

# STM/STS study on $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ single crystals

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## Abstract

To explore the evolution of electronic states from the Mott insulator to the high- $T_c$  superconductor, we performed scanning tunneling microscopy/spectroscopy (STM/STS) on  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  single crystals which show superior cleavage. Topographic images taken by constant-current scanning at 7 K show clear atomic images superposed on nano-scale patch-like or river-like irregular corrugations. Spectroscopic measurements revealed that low areas are semiconducting and the spectrum at high area is approaching to "metallic" while gap-like feature still remains near the Fermi level. Namely, background corrugations are originated from the electronic inhomogeneity.

**Key words:** scanning tunneling microscopy ; high- $T_c$  superconductor ; metal-insulator transition ;  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$

## 1. Introduction

High- $T_c$  superconductivity (HTS) emerges as appropriate concentration of carrier is introduced into the parent Mott insulator by chemical substitution of heterovalent ions. Since charged ions are leaved in so-called blocking layers which alternate with the  $\text{CuO}_2$  planes, it is possible that mobile carries are affected by randomly-distributed charged ions. This effect should bring the inhomogeneous electronic state which is most apparent near the metal-insulator transition (MIT), since two distinct ground states can be switched by small change in the carrier concentration.

Scanning tunneling microscopy / spectroscopy (STM/STS) has proven to be a powerful tool to investigate such a spatially inhomogeneous electronic state [1]. To date, most STM/STS studies on HTS have been conducted on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  because the clean surface can be easily obtained by the cleavage. However,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  is chemically unstable near MIT. Recently, we succeeded in growing single crystals of  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  (Na-CCOC) by utilizing high-pressure flux technique [2]. Na-CCOC can be doped

near MIT [3] and shows superior cleavage. Using these crystals, we investigated the electronic states near MIT of the doped Mott insulator with STM/STS.

## 2. Experimental

$\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  single crystals used in this study are  $x \sim 0.08$  ( $T_c \sim 5$  K) and  $x \sim 0.12$  ( $T_c \sim 18$  K), being close to MIT [2]. STM/STS measurements were performed with an ultrahigh vacuum STM. Samples were cleaved *in-situ* parallel to (001) planes at low temperatures (<15 K). All STM images were taken in a constant-current mode at 7 K. Tunneling spectra were obtained by numerically differentiating the current-voltage curve.

## 3. Results and Discussion

Figure 1 shows a typical STM topograph of a cleaved surface of  $\text{Ca}_{1.92}\text{Na}_{0.08}\text{CuO}_2\text{Cl}_2$ . The image was taken at a sample bias voltage of -150 mV and a tunneling current of 10 pA. A regular square lattice is clearly

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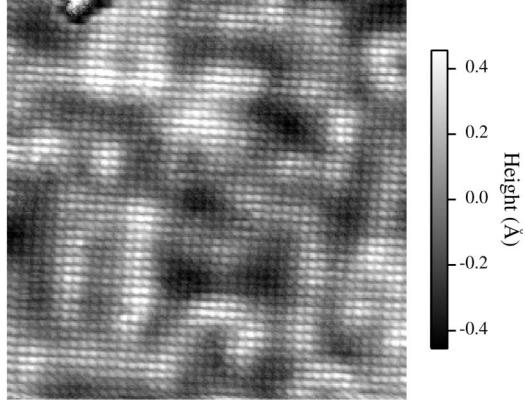


Fig. 1. An STM image of  $\text{Ca}_{1.92}\text{Na}_{0.08}\text{CuO}_2\text{Cl}_2$  ( $V_s = -150$  mV,  $I_t = 10$  pA). A scan range is  $160 \text{ \AA} \times 160 \text{ \AA}$ .

imaged. Lattice constant is  $3.8 \text{ \AA}$ , which corresponds to the  $a$ -axis length. Since all the images we observed are similar to Fig. 1, cleavage should always occur between adjacent identical layers, i.e. Ca-Cl layers.

The striking feature of Fig. 1 is the irregular corrugations superposed on the lattice image. Similar patterns, not only the river-like patterns as shown in Fig. 1 but also the patch-like patterns (for example, see inset of Fig. 2), were always observed. Therefore we believe that such irregular structures are not artifacts but characteristics of Na-CCOC near MIT. These patterns were observed to be stable in time.

Figure 2 shows differential conductance spectra taken at different positions where background corrugation is apparently high (A) and low (B). As can be seen from Fig 2, these spectra are different in overall shape depending on the positions. Therefore, we can conclude that the spatial inhomogeneity of the electronic state should be responsible for the irregular background.

At position B, V-shaped gap-like feature is evident over the energy range studied. On the other hand, the density of states (DOS) at position A tends to be energy independent at high energies while gap-like feature ( $\sim 100$  meV) still remains near the Fermi level. Namely, apparently high area seems to be approaching to "metallic" in nature. It should be noted that the absolute value of the DOS at position A should be much *larger* than the DOS at position B, because "high position" means that the feedback loop for the constant current scanning moves the tip away from the surface to compensate the large DOS.

Such nano-scale coexistence of electronically different regions is in stark contradiction to the conventional electronic screening in an ordinary metal. Actually, the Thomas-Fermi screening length for the electron gas in two dimensions is estimated to be  $\sim 0.7 \text{ \AA}$  [4], which is much shorter than the length scale of the observed irregular structure. This implies that the observed in-

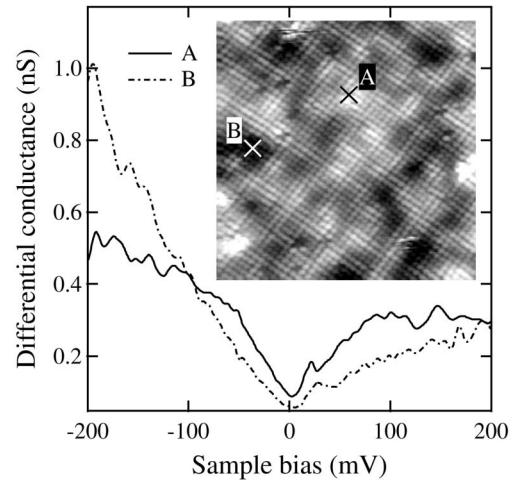


Fig. 2. Spatial dependence of normalized differential conductance in  $\text{Ca}_{1.88}\text{Na}_{0.12}\text{CuO}_2\text{Cl}_2$ . (inset) An STM image of the sample ( $V_s = -150$  mV,  $I_t \sim 50$  pA) and the position where the spectra were taken.

homogeneity is highly unconventional in origin. Such inhomogeneity is reminiscent of the electronic phase separation driven by strong interaction among electrons [5].

If the electronic phase separation occurs in an uniform system, periodic spatial modulation of the electronic states, such as stripe phase [6], is most likely. Furthermore, such a modulation should *not* be stable in time without pinning. Therefore, if the electronic inhomogeneity observed in Na-CCOC is originated from the electronic phase separation, there must be a random potential which pins and tears the original periodic pattern. It is natural to consider the dopant atoms as the source of pinning.

Even if the electronic phase separation is not completed in Na-CCOC, it is no wonder that the electronic states near MIT can be easily perturbed by small disturbance. Therefore, the potential produced by the dopant atom (Na) might promote the electronic phase separation locally. In any case, the electronic inhomogeneity observed in Na-CCOC must be the manifestation of the strong correlation among electrons.

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