

## Phonon self-energy effects due to superconductivity in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

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Raman scattering of  $A_{1g}$  phonons in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  single crystals ( $\delta=0.13$ ,  $T_c=86$  K) has been measured as a function of temperature. We report an anomalous softening in the frequency and a decrease in the linewidth of the  $A_{1g}$  phonon at  $290\text{ cm}^{-1}$  ( $\text{O}_{1,2}$   $c$ -axis in-phase vibration) below  $T_c$ . We also confirm a smaller anomalous softening in the frequency of the  $A_{1g}$  phonon at  $465\text{ cm}^{-1}$  ( $\text{O}_3$   $c$ -axis vibration), but for this phonon mode no linewidth anomaly has been found. We compare the anomalous softening and linewidth behavior in the superconducting state with theoretical calculations for isotropic  $s$ -wave, planar  $d$ -wave, and  $d_{x^2-y^2}$  gap symmetries and as for a layered superconductor model. [S0163-1829(97)09837-8]

### I. INTRODUCTION

The temperature dependence of phonon frequencies and linewidths near  $T_c$  continue to attract a considerable interest in the high-temperature superconductors (HTSC's) because phonon self-energy effects due to superconductivity can be studied. The dependence of the phonon self-energy on the electronic states above and below  $T_c$  has been widely used to estimate the value of the superconducting energy gap in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Y123),<sup>1</sup>  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y124),<sup>2</sup> and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi2212) (Ref. 3) compounds. Experimentally, these phonon anomalies in HTSC's were observed by studying the Raman spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .<sup>4</sup> Irrefutable proof that the anomalous temperature behavior of the phonons is connected with the superconducting properties of the material was obtained by studying the Raman spectra of Y123 in a magnetic field.<sup>5</sup>

The anomalous temperature behavior at  $T_c$  was also observed in the Raman spectra of Bi2212. The phonon softening below  $T_c$ , in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  single crystals, was observed in the  $465\text{ cm}^{-1}$   $A_{1g}$  mode by Burns *et al.*<sup>6</sup> and Boekholt *et al.*<sup>7</sup> However, no anomalous behavior in linewidth has been reported for this phonon. More recently, Leach *et al.*<sup>8</sup> have reported an anomalous decrease in the linewidth of the  $B_{1g}$  phonon at  $285\text{ cm}^{-1}$  near  $T_c$ . However, contrary to the  $465\text{ cm}^{-1}$  mode, no frequency anomaly has been found. A recent study of the oxygen isotope effect on the vibrational modes of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  leads us to assign the  $A_{1g}$  phonon at  $290\text{ cm}^{-1}$  as an  $\text{O}_{1,2}$   $c$ -axis in-phase vibration ( $\text{CuO}_2$  planes).<sup>9</sup> It is known that, in the high- $T_c$  compounds, the superconductivity occurs in the copper planes. Therefore, it is expected that the phonon renormalization due to the superconducting state will be stronger for modes in which the ions of the  $\text{CuO}_2$  planes participate. We report in this paper a study of the temperature dependence of the  $A_{1g}$  phonon modes at  $290\text{ cm}^{-1}$  and  $465\text{ cm}^{-1}$  in Bi2212 single crystals.

The remainder of this paper is organized as follows. In Sec. II, the experimental techniques are described. In Sec. III, polarized Raman spectra for different temperature are presented for the  $290$  and  $465\text{ cm}^{-1}$  vibrational modes, and results for the temperature dependence of the frequency and linewidth are reported. Section IV discusses the interpretation of the results based on the strong-coupling theory and finally the conclusions of this work are presented in Sec. V.

### II. EXPERIMENTAL TECHNIQUES

The  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  single crystals were grown by a conventional self-flux method employing a double crucible.<sup>9</sup> Quantitative chemical analysis by means of wavelength-dispersion spectroscopy (WDS) showed the composition of the crystals to be  $\text{Bi}_{2.15}\text{Sr}_{1.90}\text{Ca}_{0.96}\text{Cu}_{2.0}\text{O}_{8+\delta}$ . The superconducting transition temperature was determined by four-probe resistance measurement yielding a  $T_c$  of 86 K. Raman scattering experiments were carried out in backscattering geometry. The single-crystal platelets, oriented with the  $a$ - $b$  plane normal to the incident beam, were mounted with silver paint on the cold finger of a closed-cycle Displex He refrigerator. The temperature in the sample chamber was controlled by resistive heating of the cold finger. To measure and regulate the temperature in the range from 10 to 300 K we used an Artronix controller and an Au-Cr thermocouple. The laser light from an argon-ion laser operating at  $514.5\text{ nm}$  was used as the excitation source. The laser power incident on the sample was kept at 5mW and the collection time for each run was 60 min. The collected Raman signal was dispersed by a Jobin-Yvon (T64000) spectrograph and detected with a charge-coupled device (CCD) camera. During each series of measurements the grating position was kept fixed and centered at the phonon frequency under investigation. This pro-

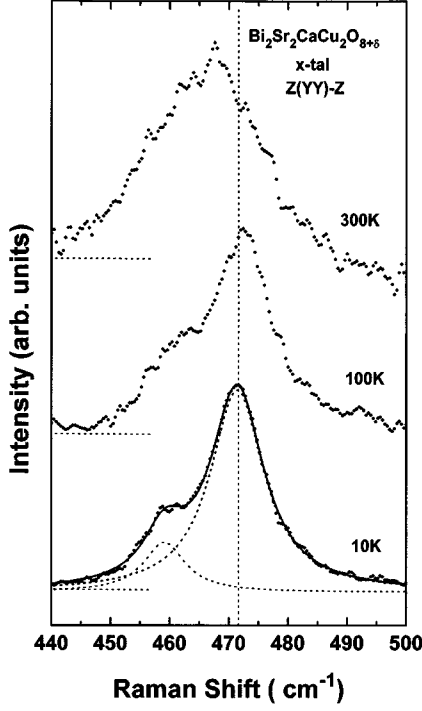


FIG. 1. Raman spectra of  $A_{1g}$  phonons at  $465 \text{ cm}^{-1}$  in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  single crystals with  $\delta=0.13$  and  $T_c=86 \text{ K}$  taken at 10, 100, and 300 K. The temperature dependence of the frequency and linewidth of the main peak at  $465 \text{ cm}^{-1}$  was fitted using a double Lorentzian, keeping constant the parameters for the lower intensity mode at  $458 \text{ cm}^{-1}$ .

cedure was necessary to avoid a possible error in the measured Raman frequency due to slight movement of the grating.

### III. RESULTS

Polarized Raman spectra for the  $Z(YY)-Z$  ( $A_{1g}+B_{1g}$ ) symmetry from the  $a-b$  plane of a single crystal of  $\text{Bi}_{2.15}\text{Sr}_{1.90}\text{Ca}_{0.96}\text{Cu}_{2.0}\text{O}_{8+\delta}$  were collected for single crystals from different batch at temperatures in the range 10–300 K. In Fig. 1 we show the Raman spectra of the  $A_{1g}$  mode at  $465 \text{ cm}^{-1}$  at three different temperatures. This phonon has been assigned to the  $c$ -axis vibration of  $\text{O}_3$  atoms in the strontium layers.<sup>9,10</sup> Two peaks at  $458$  and  $465 \text{ cm}^{-1}$  are observed in Fig. 1. In order to better isolate the temperature dependence of the frequency and linewidth of the main peak ( $465 \text{ cm}^{-1}$ ) we have used a double Lorentzian fitting, keeping constant the parameters for the lower intensity mode ( $458 \text{ cm}^{-1}$ ). Figures 2 and 3 show, respectively, the frequency and linewidth of the  $465 \text{ cm}^{-1}$   $A_{1g}$  mode as a function of temperature for two different samples. Above  $T_c$ , the frequency (Fig. 2) can be described by the normal temperature-dependent anharmonic decay. However, in the superconducting state the frequency shows an anomalous softening of about  $\Delta\omega/\omega \approx -0.5\%$ . No anomalous temperature dependence in the linewidth of this phonon is observed. The dashed line in the Fig. 3 is the predicted linewidth due to the anharmonic decay into two phonons with opposite  $q$  vectors, each having a frequency close to  $\omega_v/2$ , which is given by<sup>11</sup>

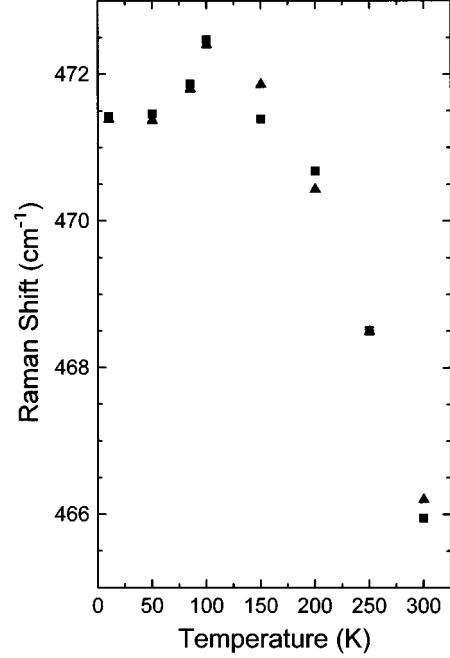


FIG. 2. Temperature dependence of the frequency of the  $Z(YY)-Z$   $A_{1g}$  phonon at  $465 \text{ cm}^{-1}$  in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  with  $T_c=86 \text{ K}$  taken for different samples represented by triangles and squares. In the superconducting state the frequency shows an anomalous softening of about  $\Delta\omega/\omega \approx -0.5\%$ .

$$\gamma(\omega, T) \approx a_1 [1 + 2n(\omega_v/2, T)] + a_2, \quad (1)$$

where  $n$  is the Bose factor,  $a_1$  and  $a_2$  are constants, and  $\omega_v$  is the frequency of the mode. The best fit to the data was

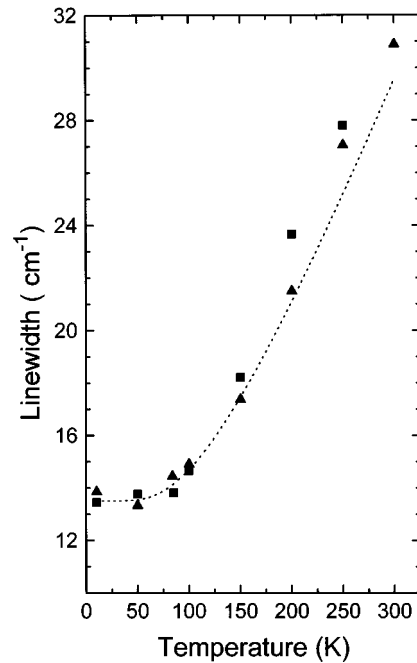


FIG. 3. Temperature dependence of the linewidth of the  $A_{1g}$  phonon at  $465 \text{ cm}^{-1}$  in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  with  $T_c=86 \text{ K}$ . The dashed line is derived from a calculation of the anharmonic decay of two phonons with opposite  $\mathbf{q}$  vectors, each having a frequency close to  $\omega_v/2$  [Eq. (1)].

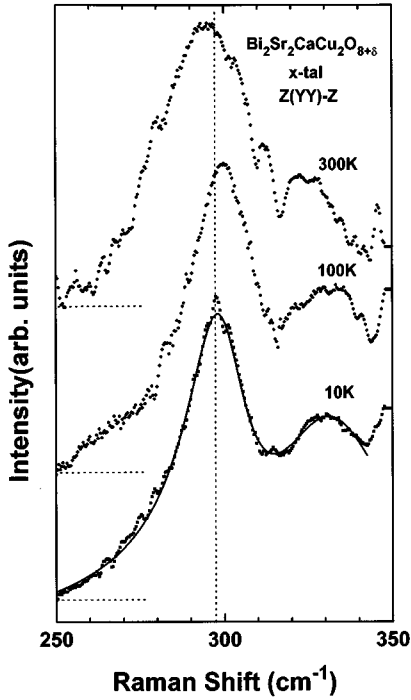


FIG. 4. Typical Raman spectra of the  $290 \text{ cm}^{-1}$   $A_{1g}$   $Z(YY) - Z$  mode in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  for three different temperatures; 10, 100, and 300 K. In the fitting procedure a Lorentzian profile was used for the symmetric lineshape of the  $327 \text{ cm}^{-1}$  mode and a Fano line shape profile was used for the slightly asymmetric line shape of the  $290 \text{ cm}^{-1}$  mode. The dashed line in this figure is the result of this fitting procedure for the spectrum at 10 K, corresponding to the Fano mode with  $q = -5.81$ ,  $\omega_v = 300.6 \text{ cm}^{-1}$ , and  $\gamma = 11.91 \text{ cm}^{-1}$  and to the Lorentzian mode with  $\omega = 329.0 \text{ cm}^{-1}$  and  $\gamma = 27.46 \text{ cm}^{-1}$ .

achieved with the fitting parameters  $a_1 = 9.02 \text{ cm}^{-1}$ ,  $a_2 = 4.95 \text{ cm}^{-1}$ , and  $\omega_v = 465 \text{ cm}^{-1}$ .

In Fig. 4 we present a typical Raman spectrum with  $Z(YY) - Z$  polarization of the  $290 \text{ cm}^{-1}$   $A_{1g}$  mode for three different temperatures. Besides the  $290 \text{ cm}^{-1}$  mode, another  $A_{1g}$  mode at  $327 \text{ cm}^{-1}$ , corresponding to the  $c$ -axis vibration of the oxygen ( $\text{O}_{4+\delta}$ ) atoms in the Bi layer,<sup>9</sup> is also observed. The phonon near  $290 \text{ cm}^{-1}$  has been identified as the  $c$ -axis in-phase vibration of the  $\text{O}_{1,2}$  atoms in the  $\text{CuO}_2$  layer.<sup>9</sup> We notice that even the  $285 \text{ cm}^{-1}$   $B_{1g}$  is also active in  $YY$  polarization, and it is not detected in Fig. 4. This phonon is much weaker than the  $290 \text{ cm}^{-1}$   $A_{1g}$ , and it can be seen with appreciable intensity in  $X'Y'$  scattering geometry [where  $X' = (1/\sqrt{2})(1,1)$  and  $Y' = (1/\sqrt{2})(1,-1)$ ].<sup>8</sup> In order to account for any mutual interference between the  $290$  and  $327 \text{ cm}^{-1}$  modes we used a combined fitting procedure to obtain the values of their frequencies and linewidths. A Lorentzian profile was used to fit the symmetric line shape of the  $327 \text{ cm}^{-1}$  mode and a Fano line shape profile was used to fit the slightly asymmetric line shape of the  $290 \text{ cm}^{-1}$  mode. Therefore, the Raman intensity is given by<sup>11</sup>

$$I(\omega) \propto \frac{(\varepsilon + q)^2}{1 + \varepsilon^2} + B + \text{Lorentzian}, \quad (2)$$

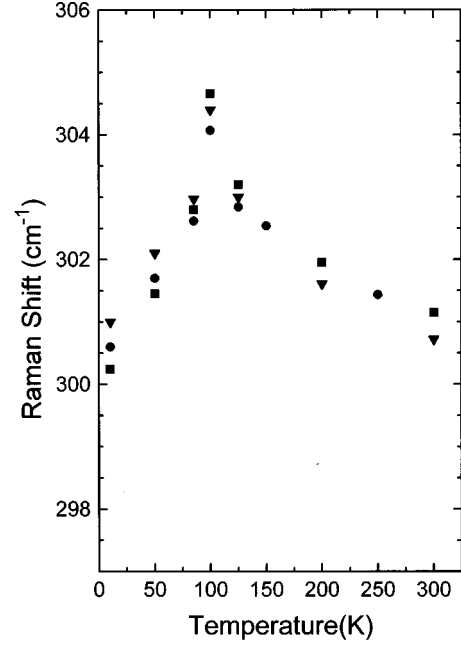


FIG. 5. Temperature dependence of the frequencies of the  $A_{1g}$   $290 \text{ cm}^{-1}$  phonon mode in three different samples (represented by squares, circles, and triangles). Above  $T_c$ , the frequency can be adequately described by the normal temperature-dependent anharmonic decay. Below  $T_c$  a softening in the frequency of about  $\Delta\omega/\omega \approx -1.3\%$  is observed.

where  $\varepsilon = (\omega - \omega_v)/\gamma$ ,  $\omega_v$  is the phonon frequency,  $q$  is the asymmetry parameter, and  $B$  is a linear extrapolated background [ $B = B_0 + 0.0012(\omega - 250)$ ] between  $250$  and  $330 \text{ cm}^{-1}$ . The dashed line in Fig. 4 is the result of applying this fitting procedure to the spectrum at 10 K. The fitting parameters for the Fano mode are  $q = -5.81$ ,  $\omega_v = 300.6 \text{ cm}^{-1}$ , and  $\gamma = 11.91 \text{ cm}^{-1}$ , and that for the Lorentzian mode are  $\omega = 329.0 \text{ cm}^{-1}$  and  $\gamma = 27.46 \text{ cm}^{-1}$ . The  $|q|$  value is nearly constant ( $\approx 3$ ) above  $T_c$ , but below  $T_c$  it increases, reaching a value of  $|q| \approx 6$  at 10 K. Anomalies of the  $q$  parameters at  $T_c$  have been reported in Y124.<sup>2</sup> The frequencies of the  $290 \text{ cm}^{-1}$  mode obtained at different temperatures for three different samples are plotted in Fig. 5. Above  $T_c$ , and below 200 K, the frequency behavior is similar to that found in Y124 by Heynen *et al.*,<sup>2</sup> while below  $T_c$  a softening in the frequency of about  $\Delta\omega/\omega \approx -1.3\%$  is observed.

In Fig. 6 the linewidth of the  $290 \text{ cm}^{-1}$  mode is plotted as a function of the temperature. The dashed line corresponds to the anharmonic decay fitted with Eq. (1), using  $a_1 = 8.26 \text{ cm}^{-1}$ ,  $a_2 = 3.25 \text{ cm}^{-1}$ , and  $\omega_v = 290 \text{ cm}^{-1}$ . Once again, above  $T_c$ , the phonon linewidth is consistent with the anharmonic decay profile, but below  $T_c$ , the phonon linewidth shows a narrowing of about  $6 \text{ cm}^{-1}$ . The onset of the frequency softening and the linewidth decrease occurs about 15 K above the value of  $T_c$  determined by dc magnetization measurements. An even higher temperature difference was found in the Y123 compounds.<sup>12</sup>

#### IV. DISCUSSION

Group theoretical analysis of Bi2212 based on a tetragonal cell (space group  $I4/mmm$ ) predicts 14 Raman-active

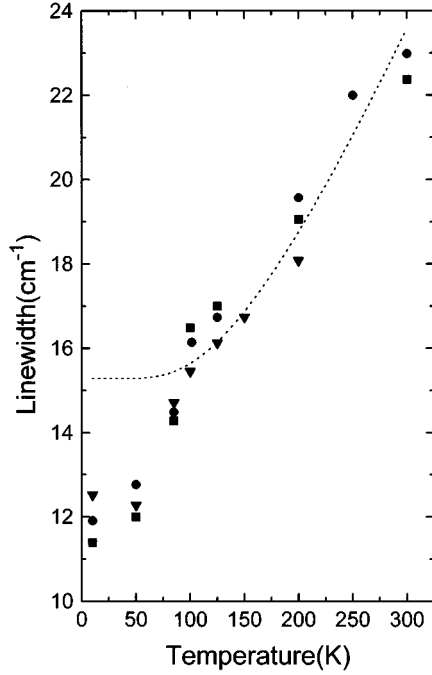


FIG. 6. Temperature dependence of the linewidth of the  $A_{1g}$   $290\text{ cm}^{-1}$  mode. Above  $T_c$ , the phonon linewidth follows the anharmonic decay curve fitted by Eq. (1) (dashed line). Below  $T_c$ , the phonon linewidth shows a narrowing of about  $6\text{ cm}^{-1}$ .

modes ( $6A_{1g} + B_{1g} + 7E_g$ ).<sup>9</sup> Prior to this work, the temperature dependence of the frequency and linewidth had been studied in 3 of these 14 Raman-active modes, i.e.,  $650\text{ cm}^{-1}$  (Ref. 7) ( $A_{1g}$ ,  $O_{4+5}$   $a$ -axis vibration, BiO layers),  $465\text{ cm}^{-1}$  (Ref. 7) ( $A_{1g}$ ,  $O_3$   $c$ -axis vibration, SrO layers), and the  $285\text{ cm}^{-1}$  (Ref. 8) ( $B_{1g}$ ,  $O_{1,2}$   $c$ -axis out-of-phase vibration, CuO layers). For the  $A_{1g}$  mode at  $650\text{ cm}^{-1}$  no anomalies in the temperature dependence of the frequency and linewidth were found. For the  $A_{1g}$  mode at  $465\text{ cm}^{-1}$  a softening of about  $1\text{ cm}^{-1}$  with onset close to  $T_c$  was found and confirmed by the present experiment (see Fig. 3). However, the temperature dependence of the linewidth was found to follow the normal anharmonic decay curve (see Fig. 4), without any detectable anomaly at  $T_c$ . Recently,<sup>8</sup> an anomalous linewidth behavior was found for the  $B_{1g}$  mode at  $285\text{ cm}^{-1}$ . But in contrast to the  $465\text{ cm}^{-1}$  mode, the frequency of the  $285\text{ cm}^{-1}$  mode did not show any anomalous behavior within the experimental uncertainty. This last result led the authors to conclude that the superconducting energy gap is larger than  $285\text{ cm}^{-1}$ . The experimental result reported here is the temperature dependence of the frequency and the linewidth of the phonon mode with symmetry  $A_{1g}$  at  $290\text{ cm}^{-1}$ . We observe a softening and a narrowing of this mode below  $T_c$ . We note the presence of an anomalous temperature dependence of the linewidth of a  $A_{1g}$  phonon in Bi2212.

In order to account for the phonon anomalies at  $T_c$ , Zeyher and Zwicky,<sup>13</sup> Nicol *et al.*,<sup>14</sup> and Devereaux<sup>15</sup> have calculated the shift of the phonon frequency and the change in the linewidth due to superconductivity with  $s$ -wave,  $d$ -wave, and  $d_{x^2-y^2}$  pairing interactions for  $q=0$  Raman-active phonons. Their main results are summarized below.

Zeyher and Zwicky<sup>13</sup> have shown that, if the electron-phonon coupling is strong enough, the phonon should soften or harden below  $T_c$ , depending on whether the phonon frequency is less than or greater than twice the superconducting gap energy. The superconductivity-induced change in the frequency of the  $\nu$  phonon is given by<sup>13</sup>

$$\Delta\omega_\nu/\omega_\nu = \lambda_\nu \text{Re}(\Sigma_\nu)/2N, \quad (3)$$

where  $\lambda_\nu$  is the electron-phonon coupling constant for the  $\nu$  phonon,  $N$  is the normal density of states per spin at the Fermi energy  $E_F$ , and  $\Sigma_\nu$  is the complex self-energy for the  $\nu$  phonon. Moreover, the phonon linewidth should decrease or increase below  $T_c$ , depending on whether the phonon energy is less than or greater than twice the superconducting gap, respectively. The phonon linewidth change  $\Delta\Gamma_\nu$  is given by<sup>13</sup>

$$\Delta\Gamma_\nu/\omega_\nu = -\lambda_\nu \text{Im}(\Sigma_\nu)/2N. \quad (4)$$

The curves for the real and imaginary parts of the phonon self-energy and the changes of phonon frequency and linewidth for different temperatures and impurity scattering rates are presented in Figs. 3–6 of Ref. 13. The most drastic effects should occur when  $\omega \approx 2\Delta$ , where  $\Delta$  is the superconducting gap. The physical reason why the phonon linewidth changes in the superconducting state is that superconductivity reduces the number of possible electronic decay channels for phonons with energy less than twice the gap, resulting in a decrease of phonon linewidth, while phonons with energy greater than twice the gap experience an increase in the quasiparticle scattering, resulting in an increase of phonon linewidth. Similarly, since energy levels of interacting excitations tend to repel phonons with energies greater than the gap we expected to harden, while phonons with energies less than the gap we expected to soften below  $T_c$ . These effects would be expected in the clean limit. However, in the dirty limit, with  $1/(2\Delta\tau) = 3$ , where  $\tau$  is the scattering time, the hardening for phonons with energy above the gap may turn into a slight softening and the expected broadening will decrease by approximately 80%. This shows that in the strong-coupling limit the effects of softening and broadening will depend on  $T/T_c$  and also on the impurity scattering rate  $1/(2\Delta\tau)$ .

Nicol *et al.*<sup>14</sup> have calculated the frequency shift and the change in linewidth, in the clean limit, due to superconductivity in the high- $T_c$  superconductors assuming a  $d$ -wave pairing interaction. They have also presented a more general model of a superconductor with nodes in the gap function and related it both to the  $d$ -wave model and to a model for layered superconductors. In the layered superconductor model the anisotropic gap function is given by  $\Delta_k = \Delta[1 + b \cos(k_z c)]$ , where  $b$  is the anisotropy parameter. Therefore, for  $b=0$  the standard  $s$ -wave result is recovered. However, for  $b \neq 0$ , in contrast to the usual isotropic  $s$ -wave picture, there are three regions of behavior: (i) Phonons with energy less than twice the minimum gap value will

soften with no change in linewidth, (ii) phonons between twice the minimum and the maximum gaps will soften and broaden, and finally, (iii) phonons with energy greater than twice the maximum gap will broaden and harden. The broadening in the intermediate region is explained because in superconductors with nodes in the gap function, particle-hole pairs can be created at arbitrarily low energy (at the nodes) and contribute to scattering. Therefore, experimental results with broadening and softening could be a signature of a gap parameter that exhibits nodes.

Devereaux<sup>15</sup> has studied the temperature dependence below  $T_c$  of the line shapes of optical phonons of different symmetry. He found that phonons with  $A_{1g}$  and  $B_{1g}$  symmetry couple differently to the electrons. As a consequence, the real and imaginary parts of the phonon self-energy peak at  $\omega/2\Delta \approx 1$  for  $B_{1g}$  symmetry and  $\omega/2\Delta \approx 0.5$  for  $A_{1g}$  symmetry. He shows that in the case of  $d_{x^2-y^2}$  pairing symmetry, phonons of  $B_{1g}$  symmetry ( $285 \text{ cm}^{-1}$ ) with energy below the peak in the imaginary part of the self-energy could have a substantial narrowing below  $T_c$ . On the other hand, phonons with  $A_{1g}$  symmetry ( $465 \text{ cm}^{-1}$ ) which lie above the peak in the imaginary part of the self-energy should not show any linewidth anomaly.

Previous results from electronic Raman scattering<sup>16</sup> (ERS) measured above and below  $T_c$  in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  single crystals with  $\delta=0.13$  ( $T_c=86 \text{ K}$ ) provide evidence that the gap is anisotropic and that its energy for the  $A_{1g}$  symmetry is close to  $2\Delta=385 \text{ cm}^{-1}$ . Assuming that this is the true gap value in this symmetry for the slightly doped samples of Bi2212, this means that the phonon modes at 290 and  $465 \text{ cm}^{-1}$  studied in this work are below and above twice the gap energy, respectively. Therefore, the normalized optical phonon frequency is given by  $\omega/2\Delta \sim 0.77$  and 1.2 for the 290 and  $465 \text{ cm}^{-1}$   $A_{1g}$  phonons, respectively.

Analyzing our experimental results based in the Zeyher's model for the isotropic  $s$  wave we would expect that below  $T_c$  and in the clean limit, the  $290 \text{ cm}^{-1}$  mode will exhibit softening and narrowing, whereas the  $465 \text{ cm}^{-1}$  mode will exhibit hardening and broadening. The prediction of softening and narrowing of the  $290 \text{ cm}^{-1}$  mode below  $T_c$  is consistent with our experimental results. However, the prediction of hardening and broadening below  $T_c$  is inconsistent with the softening and no change in the linewidth found for the  $465 \text{ cm}^{-1}$  mode. However, if the impurity scattering rate plays an important role, with  $1/(2\Delta\tau)=3$ , the hardening of the phonons above  $2\Delta$  can become a small softening (see Fig. 5 from Ref. 13), and the expected broadening will decrease by a factor of 4 compared to the clean limit.

Another possibility is that the pairing interaction has  $d$ -wave energy-gap symmetry as proposed by Nicol *et al.*<sup>14</sup> In Fig. 7 of Ref. 14 is plotted a comparison between the experimental data and the theoretical curves for three models: isotropic  $s$ -wave, planar  $d$ -wave, and a layered anisotropic superconductor model with  $2\Delta_{\min}=2\Delta_0(1-b)$  and  $2\Delta_{\max}=2\Delta_0(1+b)$  where  $\Delta_0=\Delta(T=0)$  and assuming for the anisotropy parameter  $b=0.125$  and  $2\Delta_0=380 \text{ cm}^{-1}$ . Note that the phonon mode at  $290 \text{ cm}^{-1}$  is below twice the minimum gap, [ $2\Delta_0(1-b)=332 \text{ cm}^{-1}$ ], and so according to Fig. 7 of Ref. 14, in the clean limit softening is predicted by each of the three models presented. However, the linewidth should not change in either the isotropic  $s$ -wave or the

layered superconductor model, whereas for the planar  $d$ -wave model broadening of the  $290 \text{ cm}^{-1}$  phonon is predicted. The agreement of these models with our experimental result for the  $290 \text{ cm}^{-1}$  mode is good for the frequency shift but not for the linewidth, since none of them predicted the observed narrowing of the linewidth below  $T_c$ . The phonon at  $465 \text{ cm}^{-1}$  is above twice the maximum gap [ $2\Delta_0(1+b)=427 \text{ cm}^{-1}$ ], and so according to Fig. 7 of Ref. 14 we should expect below  $T_c$  a hardening and broadening, which is inconsistent with the softening without apparently change in the linewidth that was reported in Refs. 6 and 7 and confirmed by the present experimental result.

Devereaux<sup>15</sup> has discussed the experimental results for the linewidth in Bi2212 and Y123, assuming a  $d_{x^2-y^2}$  gap symmetry. He concluded that the behavior of the linewidth at  $T_c$  of both phonons could be explained by his approach; i.e., the  $285 \text{ cm}^{-1}$  ( $B_{1g}$ ) narrows and the  $465 \text{ cm}^{-1}$  ( $A_{1g}$ ) does not show any appreciable change. He based his analyses on the different low-temperature dependence of the imaginary part of the self-energy for the  $A_{1g}$  (linear dependence) and  $B_{1g}$  ( $T^3$  dependence) channels. However, the linewidth narrowing that we found for the  $290 \text{ cm}^{-1}$   $A_{1g}$  could not be explained by the Devereaux analysis.

## V. CONCLUSIONS

We have measured the superconductivity-induced changes in the frequency and linewidth of the  $A_{1g}$  Raman-active phonons at 290 and  $465 \text{ cm}^{-1}$  in several single crystals of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ . We found that in the superconducting state the  $A_{1g}$  phonon mode at  $290 \text{ cm}^{-1}$  softened and narrowed, whereas the  $A_{1g}$  mode at  $465 \text{ cm}^{-1}$  softened with no detectable change in its linewidth. We compare the anomalous softening and linewidth behavior observed in the superconducting state with the theoretical predictions for isotropic  $s$ -wave, planar  $d$ -wave, a layered superconductor model, and  $d_{x^2-y^2}$  gap symmetries. We found that none of those theoretical predictions could account for our results regarding the narrowing of the  $A_{1g}$   $290 \text{ cm}^{-1}$  phonon mode. However, many experimental results have shown that the  $d_{x^2-y^2}$  state is a viable candidate for the pairing state of this high- $T_c$  superconductor. Since our experiment was carried out with a close optimally doped sample ( $\delta=0.13$  and  $T_c=86 \text{ K}$ ), more Raman measurements with overdoped and underdoped samples could contribute to understanding the symmetry of the superconductor gap. We would like to point out that the Raman spectroscopy measurements are not sensitive to the phase of the order parameter and, therefore, there is no way to distinguish between  $d_{x^2-y^2}$  and a strongly anisotropic  $s$ -wave gap symmetry.

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