Electron-Phonon Interactions in Superconducting $La_{1.84}Sr_{0.16}CuO_4$ Films

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We have measured quasiparticle tunneling across a junction perpendicular to the superconducting copper oxide planes. The tunneling spectra show peaks in the density of states. There are 11 minima in the second derivative d^2I/dV^2, where I is the current and V the voltage, suggesting multiple boson-quasiparticle interactions. These minima match precisely with the published Raman scattering data, leading us to conclude that the relevant bosons in superconducting $La_{1.84}Sr_{0.16}CuO_4$ films are phonons.

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Quantum mechanical tunneling [1,2] provided convincing evidence in support of the Bardeen, Cooper, and Schrieffer (BCS) theory of superconductivity [3] and established the role of phonons as the basis of the attractive potential that bound two electrons. Since the discovery of the cuprate superconductors with high superconducting transition temperatures (high T_c), there have been numerous attempts to build a superconductor-insulator-superconductor (SIS) tunnel junction, where both superconductors are made of hole-doped high-T_c materials and tunneling is through a barrier perpendicular to the copper oxide planes. The goal, as in conventional superconductors, has been to identify the mechanism of pairing and thereby distinguish between phonons and magnetic spin excitations as the relevant bosons.

Grain boundary junctions, particularly bicrystal junctions, have been investigated for two decades in high-T_c applications and in experiments dealing with the symmetry of the wave function of the superconducting state [4]. In this Letter, we use a bicrystal grain boundary modified by annealing in ozone to produce a barrier across which quasiparticles tunnel carrying information about the quasiparticle-boson interaction. A bicrystal junction is particularly attractive, because the current flow is along the copper oxide planes and the tunnel barrier is perpendicular to these planes. Hence any structure in the conductance data can provide direct information about pairing interactions.

$La_{1.84}Sr_{0.16}CuO_4$ (LSCO) films were prepared on symmetric 24° (12° + 12°) [001]-tilt $SrTiO_3$ (STO) bicrystal substrates using molecular beam epitaxy. The details of the film preparation procedure have been described elsewhere [5]. The 104 nm thick films were patterned by photolithography and Ar ion milling to form 25 μm wide junctions. A four-terminal method was used to measure the current-voltage (I-V) characteristics of the junction and film. The temperature was varied from 4.2 K to room temperature. The as-prepared junctions were annealed in a mixture of ozone and oxygen. Annealing was done in a vacuum chamber with a base pressure better than 1×10^{-7} Torr. During exposure to ozone, the gas pressure was kept at 1 Torr, and the ozone concentration of the oxygen-ozone mixture was 2.3% by weight as the ozone flowed through the chamber. The junction was annealed at 125 °C for 30 min and then quickly cooled to room temperature by flowing liquid nitrogen through the back end of the sample holder without interrupting the flow of ozone. The samples were removed from the chamber at room temperature and then measured in a liquid helium Dewar. On ozone annealing, the resistance of the junctions decreased from values above 100 Ω to values between 20 and 50 Ω. The junction with a resistance of about 20 Ω produced a well-resolved spectrum.

Figure 1 shows the change of junction resistance and that of the film as a function of temperature. These data were collected by applying a 10 μA bias current across the grain boundary. Also, shown in the inset is the I-V characteristic of the junction. The superconducting transition temperature of the film (23.5 K) is consistent with values published in the literature on LSCO films deposited on STO substrates with which there is a large lattice parameter mismatch [6]. The dynamic conductance data of the junc-

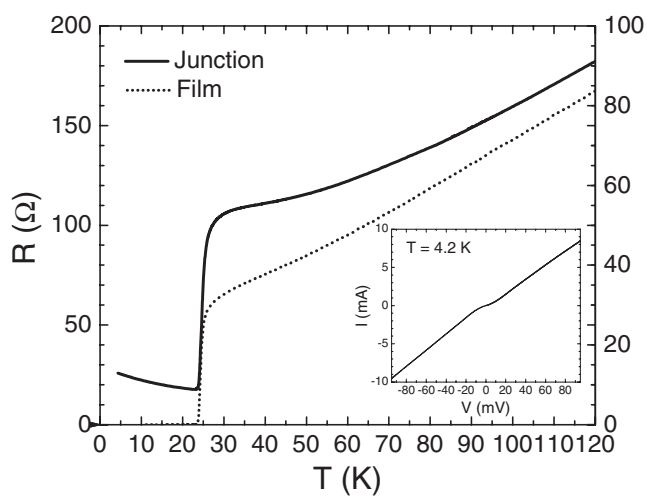

FIG. 1. The resistance of the grain boundary junction and film plotted as a function of temperature. The inset shows current-voltage (I-V) characteristics of the junction measured at 4.2 K.

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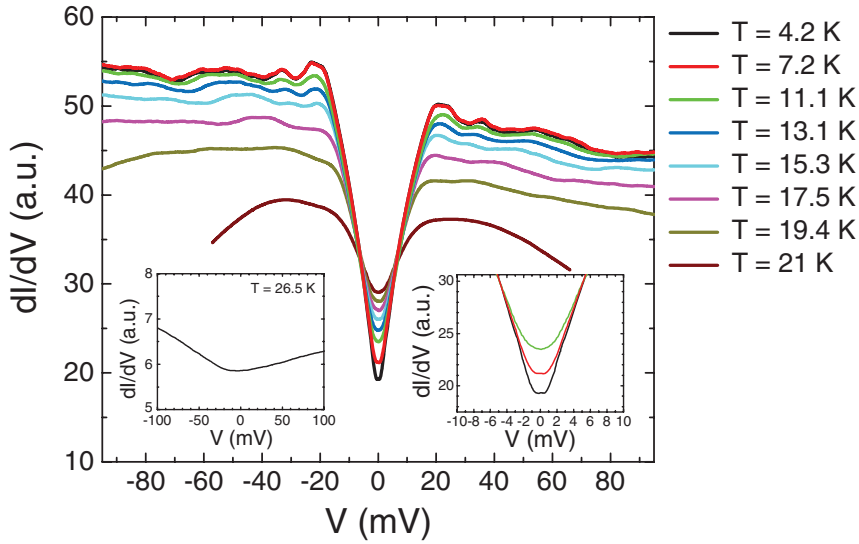

FIG. 2 (color). Dynamic conductance of the ozone annealed junction as a function of bias voltage measured at various temperatures. The inset on the right shows the variation of conductance with bias voltage near zero voltage for three temperatures to illustrate the constant conductance around zero for the 4.2, 7.2, and 11.1 K data. The inset on the left shows the conductance of the junction above the T_c of the film.

tion, measured at different temperatures, are shown in Fig. 2. At zero voltage we observe finite conductance, which increases as the temperature is increased. A closer examination of the data around zero bias (inset in Fig. 2) shows an additional feature: The conductance spectrum around zero voltage taken at 4.2 K is not rounded but flat. At 4.2 K, the flat minimum extends to approximately 630 μV. The flat feature disappears as the temperature is increased. It has been suggested that LSCO may have two gaps: a small s-wave gap and a larger d-wave gap [7]. The observation of a flat conductance curve at 4.2 K around zero bias is consistent with the suggestion of a small s-wave component. We also note that above the T_c of the film the junction produces a broad featureless conduction curve characteristic of a slightly asymmetric tunnel barrier (second inset in Fig. 2). There were no discernible features of the type seen below T_c.

The broad peaks in the density of states (DOS) are clearly observable maxima in the conductance peaks as a function of voltage. Given our tunneling geometry, we identify the first conductance peak as $2\Delta_s$, where Δ_s is the superconducting gap of approximately 10 meV at 4.2 K, yielding a BCS parameter $2\Delta_s/kT_c$ approximately equal to 9.5. A value of Δ_s equal to 10 meV is consistent with published values [8–10]. It is difficult to evaluate the gap precisely, for the first peak is not sharp and there is further rounding due to thermal smearing. The values of Δ, and the associated error bars, as a function of temperature shown in Fig. 3 were obtained as follows: The voltages at which the first conductance peaks were observed for positive and negative voltage sweeps were averaged. This gave us the upper limit to the values of the gap and the error associated with estimating the peak position. The lower limit to the value of the gap was obtained from measuring the voltages when the conductance curves deviated significantly from the almost linear increases with voltage and towards the first conductance peaks. We take the average of these two values as the gap value. The error bars indicate the voltage span associated with this procedure. The values of the gap as a function of temperature are consistent with the BCS theory.

The presence of conductance peaks reflects the coupling of quasiparticle with phonon or spin excitations. Similar peaks have been observed in SIS junctions using conven-

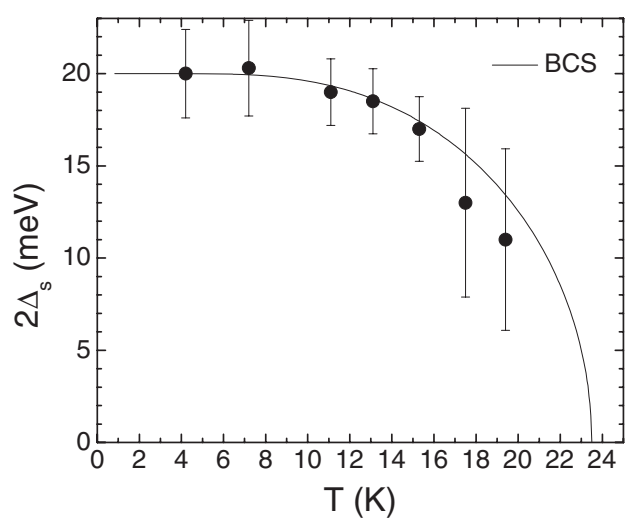

FIG. 3. Experimental values of $2\Delta_s$, where Δ_s is the superconducting gap as a function of temperature and the BCS prediction. The BCS curve is given by the equation $\Delta(T)/\Delta(0) = \tanh\{(T_c/T)[\Delta(T)/\Delta(0)]\}$ [15].

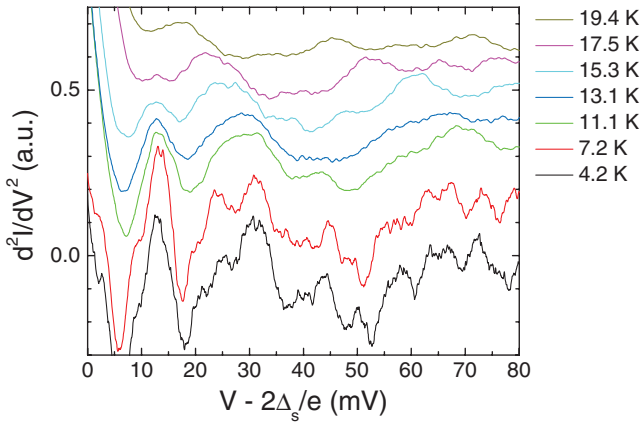

FIG. 4 (color). The second derivative of the data shown in Fig. 2 and plotted as a function of $V - 2\Delta_s(T)/e$. The minima in the second derivative, with the exception of the first minimum, are associated with peaks in the excitation spectra. The first minimum is associated with a lack of normalization of the data by the BCS density of states and the normal state density of states. It is not used for comparison with spin or phonon spectra. The curves have been shifted vertically by arbitrary amounts for purposes of viewing. However, the y scale is unchanged.

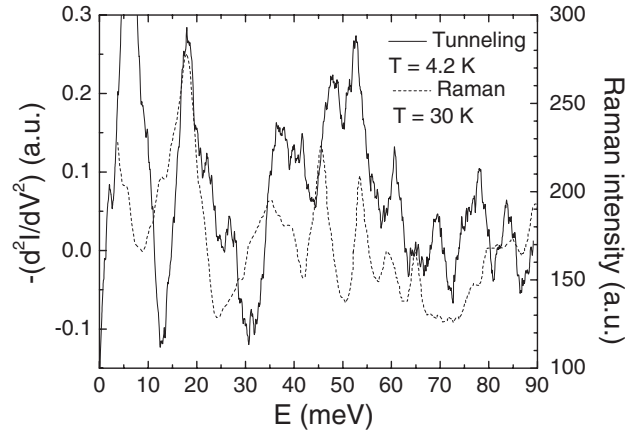

FIG. 5. The second derivative data (shown in Fig. 4 as the 4.2 K data) multiplied by (-1) are shown along with the published Raman scattering data in Ref. [11] measured at 30 K on single crystal LSCO samples with 20% Sr. The polarization of the incident and scattered light in the Raman data is parallel to the copper oxide planes of the crystal. The peak in the tunneling data at 21 meV is present in the Raman scattering data of Lampakis *et al.* [12].

tional superconductors and were the basis of the successful inversion analysis carried out by McMillan and Rowell [2]. We can obtain detailed information about quasiparticle-boson interaction by differentiating the conductance curve with respect to voltage. In Fig. 4, we show this calculated second derivative of the data shown in Fig. 2. From the minima in the second derivative, we identify 12 peaks at 4.2 K. As is usually done in conventional superconductors, we subtract the value of $2\Delta_s(T)$ from the values of the 12 peaks to rescale the DOS changes associated with quasiparticle interaction with bosons. The energies at which the minima in the second derivative curves occur in superconducting LSCO at 4.2 K are at approximately 6, 18, 21, 25, 36, 42, 47, 52, 60, 68, 77, and 82 meV. We ignore the first peak, for it can arise from a lack of normalization of the superconducting DOS by the normal state DOS and by the featureless BCS density of state. In our current geometry we cannot reliably estimate the normal state DOS, as the film resistance is much larger than the junction resistance once the film is in the normal state. Of the 11 remaining peaks associated with boson excitations, five are particularly strong, and at 4.2 K (and 7.2 K) these peaks are at approximately 18, 36, 42, 47, and 52 meV. The four strong peaks between 36 and 52 meV overlap. The background above which the peaks are visible can be divided into two parts: one between 10 and 28 meV with a peak around 18–19 meV and the other starting at 28 and peaking around 45–47 meV and continuing over the range of our measurement. Interesting features of the second derivative data, shown in Fig. 4, are the disappearance into the background of the weaker peaks between 7.2 and 11.1 K and the relative shifts in amplitude of the stronger peaks such that the minima shift on the energy scale. We have made and measured three different junctions. All three show the same strong features in the second derivative data. We have learned that the best second derivative data are obtained from junctions that show a linear I-V characteristic in the range of the derivative measurement. Otherwise, only the strong features are observed and the data resemble the data shown in Fig. 4 for T greater than 7.2 K.

The data clearly suggest that there are multiple bosons interacting with quasiparticles in superconducting LSCO films, as measured by a tunneling current across a grain boundary junction perpendicular to the superconducting copper oxide planes.

We now compare the position of the peaks in the electronic tunneling spectra with published data on phonons in $La_{1.8}Sr_{0.2}CuO_4$. We show, in Fig. 5, Raman scattering data obtained on single crystals of LSCO for compositions close to but not identical to ours. These Raman scattering data, measured with incident and scattered light polarization parallel to the copper oxide planes [11], are not significantly different from the data on microcrystalline samples with a composition identical to ours [12]; we have chosen to reproduce the data from Ref. [11] for it covers the full energy range of the tunneling data. Superimposed on the Raman data are our second derivative data measured at 4.2 K (from Fig. 4). The agreement between the two sets of data is remarkably good. Hence we conclude that the bosons responsible for peaks in the conductance spectra are phonons.

The generalized phonon density of states of LSCO has been determined by inelastic neutron scattering on powdered samples [13]. A comparison with the tunneling data

shows that the phonons associated with La (Sr) vibrations, which peak at about 28 meV and have the highest density of states peak in the neutron data, do not interact measurably with quasiparticles. This is evident from the second derivative data shown in Fig. 5, where there is a dip in the spectrum rather than a peak. If we remove the peak associated with these phonons from the neutron-derived phonon density of states, the phonon density of states would have two broad divisions: one centered around 18 meV and the other, broader one centered between 40 and 46 meV, in general agreement with the tunneling data.

While we can rule out any dominant role of La(Sr) vibrations, we are less certain as to what modes to assign to the phonon peaks, particularly the strong ones seen in the tunneling data (18, 36, 42, 47, and 52 meV). There is some disagreement in the literature. For example, the apex oxygen vibrations parallel to the copper oxide plane are assigned to the peak seen at 52 meV in Ref. [12] and to 60 meV in Ref. [11]. While Refs. [13,14] assign the phonon peaks seen above 60 meV to breathing and half breathing modes in the copper oxide plane, there is a suggestion in Ref. [11] that the 68 meV peak is due to local vibrations of O atoms in interstitial sites as Sr content increases. However, there appears to be broad agreement that the modes are associated with the copper-oxygen and oxygen vibrations.

In summary, in optimally doped superconducting LSCO films deposited on STO bicrystal substrates, multiple conductance peaks in the density of states are observed as a function of applied voltage. The data suggest multiple quasiparticle-boson interactions. The tunneling spectra agree very well with the published Raman data, leading us to the conclusion that the bosons giving rise to the peaks in the quasiparticle density of states are phonons.

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