Nanoscale One-Dimensional Scattering Resonances in the CuO Chains of $YBa_2Cu_3O_{6+x}$

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We present scanning tunneling spectroscopy measurements of the CuO chain plane in $YBa_2Cu_3O_{6+x}$, showing a ~25 meV gap in the local density of states (LDOS) filled by numerous intragap resonances: intense peaks in LDOS spectra associated with one-dimensional, Friedel-like oscillations. We discuss how these phenomena shed light on recent results from other probes, as well as their implications for phenomena in the superconducting CuO_2 plane.

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Recently there has been a great deal of interest, both experimental [1–5] and theoretical [6–15], in the study of quasiparticle scattering resonances in the high temperature superconductors. These resonances, usually associated with impurities, have a spatial and energetic structure strongly dependent on the environment from which they arise and hence have the potential to provide new insights into high temperature superconductivity at the microscopic scale. In this Letter we report on the study of resonances observed while tunneling into the CuO "chain" plane of $YBa_2Cu_3O_{6+x}$ (YBCO). Understanding the electronic nature of this plane, and its interaction with the superconducting CuO_2 plane, may prove crucial to understanding the nature of superconductivity in this material. A number of different bulk techniques, including inelastic neutron scattering (INS) [16–19], nuclear quadrupole resonance spectroscopy (NQR) [20,21], microwave penetration depth [22], and angle resolved photoemission spectroscopy (ARPES) [23,24], have been employed to determine the electronic structure of this system. Although each of these techniques has provided strong evidence for one-dimensional (1D) phenomena, their exact nature remains a mystery, as does their relationship to superconductivity. Here we report results from a direct investigation of this relationship by scanning tunneling microscopy (STM).

Spatially resolved measurements of local electronic structure can be carried out in YBCO using STM, provided that an atomically clean and flat surface can be prepared [25]. For this study, we use an STM that has been described elsewhere [26]. The YBCO samples are highly oxygenated ($x = 0.97$), twinned single crystals grown by the flux method, and have $T_c = 93$ K. The samples are cleaved in cryogenic ultrahigh vacuum at 4.2 K and immediately inserted into the STM head in order to preserve the delicate CuO chains on the surface [25]. The primary STM technique we use for this study is LDOS mapping, whereby the differential tunneling conductance $G(V, \mathbf{R}) = dI/dV$ (proportional to the LDOS) is measured as a function of energy $E = eV$ (set by the sample bias V) and position $\mathbf{R}$.

Cold cleavage of YBCO single crystals typically reveals either the CuO chain plane or the complementary BaO layer, and here we focus on the former. Figure 1a is a constant-current topograph that clearly reveals the CuO chain direction (the **b** axis). While one can see faint features associated with individual Cu and O atoms, the most obvious feature along the chains is the $\lambda \sim 1.3$ nm wavelength modulation. This is particularly true in the 100 times larger Fig. 1b, which also shows that these LDOS modulations tend to remain in phase (along the **a** axis) over approximately three neighboring CuO chains. The existence of these one-dimensional LDOS modulations has been known for some time from topographic STM measurements, although their origin and nature have been the source of much dispute [25]. In this work, to more fully understand the electronic structure of the CuO chain plane and how its spatial variations give rise to such topographic images, we applied the technique of LDOS mapping

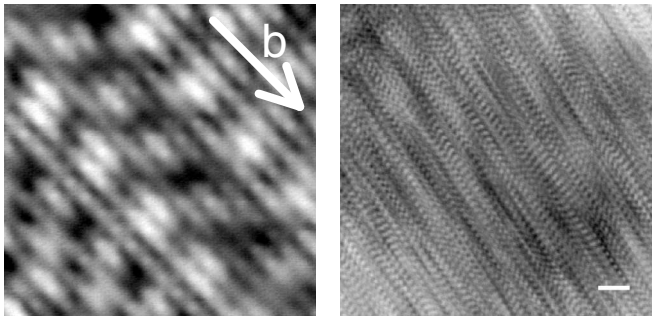

FIG. 1. (a) 50 Å STM topography of a CuO plane. The Cu and O atoms (faint round and oval features) are almost completely washed out by the much stronger LDOS modulations with wavelength ~1.3 nm along the **b** axis. (b) 500 Å topography of the same CuO chain plane, showing a characteristic tweed pattern generated by the LDOS modulations with correlation length ~4 nm along the **b** axis, and ~3 chains (1 nm) along the **a** axis. Scale bar (50 Å) shows the relative size of (a). Here $I = -50$ mV, $V = 50$ pA. All data are unfiltered and obtained at 4.2 K.

(Fig. 2). One can immediately see that the local electronic structure is highly 1D at each individual energy and that spatial variations in the LDOS occur at different locations for different energies. The complete set of spectroscopic data is best seen as a movie [27].

We may derive several significant, new results from these data. First, in each of the LDOS maps several regions show a significantly higher than average conductance. For example, the conductance map at the Fermi energy (Fig. 2b) shows zero LDOS over much of the surface, as one would expect in the presence of an electronic energy gap. However, there are also several 1D regions (resonances) that show a high amplitude, oscillating LDOS pointing along the b axis. Conductance maps at higher energies (Figs. 2c–2f) show similar behavior, with randomly distributed, strong resonances, the main difference being that they are superimposed on a steadily rising background LDOS. Eventually the black regions of zero LDOS disappear everywhere at energies above ~25 mV indicating the edge of the energy gap.

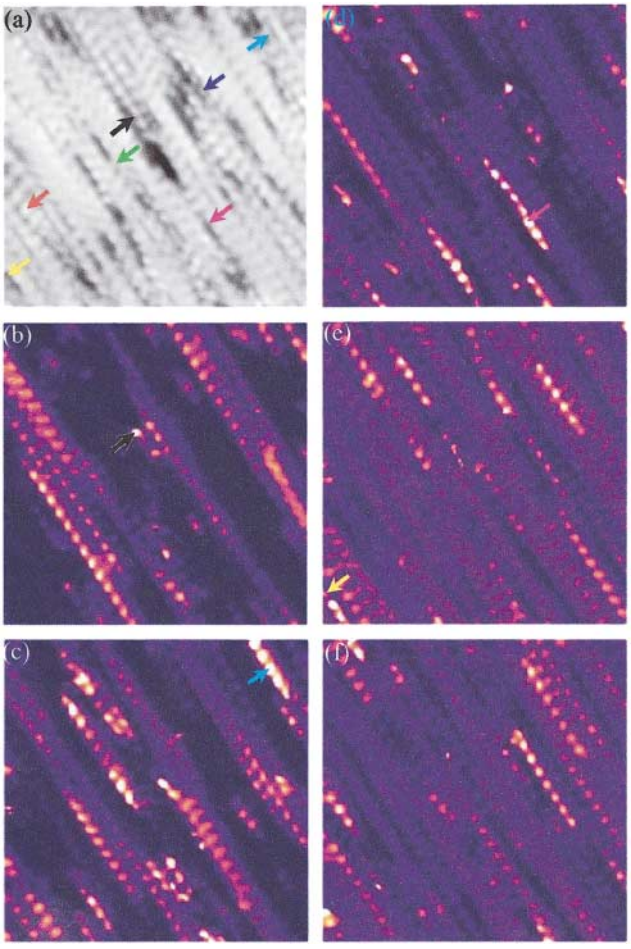

FIG. 2 (color). (a) 250 Å topography of a CuO plane, simultaneously obtained with LDOS maps (b)–(f) of equally spaced energies from 0 to 24 meV [37]. Differential conductance spectra are measured at each pixel of the topography (−200 mV, 200 pA) using a lock-in amplifier. Colored arrows indicate the locations of resonances whose spectroscopic curves are shown in Fig. 3 with the same color. The complete set of spectroscopic data is best seen as a movie [27].

Figure 3 (inset) contains typical examples of the conductance spectra taken at the point of highest LDOS for resonances occurring at several different energies. The spatial location of each of these spectra is indicated by an arrow in the topography of Fig. 2a, as well as in the appropriate LDOS image in Fig. 2. A sharp LDOS peak, of full width at half maximum linewidth approximately 3 meV, is associated with each resonance. The spectrum of a resonance is usually not particle-hole symmetric in amplitude, but careful study shows that if the high LDOS of a resonance is centered on energy Ω, a smaller local LDOS maximum also appears at $-\Omega$. For example, Fig. 3a shows a spectrum with two large resonances (−6 meV and +13 meV, black and red upward pointing arrows, respectively) each of which has shadows at opposite polarity (black and red downward pointing arrows, respectively).

We may further characterize these resonances by considering the discrete two-dimensional autocorrelation of each of the LDOS maps, $g(\mathbf{r}) = \sum_{\mathbf{R}} G(\mathbf{R})G(\mathbf{R}+\mathbf{r})$, where G is the differential tunneling conductance and the summation is over all measured locations. In Fig. 4a we plot $g(\mathbf{r})$, $\mathbf{r}$ parallel to the $\mathbf{b}$ axis, for LDOS maps at +50 and −50 mV. Several phenomena are made apparent here. First, the exponential decay length of $g(\mathbf{r})$ with $\mathbf{r}$ indicates that

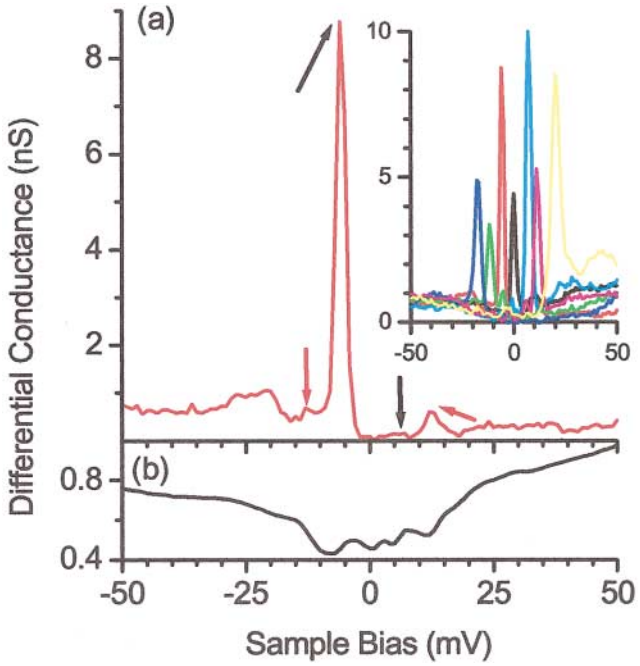

FIG. 3 (color). (a) Typical example of a spectrum measured as indicated in Fig. 2. Black arrows at ±6 meV and red arrows at ±13 meV indicate the two large resonances at this location, as well as their "shadow resonances" that always appear at the opposite polarity. The inset shows similar resonance spectra obtained at other locations as indicated in Fig. 2. (b) The average of all spectra obtained in the region of Fig. 2. The presence of a gap is evident, although it is highly asymmetric and filled in due to resonances of various energies randomly sprinkled throughout the field of view.

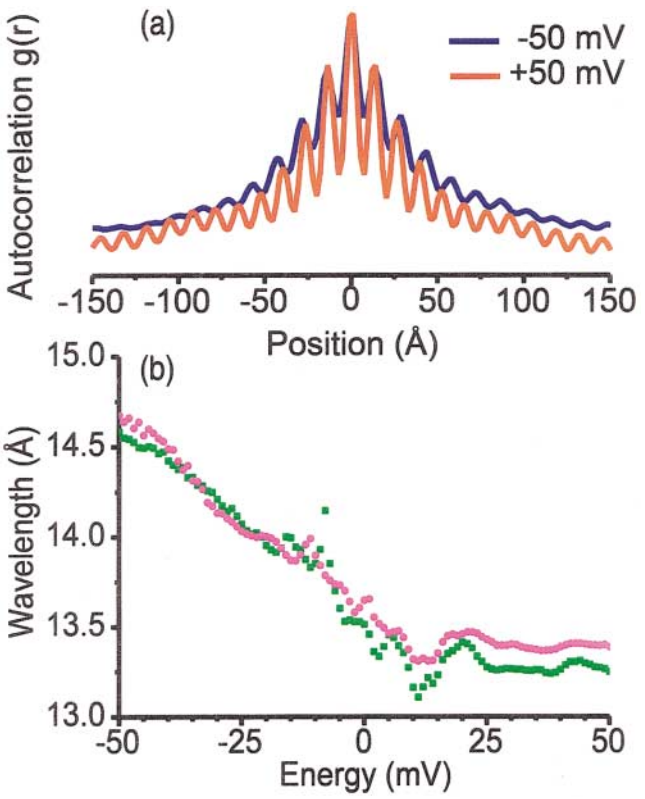

FIG. 4 (color). (a) Autocorrelation function $g(r)$ taken parallel to the **b** axis for the LDOS maps at -50 mV (blue) and $+50$ mV (red). The different resonance oscillation wavelengths are apparent, as is the exponential decay ($\sim$4 nm correlation length). (b) Dispersion relation of the resonance oscillations, measured from fitting an exponentially decaying sinusoid to the autocorrelation [as in (a)] of each of 101 LDOS maps from -50 to $+50$ mV. One of the curves (green squares) was obtained from analyzing the data of Fig. 2, while the other (magenta circles) was measured on a different crystal.

resonance oscillations are correlated only over a length of $\zeta_b \sim 4$ nm, roughly independent of the energy of the map considered. Second, the wavelength of the LDOS oscillations [the periodicity of $g(\mathbf{r})$] is not constant. By measuring the periodicity of the autocorrelation function for each LDOS map, we can extract the wavelength of LDOS oscillations as a function of energy (Fig. 4b), showing that the wavelength of these electronic states in the CuO chain falls with increasing energy. We have found similar results on multiple samples and show data taken from two (that of Fig. 2 and another) here. Dispersion relationships have been measured in a similar fashion for surface states on noble metals using the wavelength of Friedel oscillations at step edges [28], but this is the first application of this technique to a highly correlated electronic system. Finally, from autocorrelations along the **a** axis we find that, as in the case of the modulations in the topography, LDOS resonance oscillations are correlated over roughly three atomic chains. The shorter correlation along the **a** axis, compared to that along the **b** axis, may be due to stripes in the CuO_2 plane.

In light of these new observations, the original interpretation of these modulations as 1D charge density waves (CDWs) [20,25] should be revisited. Although we cannot rule out some novel CDW system in the chains, a CDW typically has a fixed wavelength, given by nesting vectors on the Fermi surface. Here we find that the modulations have a rather strong dispersion, changing wavelength by more than 10% within 50 meV of the Fermi energy.

If these modulations are not CDWs, then another explanation must be found. One possible interpretation is within the context of superconducting quasiparticle scattering. Theory predicts that quasiparticle scattering by impurity atoms in the CuO_2 plane of a d-wave superconductor creates a local electronic state (impurity state) nearby [29–32]. Quasiparticle scattering resonances have, in fact, been observed by STM in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) [1–4]. A recent theory for the electronic structure of the chain plane of YBCO postulates 1D scattering resonances in the CuO chain plane of this system if the CuO chains are themselves superconducting due to their proximity to the superconducting CuO_2 planes [33]. Under these circumstances, the quasiparticles of this 1D superconductor may then resonantly scatter (from oxygen vacancies, for example) resulting in a new type of 1D quasiparticle scattering resonance. These 1D scattering resonances would be manifest as an intragap peak in the LDOS that oscillates in space due to Friedel-like oscillations. This theory is consistent with our observation of strong resonances, distributed at random in space, and oscillating with an incommensurate wavelength.

The source of scattering leading to these resonances remains unclear. One possibility, O vacancies, should be testable by counting the number of resonances and comparing it with the expected number of vacancies — for a doping of $x = 0.97$, one would expect approximately 130 O vacancies (and hence scattering resonances) in a 250 Å field of view such as that of Fig. 2. Unfortunately, as it is often difficult to determine where one resonance ends and another begins when the density is this high, counting of resonances in this sample is difficult. Our estimate of 150 ± 30 resonances here is consistent with scattering from O vacancies as a source, but further measurements of samples at different doping levels will be required to test this possibility.

Regardless of the source of these resonances or their transition temperature, this picture of the electronic structure of the CuO chain plane meshes well with a variety of other recent low temperature observations. For example, both INS [16,18] and NQR [20,21] measurements find evidence of incommensurate 1D charge modulations that appear consistent with the LDOS oscillations directly imaged here. Furthermore, an intense and similarly dispersing peak in the ARPES spectra close to the Fermi surface has recently been observed [23].

At the same time, the presence of superconductivity in the chains, as demonstrated both by the presence of

an electronic gap and by the existence of scattering resonances, has also been suggested by infrared spectroscopy measurements that find a large anisotropy of the London penetration depth attributable to superconductivity in the chains [22]. ARPES [23] and microwave surface impedance measurements [24] also find evidence of chain superconductivity, although in both of these cases the more interesting finding is that superconductivity (as measured by the gap magnitude [23] and the spectral weight for transport [24]) within the superconducting CuO_2 plane itself is highly anisotropic, being as much as 50% higher along the **b** axis than the **a** axis.

The existence of proximity-coupled superconductivity in the chains demonstrates clearly that the CuO plane, separated only 4 Å from the CuO_2 plane, is strongly influenced by it. In light of this, the question of how the 1D electronic resonances reported here in turn influence the electronic structure of the CuO_2 plane is particularly intriguing. These observations imply significant local charge density variations over a characteristic distance of $\sim$1.3 nm. Unscreened Coulomb effects might then lead to spatial gap modulations, as postulated for BSCCO [34–36]. A complete understanding of these 1D resonance phenomena and their interactions with other electronic degrees of freedom may therefore be required to explain the directional dependence of both the superfluid density and the gap magnitude, as well as 1D signatures detected using other techniques, in the CuO_2 plane of YBCO.

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