Electronic Raman scattering of $YBa_2Cu_3O_7$ using c-axis polarization: Evidence for two characteristic superconducting energies

K. F. McCarty
Sandia National Laboratories, Livermore, California 94551

J. Z. Liu and R. N. Shelton
Department of Physics, University of California–Davis, Davis, California 95616

H. B. Radousky
Lawrence Livermore Natinal Laboratory, Livermore, California 94550
(Received 14 June 1990)

Raman scattering has been obtained with light polarized along the c axis of twin-free single crystals of $YBa_2Cu_3O_7$. For c-axis polarization, an electronic continuum is observed, similar to the continuum observed for polarization within the a-b plane. In the superconducting state, there is a small decrease in the intensity of the c-axis continuum at energies below $\sim 200\ cm^{-1}$. This change is not purely thermal in origin, since it occurs at essentially the same energy for temperatures between 4 and 65 K. This behavior differs from the large redistribution that occurs below T_c in the continuum observed for polarization within the a-b plane. If the characteristic energies for c-axis polarization ($\sim 200\ cm^{-1}$) and a-b polarization (400–500 cm^{-1}) are interpreted as superconducting energy gaps, then there is either a single anisotropic gap or two gaps.

Like the other Cu-based superconductors, $YBa_2Cu_3O_7$ has unusual properties in both the normal and superconducting state. For example, in the normal state for light polarized within the Cu-O planes, there is a strong electronic Raman continuum that is nearly energy independent.[1] While originally interpreted as interband scattering,[1] the electronic continuum has been more recently interpreted as intraband scattering that derives its unusual nature from strong electron-electron correlations.[2,3] Below T_c, this continuum redistributes; the intensity at low energies is diminished and the increased intensity at high energies gives peaks at either ~ 350 or $\sim 500\ cm^{-1}$, depending on the specific polarization geometry.[4] Similar characteristic energies have been observed by other experimental techniques and have been interpreted as the superconducting energy gap within the a-b plane ($2\Delta_{ab}$). For example, tunneling gives $2\Delta_{ab} = 4.7kT_c$ (Ref. 5) to $5.9kT_c$ (Ref. 6), and both electron-energy loss[7] and ir reflection[8] give $2\Delta_{ab} \approx 8kT_c$. All of these values are large compared to the weak-coupling BCS value of $2\Delta(T=0) = 3.53kT_c = 228\ cm^{-1}$.

However, the simple interpretation of these energies as a traditional BCS energy gap is complicated by several observations. Consider the Raman results. First, even for $T \ll T_c$, the continuum scattering remains for energies well below the energy of a weak-coupling gap.[4] Second, the peaks in the continuum scattering occur at essentially the same value for $YBa_2Cu_3O_7$ with $T_c \approx 90$ K and for $YBa_2Cu_3O_{7-x}$ with $T_c \approx 60$ K.[9] Finally, the peaks in the electronic continuum can persist well above T_c.[9] Similar complications prevent simple interpretation of the results of other techniques.[10]

While less reported than the "$2\Delta_{ab}$" values, there have been observations in $YBa_2Cu_3O_7$ of a second characteristic energy that is close to the weak-coupling BCS value. For example, the NMR results of Barrett *et al.*[11] show that the chain copper, Cu(1), has an energy gap $2\Delta = 3.52kT_c$, versus $2\Delta \approx 3.8kT_c$ to $6.2kT_c$ for the plane copper, Cu(2). In ir-reflectivity measurements along the c axis of single crystals, Collins *et al.*[8] saw a pronounced increase in reflectivity below $\sim 200\ cm^{-1}$ ($3kT_c$). In measurements of tunneling along the c axis of oriented thin films, Tsai *et al.*[6] observed a characteristic energy of $3.6kT_c$, versus $5.9kT_c$ for tunneling along the a-b planes. These results suggest that there are either two gaps or that there is a single gap that is highly anisotropic. In the latter case, the "c-axis energy gap," $2\Delta_c$, is less than $2\Delta_{ab}$.

While important, the electronic structure perpendicular to the Cu-O planes (i.e., along the c axis) is not well investigated since most crystals are only about 100 μm thick along the c axis. In this study, a Raman microprobe has been used to measure the electronic Raman scattering induced by light polarized along the c axis of $YBa_2Cu_3O_7$ single crystals. While a broad continuum is found for c-axis polarization, the temperature dependence is fundamentally different than the temperature dependence of the continuum observed for polarization within the a-b plane. Unlike the a-b plane continuum, the c-axis continuum changes by only a small amount below T_c and has no obvious peak as would be expected from the piling up of electronic states around an energy gap. However, the superconducting state does exhibit a reproducible decrease in scattered intensity for energies less than $\sim 200\ cm^{-1}$, and this change is not purely thermal in origin.

The majority of results reported here are from a twin-free crystal of $YBa_2Cu_3O_7$ about $600\times600\times55$ μm^3 in dimension. The orientation of the a and b directions in the nearly square platelet was uniquely determined by the mechanical detwinning procedure.[12] Magnetization analysis using a SQUID (superconducting quantum interference device) magnetometer showed that the onset of superconductivity occurred at 93 K and the 10–90% transition width was about 2.5 K in an applied field of 20 Oe, similar to results of previous crystals.[13] Either 488- or 514.5-nm laser light with an incident power of 0.5 mW was focused to a spot roughly 3 μm in diameter. Prior to mounting in the cryostat, the crystal was etched in a 1% solution of bromine in methanol for about 1 min to remove any potential surface impurities.[5] In order to reduce the collection of elastically scattered radiation in the 180° backscattering geometry, the surface normal of the crystal face was rotated ~20° from the direction of the incident laser beam. The crystal was mounted using silver adhesive on the cold finger of a vacuum cryostat evacuated by a turbomolecular pump. Temperatures were measured by an iron-doped gold/chromel thermocouple mounted on the cold finger adjacent to the crystal.

Raman spectra were obtained with the incident laser beam and the scattered light propagating along the $a=x$ of the $YBa_2Cu_3O_7$ crystal, that is, along the Cu-O planes. In spectra labeled $x(zz)\bar{x}$, the polarization of both the incident and scattered light was along the $c=z$ axis, while $x(yy)\bar{x}$ refers to polarization along the $b=y$ axis. As shown in Fig. 1, both polarization along and perpendicular to the c axis gives broad, intense scattering whose intensity is relatively indepenent of energy. These continua extend to at least 2000 cm^{-1},[14] well beyond the energy expected for two-phonon scattering, and they lack the fine structure expected for phonon scattering. At 295 K, the c-axis continua is about half as intense as the a-b plane continuum. Based on these observations, we conclude that the c-axis continuum, like the a-b plane continuum,[1] is of electronic origin.

The intensity of electronic Raman scattering, $S(\omega)$, is proportional to squares of tensor components of the inverse effective-mass tensor μ_k^{-1}.[15] A particular polarization geometry couples to certain components of μ_k^{-1}. Within the D_{2h} symmetry of orthorhombic $YBa_2Cu_3O_7$, c-axis polarization gives $S(\omega)\propto|(\mu^{-1})_{zz}|^2$. The present results show that there is an electronic continuum for c axis and a-b polarization [i.e., (xx), (yy), and (zz) polarizations]. Previous results have shown that there is no significant continuum scattering for (xy),[4] (xz), or (yz) polarizations.[13] This suggests that the off-diagonal components of the inverse effective-mass tensor, $(\mu^{-1})_{xy}$, $(\mu^{-1})_{xz}$, and $(\mu^{-1})_{yz}$, are small compared to the diagonal components $(\mu^{-1})_{ii}$.

The temperature dependence of the a-b plane continuum illustrated in Fig. 2 is in good agreement with results of other investigations using (yy) polarization.[1] These previous investigations had the incident and scattered light propagating along the c axis [i.e., polarization geometries of type $z(yy)\bar{z}$]. In Fig. 2, the tops of the well-studied phonon peaks are truncated to emphasize the scattering from the electronic continuum. In the normal state (upper spectrum at 115 K), the intensity of the electronic continuum is roughly constant with energy. Well below T_c, the bottom spectrum shows a substantial redistribution of the continuum; the scattering decreases in intensity with decreasing energy and has a very broad peak centered around roughly 450 cm^{-1}. At 4 K, the

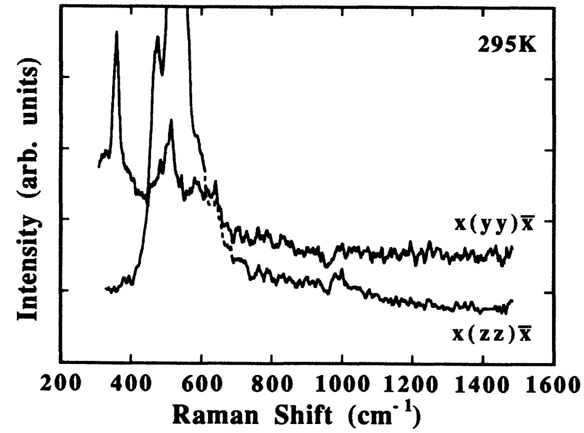

FIG. 1. Comparison of twin-free single crystal of $YBa_2Cu_3O_7$ at 295 K with polarization perpendicular (upper spectrum) or along (lower spectrum) the c axis. Absolute intensity of both spectra is the same and the abscissa is zero intensity. The phonons of the $x(zz)\bar{x}$ spectra have been truncated to emphasize the continuum.

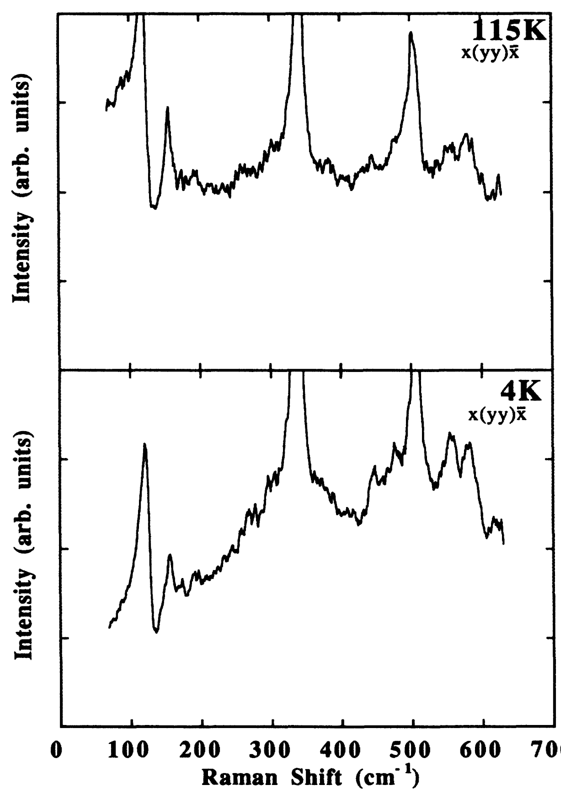

FIG. 2. Raman spectra with light propagating along the $a=x$ axis and polarized within the a-b plane (i.e., within the Cu-O planes and parallel to the Cu-O chains) of twin-free $YBa_2Cu_3O_7$ crystal.

120-cm^{-1} phonon still exhibits unmistakable antiresonant behavior (asymmetric line shape and destructive interference on the high-energy side) indicative of strong electron-phonon coupling, establishing that electronic states remain within the "gap".[1] For $T \ll T_c$, the electronic continuum of the present twin-free crystals gives broad peaks at ~ 400 and ~ 550 cm^{-1} in $z(y'y')\bar{z}$ and $z(x'y')\bar{z}$ geometries,[16] respectively, in good agreement with previous results.[4] Since the $x(yy)\bar{x}$ spectra of Fig. 2 are roughly the sum of the separate $z(x'y')\bar{z}$ and $z(y'y')\bar{z}$ results, only a broad, average peak is observed in the continuum for $T \ll T_c$.

Figure 3 illustrates the c-axis continuum above and well below T_c. These spectra were obtained from the same spot on the crystal as Fig. 2, but with the polarization of the incident and scattered light rotated by 90°. Importantly, there is not a large change in the c-axis continuum between the normal state (upper spectrum of Fig. 3) and the superconducting state (bottom spectrum). This is in contrast to the dramatic redistribution of the a-b continuum below T_c (Fig. 2). However, there is a small but reproducible decrease in the intensity of the c-axis scattering below ~ 200 cm^{-1} for the 4-K spectrum relative to the 115-K spectrum. This difference is shown in an enhanced manner in Fig. 4, where spectra are normalized by dividing by the normal-state spectrum at 115 K. The 4-K normalized spectrum shows a decrease in intensity below ~ 200 cm^{-1}. While the change between the normal state (115 K) and 4 K is small, it was reproducibly observed from the crystal whose results are shown here and from a second twin-free crystal in a $y(zz)\bar{y}$ polarization geometry.

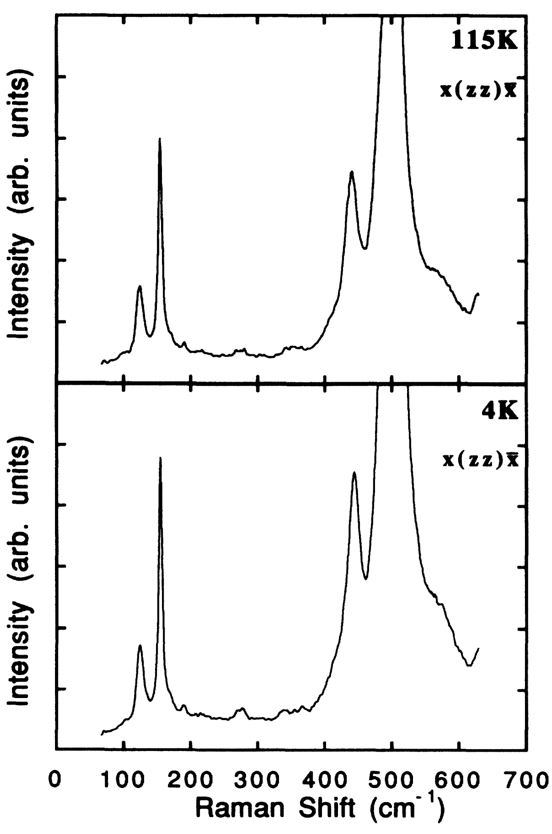

FIG. 3. Raman spectra obtained under the same conditions as Fig. 2 except with the incident and scattered light polarized along the $c = z$ axis (i.e., perpendicular to the Cu-O plains.)

There are at least two contributions to the temperature dependence of the electronic continuum—changes due to entering the superconducting state and a purely thermal effect since the Raman intensity is proportional to a thermal Bose factor $1+n(\omega)$, where

$$n(\omega)=[\exp(\hbar\omega/kT)-1]^{-1} .$$

For c-axis polarization, the change at low energy (~ 65 cm^{-1}) that occurs in the electronic continuum between 115 and 4 K is approximately the same as that expected simply from thermal Bose effects. However, spectra obtained at other temperatures give evidence that the changes that occur below T_c are not purely thermal in origin. Figure 4 shows normalized spectra at 25, 65, and 77 K, in addition to the 4-K data. At 25 and 65 K, the deviation of the normalized spectra from the horizontal baseline occurs below ~ 200 cm^{-1}, the same value as for 4 K. At 77 K, the point of deviation is somewhat smaller—about 150 cm^{-1}. If the observed changes were purely thermal in origin, then the point of deviation of the normalized spectra would be expected to shift continually downward in energy with increasing temperature. However, the 4-, 25-, and 65-K spectra all show the deviation occurring at ~ 200 cm^{-1}. Instead, the observed behavior suggests incomplete suppression of the electronic scattering within an energy gap.

The characteristic energy (~ 200 cm^{-1}) observed below T_c for the c-axis continuum is consistent with the smaller of the two characteristic energies ($3kT_c$ to $3.6kT_c$) measured by NMR,[11] ir,[8] and tunneling.[6] The present results are similar to light scattering results from another layered Cu-O superconductor ($Tl_2CaBa_2Cu_2O_8$) by Timofeev *et al.*,[17] where for $T \ll T_c$ and c-axis polarization, the normalized Raman spectrum exhibited a falloff in intensity for energies below about 150 cm^{-1}. For polarization within the a-b plane, the normalized intensity decreased for energies below about 400 cm^{-1}.

When the a-b continuum for $T \ll T_c$ is separated out into A_{1g} and B_{1g} contributions (tetragonal notation), there are obvious, broad peaks at ~ 400 and ~ 550 cm^{-1}, respectively.[16] These peaks are apparent in either the raw data, or in spectra normalized by dividing by a normal-state spectrum, as done in Fig. 4. However, there is no apparent peak in the continuum scattering for c-axis polarization in either the raw (Fig. 3) or normalized data (Fig. 4). It is possible that for $T \ll T_c$ the electronic scattering has a peak that is weak, very broad, or masked by the low-frequency phonons, making it difficult to observe experimentally. More interestingly, the lack of a peak below T_c in the c-axis continuum may be an intrinsic property of $YBa_2Cu_3O_7$.

Above T_c, the c-axis and a-b continua are qualitatively similar in nature, suggesting that they have the same origin. It is then doubtful that the continua originate from band-structures features (i.e., from interband scattering) since the dispersion of the electronic bands along the c-

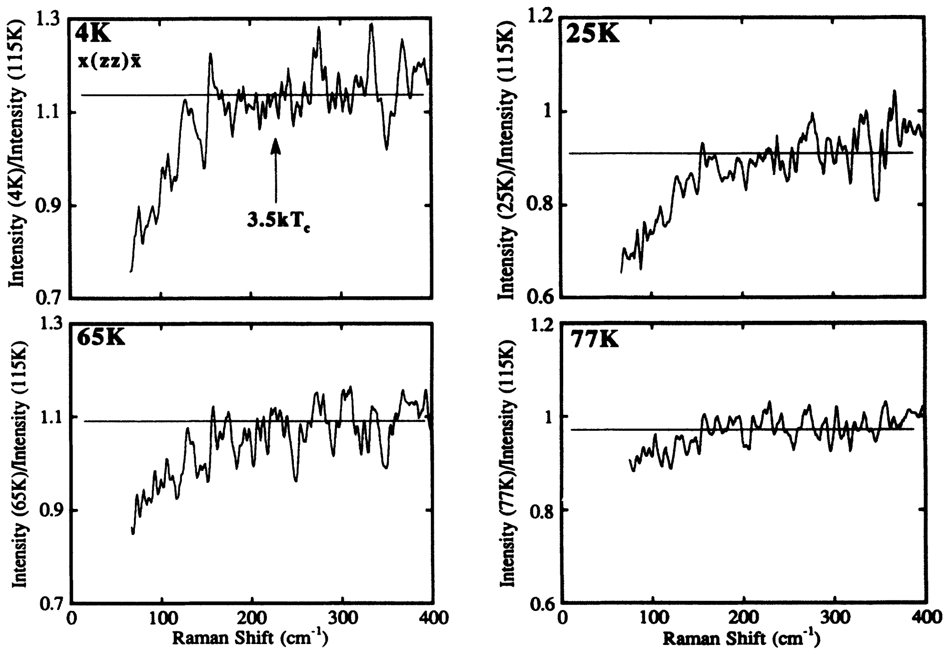

FIG. 4. Normalized spectra with c-axis polarization obtained by dividing by a normal-state spectrum (115 K). Horizontal lines are least-squares fits to the scattering intensity above 285 cm^{-1}. The vertical arrow on the 4-K spectrum shows the energy gap for a weak coupling BCS, $2\Delta = 3.53kT_c = 228$ cm^{-1} with $T_c = 93$ K.

axis direction is significantly different than along the a and b axes.[18] Therefore, it is reasonable to conclude that the continua are intraband scattering and that the unusual frequency and temperature dependence result from strong electronic correlations.[2,3] However, the c-axis and a-b plane continua do exhibit fundamentally different temperature dependence below T_c. The a-b plane continuum dramatically redistributes while the c-axis continuum changes only by a small amount. Explanation of this difference may have to await a consistent microscopic theory of superconductivity in these materials.

The present results suggest that there are two energies that characterize the superconducting state and that these differ by about a factor of 2. This suggests the existence of either two superconducting gaps or a single, anisotropic gap. Concerning the latter interpretation, Klemm and Liu[19] have shown that the physical and electronic anisotropy of $YBa_2Cu_3O_7$ is not a sufficient condition for gap anisotropy. That is, gap anisotropy can only arise in superconductors with two or more conducting layers per unit cell and where interlayer pairing dominates.[19]

The characteristic energy of the superconducting state can also be evaluated by following the behavior through T_c of the different phonons. Figure 5 shows the peak width of the 500-cm^{-1} phonon, which mainly involves vibration along the c axis of O(4),[20] the O atom between the Cu-O planes and the Cu-O chains. The peak width decreases between 295 K and T_c, but increases below T_c. The increased damping inferred from the increased peak width shows that there is an increased electronic density of states near 500 cm^{-1} below T_c. The increased damping at 500 cm^{-1} is in marked contrast to the behavior of the lower frequency Raman-active phonons. In particular, the 340- and 440-cm^{-1} phonons both exhibit damping that decreases below T_c.[14]

In summary, Raman scattering from twin-free single crystals of $YBa_2Cu_3O_7$ has been obtained for polarization both along and perpendicular to the c axis. A continuum is observed for c-axis polarization, but this continuum does not dramatically redistribute below T_c, unlike the

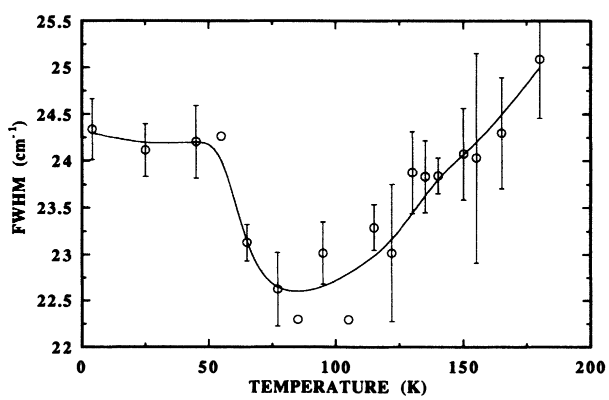

FIG. 5. Peak width of the 500-cm^{-1} phonon at half maximum intensity obtained by numerically fitting $x(zz)\bar{x}$ spectra with an asymmetric (Fano) line shape. Error bars are standard deviations of three or more measurements. Solid line is a guide to the eye.

continuum observed for polarization with the a-b plane. Below T_c, however, the c-axis continuum does show a small decrease in intensity for energies less than ~ 200 cm^{-1}. The energy at which the continuum changes below T_c (~ 200 cm^{-1}) is consistent with the lower characteristic energy (i.e., "$2\Delta_c$") observed by other techniques. Finally, the 500-cm^{-1} phonon exhibits increased damping below T_c, unlike the lower frequency phonons.

The work at Sandia National Laboratories was supported by the U.S. Department of Energy (Division of Material Sciences of the Office of Basic Energy Sciences) under Contract No. DE-AC04-76DP00789. The work at Lawrence Livermore National Laboratory and University of California–Davis was performed under the auspices of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

[1]S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **37**, 5920 (1988).

[2]A. Virosztek and J. Ruvalds, Phys. Rev. B **42**, 4064 (1990).

[3]M. V. Klein, S. L. Cooper, F. Slakey, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, in *Strong Correlations and Superconductivity,* edited by H. Fukyuama, S. Maekawa, and A. P. Malozemoff (Springer, Berlin, 1989).

[4]S. L. Cooper, F. Slakey, M. V. Klein, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **38**, 11 934 (1988).

[5]M. Gurvitch, J. M. Valles, Jr., A. M. Cucolo, R. C. Dynes, J. P. Garno, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **63**, 1008 (1989).

[6]J. S. Tsai, I. Takeuchi, J. Fujita, T. Yoshitake, S. Miura, S. Tanaka, T. Terashima, Y. Bando, K. Iijima, and K. Yamamoto, Physica C (Amsterdam) **153-155**, 1385 (1988).

[7]J. E. Demuth, B. N. J. Persson, F. Holtzberg, and C. V. Chandrasekhar, Phys. Rev. Lett. **62**, 603 (1990).

[8]R. T. Collins, Z. Schlesinger, F. Holtzberg, and C. Field, Phys. Rev. Lett. **63**, 422 (1989).

[9]F. Slakey, M. V. Klein, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **42**, 2643 (1990).

[10]For example, for a discussion of ir results, see K. Kamaras, S. L. Herr, C. D. Porter, N. Tache, D. B. Tanner, S. Etemad, T. Venkatesan, E. Chase, A. Inam, X. D. Wu, M. S. Hegde, and B. Dutta, Phys. Rev. Lett. **64**, 84 (1990).

[11]S. E. Barrett, D. J. Durand, C. H. Pennington, C. P. Slichter, T. A. Friedmann, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **41**, 6283 (1990).

[12]J. Z. Liu, M. D. Lan, P. Klavins, and R. N. Shelton, Phys. Lett. A **144**, 265 (1990).

[13]K. F. McCarty, J. Z. Liu, R. N. Shelton, and H. B. Radousky, Phys. Rev. B **41**, 8792 (1990).

[14]K. F. McCarty, J. Z. Liu, R. N. Shelton, and H. B. Radousky (unpublished).

[15]M. V. Klein, in *Light Scattering in Solids I,* Vol. 8 of *Topics in Applied Physics,* edited by M. Cardona (Springer-Verlag, Berlin, 1983), p. 153.

[16]In the notation, x' refers to polarization along the [110] direction and y' refers to polarization along the $[\bar{1}10]$ direction. In tetragonal point-group symmetry D_{4h}, $z(x'y')\bar{z}$ and $z(y'y')\bar{z}$ allow A_{1g} and B_{1g} symmetries, respectively.

[17]V. B. Timofeev, A. A. Maksimov, O. V. Misochko, and I. I. Tartakovskii, Physica C (Amsterdam) **162-164**, 1409 (1989).

[18]W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[19]R. A. Klemm and S. H. Liu (unpublished).

[20]R. E. Cohen, W. E. Pickett, and H. Krakauer, Phys. Rev. Lett. **64**, 2575 (1990).