Raman properties intrinsic to superconductivity in the Bi-Sr-Ca-Cu-O system

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Previous Raman studies of the Bi-Sr-Ca-Cu-O system have provided an abundance of interesting results including the existence of an electronic continuum which redistributes below T_c, an anomalous phonon renormalization effect, and Fano antiresonance behavior of the 290-cm^{-1} vibrational mode. We attempt in this paper to determine what connection these features may have to the superconducting behavior of this compound. In order to draw such conclusions a systematic study has been carried out on numerous $Bi_2Sr_2CaCu_2O_{8+\Delta}$ samples. Our Raman investigations indicate that it is the continuum redistribution and a linear low-energy contribution to the scattering intensity at temperatures $T \ll T_c$ that are intrinsic to superconductivity in this system.

I. INTRODUCTION

Recent Raman scattering investigations of the Bi-Sr-Ca-Cu-O high-temperature superconductor indicated the existence of a room-temperature electronic continuum having both A_{1g} and B_{1g} symmetry that was found to be coupled strongly to the 290-cm^{-1} phonon.[1] Below T_c, the 464-cm^{-1} phonon was found to soften[2] and the continuum was found to redistribute into a broad peak.[1,3] In addition to these effects, all of which find counterparts in the $YBa_2Cu_3O_{7-\delta}$ superconductor,[4] low-energy excitations were studied[5] and later assigned as intrinsic first-order excitations of $Bi_2Sr_2CaCu_2O_{8+\Delta}$. While some uncertainty still exists over the assignments of the intrinsic modes, many of the other features have received substantial verification.[6,7] What remains unclear, however, is what bearing these features may have upon the superconducting character of the Bi-Sr-Ca-Cu-O system. The systematic studies we have carried out form an attempt to address this question. We find that the behavior of the 290- and 464-cm^{-1} phonons has little relation to the superconducting state, while the continuum redistribution and a linear contribution to the low-energy scattering at temperatures $T \ll T_c$ appear to be intrinsic to the superconducting behavior of the Bi-Sr-Ca-Cu-O system. We also briefly discuss the room-temperature phonon spectrum and mention possible processes responsible for the continuum and low-energy residual scattering.

II. EXPERIMENTAL DETAILS

Various growth techniques were attempted in order to fabricate the samples used in this study. A pseudoflux technique was found to produce crystals with the sharpest transitions and afford Raman spectra with the most clarity. We took these features as an indication of high sample quality and retained this method throughout our investigations. In following this technique, the crystals were grown with a small excess of copper oxide serving as the flux. A mixture of the starting reagents Bi_2O_3, $SrCo_3$, $CaCO_3$, and CuO with cation ratio 2:2:1:2.2 was ground and placed in platinum crucibles. The materials were then heated in air in a box furnace according to the following schedule: the temperature was ramped from room temperature to 980 °C in 5 h, held at 980 °C for 10 h, ramped to 830 °C over 150 h, ramped to 500 °C over 5 h, and then furnace cooled to room temperature. Various oxygen annealing treatments were then applied. The resulting samples, thin platelets presenting an (0 0 1) face, exhibited Laue diffraction patterns of concentric rings indicating random orientation in the **a-b** plane.

The $Bi_2Sr_2CaCu_2O_{8+\Delta}$ crystals grown according to this technique still suffered from the possible presence of impurity phases and defects, thus preventing an incontest-

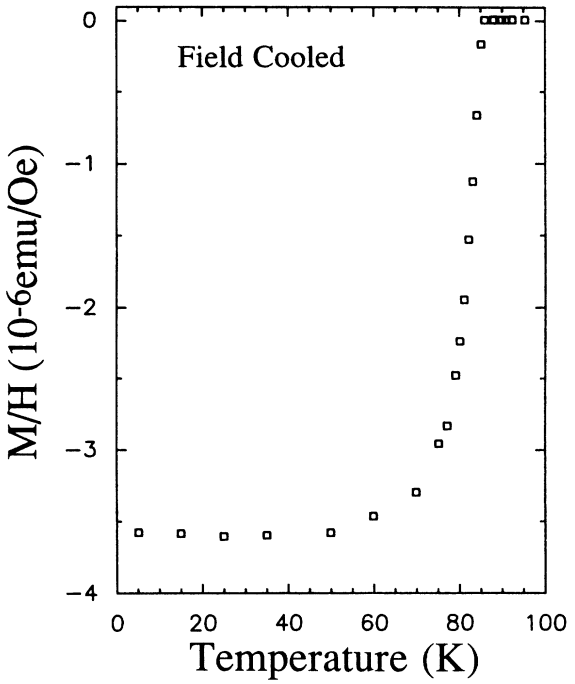

FIG. 1. dc squid magnetometry data taken in a 14-Oe field detailing the transition of a typical $Bi_2Sr_2CaCu_2O_{8+\Delta}$ crystals used in this study.

able determination of the intrinsic vibrational modes. However, the samples nonetheless exhibited superconducting behavior, allowing for general conclusions to be drawn concerning the superconducting state of the Bi-Sr-Ca-Cu-O system. Figure 1 illustrates a typical transition curve for the crystals grown by this method. The Meissner onset occurs at $T_c = 84$ K with the transition to flux exclusion occurring over a 20-K range. The different annealing treatments used were found to have varying effects on the transition widths and were therefore examined for possible effects on the excitations in the optical spectra.

The samples were mounted on a rotation stage and placed in a liquid-helium cryostat that allowed for temperature control down to 4 K. The cryostat was evacuated and the samples were aligned in a near-backscattering geometry with the polarized 5145 and 4880-Å lines of an argon-ion laser providing the incident radiation. The scattered light was dispersed by a triple-stage monochromator and detected by a nitrogen-cooled photomultiplier tube. As laser heating was found to be a significant problem, power densities were maintained below 8 W/cm^2 during the low-temperature runs.

III. RESULTS AND DISCUSSION

$Bi_2Sr_2CaCu_2O_{8+\Delta}$ crystallizes into a pseudotetragonal structure ($a = 5.399$ Å; $b = 5.414$ Å) (Ref. 8) and can therefore be approximately described by a D_{4h}-$I4/mmm$ space group. Symmetry analysis then obtains $6A_{1g} + B_{1g} + 7E_g$ allowed Raman-active modes. Because of the orientational disorder of the **a-b** plane in our samples, excitations of B_{1g} symmetry can be visible in both the polarized and depolarized geometries. Thus, seven of the allowed modes can be coupled to in the polarized (x,x) geometry ($= A_{1g} + B_{1g}$ *tetragonal*) and the depolarized (x,y) geometry ($= B_{1g}$ *tetragonal*). In the presence of defects and impurity phases these strict selection rules may be relaxed, allowing for infrared-active modes and a superposition of impurity phase modes to appear in the spectra.[9]

A typical room-temperature spectrum of the described geometries is shown in Fig. 2, and a detailed view of the low-energy modes is shown in Fig. 3. While the spectra seem to be consistent with previous work,[1,7,10] there exist some marked differences. The low-energy spectrum is in agreement with Sapriel *et al.*,[7] yet it was found that the intensity of these peaks varied dramatically from sample to sample and would even vary within the same sample upon cleaving. Since the majority of higher-energy features persisted under these changes, and given that the Bi-O layers are only weakly bonded, it is possible that the 25-, 50-, and 59-cm^{-1} peaks are due to vibrations of these layers and are not among the seven normal modes of the ideal crystal.

In the higher-energy spectra, modes are apparent at 116, 195, 290, 380, 464, 620, and 640 cm^{-1}. Because of the strength of the 290-cm^{-1} mode in the depolarized spectrum it is thought to be the B_{1g} mode of the crystal.[10] Several features complicate the normal mode assignments of the room-temperature state, however. The

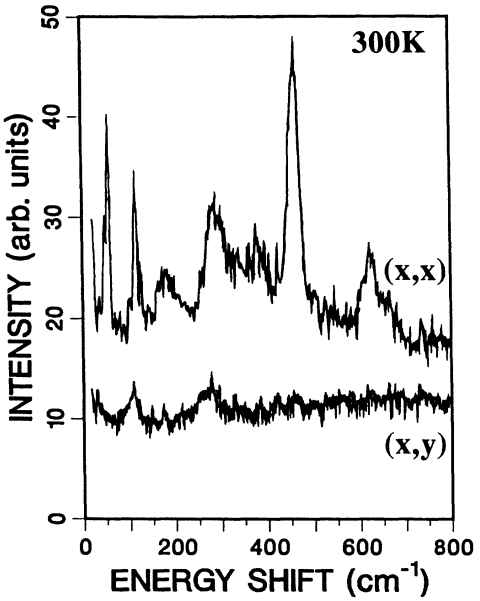

FIG. 2. Room-temperature spectrum of $Bi_2Sr_2CaCu_2O_{8+\Delta}$ in the polarized (x,x) [$= A_{1g} + B_{1g}$ (*tetragonal*)] and the depolarized (x,y) [B_{1g} (*tetragonal*)] geometries.

depolarized scattering intensity of the 116-cm^{-1} mode cannot be attributed merely to "leakage" of the A_{1g} spectra as no other modes, most notably the strong 464-cm^{-1} mode, show a B_{1g} component. Instead, if this mode is due to the Bi vibrations, a relaxing of the selection rules brought on by possible Bi-O plane deformations could ac-

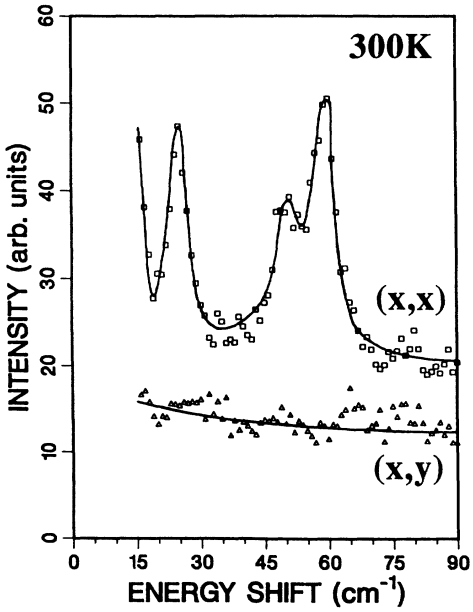

FIG. 3. A detailed view of the low-energy phonons in the polarized and depolarized geometries at room temperature. The line serves as a guide to the eye.

count for the depolarized component.[9] Further, an additional 325-cm^{-1} mode appears in some samples at room temperature and in all samples at temperatures $T \sim T_c$, a behavior quite similar to the appearance at low temperatures of the intrinsic 430-cm^{-1} phonon in single crystals of the $YBa_2Cu_3O_{7-\delta}$ superconductor.[4] Finally, detailed examination of the 464-cm^{-1} mode reveals a splitting at low temperatures into peaks at approximately 455 and 469 cm^{-1}. Such a splitting could indicate the possible superposition of spectra from different phases of the Bi-Sr-Ca-Cu-O system.

Two features that appear consistently in the room-temperature spectra in all the samples studied are an asymmetry of the 290-cm^{-1} phonon, interpreted as an antiresonance on the low-energy side of the mode,[3] and a strong background continuum of both A_{1g} and B_{1g} symmetry. For reasons similar to those discussed in our earlier work on $YBa_2Cu_3O_{7-\delta}$,[4] the continuum is believed to constitute real inelastic electronic scattering. Information provided by electronic structure calculations reveal that it is the Bi, Cu, and O atoms which contribute bands near the Fermi energy.[11] If such a conventional metallic interpretation were correct then it is possible that this continuum results from electronic scattering within and between the Cu-O(1,4) planes, the O(2) bridging site, or the Bi-O(3) planes, with a significant interband component due to a band crossing occurring at the Fermi energy.[12] Another possibility, more consistent with current Raman results from the 60-K phase of $YBa_2Cu_3O_{7-\delta}$,[13] is that inelastic scattering from fluctuations in a highly correlated electronic liquid is responsible for the normal-state continuum.[14] Both processes find parallels in descriptions of the midinfrared absorption band seen by ir reflectivity techniques in the Y-Ba-Cu-O superconductor as due to direct electronic excitations,[15] or as due to a dynamic interaction with a frequency-dependent relaxation rate,[16] respectively.

Figure 4 displays a feature of the Bi-Sr-Ca-Cu-O system that appears consistently at low temperatures: a prominent redistribution of the electronic continuum. As the temperature is dropped below T_c, the low-energy electronic scattering begins to be suppressed due both to the changing Bose factor $[1+n(\omega)]$ and the gradual opening of the superconducting "gap." At 15 K the continuum has developed into a broad asymmetric distribution in both the (x,x) $(=A_{1g}+B_{1g})$ spectrum peaking at roughly 320 cm^{-1} and in the (x,y) $(=B_{1g})$ spectrum peaking at roughly 490 cm^{-1}, believed to originate from direct quasiparticle excitations. Although the redistribution occurs anisotropically, the complexity of the band structure, evidenced by recent infrared results,[17] precludes assignment of this feature to actual gap anisotropy. Strikingly, the line shape of the A_{1g} dominated gap distribution is nearly identical to that of the A_{1g} gap distribution of $YBa_2Cu_3O_{7-\delta}$ (Ref. 18) with the $Bi_2Sr_2CaCu_2O_{8+\Delta}$ peak only slightly down shifted. Further, the redistribution bears a conspicuous resemblence to the density of states observed below T_c through photoemission techniques.[19]

The linear low-energy contribution to the electronic

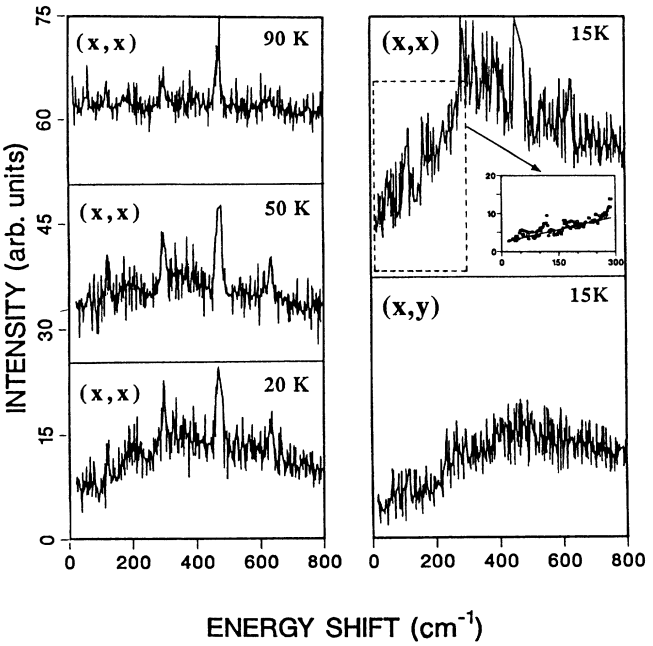

FIG. 4. Low-temperature spectra elucidating the redistribution of the continuum. The low power densities used in these runs tend to obscure the weaker phonon features observed at room temperature. The more intense phonons have been truncated to make the features of the quasiparticle distribution more apparent. The inset illustrates the linear character of the low-energy polarized spectra.

scattering in the (x,x) spectra below 2Δ, evident in the inset of Fig. 4, was also found to appear consistently in the various samples examined. While previous Raman data also exhibited low-energy scattering, the contribution appeared nearly quadratic and the peak positions of both this broad electronic feature and the phonons were different from those of the system investigated here.[1] This incomplete suppression below the pair breaking energy, also evident as a linear contribution in the $YBa_2Cu_3O_{7-\delta}$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$ compounds,[4,20] may possibly arise from normal electron transitions from "gapless" regions of the Fermi surface which, according to the interband model, would exist in the vicinity of the suggested band crossing.

Recent Raman investigations have revealed a softening of the 464-cm^{-1} phonon.[2] In our investigations, this softening did not appear consistently from sample to sample and did not scale directly with T_c, as determined by the redistribution of the continuum. This may indicate that the renormalization effect of the 464-cm^{-1} mode is related to a structural deformation at low temperatures and is not intrinsic to superconductivity of the Bi-Sr-Ca-Cu-O system. Our studies of the various samples also revealed that no apparent softening of the 290-cm^{-1} phonon occurred as the temperature was brought below T_c. Surprisingly, while the 290-cm^{-1} mode finds a

counterpart in the antiresonance character of the 330-cm^{-1} mode in $YBa_2Cu_3O_{7-\delta}$, distinguishing it from the 330-cm^{-1} mode is the absence of any renormalization effects.

IV. CONCLUSIONS

Room-temperature analysis of numerous $Bi_2Sr_2CaCu_2O_{8+\Delta}$ samples indicated the likely presence of impurities and deformations. However, while admitting the possibility of defects precludes a precise determination of the first-order phonon spectra, we recognize that the samples exhibited significant superconducting behavior that allows for general conclusions to be drawn concerning the nature of their superconductivity. Specifically, our data indicate that the 464-cm^{-1} softening and the 290-cm^{-1} antireresonance appear to have little relation to the actual superconducting state in $Bi_2Sr_2CaCu_2O_{8+\Delta}$. Alternatively, the consistently apparent low-temperature development of the electronic continuum in our Raman spectra constitutes strong evidence that the broad asymmetric peaks of $A_{1g}+B_{1g}$ and B_{1g} symmetry and the linear low-energy contribution to their quasiparticle distribution are intrinsic to superconductivity in the Bi-Sr-Ca-Cu-O system. Perhaps even more compelling evidence for the latter claim is in the striking similarity these features bear to those of the $YBa_2Cu_3O_{7-\delta}$ superconductor.

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