Impurity-Induced Bound Excitations on the Surface of $Bi_2Sr_2CaCu_2O_8$

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(Received 22 March 1999)

We have probed the effects of atomic-scale impurities on superconductivity in $Bi_2Sr_2CaCu_2O_8$ by performing low-temperature tunneling spectroscopy measurements with a scanning tunneling microscope. Our results show that nonmagnetic defect structures at the surface create localized low-energy excitations in their immediate vicinity. The impurity-induced excitations occur over a range of energies, including the middle of the superconducting gap, at the Fermi level. Such a zero bias state is a predicted feature for strong nonmagnetic scattering in a d-wave superconductor.

PACS numbers: 74.50.+r, 73.20.Hb, 74.72.Hs

There is now a great deal of evidence that the superconducting state in a number of high-T_c superconductors has a dominant $d_{x^2-y^2}$ symmetry [1]. One key evidence is that nonmagnetic impurities, which only affect conventional s-wave superconductors weakly, can act as strong pair breakers in the high-T_c superconductors [2,3]. However, to date, there are no atomic scale studies of superconductivity in the immediate vicinity of individual impurities in a high-T_c superconductor. Such experiments are motivated by recent theoretical studies of the local response of a d-wave superconductor to individual impurities. These theories [4,5] predict local signatures of d-wave pairing and emphasize the importance of local variations in the electronic properties of a d-wave superconductor [6–8]. There is also now growing theoretical and experimental evidence that quasiparticle scattering from surfaces and twin boundaries of d-wave superconductors gives rise to effects that have no analog in conventional s-wave superconductors [9–14].

The scanning tunneling microscope (STM) offers a direct method to examine the spatial variation of the electronic properties in the superconducting state near defect structures [15]. In this paper, we report on STM measurements of the local density of states (LDOS) near regions of a d-wave superconductor that have been perturbed by the presence of atomic-scale impurities. Our results show that nonmagnetic impurities induce low-energy excitations in a d-wave superconductor, which are localized on length scales comparable to the superconducting coherence length. Such impurity-bound excitations for nonmagnetic impurities are a predicted signature of a d-wave superconductor [5] and are in stark contrast to the behavior of conventional s-wave superconductors, in which to create similar effects, the impurities need to be magnetic [15]. More specifically, we observe that the impurity-induced excitations for a d-wave superconductor can occur as a pronounced and narrow resonance at energies close to the Fermi level, E_F. Such a zero bias feature has been predicted to occur for impurity scattering in d-wave superconductors in the unitarity limit [5] or for strong impurities when considering the order parameter suppression [16]. From a different perspective, a zero bias resonance has also been predicted and observed for Andreev scattering from interfaces at which quasiparticles experience a sign change of the d-wave order parameter and form a surface bound state at E_F [10,11,17,18]. The similarity suggests that multiple Andreev scattering similar to that proposed at interfaces [10] is at work in the bulk at strongly scattering impurities.

We performed our experiments using an ultrahigh vacuum (UHV) STM which operates at low temperatures. The $Bi_2Sr_2CaCu_2O_8$ single-crystal samples were grown using a directional solidification technique and were reoxygenated prior to the STM measurements. The experiments reported here were carried out on overdoped single-crystal samples with a superconducting transition temperature at 74 K and a transition width of 3 K, as characterized by magnetometry measurements. Samples were introduced into the UHV chamber at room temperature and mechanically cleaved prior to STM measurements performed at low temperatures ($T = 5$ K.) We used a polycrystalline Au wire as our tip; however, the chemical identity of the last atom on the tip is unknown. The local quasiparticle density of states of the $Bi_2Sr_2CaCu_2O_8$ surface was obtained from measurements of the differential conductance dI/dV (where I is the current) of the STM junction versus sample bias voltage V (with respect to the tip) performed under open feedback loop conditions.

Figure 1 shows a constant current STM topograph of the cleaved $Bi_2Sr_2CaCu_2O_8$ surface. The weakest bond in the crystal is between the two adjacent BiO layers; therefore it is most likely that the topmost atomic layer of a cleaved sample is BiO [19]. The image in Fig. 1 shows a long length scale modulation (period of 27 Å) which has been previously observed with the STM and has been associated with the relaxation of Bi atoms in BiO layer [19]. Imaging the $Bi_2Sr_2CaCu_2O_8$ surface in several regions showed that there are intrinsic defects on the surface. The intrinsic impurities are difficult to

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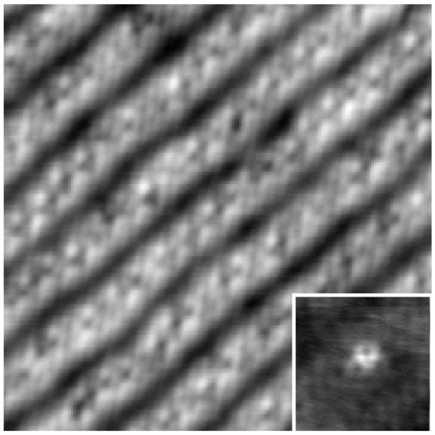

FIG. 1. Constant current STM topograph (200 Å × 200 Å) of the $Bi_2Sr_2CaCu_2O_8$ surface; $R_J = 250$ MΩ, $V = 0.25$ V. Inset: a topograph of a native surface defect (50 Å × 50 Å); $R = 20$ MΩ, $V = 0.1$ V. The contrast (black to white) in the main image and the inset corresponds to an apparent corrugation of 0.8 and 0.3 Å, respectively.

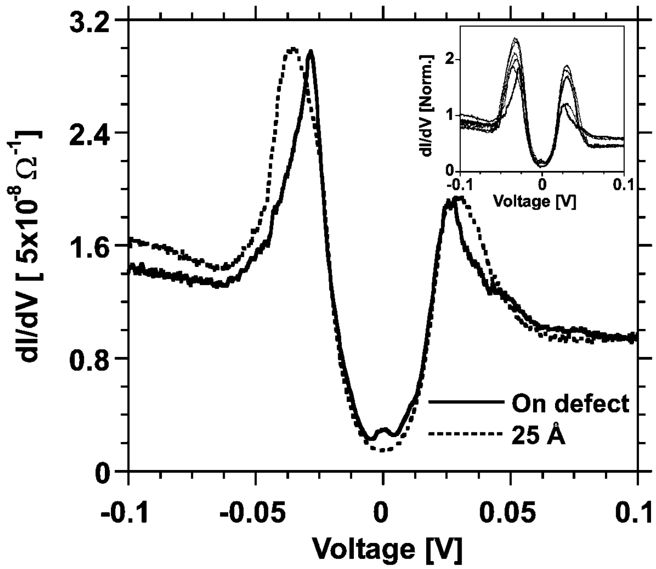

FIG. 2. Tunneling spectroscopy near an intrinsic surface defect shown in the inset of Fig. 1. Inset: the normalized spectra taken on different locations on two different samples; the data in the inset is normalized by the values of $1/R_j$ at -0.1 V. The voltage refers to sample bias.

identify, except in some cases, such as that shown in the inset of Fig. 1, where defects appeared as protrusions in STM topographs.

The intrinsic defects are of fundamental interest, since they are considered crucial to understanding the deviations of low-temperature properties of high-T_c superconductors from those expected for a clean d-wave superconductor [2,3,6,7]. Our STM measurements near intrinsic surface defects show that such defects indeed modify the LDOS of the $Bi_2Sr_2CaCu_2O_8$ surface. For example, Fig. 2 shows the measurements of LDOS with the tip "on" and "off" the intrinsic surface defect shown in the inset of Fig. 1. There is a clear enhancement of the LDOS at low energies at this impurity site, as compared to that measured at a lateral distance of about a coherence length away. The change in dI/dV near E_F corresponds to about 20% of that measured at voltages above the superconducting gap. However, we found other intrinsic surface defects which did not modify the low-energy LDOS as much, but affected only the quasiparticle peaks or the LDOS background measured at higher voltages. Overall, the STM spectra over many regions of the "bare" surface, away from any surface defects, were comparable to those previously reported in the overdoped regime [20]. In the inset of Fig. 2 we show a collection of spectra from different regions of two samples with similar doping levels. The values of the maximum gap ($2\Delta_{max}/k_b T_c \sim 9$), the asymmetric background, and other features of our spectra, such as the width of the quasiparticle peaks, are similar to those previously reported by Renner *et al.* for a sample with a similar doping level and T_c.

The intrinsic surface defects that do modify the LDOS at low energies can be considered as evidence for impurity-induced excitations due to nonmagnetic scattering in a d-wave superconductor. However, the magnetic state of such defects is unknown; hence to illustrate the main point of this work, we focus the rest of this paper on ostensibly nonmagnetic defects created with the Au STM tip. Such defects were deposited onto the surface by bringing the Au STM tip close enough to the surface to cause transfer of atoms from the tip to the sample. We monitored the current through the STM junction during this procedure and retracted the tip once the current began to saturate, signaling the formation of a small contact. In the regime of close contact, it has been shown that an STM junction resistance, $R_J \sim 25$ kΩ, is indicative of the formation of a single metal atom contact between the tip and the surface [21]. The STM topographs of the $Bi_2Sr_2CaCu_2O_8$ surface measured after making such contacts revealed the deposition of atoms from the tip onto the sample, similar to that observed when Au tips contact other conducting surfaces. An example of tip-deposited defects is shown in the topograph in Fig. 3A, which shows a 36 Å square area of the surface with two defects appearing as protrusions with an apparent height of 0.8 Å.

The LDOS of the $Bi_2Sr_2CaCu_2O_8$ surface is dramatically modified by defects deposited from the Au STM tip. For the defect in the center of Fig. 3A these modifications are demonstrated by the data in Fig. 4A. This figure shows measurements of the LDOS with the tip over the defect structure (centered at maximum height) and at lateral distances away (in the y direction, as indicated in Fig. 3A). Comparing these spectra shows that the defect induces low-energy excitations, within the superconducting gap, in its immediate vicinity. At the impurity site, the value of dI/dV measured close to E_F is about 5 times larger than that measured at voltages above the superconducting

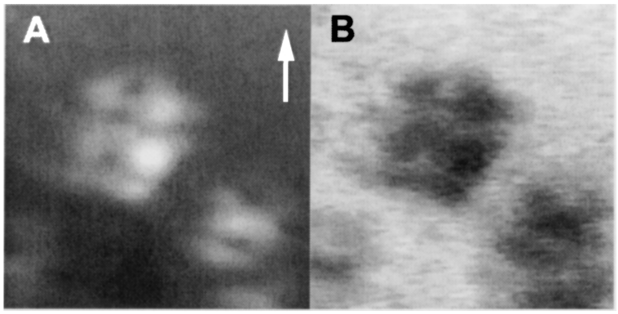

FIG. 3. (A) STM topograph (36 Å × 36 Å) of atomic-scale defects deposited from the tip; $R_J = 160\ \mathrm{M}\Omega$, $V = 0.032$ V. Black to white corresponds to 0.8 Å. These defects appear as protrusions also at higher V's. (B) Simultaneously acquired dI/dV map. Black to white corresponds to a 50% change in the signal. The areas where dI/dV is reduced (dark) correspond to the position of the bound state [22].

gap. A closer examination of data in Fig. 2A shows that the impurity-induced resonance is made of two asymmetric peaks—one above and one below E_F (within 1 meV). It is also interesting to note that this asymmetric behavior is similar to that of the quasiparticle peaks measured with tip over a region far away from the impurity.

The enhancement of the low-energy excitations is a common characteristic among the different defects deposited from the Au STM tip. This behavior is illustrated in Fig. 4B for another defect. The inset of this figure also shows difference spectra for several different defects with similar behavior (see caption for details). Another common characteristic is that the impurity-induced excitations are localized to within lateral distances of about 20 Å around the impurities. This spatial characteristic was also imaged by measuring the ac dI/dV at a fixed voltage while scanning the tip in constant dc current mode. Such an image is shown in Fig. 3B, along with the constant current topographs (Fig. 3A) acquired simultaneously from an area of the surface which includes two defect structures. The bound excitations for each of the defects are localized at the dark regions in this gray scale image [22].

The data above demonstrated the central result of this paper, that nonmagnetic defects alter the local LDOS of $Bi_2Sr_2CaCu_2O_8$ surface by inducing low-energy excitations. These excitations are bound to the impurities on length scales comparable to the superconducting coherence length. We emphasize that similar experiments on a Nb surface have previously shown the LDOS of a conventional superconductor to be insensitive to the presence of atomic-scale nonmagnetic defects deposited from an Au tip [15].

Theoretical works on impurity scattering in a d-wave superconductor have predicted that an isolated nonmagnetic defect gives rise to a semibound excitation with energy $E_B < \Delta_{\max}$ [5]. In this theoretical picture, E_B is determined by the strength of the impurity scattering potential, with $E_B = E_F$ for scattering in the unitarity limit. More recent efforts show that including the local suppression of the superconducting order parameter in the calculations drives the effective scattering strength of even a strong impurity of the unitarity limit [16]. The impurities discussed above modify the LDOS over a range of energies, many of which induce sharp resonances very close to E_F, and are in the unitarity limit. The asymmetric or splitting of measured resonances near E_F supports the possibility that impurities locally break the electron-hole symmetry [5]. However, the underlying electronic states of $Bi_2Sr_2CaCu_2O_8$ have also been suggested as a cause for the asymmetry [23].

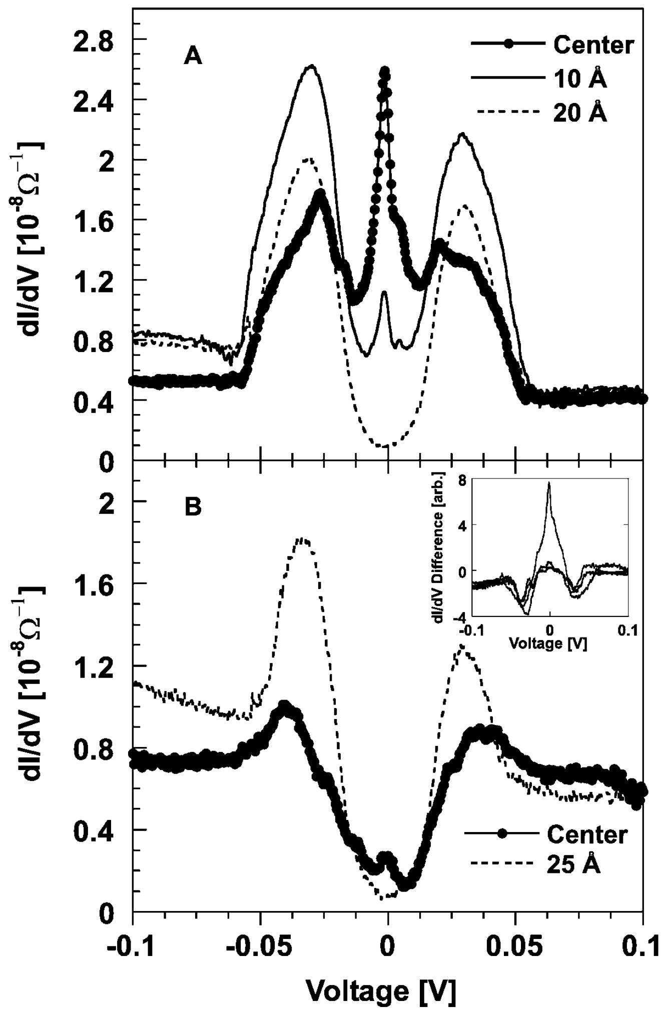

FIG. 4. (A) Tunneling conductance near the defect shown in Fig. 3A; the distnaces indicated are those lateral from the center of the defect structure along the direction indicated in Fig. 3A. (B) Spectra taken near another tip-induced defect. The inset shows differences in the spectrum with the tip on and off different defect structures.

The spatial structure of the resonance for an isolated impurity has been predicted to be cross shaped, reflecting the anisotropy in the superconducting order parameter [5]. Theoretical efforts have emphasized that the spatial and angular character of single-impurity resonances greatly affect their overlap and the nature of the many-impurity state. The overlap between these resonances for bulk impurities determines the formation of low-energy impurity bands and the behavior of the thermodynamic properties at low temperatures [5,6]. The single impurity-induced excitations measured here appear to be localized to a region of about a coherence length, and do not show the predicted cross-shaped pattern, which has a delocalized nature along the nodes of the d-wave order parameter. More detailed high-resolution spatial measurements may be required to resolve this fine structure.

The observation of the impurity-induced excitation is also intriguing within the context of local electronic properties of a d-wave superconductor near other spatial perturbations such as surfaces, crystal twins, and grain boundaries. The scattering from these boundaries is expected to give rise to Andreev bound states whenever the incident and reflected quasiparticles experience the sign change of the d-wave order parameter, i.e., when the boundary is normal to the direction in momentum space along d-wave nodes [10,13,14]. Directional tunneling spectroscopy in planar tunnel junction [11], point contact spectroscopy [17], and grain boundary tunnel junctions [18] has shown evidence for such Andreev states. The experimental data reported here show that the scattering at isolated atomic-scale impurities can also induce similar resonances at E_F. In fact, a theoretical connection between scattering processes at impurities and those at interfaces can be made within a semiclassical approximation [24,25]. Perturbations such as defects or surfaces cause scattering and interference between electronic states from different regions of k space. These processes, together with the sign change of the order parameter inherent to a d-wave superconductor, give rise to the zero energy resonances observed in the experiments.

In conclusion, we have shown that ordinary nonmagnetic impurities can induce localized low-energy excitations in a d-wave supercondutor. For some of the impurities, we observed the impurity-induced resonance to be essentially in the middle of the gap at E_F, as predicted for impurity scattering in the unitarity limit. Such a zero bias state is also the hallmark of Andreev scattering in a d-wave superconductor whenever scattering of the quasiparticles can explore the sign change of the d-wave order parameter.

The experimental data described here were obtained at IBM Almaden Research Center. It is our pleasure to thank L. H. Greene, D. J. Van Harlingen, J. A. Sauls, G. Blumberg, D. K. Campbell, and especially A. V. Balatsky, M. E. Flatté, A. Shnirman, I. Adagideli, and P. M. Goldbart for fruitful discussions.

Note added.—After submission of this manuscript, we have become aware of another STM study of defects in $Bi_2Sr_2CaCu_2O_8$ [26].

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