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# Electronic Raman scattering from $Bi_2Sr_2CaCu_2O_{8+\delta}$: Doping dependence of the pseudogap and anomalous 600 $cm^{-1}$ peak

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Raman spectra of both overdoped and underdoped single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ have been studied as a function of temperature. A substantial depletion of spectral weight at low energies is observed in the underdoped samples at temperatures well above $T_c$ and a peak centered near 600 $cm^{-1}$ is observed in the normal-state spectra of the optimally and underdoped crystals, confirming a recent report of such a peak in underdoped crystals. This peak shows little dependence on doping or temperature and there is no apparent relationship between the doping dependence of the anomalous peak at 600 $cm^{-1}$ and the pair-breaking peak observed below $T_c$. In contrast, the onset temperature of the normal state depletion, the depth of depletion, and both the position and intensity of the pair-breaking peak are all dependent on sample doping. The depletion of normal-state spectral weight in the underdoped materials is attributed to the opening of the pseudogap but the origin of the 600 $cm^{-1}$ peak remains unclear. [S0163-1829(98)50518-8]

The high-temperature superconducting cuprates possess many curious properties compared to conventional superconductors, not the least of which is the gaplike feature which appears in the normal state of underdoped cuprates.[1,2] In the normal state below a characteristic temperature, $T^*$, a gap forms in the electronic excitation spectrum. This gap, commonly referred to as the pseudogap, may be observed with a variety of experimental techniques including angle-resolved photoemission spectroscopy (ARPES),[3–6] NMR,[7,8] and electronic specific heat measurements.[9] The ARPES measurements indicate that the pseudogap has the same $d_{x^2-y^2}$ symmetry as the superconducting gap, and a number of suggestions have been made regarding the source of the pseudogap and its relationship to the superconducting gap.[10–13] In common with explanations of the origin and nature of the pairing state in the high-$T_c$ superconductors, there is little consensus amongst theoretical descriptions of the pseudogap and no single explanation seems appropriate in light of the sometimes contradictory experimental evidence. However, it is clear that any description of superconductivity in the cuprates must provide an understanding of the details of both the pseudogap and the superconducting gap.

Raman scattering from electronic excitations has been used to directly probe the magnitude and symmetry of the superconducting gap in a variety of high-$T_c$ materials.[14–21] By selecting appropriate polarizations of the incident and scattered light, Raman scattering may be made sensitive to scattering from different portions of the Fermi surface. Measurements have revealed the formation of a broad peak in the superconducting state, the shape, magnitude, and position of which exhibit a strong dependence on both doping and scattering symmetry. In $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) the peak position and magnitude are maximal in the $B_{1g}$ symmetry,[22–24] which selects those portions of the Fermi surface around $(0,\pm\pi)$ and $(\pm\pi,0)$. These measurements are consistent with the available ARPES data indicating a superconducting gap of predominantly $d_{x^2-y^2}$ symmetry.[25–27] The normal-state Raman spectrum of the cuprate superconductors shows a broad featureless continuum extending to high energies, quite unlike that expected from a normal metal.[19,24,28] Phenomenological models explaining the unusual normal-state Raman spectrum of the cuprates and other anomalous normal-state properties were forwarded some time ago[29–31] but the origin of the electronic Raman continuum, both in the normal and superconducting states, remains the subject of some controversy.[23,32,33]

Recent electronic Raman-scattering measurements[34–37] have added to the evidence of a pseudogap in the normal state of underdoped high-$T_c$ superconductors. Those measurements on Bi2212 (Refs. 34, 36, and 37) show a depletion of spectral weight in the normal state of underdoped crystals which appears to be maximal in the $B_{1g}$ scattering symmetry, analogous to the pseudogap indicated by ARPES measurements. Most recently, a feature of $B_{1g}$ symmetry, appearing at 600 $cm^{-1}$, has been reported in the normal-state electronic continuum of underdoped Bi2212 crystals.[37] Here we confirm the existence of this feature in the underdoped materials and show that it is also present in spectra taken from an optimally doped crystal. We observe the temperature and doping dependent changes in the normal-state spectra of the underdoped samples, consistent with the formation of a pseudogap reported previously in the literature, while the 600 $cm^{-1}$ peak shows only weak doping dependence in both position and width.

Single crystals of Bi2212 were prepared by a traveling solvent floating zone method using an infrared imaging furnace.[38] Oxygen was unloaded by high-temperature anneals in low oxygen pressures, with rapid quenching. The $T_c$ of each crystal was determined via magnetic susceptibility measurements. Raman spectra were measured with the 514.5 nm line of an argon ion laser with a typical incident power of 50 mW and area of 0.025 $cm^2$. Measurements using lower laser powers indicated that the sample was heated locally by less than 10 K at 50 mW incident power. This minimal sample heating will be ignored when sample temperatures are quoted. Scattered light was collected in the backscattering geometry, with a Jobin Yvon U1000 double monochromator and a charge coupled device used to disperse and detect the scattered light. A Rayleigh line rejection filter was used, restricting the spectra to Raman shifts of 200 $cm^{-1}$ and above. Polarization resolved Raman measurements were performed in the $XX$, $XY$ and $X'Y'$ geometries, where $X$ and $Y$ are parallel to the Cu-O bonds, and $X'$ and $Y'$ are at 45° to $X$ and $Y$. Here we will quote all symmetry selection rules with reference to the tetragonal $D_{4h}$ point group of the Cu-O planes, rather than the orthorhombic unit cell.[16,19] The $XX$ polarization selects $A_{1g}+B_{1g}$ symmetry, $XY$ polarization selects $B_{2g}$ symmetry and $X'Y'$ polarization selects $B_{1g}$ symmetry excitations. The $B_{1g}$ channel selects excitations of $d_{x^2-y^2}$ symmetry and hence should detect the maximum magnitude of the pseudogap and the superconducting gap.[4,5,22,23,32] In common with previous measurements on Bi2212,[16] we observed only a weak superconductivity-induced redistribution of the electronic continuum below $T_c$ in the $XX(A_{1g}+B_{1g})$ and $XY(B_{2g})$ geometries for the underdoped samples and no evidence of a pair-breaking peak. As pseudogap and superconductivity-induced changes in the continuum for the underdoped regime were of greatest interest, the measurements presented here are those performed in the $X'Y'(B_{1g})$ geometry.

Electronic Raman spectra from four Bi2212 crystals collected at temperatures between 300 and 10 K are shown in Fig. 1—they are, respectively, (a) overdoped, (b) near optimally doped, (c) and (d) underdoped. In order to emphasize the temperature dependent changes, the spectra shown have been divided by their respective 300 K spectra and adjusted for the thermal Bose occupation factor at the appropriate temperature. As we are interested only in the magnitude of change from the 300 K spectrum, the distortion of the continuum shape resulting from the division procedure[18] is not of concern. The resulting relative spectra were then normalized to unity at 1000 $cm^{-1}$ and offset by equal amounts along the vertical axis. The zero for each spectrum is shown as a thick mark on the vertical axis.

The overdoped crystal of Fig. 1(a) has a $T_c$ of 83 K. Those spectra taken at 200, 100, and 80 K show little change with temperature, exhibiting the broad, featureless continuum characteristic of the high-$T_c$ cuprates, even at a temperature very slightly below $T_c$. A common feature of these three spectra is the slight increase of spectral weight toward low energies extending from approximately 350 $cm^{-1}$. This increase is expected from the temperature dependence of the low energy ($\omega \rightarrow 0$) part of the normal-state response function, predicted by phenomenological models of the normal state.[19,29,30] Both the 50 and 10 K spectra exhibit the characteristic depletion at low energies and formation of a peak in the superconducting state. The near optimally doped sample ($T_c = 89$ K) shown in Fig. 1(b) displays different temperature-dependent behavior to that of the overdoped crystal. At 150 K, the increase in spectral weight toward low energies now extends from approximately 700 $cm^{-1}$ when compared to the level at 1000 $cm^{-1}$. In contrast, the 110 K spectrum shows an almost flat spectrum over the entire range up to 1000 $cm^{-1}$. The 80 K spectrum shows greater depletion at low energies, but no evidence of the peak which appears clearly in the 10 K spectrum. The absence of a pair-breaking peak at 80 K is most probably due to laser heating

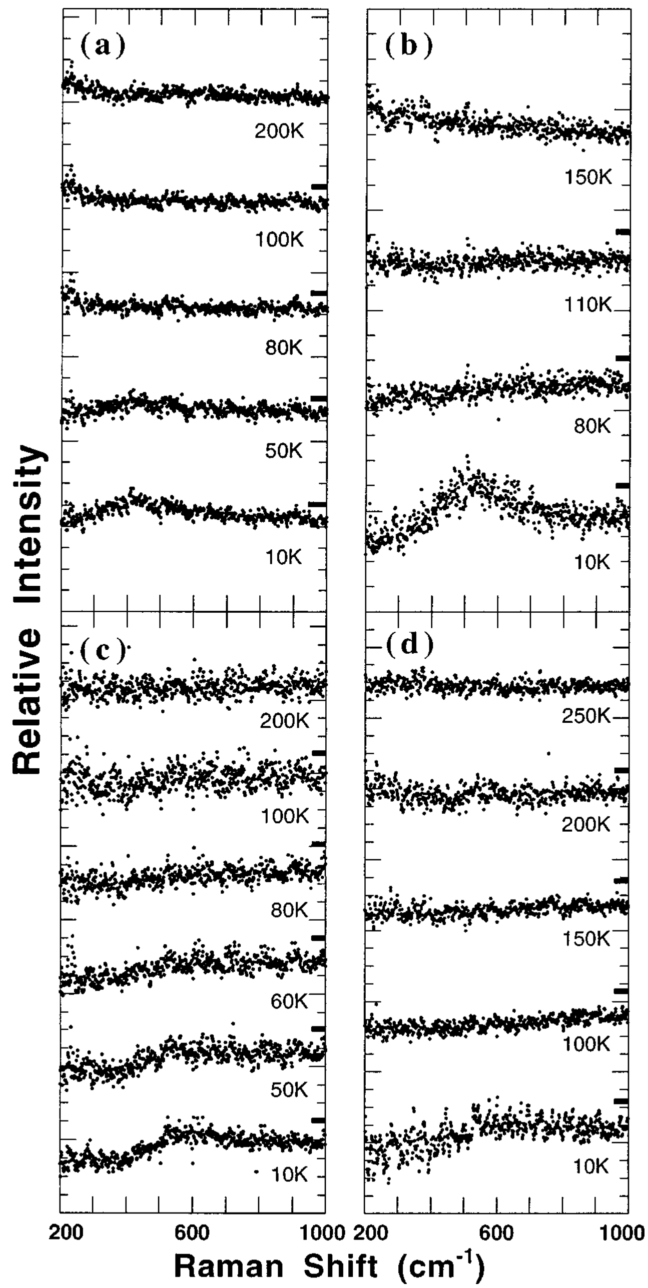


FIG. 1. Relative Raman spectra $[I_{(T)}(\nu)/I_{300\,K}(\nu)]$ for an overdoped, a near optimally doped and two underdoped single crystals of Bi2212, taken in the $B_{1g}$ scattering symmetry. The spectra have been normalized to unity at large frequencies and are offset along the $y$ axis for clarity. The zero for each offset spectrum is indicated by a heavy dash on the right of the frame. Sample details are: (a) overdoped, $T_c = 83$ K; (b) near optimally doped, $T_c = 89$ K; (c) underdoped, $T_c = 80$ K; and (d) underdoped, $T_c = 68$ K. The underdoped samples exhibit a normal-state depletion of spectral weight at low frequencies not seen in the optimally doped or overdoped samples.

of the sample and the weakness of the pair-breaking peak at temperatures only slightly below $T_c$.

Figures 1(c) and 1(d) both show spectra from underdoped crystals with $T_c$'s of 80 and 68 K, respectively. Considering the moderately underdoped sample first, the 200 K spectrum of Fig. 1(c) is flat, in contrast to the higher-temperature spectra from the overdoped and near optimally doped samples of Figs. 1(a) and (b). At 100 K a very slight depletion between 300 and 500 $cm^{-1}$ is observed, which is seen to deepen and broaden in the 80 K spectrum. Below $T_c$, the 60, 50, and 10

K spectra show the evolution of the pair-breaking peak from the continuum. There is no evidence of this peak persisting above $T_c$, rather it appears below $T_c$ and increases in magnitude as the temperature is reduced. Turning next to the most heavily underdoped crystal, the normal state behavior of Fig. 1(d) is qualitatively similar to that of Fig. 1(c), but is observed at substantially higher temperatures. Considering the normal state spectra of Fig. 1(d), the 250 K spectrum is flat while the 150 and 100 K spectra show a small but definite depletion at low energies extending up to around 600 $cm^{-1}$. In the superconducting state, the 10 K spectrum shows the formation of a broad, weak peak in the region of 600 $cm^{-1}$. This decrease in the magnitude of the superconductivity-induced peak in the underdoped regime has been reported previously[16] and corresponds to a doping region where pair-breaking peaks in the $A_{1g}$ and $B_{2g}$ continua are typically not observed.

This depletion of normal-state spectral weight in the $B_{1g}$ scattering symmetry is consistent with reports from ARPES measurements of the pseudogap.[3–5] In these measurements, a gaplike feature is seen to open at a temperature $T^*$ of around 170 K for crystals of moderate underdoping ($T_c = 83$ K) and is present at 300 K for an extremely underdoped sample of $T_c = 10$ K. An overdoped sample near optimal doping ($T_c = 87$ K) showed the persistence of a very small, if not vanishing, gap into the normal state to a temperature of 95 K. Very recent ARPES measurements on an optimally doped Bi2212 crystal also provide evidence of a depletion of spectral weight along the principal axes $(0,\pm\pi)$ and $(\pm\pi,0)$ in the normal state.[6] In common with these measurements, we do not observe any reduction in spectral weight above the $T^*$ temperatures determined by ARPES, nor was any normal-state depletion observed in scattering symmetries other than the $B_{1g}$ symmetry. The depletion of the spectral weight is seen to increase with temperature below $T^*$ and to merge smoothly with the superconductivity-induced continuum changes below $T_c$ in both ARPES (Refs. 3–5) and the present Raman measurements.

Figure 2 shows typical unnormalized spectra from two underdoped crystals and an optimally doped crystal in the normal state. The raw spectra have been scaled such that the intensity of the 280 $cm^{-1}$ phonon are identical in each spectrum. An anomalous peak appears at around 600 $cm^{-1}$ in all spectra and shows very little doping dependence, in contrast with the pair-breaking peak which appears in the below-$T_c$ spectra of Fig. 1. The spectrum shown in Fig. 2(a) was taken at 250 K from the underdoped crystal of $T_c = 68$ K. The 600 $cm^{-1}$ feature is quite broad in contrast to the other spectra. The 300 K spectrum, Fig. 2(b), of the moderately underdoped sample with $T_c = 80$ K shows a definite narrowing of the anomalous peak and a shift in position to slightly below 600 $cm^{-1}$. Figure 2(c) shows the 300 K spectrum of an optimally doped crystal with $T_c = 90$ K. Here, the peak lies around 580 $cm^{-1}$ and has narrowed significantly compared to the spectra of Fig. 2(a) and (b). The overdoped crystal shown in Fig. 1(a) did not exhibit any discernible normal-state peak in this vicinity.

That neither the 280 $cm^{-1}$ phonon mode nor the anomalous 600 $cm^{-1}$ peak show significant temperature dependence is demonstrated by the relative spectra of Fig. 1. Temperature-dependent changes in the position or intensity

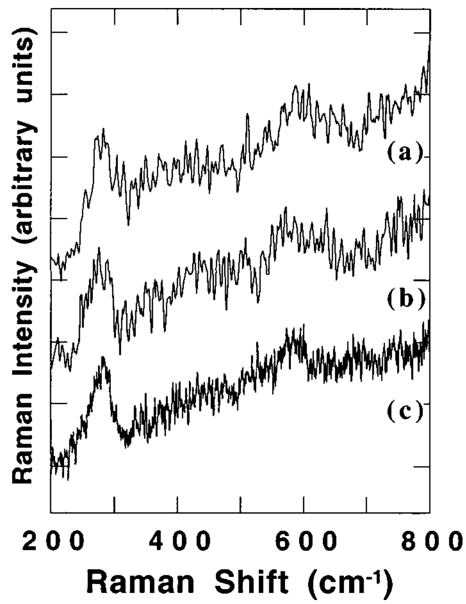


FIG. 2. Raman spectra taken from two underdoped samples, (a) and (b), and an optimally doped sample, (c), in $B_{1g}$ symmetry. The spectra have been scaled so that the 280 $cm^{-1}$ phonon peak is of equal intensity. Spectrum (a), taken at 250 K, is from the underdoped sample with $T_c = 68$ K [Fig. 1(d)]; spectrum (b), taken at 300 K, is from the underdoped sample with $T_c = 80$ K [Fig. 1(c)]; and spectrum (c), taken at 300 K, is from an optimally doped sample with $T_c = 90$ K. The $B_{1g}$ symmetry phonon at 280 $cm^{-1}$ is clearly visible, as is a relatively sharp peak near 600 $cm^{-1}$. This anomalous 600 $cm^{-1}$ peak both softens and narrows slightly as the hole doping is increased from underdoped to optimally doped. The overdoped sample [Fig. 1(a)] did not exhibit a discernible peak in this region.

of these features would appear as relatively sharp peaks (or troughs) in the regions of 300 and 600 $cm^{-1}$, which are not seen in the spectra of Fig. 1. Blumberg *et al.* (Ref. 37) observe an increase in the integrated 600 $cm^{-1}$ peak intensity of about a factor of 2 on cooling from 300 to 100 K in an underdoped crystal of $T_c = 68$ K. A doubling of intensity of the 600 $cm^{-1}$ peak at 100 K would be clearly visible in the spectra of Figs. 1(b), 1(c), and 1(d), where the relative spectra are seen to be quite flat, indicating that any temperature dependence of the peak intensity in our data must be somewhat weaker than a factor of 2. The feature appearing here in Fig. 2 does appear to have some weak dependence on doping, although much less than the pair-breaking peak in the superconducting state. Our data show that as the doping is changed from underdoped to optimally doped, the peak shifts in position from around 600 to approximately 580 $cm^{-1}$ while simultaneously becoming narrower and less intense. Over a similar doping range, the $B_{1g}$ pair-breaking feature in the superconducting state shifts monotonically from 600 to around 510 $cm^{-1}$ while becoming narrower and more intense. Taking this behavior into account, the correspondence of the positions of the two peaks in the underdoped crystals is most likely coincidental.

Blumberg *et al.* establish that the anomalous 600 $cm^{-1}$ feature is most unlikely to be phononic in origin and attribute it to a coherent bound state, which they associate with the pseudogap and antiferromagnetic ordering in the underdoped materials.[37] The occupancy of this bound state increases as the temperature is reduced, leading to a depletion of spectral weight at low frequencies and the observed pseudogap. They also raise the possibility that this anomalous peak is evidence of the preformed Cooper pairs proposed as an explanation of the pseudogap by some authors.[10,11] Arguing against this interpretation is the presence of the peak in the 300 K spectrum of the moderately underdoped and optimally doped crystals. In the first instance, the anomalous peak is present well above the temperature where spectral weight begins to be lost, as observed both in the Raman data of Fig. 1 and the ARPES measurements.[3–5] In the second instance, the magnitude of the pseudogap at optimal doping is very small[6] and significant changes in the low-frequency Raman spectra, which could be identified as a pseudogap, are absent from our spectra. If the appearance of the anomalous 600 $cm^{-1}$ peak was a pair-breaking feature, due to the Cooper pairing of holes above $T_c$ without long-range phase coherence, then changes to the low-frequency spectral weight would be expected as a function of temperature and the positions of the normal state and superconducting state peaks should coincide. Neither of these expectations are fulfilled by the behavior of the anomalous 600 $cm^{-1}$ peak.

Another explanation of the 600 $cm^{-1}$ peak is that it is the collective mode proposed by Shen *et al.* to explain the anomalous temperature and lineshape dependence of the normal-state ARPES spectra of underdoped Bi2212.[39] In the normal state, below $T^*$, the ARPES spectra observed at the $(\pi,0)$ to $(\pi,\pi)$ Fermi level crossing show an edgelike shape with a broad maximum in the region of 100–200 meV and a leading edge shifted to higher binding energies—the pseudogap. In contrast, the (0,0) to $(\pi,\pi)$ crossing spectra show a relatively sharp quasiparticle peak at the top edge of the step and no pseudogap. In their model, the broad peak seen in the $(\pi,0)$ to $(\pi,\pi)$ spectra is due to collective excitations, which couple strongly to the photohole, suppressing the quasiparticle peak observed along (0,0) to $(\pi,\pi)$. The spectral function of the collective mode peaks near $(\pi,\pi)$ in underdoped crystals, while it becomes weak and broad in momentum in the overdoped regime. There are two difficulties in identifying the 600 $cm^{-1}$ peak with such a collective mode. First, the energy scales indicated by ARPES are much higher than the observed peak: 100–200 meV corresponds to a Raman shift of 800–1600 $cm^{-1}$. Second, the 600 $cm^{-1}$ peak is relatively sharp and is present only in the $B_{1g}$ symmetry (which selects scattering from the Fermi surface around the principal axes) while the proposed collective mode is comparatively broad and peaked around $(\pi,\pi)$.

In conclusion, electronic Raman scattering from underdoped Bi2212 single crystals shows the formation of pseudogap below a characteristic temperature $T^*>T_c$, evidenced by a depletion of spectral weight at low frequencies. The near optimally doped and overdoped crystals studied showed no evidence of pseudogap formation at temperatures significantly above $T_c$. The results are consistent with previous reports of the pseudogap by ourselves and others using Raman spectroscopy[34–37] and observations made by other techniques.[3–9] Below $T_c$, a characteristic superconductivity-induced reorganization of the electronic continuum occurs,[16–19,22–24] with the formation of a pair-breaking peak. We also observe an anomalous peak appearing at 600 $cm^{-1}$ in the spectra of the underdoped and optimally doped crystals. This relatively sharp peak is present at 300 K, shows no discernible temperature dependence and only weak doping dependence, softening and narrowing as the doping is increased from underdoped to optimally doped. The peak does not appear in spectra from the overdoped crystal and its change in position with doping is much less than that of the pair-breaking peak in the superconducting state. There is no clear correspondence in position of these peaks.

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