Doping dependence of the superconducting gap in $Bi_2Sr_2CaCu_2O_{8+\delta}$

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$Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals with varying hole concentrations ($0.12<p<0.23$) were studied to investigate the effects of doping on the symmetry and magnitude of the superconducting gap [$\Delta(\mathbf{k})$]. Electronic Raman scattering experiments that sample regions of the Fermi surface near the diagonal (B_{2g}) and principal axes (B_{1g}) of the Brillouin zone have been utilized. The frequency dependence of the Raman response function χ'' at low energies [$\omega<\Delta(\mathbf{k})$] is found to be linear for B_{2g} and cubic for B_{1g} ($T<T_c$). The latter observations have led us to conclude that the doping dependence of the superconducting gap is consistent with $d_{x^2-y^2}$ symmetry, for slightly underdoped and overdoped crystals. Studies of the pair-breaking peak found in the B_{1g} spectra demonstrate that the magnitude of the maximum gap ($|\Delta_{\max}|$) decreases monotonically with increasing hole doping, for $p>0.12$. Based on the magnitude of the B_{1g} renormalization, it is found that the number of quasiparticles participating in pairing increases monotonically with increased doping. On the other hand, the B_{2g} spectra show a weak ''pair-breaking peak'' that follows a paraboliclike dependence on hole concentration, for $0.12<p<0.23$.

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I. INTRODUCTION

One of the important questions to be answered in identifying the microscopic origin of superconductivity in cuprates is the nature of the superconducting gap. A great deal of attention[1–10] has been focused on identifying the symmetry of the pairing state since it is believed that this information will provide constraints that will lead to the identification of the pairing mechanism. For example, it has been suggested[11–16] that pairing in high-temperature superconductors (HTSC's) is induced by the exchange of antiferromagnetic spin fluctuations and in this case the pairing state would necessarily have $d_{x^2-y^2}$ symmetry. From the many experiments carried out in this context, a consensus view has emerged[17] that associates $d_{x^2-y^2}$ symmetry with the pairing state in optimally hole-doped cuprates. However, this consensus is lacking (see Ref. 18 for a review) in the results of angle resolved photoemission,[2,19–24] tunneling,[25,26] infrared,[27] and Raman spectroscopy[10,28–40] experiments carried out on overdoped and underdoped compounds, where it appears that the material properties are very different from those of the optimally doped versions. Since an appropriate model of the normal state must be capable of predicting the effects of doping, it is clear that additional experiments are required if one is to gain a complete understanding of superconductivity in the high-T_c cuprates.

Raman scattering has been widely used[3–10,31,32,34,41,42] to investigate electronic excitations in superconductors. In electronic Raman scattering experiments, one may investigate various parts of the Fermi surface by a simple choice of the incident and scattered polarization vectors. The B_{1g} spectra sample[3,5–7] regions of the Fermi surface located near the Brillouin zone (BZ) principal axes [i.e., $(\pm\pi,0),(0,\pm\pi)$], while B_{2g} spectra sample regions located near the diagonal directions in the BZ. When Raman results are interpreted[3–9] in terms of the conventional model,[43] the gap is found to have maxima along the $(\pm\pi,0)$ and $(0,\pm\pi)$ directions and nodes (or minima) along the diagonal directions. The results are consistent with $d_{x^2-y^2}$ symmetry and are thus in agreement with the outcome of several other experiments (see Scalapino[17] for a review). The maximum values of the gap are found to scale with T_c ($2\Delta_{\max}\sim 8k_BT_c$) between optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212),[3] $YBa_2Cu_3O_{7-\delta}$ (Y123),[5] and $La_{2-x}Sr_xCuO_4$ (La214).[9] In Bi2212, the value derived from Raman experiments ($2\Delta_{\max}\sim 500\ cm^{-1}$) is also in good agreement with the results of photoemission experiments ($\Delta_{\max}\approx 30\ meV = 240\ cm^{-1}$).

The first Raman investigation of the influence of doping was carried out on Y123 (Ref. 5) and it was found that, although the symmetry appeared to be independent of doping, the B_{1g} pair-breaking frequency ($2\Delta_{\max}$) decreased much more rapidly than T_c as the doping level was increased beyond optimal. Later, Kendziora *et al.*[10] carried out measurements on both heavily overdoped and underdoped Bi2212. In the heavily overdoped region they also found that $2\Delta/k_BT_c$ decreased and that the B_{1g} and A_{1g} peak frequencies approached equality, and suggested that this implied the existence of an isotropic gap. The low-energy frequency dependence of their measured B_{1g} and A_{1g} spectra also appeared to be compatible with this interpretation. However, it was pointed out by Hewitt *et al.*[31] that the gap cannot be isotropic if the Bose-factor corrected spectra from all scattering geometries are considered. Hackl *et al.*[33] also carried out experiments on a heavily overdoped crystal of Bi2212 and interpreted their results in terms of a disordered *d*-wave model proposed by Devereaux.[44]

In an attempt to gain additional insight into the influence of doping on the superconducting order parameter in HTSC's we have carried out Raman scattering experiments on overdoped (OD) and underdoped (UD) Bi2212 crystals with critical temperatures $T_c = 82,85,86,90.5$ K (UD) and 89,87,83,70,55 K (OD). Spectra have been obtained in the B_{1g} and B_{2g} scattering geometries in both the superconducting and normal state. The B_{2g} spectra of overdoped compounds, which were not carefully investigated in previous studies,[10] have provided important information regarding the

TABLE I. Bi2212 sample properties—see Ref. 65 for details.

Sample	T_c	Doping	p
Bi-Y(0.40)-2212	30 K	UD	0.0696
Bi2212	51 K	UD	0.0865
Bi2212-^{18}O	51 K	UD	0.0865
Bi-Y(0.07)-2212	70 K	UD	0.1062
Bi2212-^{18}O	82 K	UD	0.1237
Bi2212	85 K	UD	0.1296
Bi2212	86 K	UD	0.1319
Bi2212	90.5 K	UD	0.1460
Bi2212-^{18}O	89 K	OD	0.1799
Bi2212	87 K	OD	0.1857
Bi2212	83 K	OD	0.1944
Bi2212	70 K	OD	0.2138
Bi2212	55 K	OD	0.2298

symmetry of $\Delta(\mathbf{k})$. These spectra sample regions of the Fermi surface that are located near the diagonal directions in the Brillouin zone and hence can be used[5–7] to directly probe for the existence of *d*-wave type gap nodes. Our results suggest that the superconducting gap possesses $d_{x^2-y^2}$ symmetry, for the doping range $(0.12<p<0.23)$ investigated—slightly underdoped to overdoped.

II. EXPERIMENTAL RESULTS

A. Sample properties: $Bi_2Sr_2CaCu_2O_{8+\delta}$

In cuprates, the addition (removal) of oxygen increases (decreases) the Cu valence[45] and therefore the hole concentration. Thus single crystals of Bi2212 were subjected to various oxygen-rich or oxygen-poor environments in order to vary the hole concentrations, spanning the doping range $0.07<p<0.23$. The superconducting transition temperatures (measured by the onset of the drop in magnetization or the zero of resistance) and hole concentrations are listed in Table I. Hole concentrations for each crystal are estimated using the empirical relation of Tallon and Presland,[46,47] assuming $T_{c,\max}=92$ K.

B. Raman scattering

Raman vibrational spectra in the frequency range 20–1000 cm^{-1} were obtained using the 514.5 nm line of an argon ion (Ar^+) laser as the excitation source. The Raman measurements were carried out in a quasibackscattering geometry, with the incident laser beam directed nearly perpendicular to the freshly cleaved (**a**,**b**) face of the crystal.

Bi2212 has an orthorhombic (D_{2h}) structure with the **a** and **b** axes oriented at 45° to the Cu-O bonds. In Raman experiments it is customary (since $a\approx b$) to assume a tetragonal structure (D_{4h}) with axes parallel to **a** and **b**. To facilitate comparison with other cuprates, however, we will consider a tetragonal cell with **x** and **y** axes parallel to the Cu-O bonds. Another set of axes, $\mathbf{x}'$ and $\mathbf{y}'$ are rotated by 45° with respect to the Cu-O bonds. Considered within the tetragonal point group (D_{4h}), the $\mathbf{x}'\mathbf{y}'$ (B_{1g}) scattering geometry means that the incident (scattered) light is polarized along $\mathbf{x}'(\mathbf{y}')$ and selection of this scattering channel enables coupling to excitations having B_{1g} symmetry. Similarly, the **xy** geometry allows coupling to B_{2g} excitations, which transforms as $d_{\mathbf{x}\cdot\mathbf{y}}$. Finally, the diagonal scattering geometry $\mathbf{x}'\mathbf{x}'$ allows coupling to $A_{1g}+B_{2g}$ and **xx** to $A_{1g}+B_{1g}$ excitations. Thus, by choosing the polarization of the incident and scattered light appropriately, one may select different components of the Raman tensor and thus various symmetry properties of the excitations.

The B_{1g} and B_{2g} symmetries probe[5–7] complementary regions of the Fermi surface (FS), while the A_{1g} spectra correspond to an approximate average over the entire FS. In particular, the B_{1g} Raman spectrum samples the FS along the $(0,\pm\pi)$ and $(\pm\pi,0)$ directions whereas the B_{2g} spectum samples the $(\pm\pi,\pm\pi)$ directions. That is, the B_{1g} spectra sample the BZ principal axes while the B_{2g} spectra sample the BZ diagonals, and are therefore used as complementary probes to obtain information about the **k** dependence of the gap.

The spectra presented in this section have been corrected for the Bose thermal factor. Therefore, the spectra shown are proportional to the imaginary part of the Raman response function (χ'').

1. B_{1g} renormalization

Spectra obtained from the cuprates at room temperature are characterized[48] by a rather featureless continuum, extending from $\hbar\omega\sim 0$ to 2 eV. When the samples are cooled below T_c the spectral weight at low energies (<100 meV) may be redistributed to higher energy and gaplike peaks appear in the spectra. In Bi2212 the superconductivity induced renormalization observed in the B_{1g} spectra (see Fig. 1 and Table II) produces a peak whose energy remains relatively constant (for $p<0.16$), but decreases drastically with increasing hole concentration in the overdoped regime ($p>0.16$). When the peak energy is compared (Fig. 2) with the maximum SC gap ($\Delta_{\max}$) values reported by ARPES (Ref. 24) and tunneling,[25,49] the results are striking. The doping dependence and energy of the B_{1g} peak position corresponds very well with the values of $2\Delta_{\max}$ obtained from ARPES measurements on similarly doped samples (see Fig. 2). This supports the previous association of the peak frequency in the B_{1g} spectra with the maximum ($2\Delta_0$) in a $d_{x^2-y^2}$ gap function. This association is also supported by the low frequency dependence of χ'' at low temperatures, as will be discussed in Sec. II B 3.

The ratio $2\Delta_0/k_BT_c$ has also been plotted as a function of p in Fig. 3, where the results reveal that this ratio decreases monotonically with increasing hole concentration. A linear least-squares fit to the data is well described by the empirical relation

$$\frac{2\Delta_{\max}}{k_BT_c}=(15\pm1)-(38\pm5)p \qquad (1)$$

for $0.12<p<0.24$.

It can be seen in Fig. 1 that, as p is reduced, there is a reduction in the fraction of spectral weight redistributed at

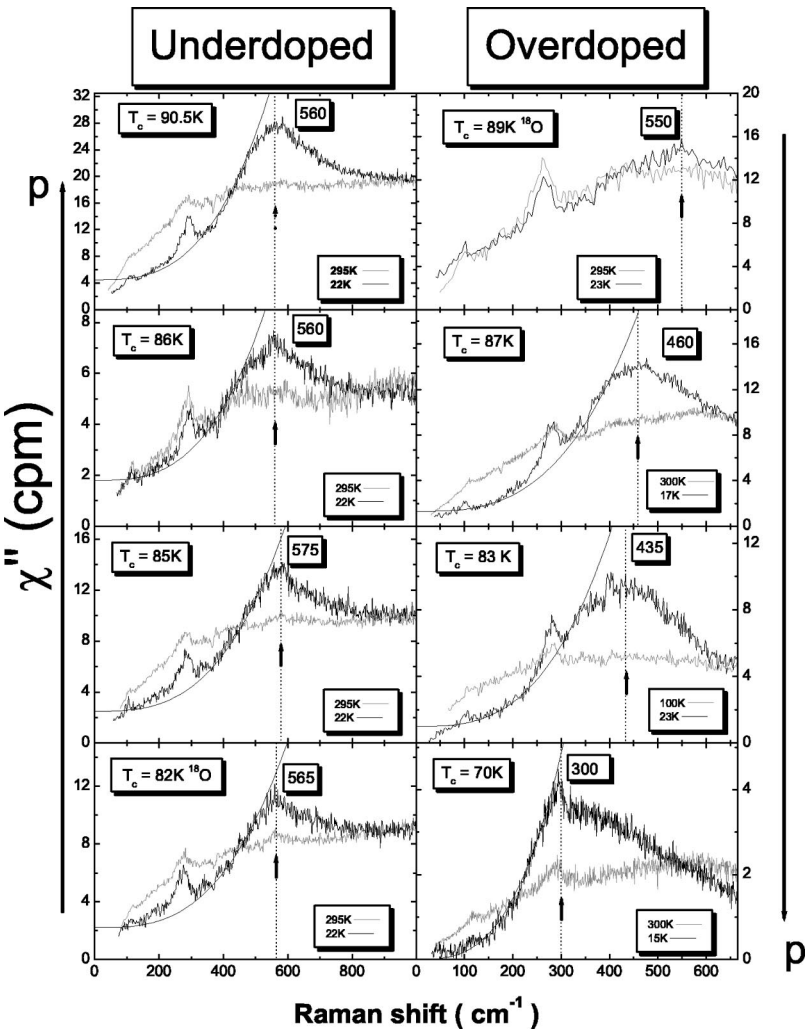

FIG. 1. The B_{1g} $(\mathbf{x}'\cdot\mathbf{y}')$ spectra at temperatures above and below T_c, for underdoped samples with T_c's of 82, 85, 86, and 90.5 K, and for overdoped samples with T_c's of 89, 87, 83, and 70 K.

low frequencies. Quantitatively, this redistribution was estimated by taking the ratio of the spectral weight above and below T_c. The frequency range of interest is selected to envelope the region where increased scattering in the superconducting state is observed. Within this region, the points at which the normal and superconducting state spectra cross defines the upper and lower bounds on the integration. In this range, the ratio of the integrated intensity of the superconducting (A_2) vs normal state (A_1) spectra are calculated, and the results are presented in Fig. 4. The redistributed spectral weight is reduced (Fig. 4) with decreasing hole concentration, indicating that fewer quasiparticles are participating in superconductivity. It may be that the quasiparticle pairs are being destroyed by some collective excitation of the crystal whose strength increases with decreasing doping. The missing spectral weight may be most likely redistributed to higher energy, as recently suggested by the work of Naeini *et al.*[50] In their study of La214 it was found that the B_{1g} spectral weight that is lost at low energies ($\omega \leqslant 800$ cm^{-1}) is transferred to the higher-energy region normally occupied by multimagnon scattering. Taken together, the results suggest that the quasiparticle density near $(\pi,0)$ is reduced by magnetic excitations of some type. Of course, this suggestion requires further quantitative analysis.

TABLE II. Values of the cubic (b) and constant (a) terms used in a fit ($I=a+b\omega^3$) to the low frequency spectra of Fig. 1—UD =underdoped; OD=overdoped.

p	OD or UD	T_c (K)	(a)	(b)
0.124	UD	82	2.2	0.06×10^{-6}
0.130	UD	85	2.5	0.07×10^{-6}
0.132	UD	86	1.8	0.05×10^{-6}
0.146	UD	90.5	4.5	0.18×10^{-6}
0.186	OD	87	1.3	0.18×10^{-6}
0.194	OD	83	1.0	0.18×10^{-6}
0.214	OD	70	0.0	0.18×10^{-6}

2. B_{2g} renormalization

A redistribution of spectral weight also occurs below T_c in the B_{2g} channel (Fig. 5) but it is difficult (except in the case of the 83 K overdoped sample) to identify any peak formation in the low-temperature B_{2g} spectra of Fig. 5. In the depleted regions of the spectra the intensity rises linearly at low frequencies then levels off at a frequency we will designate as ω_0 (a linear-to-constant crossover frequency). A linear fit is made to the low-frequency data and ω_0 is defined

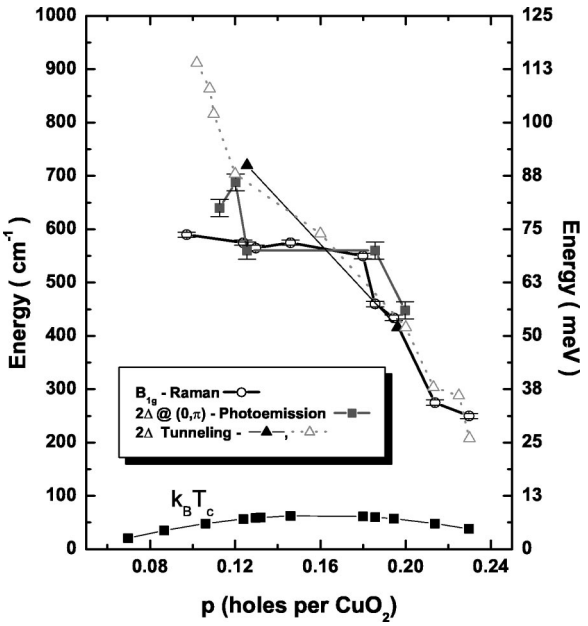

FIG. 2. The peak position of the superconductivity induced redistribution in the B_{1g} spectra as a function of doping in Bi2212. The corresponding values of $2\Delta_{\max}$ derived from the ARPES results of Mesot *et al.* (Ref. 24) (filled squares) , and the tunneling data of Miyakawa *et al.* (Ref. 25) (filled triangles) and Ozyuzer *et al.* (Ref. 49) (open triangles) are shown for comparison. In all cases Tallon's relation was used to determine the hole concentration, assuming $T_{c,\max}=92$ K.

by the point at which the line departs from the experimental data points. This frequency can be taken as a measure of the extent of the depleted region and thus provides an estimate of the B_{2g} "gap" energy.[6] It is interesting to note that ω_0 has a parabolic dependence on hole concentration (Fig. 6) and in contrast to $2\Delta_{\max}$ (B_{1g}) actually scales with T_c throughout the doping range, consistent with the results obtained in Raman experiments by Opel *et al.*[8] and Sugai and Hosokawa.[51]

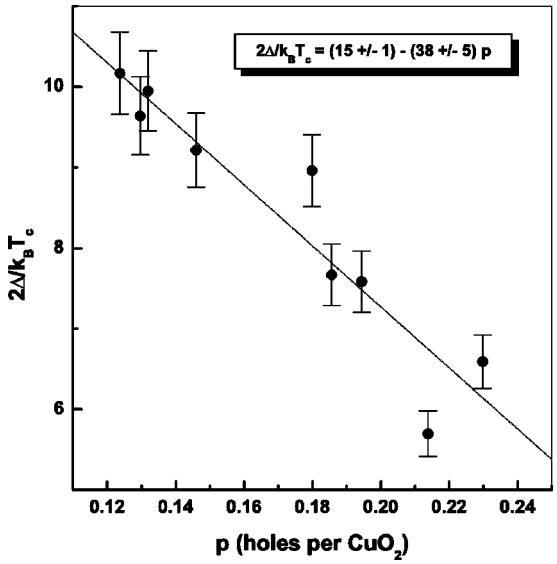

FIG. 3. The hole concentration dependence of $2\Delta_{\max}/k_BT_c$.

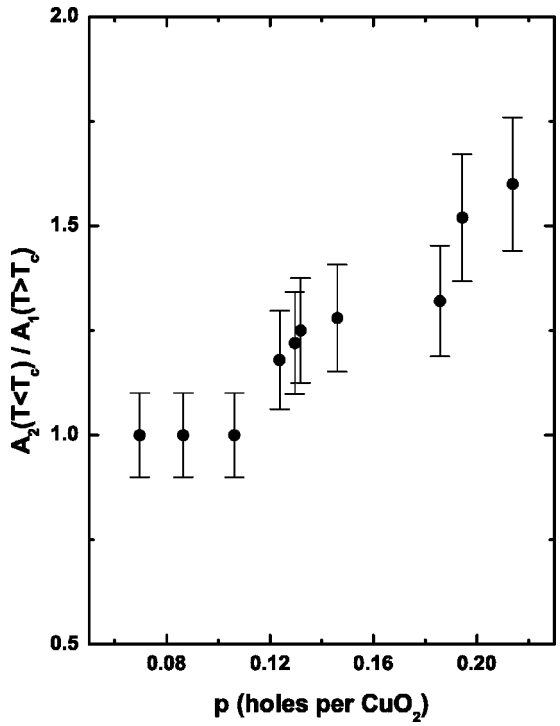

FIG. 4. The hole concentration dependence of the ratio of the redistributed spectral weight in the normal and superconducting state. The ratio is taken in the region of the spectra where increased scattering is seen in the superconducting state (see text). The lower three data points are taken from Ref. 40.

Thus, in the underdoped regime, the results obtained seem to be incompatible with the existence of a single, simple *d*-wave gap. On the other hand Sugai and Hosagawa[51] have suggested that the values of $2\Delta_{\max}$ obtained from the B_{1g} spectra scale with the frequency of the two-magnon peak. This observation suggests that B_{1g} excitations are magnetic in origin. Although not the topic of this paper, it remains to be seen whether the holon-spinon phase diagram model of Anderson[52–55] and Lee[56–59] may offer an explanation of these results.

In the overdoped regime one can observe superconductivity induced peaks in the B_{1g} channel. In this region ($p \geqslant p_{\text{opt}}$) both the values of $\omega_{\text{peak}}(B_{1g})$ and $\omega_0(B_{2g})$ decrease with increasing doping. However, $\omega_{\text{peak}}(B_{1g})$ decreases much more rapidly than does $\omega_0(B_{2g})$ and as a result the peak frequencies become almost equal for $p\approx 0.25$. This behavior, which is similar to that observed in doping studies of La214,[39] appears to be inconsistent[6] with the existence of a gap with $d_{x^2-y^2}$ symmetry. Thus, although the B_{1g} and B_{2g} spectra of optimally doped compounds[4,6,9] imply the existence of a *d*-wave gap, there are some puzzling discrepancies in this interpretation in both the underdoped and overdoped regions. In an attempt to gain additional insight we will now turn to an investigation of the dependence of χ'' on ω in the low-energy region of the spectrum.

3. Frequency dependence of χ'' at low energies

The $(T/T_c\rightarrow 0)$ frequency dependence of scattering in the low-energy regime (i.e., below ω_{peak}) provides a further

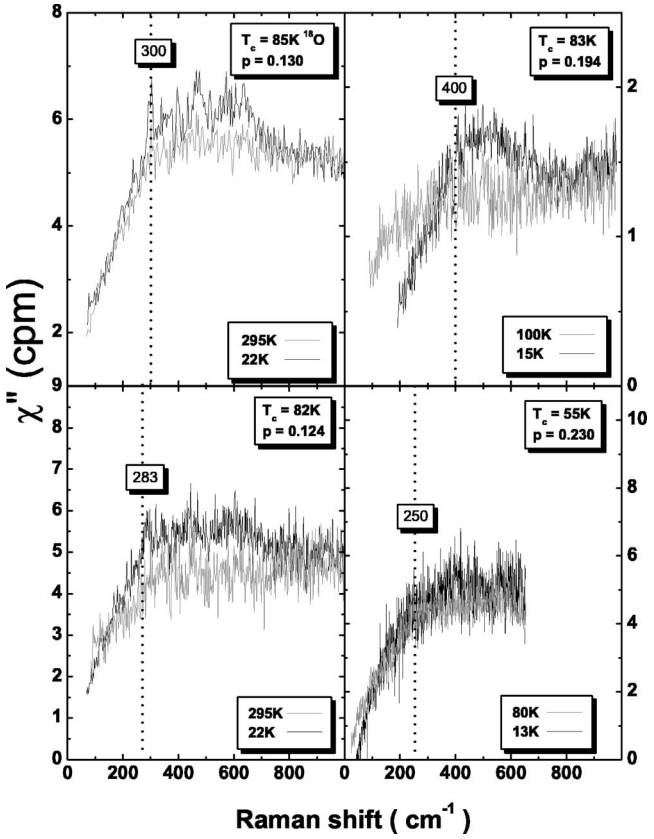

FIG. 5. Doping dependence of the B_{2g} ($\mathbf{x}\cdot\mathbf{y}$) Raman spectra at temperatures above and below T_c, for underdoped (UD) samples with T_c's of 82 and 85 K, and for overdoped (OD) samples with T_c's of 83 and 55 K.

test[4,5] of the Cooper pair symmetry. In the B_{2g} geometry, the observed frequency dependence of the response function remains linear in ω, regardless of the sample T_c (Fig. 5). The only exception is found in examining the low energy region of the B_{2g} spectra (Fig. 7) for the 87 K (OD) sample. One observes a change in slope of the Raman response function at an energy of $\omega \approx 90$ cm^{-1} or $\epsilon \approx 11$ meV. Below this energy the scattering is constant and rises linearly at frequencies above 90 cm^{-1}. These experiments have been repeated and are consistent with that described here. Thus we are confident that the observations are intrinsic and not an experimental artifact. In an ARPES investigation of a similarly overdoped ($T_C = 87$ K) Bi2212 crystal, Ding *et al.*[19] found that the SC gap function exhibited an extended node in the $(\pi,\pi),(-\pi,-\pi)$ directions in the BZ. The modulation direction corresponds to the $(0,0)\rightarrow(\pi,\pi)$ region of the Fermi surface of Bi2212. Ding *et al.*[60] have proposed that the extended node feature ($p \approx 0.186$) is an artifact of umklapp scattering, resulting from scattering of the outgoing electron by the wave vector of the modulation q_M $(0.21\pi, 0.21\pi)$. The extended node artifact near (π,π) should be manifest in the density of excited states by an increased scattering at low energies. Therefore, we contend that the increased, and constant, scattering found at low energies in the B_{2g} channel (for this particular crystal) is consistent with umklapp scattering from the modulation. Umklapp processes scatter a quasiparticle out of the first BZ. In this case, a quasiparticle on the Fermi surface can be scattered by an integral multiple of q_M. Therefore, in the extended zone scheme, the quasiparticle may thereby find itself on another portion of the Fermi surface for which the Fermi velocity is opposite to that which it possessed before being scattered. Thus, this scattering process may reverse the Fermi velocity of quasiparticles with wave vectors along the direction of the modulation wave

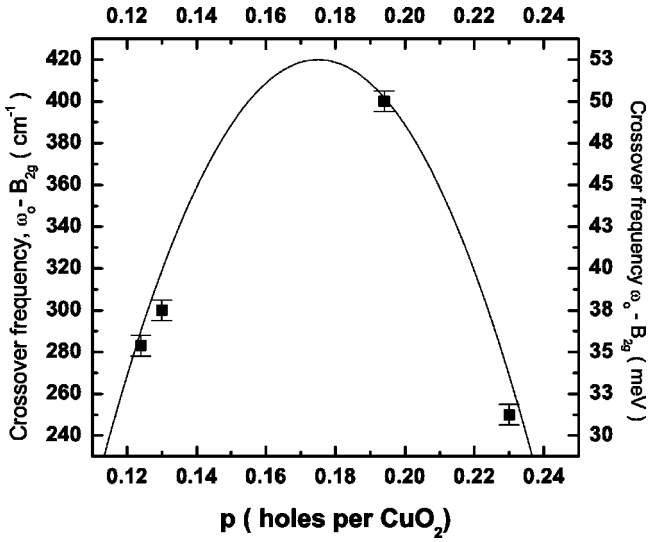

FIG. 6. The hole concentration dependence of the linear-to-constant crossover position in the B_{2g} spectra of $T_c = 82{,}85$ K underdoped and $T_c = 83{,}55$ K overdoped Bi2212 crystals.

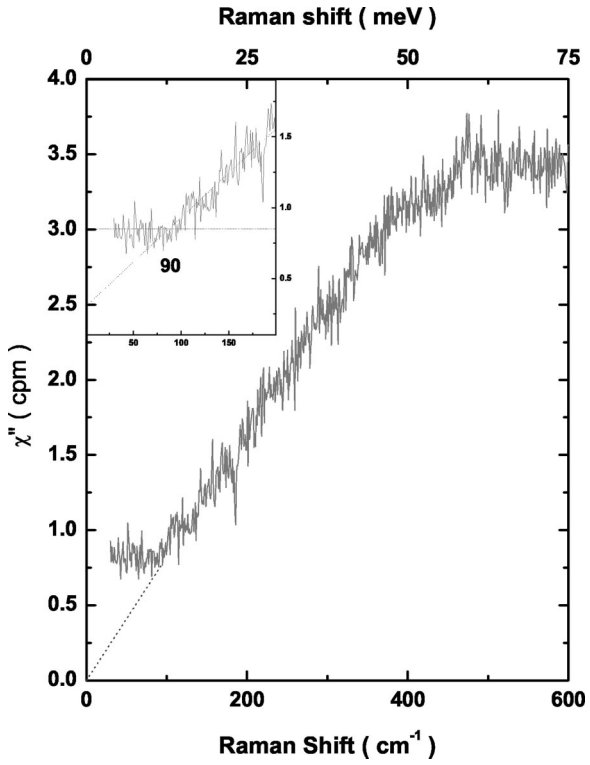

FIG. 7. The B_{2g} Raman spectra for a $T_c = 87$ K overdoped sample, showing the low-frequency dependence in the inset.

vector. This scattering process may destroy the coherence that is required for pairing, leading to a destruction or depression of the gap along the (π,π) direction in k space. The effect would therefore be seen in the B_{2g} scattering geometry.

The results shown in Fig. 7 suggest that for this particular doping level, χ'' is nonzero for ω near zero. This result must be considered to be somewhat suspect in that χ'' is expected to go to zero as ω goes to zero, since the phase space available to electronic excitations disappears. However, if χ'' is nonzero at $\omega=0$, and since $I=(1+n)\chi''$ ($n=$Bose factor), one can see that the scattering intensity will become very large as ω goes to zero. The usual interpretation of a large amount of scattering at low frequencies is to simply assume $\chi''\rightarrow 0$. For these reasons we have checked this result very carefully and have found it to be reproducible, and appearing only for this doping level. The latter point is important since the surface quality of all the samples studied was about the same. In particular the surface of the sample concerned did not have any distinguishing characteristics that we could identify. Thus it appears that the scattering at $\omega\rightarrow 0$ must be accommodated through the appearance of new states. It is possible that, in this case, these states are due to an extended zero gap in the nodal region of the *d*-wave gap.

In the B_{1g} spectra of Fig. 1 the renormalization is quite strong in the range of hole concentrations covering the T_c's 82 K (UD) to 70 K (OD) samples. In all but one spectra ($T_c=89$ K OD) a cubic low-frequency dependence is observed, below the $2\Delta_0$ pair-breaking peak.

It is also evident that there is poorer agreement with a cubic fit in the underdoped regime, where also the peak in the superconducting state appears at a relatively constant value around 565 cm^{-1}. Recent scanning tunneling spectroscopy studies of underdoped Bi2212 (Refs. 61–63) reveal inhomogeneities on a length scale of 30 Å. These inhomogeneities consist of well-defined superconducting regions coexisting with dominating semiconducting areas. As the hole concentration is increased towards optimal doping the superconducting regions grow at the expense of the semiconducting regions. The results are interpreted in terms of an inhomogeneous distribution of oxygen, giving rise to a variation in T_c and hole concentration. The poorer agreement (Fig. 1) with a cubic fit is thought to be due to this intrinsic disorder, giving rise to a linear component to the scattering at low frequencies, as described by Devereaux *et al.*[44] In other cuprate[8,34,36,39,41,50] superconductors there is no redistribution of B_{1g} spectral weight below T_c in the underdoped regime ($p<0.16$), in contrast to the results presented here. If it is assumed that Bi2212 is more inhomogeneous than other cuprate superconductors, the contradiction is resolved. The STM measurements confirm our prediction (made when the paper was submitted, and before the STM work) that underdoped Bi2212 crystals contain locally varying hole concentrations—small fractions of the crystal have a local value of $p=0.16$ and others $p<0.16$. Thus the peak observed at 565 cm^{-1} corresponds to superconducting regions with $p=0.16$. As the hole concentration is reduced from optimal, semiconducting regions grow at the expense of the superconducting regions. In this picture of granular superconductivity, microscopic superconducting grains are separated by nonsuperconducting regions and Josephson tunneling between grains establishes the macroscopic superconducting state.[63] The superconducting regions are characterized by a constant value of the gap in the local density of states. Consequently, when the doping level is reduced below optimal the B_{1g} peak would remain fixed near its value at optimal doping and be reduced in intensity with decreased doping as the semiconducting regions grow, as observed.

4. Interpretation: Power laws

Pairing functions such as an anisotropic *s*-wave or a *d*-wave gap are consistent with states lying below some maximum gap value. For a *d*-wave gap of the form $d_{x^2-y^2}$, electronic Raman spectra in the B_{2g} and B_{1g} channels are predicted[4–6] to display a linear (in B_{2g}) and cubic (in B_{1g}) power law behavior below $\omega\sim\Delta$. Conversely, the Raman response function in the low-energy regime for an isotropic *s*-wave gap should be[44] characterized by the absence of states below the gap, expressed in experimental terms by exponentially activated behavior.

Down to the lowest frequency measured, the B_{1g} and B_{2g} spectra from all samples show scattering below the gap peaks which appear in the spectra below T_c. In particular, at all doping levels the B_{2g} response function shows a linear rise in scattering at low frequencies for $T<T_c$. Therefore, the results are consistent with any gap function that posesses nodes (as a line or point) on the Fermi surface near $(\pm\pi,\pm\pi)$.

In the hole concentration range $0.12<p<0.23$, the **linear** and **cubic** frequency dependences found for the B_{2g} (Fig. 5) and B_{1g} (Fig. 1) spectra, respectively, are consistent with the behavior predicted for a $d_{x^2-y^2}$ gap, and thus completely inconsistent with an isotropic *s*-wave gap.

The cubic power law for a $d_{x^2-y^2}$ pairing state was derived in the limit $\omega\rightarrow 0, T\rightarrow 0$. However, even at the temperatures used in these studies, i.e., $0.20<T/T_c<0.28$, the power laws are still consistent with a *d*-wave gap. This suggests that the gap opens quite quickly below T_c.

Despite the presence of cation disorder, oxygen intercalation, *b*-axis modulation, and orthorhombicity that are common to Bi2212, the low-frequency power laws appear to persist throughout the doping range. The low-frequency scattering in the B_{1g} channel is found to be consistent with a cubic frequency dependence. In B_{2g} spectra, a linear-in-ω scattering is found for all samples studied, which indicates that there are nodes in the gap function near $(\pm\pi,\pm\pi)$. Therefore, the combined (for $\omega<\omega_{\rm peak}$) power-law behavior (ω in B_{2g} and ω^3 in B_{1g}) points to the existence of a $d_{x^2-y^2}$ gap function for the doping range studied.

III. DISCUSSION

In the B_{1g} scattering geometry, the superconductivity induced renormalization peak frequency changes with doping. Below a critical doping level ($p\approx 0.12$) the renormalization is not present (see Ref. 40). With increasing hole concentra-

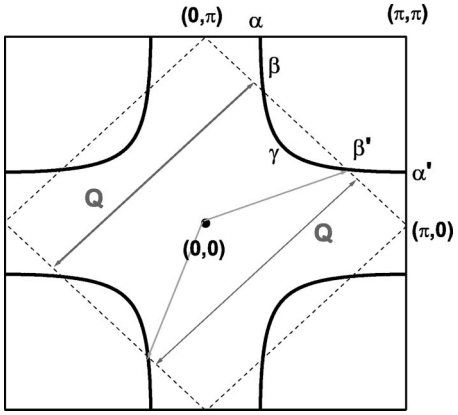

FIG. 8. A model of the Fermi surface in cuprates (solid line) and the magnetic Brillouin zone boundary (dashed line). Quasiparticles near β' *can* exchange an AFM wave vector (π,π) while those near γ *cannot*. Hence the former are highly scattered ''hot'' quasiparticles, and the latter are referred to as ''cold'' quasiparticles.

tion the peak energy remains relatively constant to $p \approx 0.18$ and then drops rather abruptly, by approximately 50% over the hole concentration range $0.18 \leqslant p \leqslant 0.23$ (i.e., overdoped regime). In the latter range, the B_{1g} peak energy and doping dependence can be plotted on a curve that matches the $2\Delta_{\max}$ feature observed in ARPES and tunneling spectroscopy measurements. Provided that the ARPES results do indeed measure 2Δ, these considerations provide substantial support for the assignment of the B_{1g} renormalization peak to $2\Delta_{\max}$.

One reason for the lack of a pair-breaking peak relies on the fact that the low-energy B_{1g} spectral weight is reduced[34,39,41] substantially with underdoping. If the quasiparticles are scattered away from the $(\pm\pi,0)$ regions of the Fermi surface, then the resulting B_{1g} spectra would show a reduced intensity. A mechanism for such anisotropic scattering lies in the description of Raman scattering in the nearly antiferromagnetic Fermi liquid model.[16,64] In the model, the presence of antiferromagnetic spin fluctuations, which are strongly peaked near the antiferromagnetic ordering vector $Q \approx (\pi,\pi)$, give rise to a enhanced scattering of quasiparticles on regions of the Fermi surface that are located near the BZ axes. For example, in such a process a quasiparticle can be scattered from $(\pi,0)$ to $(0,-\pi)$ by emitting a (π,π) magnon and back to $(\pi,0)$ by emitting a $(-\pi,-\pi)$ magnon (Fig. 8). Since the regions of the FS located near the diagonals are far from resonance with Q, the quasiparticles in this region are much more weakly scattered. This gives rise[16] to the terms ''hot spots'' for regions of the FS near the BZ axes and ''cold spots'' for those near the diagonals. As the doping level decreases and the antiferromagnetic fluctuations grow and become more strongly peaked near Q, the scattering will increase and hence the B_{1g} spectral weight will decrease further. Correspondingly, one would expect that Cooper pairing of the highly damped ''hot'' quasiparticles to become increasingly unlikely in the underdoped regime. On this basis, the absence of a pair-breaking peak in the B_{1g} channel for low doping levels ($p < 0.12$) is thus to be expected. This picture also accounts for the rapid reduction, with decreasing hole concentration, of the B_{1g} spectral weight that is involved in superconductivity.

It is also interesting to note that the B_{1g} spectra obtained from underdoped Bi2212 appear to differ from that obtained from underdoped La214 and Y123. In the latter two compounds the B_{1g} spectra change much more abruptly when the doping level is reduced below optimum. In these compounds a strong $2\Delta_{\max}$ peak is observed in the B_{1g} spectra obtained from optimally doped materials, but such a peak is completely absent[34,36,39,41,42] in the underdoped compounds. In Bi2212, however, a relatively strong B_{1g} peak is still observed in the underdoped compounds (see Ref. 51 and Fig. 2). In addition, the B_{1g} spectral weight drops rapidly as one enters the underdoped regime[34,39,41] of La214 or Y123 but decreases more slowly with underdoping in Bi2212. It thus appears that the optimally doped state is more sharply defined in both La214 and Y123 than it is in Bi2212. This is attributed to the cation disorder and superstructural modulation—traits unique to Bi2212. These comparisons suggest that the inhomogeneity in hole concentration is greater in underdoped Bi2212 as compared with underdoped La214 or Y123. As such, granular superconductivity would be more pronounced in the underdoped state of Bi2212.

IV. CONCLUSIONS

The hole concentration in single crystals of Bi2212 has been varied from 0.10 to 0.22 by varying the oxygen concentration and by Y substitution. It has been found that the $2\Delta_{\max}$ peak in the B_{1g} spectrum increases in energy as the hole concentration is reduced from $p=0.22$ to $p=0.12$ according to the empirical relation $2\Delta/k_BT_c = (15\pm1) - (38\pm5)p$. Both the magnitude of $\Delta_{\max}$ and its' doping dependence, as determined from the Raman spectra, are in good agreement with the results of ARPES measurements[24] of the leading edge shift that occurs below T_c. These results provide support for the association of the 2Δ peak of the B_{1g} spectra with the superconducting gap energy as determined by ARPES measurements. It is also found that the strength of the B_{1g} renormalization, that occurs below T_c, becomes weaker as the hole concentration is reduced from $p=0.22$ to $p=0.12$ and cannot be observed in crystals with hole concentrations less than $p \approx 0.12$. This observation is consistent with the selective scattering of quasiparticles on regions of the Fermi surface that are located near the k_x and k_y axes of the Brillouin zone. A possible mechanism for this scattering is provided by antiferromagnetic spin fluctuations[16,39,41,64] which grow in strength as the hole concentration of the crystals is decreased.

The B_{2g} spectra show a very weak renormalization at T_c for two of the four crystals studied in this work. The crossover frequency (ω_0) exhibits a parabolic dependence on hole concentration–similar to that found for T_c. In fact ω_0 appears to scale with T_c according to the relation $\hbar\omega_0 \approx 5k_BT_c$, as has been suggested by others.[34,36,41] The B_{2g} response function, at $T=20$ K, increases linearly at low frequencies in most of the samples studied. This observation is consistent[4] with the presence of nodes in the superconducting gap, in the direction $|k_x| = |k_y|$. The only exception to

this linear behavior at low temperature was observed in the B_{2g} spectrum of an overdoped crystal with $T_c = 87$ K. In this case the scattered intensity remained constant for all frequencies $\omega \leqslant 90$ cm^{-1}. It is interesting that in ARPES experiments carried out on an overdoped crystal with the same T_C it was found that gap was zero over an extended region of the FS, which could be consistent with $\chi'' \approx$ constant below a certain frequency. This constant is believed to be an artifact associated with umklapp scattering from the superstructural modulation.

Finally, it should be noted that results obtained here for the doping dependence of the spectra are, in most respects, similar to those obtained in other cuprates.[8,34,36,39,41,50] One exception appears to be the fact that in the underdoped regime the spectral weight depletion, and the strength of the B_{1g} renormalization in Bi2212, decrease less abruptly as p is decreased below 0.16.

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