Raman Scattering Study on Fully Oxygenated $YBa_2Cu_3O_7$ Single Crystals: x-y Anisotropy in the Superconductivity-Induced Effects

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The Raman scattering spectra of fully oxygenated twin-free $YBa_2Cu_3O_7$ crystals have been investigated. In addition to the out-of-plane and the in-plane anisotropy in all A_g phonon lines in the normal state, pronounced superconductivity-induced x-y anisotropy has been discovered in the softening and broadening of the 340 cm^{-1} line below T_c. This suggests a substantial contribution of the chain superconductivity with a pairing symmetry different from that for the plane, or indicates that the superconducting gap amplitudes are different in the k_x and k_y directions ($\Delta_x \neq \Delta_y$), as expected in the case of $d + s$ wave gap. [S0031-9007(97)05120-X]

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One of the important issues for understanding the mechanism of high-T_c superconductivity is the determination of the symmetry and magnitude of a superconducting gap. Raman scattering is one of the techniques that can be used to study the superconducting gap, since it can detect a gap in the density of states at the Fermi energy. It has been established that the electronic Raman scattering of the gap excitation is strongly dependent on configuration of the incident and scattered photon polarization [1,2]. Assuming the CuO_2 plane to be tetragonal, the observed polarization dependence is well accounted for a $d_{x^2-y^2}$ paring state [3].

Most of the high-T_c cuprates, however, are distorted from an ideal tetragonal structure, resulting from the existence of the CuO chain, incommensurate superstructure, or structural phase transition, etc. [4]. Theoretically, it is predicted that the orthorhombic distortion mixes a s-wave component into the original d-wave state and, as a result, leads to the magnitude of the gap being inequivalent between the x and y directions [5], although there has been no clear experimental observation. Heyen *et al.* have reported a striking x-y anisotropy in the Raman scattering of $YBa_2Cu_4O_8$ with double CuO chains [6]. This may imply that the paring symmetry is not a pure $d_{x^2-y^2}$. However, the effects of the chain and/or orthorhombic distortion are still open questions.

In this study, we have measured the Raman scattering spectra (RSS) of highly oxygenated and untwinned single crystals of $YBa_2Cu_3O_y$ (YBCO). We focus our attention on the superconductivity-induced effects on the B_{1g}-like phonons with a frequency of about 340 cm^{-1}, because it can sensitively probe the electronic excitation through the electron-phonon interaction.

The high quality YBCO single crystals were grown by a top-seeded pulling technique and oxygenated under uniaxial pressure in order to obtain the orthorhombic twin-free samples as described previously [7]. The crystals with typical volume of 10 mm^3 and optimal T_c of 92–93 K with a very narrow transition width $\Delta T_c \leq 0.2$ K were postannealed at 320 °C for higher oxygenation. This postannealing enhances the in-plane anisotropy and makes the oxygen content close to "$O_{7.0}$," which results in the overdoped state with lower $T_c = 86$ K and ΔT_c of 0.4 K. To study RSS, two fully oxygenated crystals were used, which had been grown and annealed individually. The results for these two crystals agree very well.

For RSS measurement at low temperatures, the samples were mounted on a closed-cycle UHV cryostat. The temperature stability was better than 1 K. The 514.5 nm line of Ar-Kr laser was employed for an excitation light source. The power density on the sample surfaces was adjusted to be 0.2–1 W/cm^2, and, consequently, laser heating at an illuminated spot was less than 3 K in all experiments. The xx and yy polarized RSS were obtained in the pseudobackscattering configuration from the same mirrorlike points of crystals by simply rotating the polarization analyzer. The RSS was analyzed by a triple-stage spectrometer (Jobin-Ivon T64000) with a liquid-nitrogen cooled CCD detector. The spectral resolution was 1–3 cm^{-1}. All spectra were corrected for the frequency response of the spectrometer and the detector.

The xx, yy, and zz polarized RSS of YBCO single crystals at $T = 290$ K are presented in Fig. 1, where five phonon lines of orthorhombic A_g symmetry and the electronic continua are clearly seen [1,8]. It should be noticed that in these RSS there appears no additional line which are usually observed in oxygen deficient or disordered YBCO [9]. This demonstrates that the oxygen content of our samples is almost stoichiometric "$O_{7.0}$."

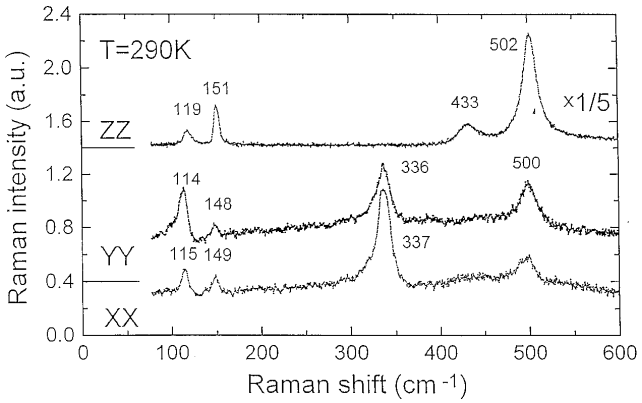

FIG. 1. Room temperature Raman spectra of a fully oxygenated twin-free $YBa_2Cu_3O_7$ single crystal with $T_c = 86$ K in the xx, yy, and zz polarizations.

In RSS, the frequency and linewidth of every nondegenerated A_g vibration is renormalized by the interaction with the anisotropic electronic system. This leads to the polarization-dependent peak frequency ω and damping Γ of phonon line. For example, reflecting the large out-of-plane anisotropy in the electronic continuum, the 120 cm^{-1} mode shows a strong out-of-lane anisotropy in the peak frequency $\omega_{zz} > \omega_{xx}, \omega_{yy}$. Also the line shape of this mode is asymmetric (the Fano-like shape), which is pronounced in the yy spectrum with a strong electronic continuum. On the contrary, the line shape in the zz spectrum where the electronic intensity is very weak, is well described by a Lorentzian. Similarly, an asymmetric line shape of the 340 cm^{-1} mode is indicative of the strong interaction with the electronic continuum [1,8]. In other words, the phononic RSS can be a good probe of the electronic RSS.

When the samples are cooled, dramatic changes are observed in all A_g phonon lines below T_c, i.e., the hardening of the 430 and 500 cm^{-1} modes and the softening of the other three lines at low frequencies. The most important finding is a significant x-y anisotropy in the 340 cm^{-1} line. In Fig. 2, temperature dependencies of the RSS for the 340 cm^{-1} mode are shown for xx and yy polarizations, where the intensities are normalized, for convenience, at the peak position after subtracting the flat background with an intensity at 250 cm^{-1}. One can immediately see that the softening below T_c (= 86 K) in the xx spectrum is more pronounced than in the yy spectrum. A difference of the peak frequencies is about 2 cm^{-1} at 10 K. Another distinctive feature is that the broadening at intermediate temperatures between T_c and 10 K is more remarkable in the xx polarization than in the yy.

In order to discuss this x-y anisotropy in detail, we have performed the least-squares fit to the RSS in the spectral region between 175 and 400 cm^{-1} in terms of a standard Fano profile $I(\omega) = I_0(\varepsilon + q)^2/(1 + \varepsilon^2) +$ background, where we have assumed a quadratic ω

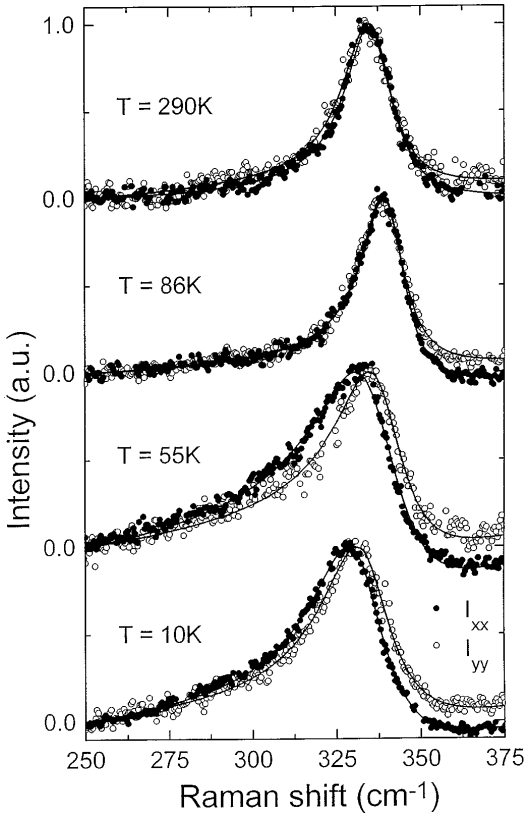

FIG. 2. The 340 cm^{-1} Raman peak obtained at different temperatures in the xx (solid circles) and the yy (open circles) polarizations, normalized to the peak intensity after subtracting a flat background with intensity at 250 cm^{-1}. The solid curves are the results of the fitting using the formula $I = I_0(\varepsilon + q)^2/(1 + \varepsilon^2) + A + B\omega + C\omega^2$, where $\varepsilon = (\omega - \Omega)/\Gamma$. The first term corresponds to the Fano profile and the other terms $A + B\omega + C\omega^2$ describe the background related to the electronic Raman scattering.

dependence of the background [8,10]. The parameter ε is defined as $\varepsilon = (\omega - \Omega)/\Gamma$ and q is the asymmetric parameter. Here the frequency Ω and linewidth Γ are renormalized by the real and imaginary parts of the electronic response $\chi(\omega) = -R(\omega) + i\pi\rho(\omega)$ as $\Omega = \Omega_0 + V^2R$ and $\Gamma = \Gamma_0 + V^2\pi\rho$, respectively, where Ω_0 and Γ_0 are the uncoupled frequency and damping, and V is the coupling constant. As demonstrated by the solid lines in Fig. 2, the fitting results are satisfactory. Figure 3 presents the T dependence of the obtained fitting parameters Ω, Γ, and q. In the normal state, there are small differences $\Omega_{xx} - \Omega_{yy} \sim 1$ cm^{-1} and $2\Gamma_{yy} - 2\Gamma_{xx} \sim 1$ cm^{-1} over the whole T range (100–300 K). This normal state anisotropy could arise from a difference of the coupling constant V in difference polarizations ($V_{xx} \neq V_{yy}$).

In the superconducting state, the well-known softening and broadening of this phonon are clearly seen. Overall features of the superconductivity-induced anomalies (the steplike softening and a maximum broadening at a certain

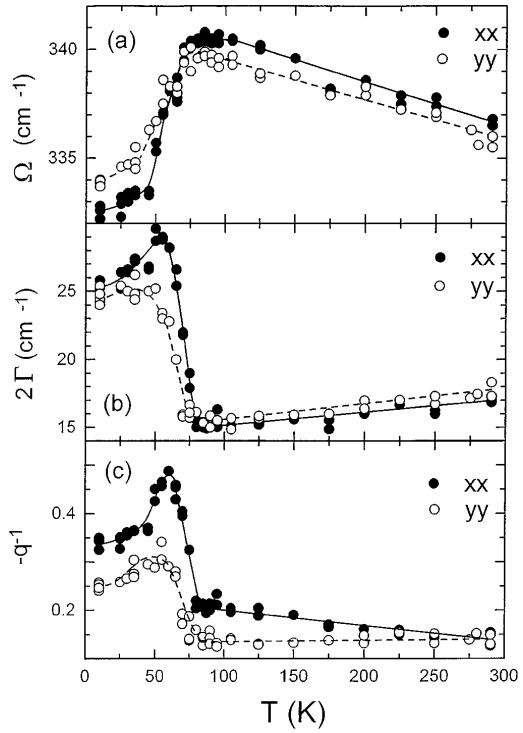

FIG. 3. Temperature dependences of the frequency Ω (a), the linewidth 2Γ (b), and the asymmetric parameter q^{-1} (c) for the 340 cm^{-1} mode in the xx and yy polarizations. The lines are guides to the eye only.

temperature below T_c) agree roughly with those expected for $d_{x^2-y^2}$ symmetry rather than for s–wave superconductors [11,12], in which broadening is expected only for the hardening phonons [13]. A striking result is that the superconductivity-induced effects depend on polarization configuration, as is expected from Fig. 2. For the xx polarization, a dramatic softening ($\Delta\Omega_{xx} \cong 7$ cm^{-1}) occurs between 70 and 40 K, and the total softening is about 8 cm^{-1}. By contrast, in the yy polarization, the total softening is smaller ($\Delta\Omega_{yy} \cong 5.5$ cm^{-1}) and the temperature dependence is weaker. As a result of this xy difference in softening behavior, the changeover from $\Omega_{xx} > \Omega_{yy}$ to $\Omega_{yy} > \Omega_{xx}$ takes place around 65 K. The broadening of the linewidth is also polarization dependent. In the xx spectrum the linewidth has a maximum at 55–60 K, whereas in the yy spectrum at 45–50 K or below. Also in the q^{-1} parameter which is roughly proportional to $V^2\rho$, maxima are observed at almost the same temperatures. All these anomalies in the phonon parameters arise from the superconductivity-induced changes in the renormalization terms associated with the coupling to the electronic excitation $\chi(\omega)$ [14]. Therefore, the x-y anisotropy of these phonon anomalies must also originate from the x-y anisotropy in the contribution of the electronic part.

A naive interpretation of the observed x-y anisotropy is that it is due to the chain contribution. In fact, infrared and penetration depth measurements have revealed a significant contribution of the chain superconductivity in overdoped YBCO [15]. A coupling of the 340 cm^{-1} phonon with the chain electronic excitation is not expected to be strong, because this phonon mode does not involve vibrations of the atoms in the chain [16]. However, the coupling could be enhanced by a resonance of this phonon energy and the interband energy between the chain and the plane bands [6]. Since these two bands are close to each other along the X-S direction in the two-dimensional Brillouin zone [17], the effect of the coupling is observed mainly in the yy spectrum. In the superconducting state, the 340 cm^{-1} phonon must be strongly affected by the gap opening in the chain. If the chain superconductivity is induced mainly by the attractive interaction within the one-dimensional chain, the gap function cannot be a d wave with nodes but should be a s wave. In this case, the Raman response should be quite different from that for $d_{x^2-y^2}$ symmetry in the plane superconductivity. Consequently, the phonon self-energy effect is observed to be different in the yy spectrum from that in the xx spectrum which reflects only the $d_{x^2-y^2}$ gap in the plane.

On the other hand, if the chain superconductivity has the same symmetry as that for the plane, as in the case of proximity-effect induced superconductivity [18], the chain contribution to the yy spectrum cannot create the observed x-y anisotropy. Then we must take into account more explicitly the effect of orthorhombic distortion of the plane. In the orthorhombic system, the tetragonal A_{1g} channel for the electronic Raman scattering is mixed into the tetragonal B_{1g} channel, giving inequivalent Raman vertices $\gamma_{xx} \neq \gamma_{yy}$. This A_{1g}-B_{1g} mixing enables the B_{1g} phonon to interact with the A_{1g} electronic channel. The Raman vertices for the xx and yy channels in this case are expressed as $\gamma_{xx}(\mathbf{k}) = \delta\gamma_{A1g}(\mathbf{k}) + \gamma_{B1g}(\mathbf{k})$ and $\gamma_{yy}(\mathbf{k}) = \delta\gamma_{A1g}(\mathbf{k}) - \gamma_{B1g}(\mathbf{k})$, respectively, where δ is the mixing rate. One can clearly see in this expression that the A_{1g}-B_{1g} mixing gives rise to an anisotropic contribution of the electronic state at the Fermi level. For a nearly cylindrical Fermi surface [3], these vertices can be approximately represented as $\gamma_{xx}(\phi) = \delta\gamma_{A1g}\cos 4\phi + \gamma_{B1g}\cos 2\phi$ and $\gamma_{yy}(\phi) = \delta\gamma_{A1g}\cos 4\phi - \gamma_{B1g}\cos 2\phi$, respectively, where ϕ is the azimuthal angle of the $\mathbf{k}$ vector. In the case for $\gamma_{A1g}, \gamma_{B1g} > 0$, the magnitude of γ_{xx}^2 at $\phi = 0$ is larger than that at $\phi = \pi/2$, so that the xx spectrum reflects mainly the electronic states around $(\pm\pi, 0)$, while the yy spectrum reflects those around $(0, \pm\pi)$. Therefore, it turns out that the observed x-y anisotropy indicates the difference of the maximum gap values between the $\mathbf{k}_x$ and $\mathbf{k}_y$ directions. Theoretically, it is predicted that the orthorhombic distortion leads to an admixture of the s-wave component with the d-wave one [5]. The only realistic symmetry which gives $\Delta_x(0) \neq \Delta_y(0)$ is the $d + s$ symmetry with the gap function $\Delta = \Delta_d(\cos\mathbf{k}_x - \cos\mathbf{k}_y) + \Delta_s(\cos\mathbf{k}_x + \cos\mathbf{k}_y)$.

In this $d + s$ wave scenario, it is worth estimating roughly the gap magnitude and the amount of s-wave mixing. The observation of the maximum $\Gamma_{xx}(T)$ near $T = 55$ K implies $2\Delta_x(55\text{ K}) \cong \Omega_0 \cong 350\ \text{cm}^{-1}$ [19]. Assuming the BCS-like T dependence of $\Delta(T)$, we obtain $2\Delta_x(0) = 400\ \text{cm}^{-1} = 6.7kT_c$. For the yy spectrum, the maximum $\Gamma_{yy}(T)$ is observed around 45 K, $2\Delta_y(0) = 370\ \text{cm}^{-1} = 6.2kT_c$. Therefore, $2\Delta_x(0)/2\Delta_y(0) \cong 1.1$, which leads to a small amount of admixture of $\Delta_s \cong 0.05\Delta_d$. Indeed, our preliminary calculation with the Green's function [14] well represents the observed x-y anisotropy in both the frequency and linewidth, by using $5 \sim 10\%$ admixture of the A_{1g} channel with the B_{1g}. Furthermore, we can estimate the value of $2\Delta_d$ as $\Delta_x + \Delta_y = 2\Delta_d = 385\ \text{cm}^{-1} = 6.5kT_c$. In comparison, we also estimate the $2\Delta_d$ value in the case of another scenario with the s wave chain contribution as mentioned above. In this case, the xx spectrum reflects the inplane gap, giving $2\Delta_d = 2\Delta_x = 400\ \text{cm}^{-1} = 6.7kT_c$. These estimated values are in good agreement with the previously reported values for overdoped YBCO [14,20].

At the moment, we cannot judge whether the observed x-y anisotropy is governed by the contribution of the chain superconductivity with s symmetry or by the $d + s$ wave superconductivity in the plane. The origin of the s component is also an unresolved problem. There is a possibility, other than the chain superconductivity or the simple orthorhombicity, that the overdoped electronic state causes an admixture of the s-wave component [21]. In order to clarify these problems, further systematic studies are required, for example, by intentionally destructing the chain superconductivity or changing the doping level [22].

In summary, precise temperature and polarization dependencies of RSS have been investigated for fully oxygenated twin-free YBCO crystals. It was found that the superconductivity induced effects on the 340 cm^{-1} B_{1g}-like mode are roughly described by the model for d-wave superconductors, but are different in the xx and yy spectra. This x-y anisotropy cannot be explained by a simple $d_{x^2-y^2}$ model for the tetragonal CuO_2 plane. If there is an independent superconducting channel in the chain with a different pairing symmetry from that of the plane superconductivity, the observed x-y anisotropy could be attributed to the contribution of the chain superconductivity in the yy spectrum. Another possibility is that it is governed by the difference in the gap magnitudes in the $\mathbf{k}_x$ and $\mathbf{k}_y$ directions, as in the case of $d + s$ wave superconductivity ($\Delta_x \neq \Delta_y$), which can be probed by the B_{1g}-like phonon, owing to the A_{1g}-B_{1g} mixing due to the orthorhombic distortion of the plane. To clarify the origin of the s component is a future study.

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