The absence of superfluid response in \(ac\) and \(bc\)-plane optical conductivities of optimally-doped \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}\) single crystals in the surface region

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The optical properties of optimally-doped \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}\) (Bi2212) have been measured normal to the edge planes \([ac\text{ plane, } bc\text{ plane, and } (110)\text{ plane}]\), for light polarized parallel to nodal and anti-nodal (gap) directions, respectively. While the superfluid contribution can be obtained from the optical conductivities in the \((110)\)-plane, it is unobservable in the \(ac\) and \(bc\)-planes. This apparent asymmetry implies that the edge region of high-\(T_c\) cuprates is unusual and further supports a \(d\)-wave symmetry of the superconducting order parameter.

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Understanding the microscopic mechanism of high-temperature (high-\(T_c\)) superconductors remains one of the fundamental challenges of condensed matter physics. Phase-sensitive techniques \([1, 2, 3, 4, 5]\) imply a \(d\)-wave symmetry of the superconducting order parameter. Angle-resolved photoemission (ARPES) results in Bi2212 \([6]\) clearly show an anisotropic energy gap. However, \(ab\)-plane optical conductivity measurements on the same material do not show large anisotropies with light (electric field vector) polarized parallel to \(a\)-axis, \(b\)-axis, or anti-nodal directions \([7, 8]\) even below \(T_c\). This can be understood since ARPES is a \(k\)-dependent measurement, whereas the optical conductivity is averaged over the Fermi surface. In general, one would expect the same kind of optical results for the edge planes \([the\ ac\text{-plane, } bc\text{-plane, and } (110)\text{-plane}]\). These edge regions of high-\(T_c\) superconductors were studied extensively by tunneling experiments on \(\text{YBa}_2\text{Cu}_3\text{O}_{6+x}\) \([4, 9, 10, 11, 12, 13]\) and more recently on Bi2212 by Greene and co-workers \([14]\). One particularly intriguing feature is the zero bias conductance peak (ZBCP) observed on the \(ac\) or \(bc\)-faces, coupled with the absence of a gap feature when tunneling into \(ab\)-plane. This is contrasted with the observation of a weaker ZBCP when tunneling into the \((110)\)-plane, with the appearance of a superconducting gap \([14]\). We emphasize that for this work we take the crystallographic \(a\) and \(b\) axis along the Cu-Cu bonds as the nodal direction, whereas the \([110]\) direction (the anti-nodal or gap-maximum direction) is along the Cu-O bonds.

In the superconducting state a particle bound state forms at the Fermi surface when the node of a \(d\)-wave order parameter is normal to a reflecting surface \([15]\), such as the \(ac\) and \(bc\)-faces of Bi2212. Particles reflecting from such surfaces experience a change in the sign of the order parameter along their classical trajectory and subsequently undergo Andreev reflection. Constructive interference between incident and Andreev-reflected particles leads to the formation of bound states confined to the surface. These bound states will produce a ZBCP in a tunneling spectrum \([16, 17, 18]\). Andreev scattering causes strong pair breaking, which leaves a surface region depleted of superfluid. The motivation of this study is to examine systematically these surface regions in Bi2212 by measuring the optical conductivities. The question is whether the picture used to explain the tunneling measurements, which probe a surface region of the order of \(\approx 10\) nm, can be used to describe the wider surface region probed by infrared radiation, which is typically \(\approx 100\) nm.

In this Letter, we report characteristically different behavior observed in the \(ac\) and \(bc\)-plane conductivities of optimally doped Bi2212 as compared to the \((110)\)-plane conductivities below \(T_c\). While the superfluid contribution can be measured in the optical conductivities in the \((110)\)-plane, it is much smaller in the \(ac\) and \(bc\)-plane. This apparent asymmetry implies that the edge region in high-\(T_c\) \(d\)-wave superconductors has unusual properties that are different from the bulk.

The \(ab\)-plane optical conductivity of optimally-doped Bi2212 has been measured extensively \([2, 3, 10, 15, 20, 21]\). However, because of the large \(c\)-axis dimension required to carry out optical measurements on the \(ac\), \(bc\) and \((110)\) faces, only one brief study was previously reported \([22]\). For this study, large optimally-doped Bi2212 single crystals are grown using the traveling-surface-floating-zone (TSFZ) method. The typical size of these crystals for the edge experiments is \(5 \times 3 \times 1\) mm\(^3\) along the three principle crystallographic axes. Cleaved \((001)\) surfaces are used for the \(ab\)-plane measurements. However, to study the edge regions, polished \((100)\), \((010)\) and \((110)\) surfaces are required. Considerable care has been taken during polishing due to the mica-like nature of Bi2212. Polishing has been done by hand, and always along the planar direction. A final polish with 0.1 \(\mu\)m diamond films allows optical surface quality to be achieved. The surface quality of our polished samples should be com-
The ab-plane reflectivity is determined by evaporating a gold parallel to that of the samples used in the tunneling experiments on Bi2212 [14], which have been found to have a surface roughness of ≈ 80 Å measured by AFM. The Bi2212 crystals are mounted on an optically-black cone, and the temperature-dependent polarized reflectance is measured in a near-normal-incidence arrangement from ≈ 50 to over 16,000 cm⁻¹ on a Bruker IFS 66v/S. The absolute reflectivity is determined by evaporating a gold film in situ over the sample [23]. This comparison to the gold reflectivity provides an absolute reflectivity scale. The optical conductivities are then determined from a Kramers-Kronig analysis.

The temperature-dependent ab-plane conductivity data is shown in Fig. 1 for a single-crystal Bi2212 sample with for light polarized along the a axis (E || a). In agreement with the previous results [7], there is only a weak dependence of the conductivity on the direction of the polarization within the ab-plane. However, strong phonon anisotropy has been observed in our ab-plane conductivity measurements [8, 24]. The superfluid response is observed in the ab-plane conductivities below Tc, as σ₁ decreases with temperature according to the Ferrell-Glover-Tinkham sum rule accompanied by a simultaneous increase in σ₂. The ab-plane data is presented here as a reference to show the large difference from the edge plane data presented in the next figure.

The temperature-dependent ac-plane conductivity data is shown in Fig. 2 for a single-crystal Bi2212 sample for E || a. No superfluid response is observed in either σ₁ or σ₂. (a) Temperature-dependent σ₁; (b) temperature-dependent σ₂. Inset: the experimental configuration.

In both cases, σ₁ at room temperature is similar, but significantly lower than the ab-plane value. However, it can be seen that as the temperature is lowered below Tc, which is ≈ 91 K for these optimally-doped samples, the behavior of the (110)-plane conductivity data is much closer to the ab-plane data, showing the characteristic decrease of σ₁ as normal carriers start to condense into superfluid which leads to a significant increase of σ₂ below Tc. The behavior of the ac-plane conductivity around and below Tc is very different. As the temperature changed from 100 to 80 K, both σ₁ and σ₂ show a significant increase, particularly in σ₂ below 500 cm⁻¹ [Fig. 2(b)]. As the temperature is lowered further, no noticeable changes are observed in σ₁ or σ₂. Similar results are obtained for the bc-plane conductivity as compared to the ac-plane conductivity.

The essence of the our results is the difference between Fig. 2 and Fig. 3 where the conductivities in the surface regions are compared for a surface with a normal along
a nodal direction and a surface with a normal along an anti-nodal direction. It immediately shows that while
the superfluid contribution to optical conductivity can be observed in the surface region of the (110)-plane, it is
unobservable in the surface region of the ac or bc planes. This apparent asymmetry implies that the surface region
in the high-Tc d-wave superconductors has unusual properties that are different from the bulk \[25\].

The comparison with the ab-plane conductivities shows that the conductivities in these edge regions at room temperature are reduced by about a factor of two, and this is no doubt due to the polishing process. To further understand the role of disorder induced by the polishing process, we have added a set of data to show that with a coarser polishing finish (1 \(\mu\)m diamond film) the conductivity of the bc-plane in the normal state is even more drastically reduced, as shown in Fig. 4. There is a large spectral feature at 627 cm\(^{-1}\) that appears as an anti-resonance dip in \(\sigma_{ab}\). This anti-resonance dip is also observed in \(\sigma_{bc}\) of the better-polished surfaces as shown in Fig. 2(a) and Fig. 3(a), albeit with less spectral weight, but not in the ab-plane conductivity data. It is due to ab-plane carriers coupling to a c-axis LO phonon \[24\], but not caused by direct absorption of c-axis TO phonons \[20\]. In the insert of Fig. 3(a), room temperature reflectance data is given with the E \(\parallel\) b and E \(\parallel\) c on this
bc face. Features associated with c-axis TO phonons are absent in the E parallel to b-axis spectrum. We therefore
conclude that there is no significant contamination by c-axis phonons in the conductivity data with E \(\parallel\) b. This indicates that even with this coarser polishing finish, the planar structure of the Bi2212 is preserved in these polished surface regions. Still, with coarser polishing there is little evidence of superfluid response in \(\sigma_{ac}\) or \(\sigma_{bc}\) similar to what is observed on better polished ac and bc surfaces.

The surprising aspect of our results is the characteristically different behavior of the optical conductivities in the interface regions of a surface with the normal along a nodal direction, compared to that of a surface with the normal along an anti-nodal (gap) direction. While the superfluid contribution to optical conductivity can be measured on the (110)-plane, it is unobservable on the ac or bc planes. The superconductivity as probed by infrared techniques may behave in a way similar to what Greene and co-workers have found in their tunneling experiments \[14\]. In the surface region where the node of a d-wave order parameter is normal to a reflecting surface like the ac and bc faces of a high-Tc superconductor, Andreev scattering causes strong pair breaking which leaves a surface region depleted of superfluid. This may explain

**FIG. 3:** The (110)-plane conductivities, the superfluid response is observed in \(\sigma_{ac}\) and \(\sigma_{bc}\) in this case. (a) Temperature-dependent \(\sigma_{ac}\); (b) temperature-dependent \(\sigma_{bc}\). Inset: the experimental configuration.

**FIG. 4:** The bc-plane conductivity data of an optimally doped Bi2212 single crystal that has a coarser surface finish for E \(\parallel\) b. No superfluid response is observed in either \(\sigma_{ac}\) or \(\sigma_{bc}\). (a) Temperature-dependent \(\sigma_{ac}\). Inset: the room-temperature reflectance data for E \(\parallel\) b and E \(\parallel\) c, respectively. (b) Temperature-dependent \(\sigma_{bc}\). Inset: the experimental configuration.
why no superfluid response is observed in ac and bc-plane conductivity. The situation is different for the surface region for which the normal is an anti-nodal direction. Ideally, there should be no Andreev scattering because the superconducting pairs do not suffer a change of sign in the order parameter under a reflection on this interface. This explains why a superfluid response is observed in the (110)-plane conductivity, albeit with less magnitude compared to ab-plane data, and there is a superconducting gap when tunneling on (110)-plane accompanied by a less pronounced ZBCP.

The small jump in $\sigma_1$ and $\sigma_2$ from 100 to 80 K deserves some more discussion. A careful study reveals that the increase almost exclusively occurs within a few degrees of $T_c$. We speculate that this jump is related to the formation of Andreev bound states in the surface region of ac and bc plane as a result of, e.g. a reduction in scattering rate when bound states are formed below $T_c$. The Andreev bound state should deplete the superfluid to a depth of order the coherence length $\xi_0 \sim 100 \text{Å}$. The classical skin depth is defined as $\delta = c/\sqrt{2\pi\sigma_1\omega}$, which is of the order of microns and much greater than the mean-free path, so that since $\delta \gg \xi_0$ the infrared should still probe the superfluid in the bulk. This is seemingly at odds with the observation of no further change in $\sigma_1$ and $\sigma_2$ for $T \ll T_c$. Within the BCS theory, $\xi_0$ can be defined in terms of the Fermi velocity $v_F$ and the energy gap $\Delta$, $\xi_0 = \hbar v_F/\pi \Delta$. However, the energy gap is thought to have a momentum dependence, thus $\Delta \equiv \Delta_k$. If $\Delta_k \to 0$ in the nodal direction, then $\xi_k$ may become quite large, i.e. $\xi_k \approx \delta$, which would suggest for certain geometries the influence of the Andreev bound state might extend over a larger region than previously thought [27].

The role of disorder induced by the polishing process also deserves some further considerations. This kind of problem seems to be reminiscent to the “two-length scale” problem in X-ray scattering [28, 29]. For example, in the case of UO$_2$ [30] and SrTiO$_3$ [31], it is found that mechanical processing causes an increase in dislocation density in the surface region that can be as deep as 500 nm. However, we do not think that random disorder can explain the asymmetry we have observed in our optical measurements nor the asymmetry observed in the tunneling experiments. Of course, if the polishing process caused different amounts of damage on two types of surfaces this could happen, but the data shows there are no large changes in the normal-state conductivity for the two cases. This issue of the extent of the depletion region remains to be understood.

In conclusion, we have observed characteristically different behavior in the ac and bc-plane optical conductivities of optimally-doped Bi2212 single crystals, as compared to the (110)-plane conductivity below $T_c$. Our observation implies that optical measurements are also sensitive to the d-wave nature of the superconducting order parameter in high-$T_c$ cuprates.

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