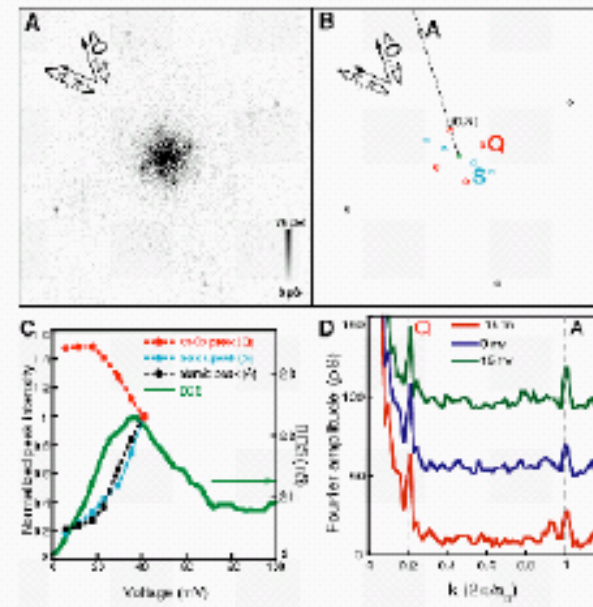
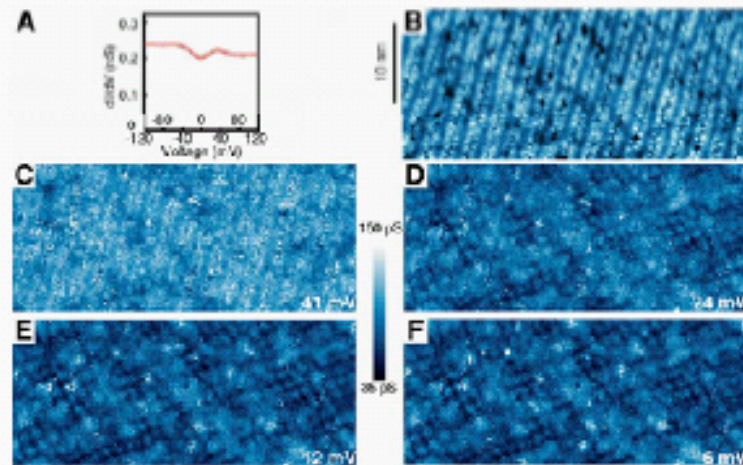
Charge ordering  
FS nesting at antinodal region

FAQs :

## Universal among cuprates?

Vershinin, Yazdani et al. Bi in the high T pseudo gap state

dispersionless  $\sim 4.7$  a self organization of electrons



Davis G (McElroy et al.)

underdoped Bi

not specific to oxchlorides

link between quasi-particle scattering and 4a checkboard?

## Summary

- $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  as a key material for high- $T_c$  physics

- Discovery of  $4a \times 4a$  checkerboard CDW

Previously observed “Kishimen” is a superposition of checkerboard and nano-inhomogeneity

- **E**-scale of a few 100 meV suggests intimate link to the pseudo-gap physics

- Antinodal FS nesting gives  $4a$  periodicity (ARPES)

- Bulk evidence for CDW not yet observed (exploration in progress)

- Evolution of antinodal CDW state into d-wave SC preventing or helping somehow?