Surface and Superconducting Properties of Cleaved High-Temperature Superconductors

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High-resolution electron-energy-loss spectroscopy is used to characterize the resistivity, vibrations, and electronic structure of $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$ single crystals cleaved in ultrahigh vacuum. Cleaved surfaces show a variety of terminations with different properties. Spectroscopy on superconducting regions reveal energy gaps in the *a-b* plane corresponding to $(7.8\pm0.3)k_BT_c$. The superconducting gap in $YBa_2Cu_3O_7$ shows a non-BCS temperature dependence and appears to be related to a delocalized excitation near 45 meV that persists well above T_c.

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The origin and nature of superconductivity in the new class of high-temperature superconductors is actively debated, with little concensus as to the energy gap or the origin of the wide differences $[(2-8)k_BT_c]$ measured by different techniques.[1-5] Photoemission studies of cleaved surfaces can provide important new information about the empty states,[6] energy-band structure,[7,8] and shifts in the Fermi edge at low temperatures associated with the formation of a gap.[9,10] Given the range of measured gaps as well as the possibility that the surface itself may modify these properties, we have used high-resolution electron-energy-loss spectroscopy (HREELS) to determine the nature of the surfaces of two widely studied systems. Our studies reveal striking surface inhomogeneities, the detailed temperature dependence of the gap, and a well-defined excitation far above T_c that appears related to electron pairing and superconductivity.

Low-energy electron scattering can be quantitatively analyzed using dipole scattering theory.[11] For small momentum transfer the scattering probability is $P(\mathbf{k},\mathbf{k}')=A(\mathbf{k},\mathbf{k}')(n_\omega+1)\mathrm{Im}g(\mathbf{k}_\parallel-\mathbf{k}'_\parallel,\omega)$, where $n_\omega=1/[\exp(\hbar\omega/kT)-1]$ is the Bose-Einstein factor, $\hbar\omega$ the loss energy, and $\mathbf{k}$ and $\mathbf{k}'$ the incident and scattered wave vectors. $A(\mathbf{k},\mathbf{k}')$ represents a kinematic prefactor depending on the scattering conditions while Img is the loss function. We have derived the loss function for a set of stacked conducting layers separated by dielectric slabs where both the polarizability and free-carrier scattering contributions to the conducting layers are included.[12] Using this model and our scattering data we have determined the frequency-dependent resistivity of these layers. The absolute accuracy of the resistivities we determine are limited by errors in calibrating the spectrometer acceptance angle due to uncertainties in sample perfection, and are estimated to be $\pm50\%$. We note that the most metallic layers found for either 2:2:1:2 or 1:2:3 effectively screen the incident electric field to make our measurements sensitive to only the topmost metallic layers. For 1:2:3 this also makes the loss signal proportional to the layer resistivity and prevents us from detecting bulk excitations (e.g., phonons). For our scattering conditions the losses between 10 and 100 meV arise from electron interactions over a distance of 10^2–10^3 Å which sets a lateral scale to the local resistivity we probe.

Measurements were performed in a UHV system operating at 6×10^{-11} Torr which houses our single-pass 2.5-cm-diam hemispherical-analyzer-based electron-energy-loss spectrometer. For this work the analyzer is operated with a pass energy of 70–90 meV and acceptance angles of 1.1°–1.6°, and is fixed at a 90° angle to a comparably monochromatized incident beam. Angle-dependent measurements confirm that the loss features reported here arise from dipole scattering. The spot focusing of our hemispherical-analyzer system (found to be ~70 μm diam) proved crucial in these studies as it has allowed us to study small flat regions of these surfaces and identify different surface terminations.

The single-crystal 1:2:3 samples[13] exhibited T_c's of 93 K with a 10%-to-90% transition width (ΔT) of 0.3 K. The 2:2:1:2 samples[14] had T_c's of mostly 85 K and $\Delta T=3$ K, with some samples having T_c's of 75 or 91 K. After HREELS the samples were removed for detailed microscopic investigation and T_c measured again by ac susceptibility. Overall, twelve thin samples of each crystal (<1 mm$\times$0.5 mm) were mounted using conductive epoxy onto a copper cold finger at the end of a rotatable tube containing an Air Products crytotip. The sample temperature was calibrated from a Chromel-Alumel thermocouple on the cold finger. Cleavage was performed by pulling off a small metal tab *in vacuo* that was epoxied onto the top surface of the sample, usually exposing several small flat regions for each cleave. The epoxy near the sample edges could be detected and distinguished by its characteristic hydrocarbon vibrations.

Figure 1 shows a series of loss spectra for 2:2:1:2 taken after cleavage at 22 K. Typical of all 2:2:1:2 cleaves we find features that depend on the beam location on the sample. The overall level of the loss background reflects the resistivity of the exposed terminal layer(s), which varies here likely from inhomogeneities in doping, e.g., due to variations in oxygen content.[15] Here the least-resistive spectrum (dotted line) corresponds to a resistivity of 20 $\mu\Omega$ cm, the intermediate spectrum (dashed line) to 30 $\mu\Omega$ cm, and the most-resistive spectrum (solid line)

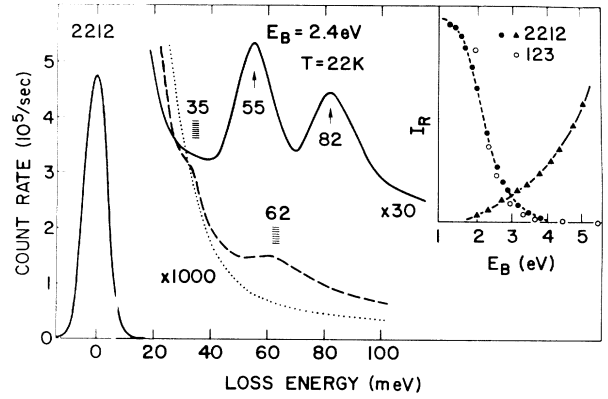

FIG. 1. Electron-energy-loss spectra for 2:2:1:2 obtained at 22 K as discussed in the text. Inset: The low-resistivity termination (circles) has a different specular reflectivity than the high-resistivity termination (triangles) which we use to isolate and study these different regions.

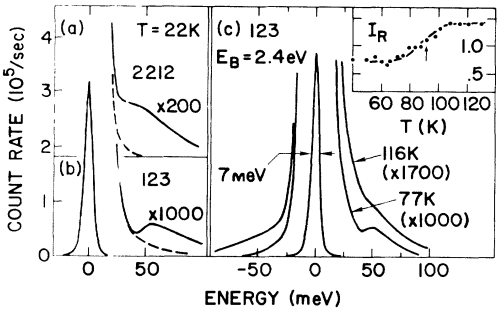

FIG. 2. Electron-energy-loss spectra from metallic regions of the surface at $T=22$ K for (a) 2:2:1:2 and (b) 1:2:3. The dashed lines in (a) and (b) correspond to the spectrometer background determined from the gain side. Postmortum analysis of these samples shows a broad T_c between 70 and 90 K for (a), and between 93 and 93.5 K for (b). The temperature dependence of (b) near T_c is shown in (c). The specular reflectivity vs temperature for (b) is shown in the inset.

to 1000 $\mu\Omega$ cm. The loss spectrum with features at 55 and 82 ± 1 meV is associated with the most-resistive layers and cover at least 10% and on average $\sim 30\%$ of the surface on *all* our 2:2:1:2 samples, independent of T_c or cleavage quality. These two vibrations correspond most closely to the infrared modes involving oxygen vibrations out of the Bi-O planes and between the Bi and Cu atoms,[16] respectively. Our layer-dependent dielectric model cannot account for this high resistivity by a few terminal Be-O layers atop a metallic substrate and requires a resistive layer ~ 100 Å thick. This dielectric modeling together with the lack of differences between this region and the metallic regions by both micro-Raman and UHV Auger microprobe analysis suggest small doping variations in these regions. At $T=298$ K we always find the more-resistive layers to have vibrations at 51 and 81 meV, where the occasional shift of the 51-meV vibration for $T < T_c$ shown in Fig. 1 can be associated with superconductivity.[17]

The more-metallic surfaces in Fig. 1 strongly screen the incident fields and prevent the bulk vibrations from being observed. In the dashed spectrum the low-energy loss near ~ 35 meV occurs independent of the 62-meV feature and is occasionally seen at $T=298$ K. This most likely corresponds to surface analogs of either of two bulk modes[16] both of which involve Sr vibrating against the Cu-O planes. The asymmetric feature with its maximum at ~ 62 meV is only seen at low temperatures and corresponds to the superconducting gap.

To observe the energy gap associated with the superconducting transition we isolate structureless metallic regions of the sample at 298 K and cool the sample to low temperatures. Some regions of the sample then exhibit the humplike loss feature shown in Fig. 2(a). This particular spectrum is not from a freshly cleaved 2:2:1:2 sample as used in Fig. 1 and reflects some broadening arising from a range of T_c. ac susceptibility measurements performed later in air with a pickup coil facing this surface show a broad T_c starting at 70 and ending at 90 K. In general, we find that both superconductors studied degrade with exposure to the electron beam for $T > T_c$ or from sitting in UHV at 298 K.

In contrast to 2:2:1:2, the 1:2:3 crystals exhibit only lower-resistivity terminations. A spectrum of 1:2:3 cleaved at 298 K and cooled within 20 min to 22 K is shown in Fig. 2(b). We have confirmed that this feature is associated with superconductivity for this and other samples by performing loss measurements as a function of temperature. As shown in the inset of Fig. 2(c), the reflectivity of the surface, I_R, changes over a temperature range about the bulk T_c of 93 K. The loss spectrum slightly above T_c reveals the near disappearance of this asymmetric peak, which we now directly associate with the superconducting energy gap. The small residual structure above T_c in Fig. 2(c) may be related superconducting fluctuations[18] and is discussed later. At 125 K the normal-state resistivity between 30 and 50 meV corresponds to 7 $\mu\Omega$ cm, which is substantially lower than the dc resistivity.[19] In general, we find that about $\frac{1}{3}$ of the 1:2:3 surface *areas* examined show superconductivity—compared to only about (5–10)% for 2:2:1:2. This smaller fraction for 2:2:1:2 is consistent with its larger transition width.

From Fig. 2 it is clear that the size of the onset corresponding to the gap in 1:2:3 changes with temperature. To compare the response associated with these gap excitations to each other and other results,[1-5] we take the ratios of the superconducting to normal-state spectra after correcting both for the spectrometer background. Here the background is established from the gain side of the spectra. As noted earlier, taking such rations removes the kinematic prefactors in the individual loss spectra and to first order corresponds to the ratio of superconducting to normal-state resistivities. As shown in Fig.

3(a) the gap for 1:2:3 is 55 and 45 meV at 22 and 80 K, respectively, and extrapolates to a value of $6.9k_BT_c$ at $T=0$. The largest gap found was 70 meV ($8.7k_BT_c$) from a cleave at 22 K which also produced a highly stepped, irregular surface. The sharpest gap structures for 2:2:1:2 were observed for samples with $T_c=85$ and 91 K, and show values of 58–60 meV. For the range of T_c's studied on both materials the average value of the gap is $(7.8\pm0.3)k_BT_c$, consistent with recent ir work on 1:2:3.[5] In contrast, recent tunneling measurements on chemically treated 1:2:3 crystals show a significantly smaller gap and a high conductance in the gap.[2] Based on our results we associate these with modified surface layers probably formed during passivation. Likewise it is not surprising that Andreev scattering using a metal layer[3] shows a smaller gap than those without such a layer.[4]

To ellucidate the nature of superconductivity, we plot the ratio of the gap position (obtained from the center of the onset in the loss spectra) relative to its position at 22 K in Fig. 3(b) and compare this to BCS theory[20] (dashed line). As superconductivity disappears the energy gap, or energy for Cooper pairing, is only slightly reduced and does not follow BCS theory. The height of the superconducting onset, H, reflects the number of Cooper pairs and approaches zero. Even at 80 K the gap shown in Fig. 3(a) is well defined and only weakly shifted. At higher temperatures the gap approaches a terminal value near 45 meV—very close to the LO phonon at 39 meV.[5]

The weak feature at 45 meV, which persists above T_c for superconducting samples, is sensitive to beam exposure and is thereby difficult to observe. Figure 4 shows the time-dependent loss spectra of another 1:2:3 surface, freshly cleaved and examined at $T=298$ K. Here we find that an electron dosage of $\sim10^6$ electrons/cm^2 reduces the excitation near ~45 meV without significantly changing the elastic peak or scattering background, i.e., the surface resistivity or screening, and implies it is neither a surface phonon nor interband transition. The evolution of the superconducting gap to this same value with increasing T argues that it is intimately related to superconductivity. Further, the low exposure of incident electron (10^{-9} per unit cell) suggests some type of collective excitation which is strongly influenced by defects produced during irradiation (most likely electron stimulated desorption of oxygen). We note that this irradiated surface shows a superconducting gap of 40 meV with a markedly increased background.

The low resistivities we determine are also significant. Namely, our values are substantially lower than those determined in macroscopic measurements.[5,20] Part of this may be attributed to the occurrence of atomic-scale layering defects on a larger length scale than we probe with HREELS. This low resistivity as well as the low-energy collective excitation and its sensitivity to irradiation, in addition to the previously cited electronic structure of 1:2:3,[21] are consistent with acoustic plasmons—a long-proposed mechanism for excitonic superconductivity.[22] Clearly, our results provide new information to be considered in evaluating other mechanisms of superconductivity as well.

In summary, we observe a superconducting energy gap of $\sim8k_BT_c$ for both 2:2:1:2 and 1:2:3 surfaces and a temperature dependence for 1:2:3 which indicates non-BCS behavior. We show these cleaved materials exhibit inhomogeneities which are severe on 2:2:1:2 and raise questions about interpreting a variety of previous macro-

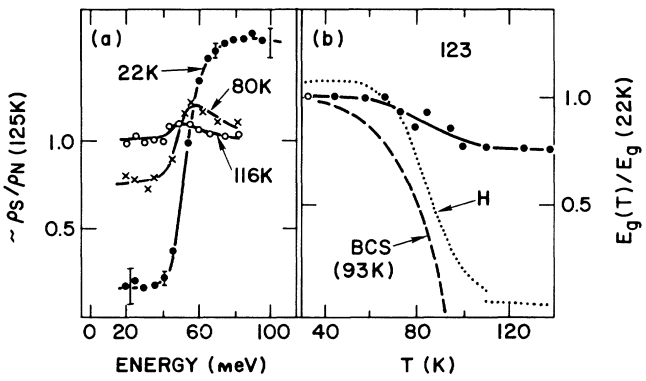

FIG. 3. (a) Ratio of the superconducting loss spectra at different temperatures to the normal-state loss spectra at 125 K showing the evolution of the gap to another excitation above T_c, and (b) the evolution of the loss-spectra onset with temperature (solid line). The dotted line, H, shows the height of the superconducting onset in the loss spectra above and below the gap. The discontinuity in H at 116 K indicates the change in the spectrum arising from electron-beam damage above T_c. The resistivity below the gap at 22 K varies for the samples studied and is found to depend on cleavage quality and electron-beam irradiation above T_c. The data shown here are from our "best," i.e., optically flat, cleave.

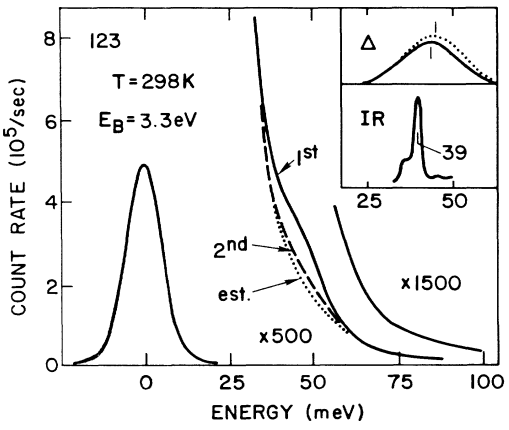

FIG. 4. Successive electron-energy-loss spectra (at $T=298$ K) for a freshly cleaved sample. Inset: The difference between spectra 1 and 2 (solid line), and between spectra 1 and an estimated background (dotted line). The ir optical phonon (Ref. 5) is also shown.

scopic measurements, *including the intrinsic layer resistivity*. Finally, we provide evidence for a delocalized excitation existing well above T_c which appears associated with superconductivity.

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