Scanning tunneling microscopy investigations of the local structure of $Tl_2Ba_2CaCu_2O_8$ single crystals

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(Received 28 July 1989; accepted for publication 19 September 1989)

The in-plane structure of single-crystal samples of $Tl_2Ba_2CaCu_2O_8$ has been imaged at room temperature using a scanning tunneling microscope. Atomic-resolution surface images exhibit areas in which the structure has tetragonal symmetry (peak spacing 2.5 ± 0.2 Å) and regions in which the structure is distorted from tetragonal symmetry. The lattice spacing indicates that the observed structure corresponds to the in-plane thallium and oxygen positions. The observation of both sites also suggests that the Tl-O band makes a significant contribution to the density of states near the Fermi level. In addition, a weak one-dimensional superlattice (period 10 ± 0.5 Å) which shows short-range order has been observed.

The recent discovery of high-temperature superconductivity in the Tl-Ba-Ca-Cu-O system has produced a family of superconducting phases with transition temperatures (T_c) above 100 K.[1-5] The highest documented T_c in these thallium materials (125 K) has been recorded for the $n = 3$ member of the series of compounds that have the general structural formula $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1$–3).[4] The tetragonal crystal symmetry and average atomic positions of this series of materials have been well characterized using x ray,[2-5] neutron,[6] and electron[2,7] diffraction. Other more localized features such as the syntactic intergrowth of different phases,[7,8] thallium and oxygen positional disorder,[3,6] and cationic substitution at the Ca and Tl sites[3,9] are not well understood. Since the superconducting properties of the thallium materials are strongly dependent on these local structural features, it is important to characterize them in greater detail. In this letter we use the scanning tunneling microscope (STM) to obtain real-space images of the in-plane structure of single-crystal $Tl_2Ba_2CaCu_2O_8$ (Tl-2212). Atomic-resolution surface images are found to exhibit areas in which the structure has the tetragonal symmetry characteristic of the bulk crystal and small regions in which the structure is distorted from this ideal tetragonal symmetry. In addition, we have imaged a weak one-dimensional superlattice (period, 10 ± 0.5 Å) that has only short-range order.

The crystal growth procedure for the preparation of Tl-2212 crystals has been described previously.[8] Briefly, crystals were grown from a melt composition of $Tl_2Ba_{0.5}Ca_{1.5}Cu_2O_x$ made up of high-purity (>99.99%) oxides that were stored and processed in an argon atmosphere dry box. This mixture, sealed in a Pt crucible with a wired on Pt foil lid, was rapidly heated in a vertical tube furnace under one atmosphere of oxygen to 950 °C. The crucible was maintained at 950 °C for 1 h, cooled to 700 °C over 12.5 h, and finally cooled to 25 °C in 5–6 h. The resulting plate-like crystals were analyzed using energy dispersive x-ray analysis (EDS) and x-ray precession photography. EDS was performed on both crystal faces to identify samples with 2212 composition. Futher x-ray diffraction analysis of these crystals showed only minor intergrowths of the $Tl_2Ba_2Ca_2Cu_3O_{10}$ phase and demonstrated that the c axis was perpendicular to the crystal surface.

The STM images were acquired using a commercial instrument (Nanoscope, Digital Instruments, Inc., Santa Barbara, CA) operated in air. The calibration of the piezodrive and the analysis of images has been described previously.[10] Gray-scale images were obtained in the constant current mode; white areas in these images correspond to surface protrusions and/or a high local density of states. The plate-like samples were cleaved with a sharp razor prior to imaging and mounted in the STM with the tip parallel to the c axis of the crystal. With this orientation images correspond to the in-plane surface structure. Several single-crystal samples were investigated in this study; the reported images are representative of these samples.

An atomic-resolution image of Tl-2212 recorded with a sample versus tip bias voltage of -580 mV and a tunneling current of 0.2 nA is shown in Fig. 1(a). Under these bias conditions tunneling occurs from filled states in the sample (near the Fermi level) to empty states in the tip. The peaks in this image define a square lattice that is consistent with the tetragonal symmetry of the crystal determined by diffraction [Fig. 1(b)].[2-7] Similar images were also recorded with a positive bias of 200 mV; in fact, for bias voltages between -600 and 200 mV we observe little change in images of the Tl-2212 surface. The average peak spacing determined from several images is 2.5 ± 0.2 Å. This peak spacing is similar to the average in-plane Tl-O separation reported in diffraction studies [2.48 Å, Fig. 1(b)][3] but is significantly larger than the in-plane Cu-O distance (1.93 Å). We therefore assign the observed surface structure to the Tl and O sites, although additional studies are necessary to confirm this point.

The observation of both atomic positions suggests that the Tl and O sites make similar contributions to the density of states near the Fermi level. These results differ from STM images of $Bi_2Sr_2CaCu_2O_8$ which only exhibit the Bi sites,[11] but are consistent with recent electronic structure calculations that predict an antibonding Tl($6s$)-O($2p$) band near

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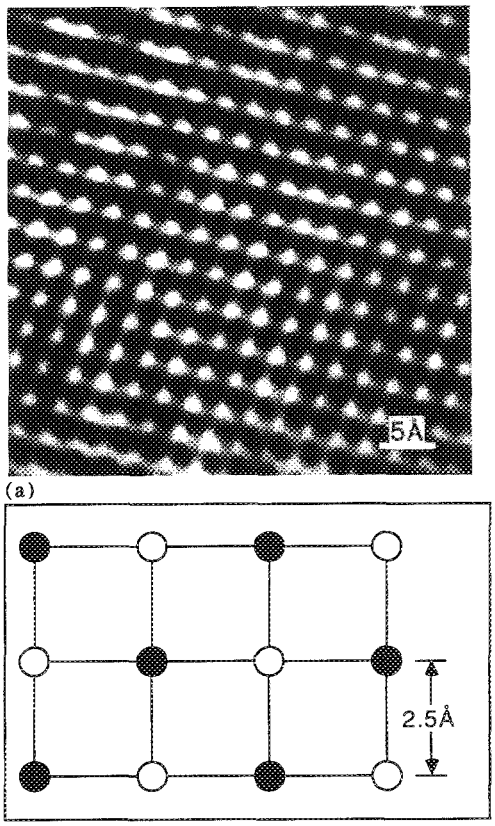

FIG. 1. (a) 40×40 Å STM image of single-crystal $Tl_2Ba_2CaCu_2O_8$ recorded with a bias voltage of − 580 mV and a tunneling current of 0.2 nA. The structure in the image has tetragonal symmetry with a spacing of 2.5 ± 0.2 Å between surface sites. (b) Schematic diagram of the ideal tetragonal Tl-O plane. The filled and open circles represent the thallium and oxygen sites, respectively.

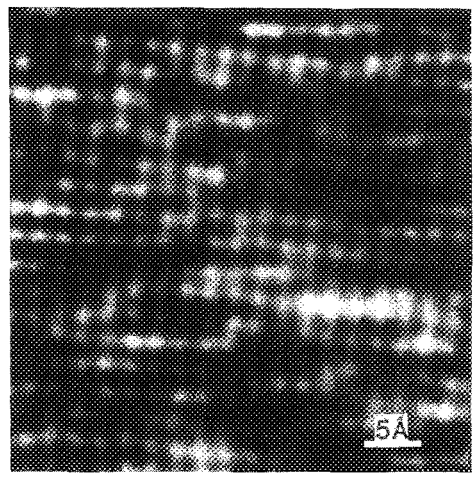

FIG. 2. 40×40 Å image of Tl-2212 recorded with a bias voltage of − 580 mV and a tunneling current of 0.2 nA. Several regions in this image exhibit structure that is distorted from tetragonal symmetry.

the Fermi level of Tl-2212.[12] This "antibonding" band must be partially filled; however, since our images were acquired while tunneling from occupied sample states. It is possible that carriers are produced in the Tl-O band by charge transfer from the Cu-O band, calcium substitution at thallium sites, and/or oxygen vacancies.[3,9]

The STM image of Tl-2212 [Fig. 1(a)] exhibits little disorder. Diffraction analyses of Tl-2212[3,6] have shown that a better refinement of the Tl and O in-plane sites occurs when the oxygen positions are allowed to randomly shift from their ideal positions [Fig. 1(b)] in the tetragonal unit cell. The ~0.6 Å difference in the two Tl-O distances reported for the refined structure[3] is not detected in STM images such as Fig. 1(a), although this difference is within our experimental resolution of ± 0.2 Å. Our STM results also differ from a recently proposed structural model in which both the in-plane Tl and O sites are shifted in a correlated fashion from the ideal tetragonal positions.[13]

There are several factors that may contribute to these structural discrepancies. First, the surface structure probed with the STM may not be representative of the bulk structure determined by diffraction methods (i.e., cleavage along the Tl-O or Cu-O sheets will break relatively short bonds and promote reconstruction). In addition, the structure may not be uniformly disordered but may consist of small domains with either tetragonal or lower symmetry; such domain structure would not be easily detected via diffraction. We believe that this latter possibility reflects the true surface structure of Tl-2212. For example, the structure in Fig. 2 is highly distorted in several areas. It is unlikely that these distorted regions are due to tip effects[14] since the surrounding areas exhibit tetragonal symmetry. The origin of these structural distortions is not certain, although they may be due to cation substitution and/or oxygen vacancies.[3,6,9]

In large-area images of Tl-2212 we also observe one-dimensional superlattice modulations (Fig. 3). The average period of these modulations (determined from five images) is 10 ± 0.5 Å and the amplitude is 0.4 ± 0.2 Å. Although the

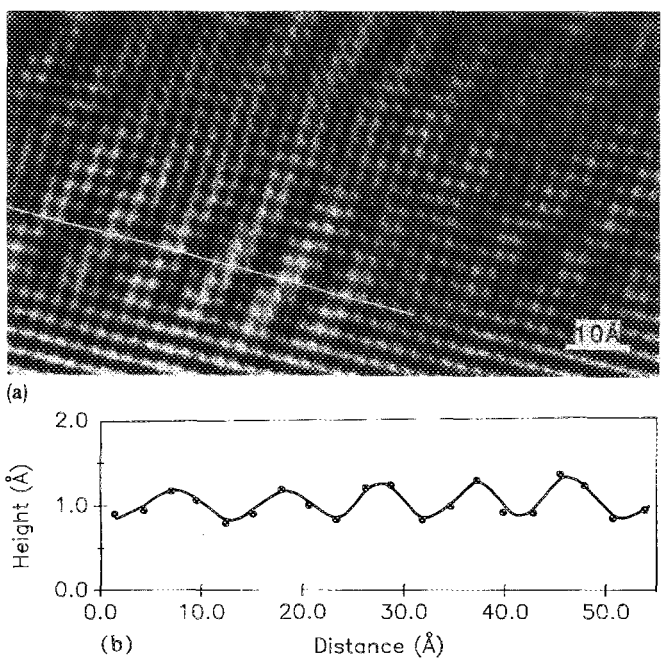

FIG. 3. (a) Large-area image that shows the one-dimensional superlattice modulations with a 10 ± 0.5 Å period. The image was recorded with a bias voltage of − 200 mV and a tunneling current of 0.2 nA. (b) Profile of the surface corrugation measured along the line in (a).

vertical corrugation determined in our STM experiments may not reflect the actual modulation of the atomic positions, this corrugation is substantially smaller than the 4 Å corrugation determined by STM for superlattices in $Bi_2Sr_2CaCu_2O_8$.[15] In addition, the superlattice modulations that we observe exhibit only short-range order (50–80 Å) compared with > 600 Å for the bismuth system.[11] Weak superlattice reflections have also been observed in selected area electron diffraction studies of Tl-2212[7,16]; however, the superlattice period determined in these diffraction investigations (23 Å) is significantly larger than we have found. This discrepency may be due to fundamental differences between the bulk and surface structure, although it is also important to recognize that modulations were detected by diffraction only after heavy exposure to electrons.[16] Additional investigations (currently in progress) will be necessary to resolve these differences and to determine the origin of this interesting structure.

In summary, we have used the STM to image single-crystal samples of $Tl_2Ba_2CaCu_2O_8$ with atomic resolution. We have observed surface structure with tetragonal symmetry and a lattice spacing of 2.5 ± 0.2 Å which is consistent with imaging the in-plane thallium and oxygen atomic positions. The observation of both atomic positions suggests that the Tl and O sites make substantial contributions to the density of states near the Fermi level. In addition to the tetragonal structure, locally disordered regions have been observed indicating that large temperature factors determined in diffraction studies may not be due to a uniformly disordered structure. Furthermore, we have also detected weak one-dimensional superlattice modulations, with a 10 ± 0.5 Å period, which exhibit only short-range order.

C. M. L. acknowledges support of the work at Columbia University by the National Science Foundation (Presidential Young Investigator Program) and the David and Lucile Packard Foundation. The work at Sandia National Laboratories was supported, in part, by the United States Department of Energy, Office of Basic Energy Sciences, under contract No. DE-AC04-76DP00789. The technical assistance of M. A. Mitchell is gratefully acknowledged.

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