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Superconductivity-induced effect on ''Raman-forbidden'' modes in underdoped $YBa_2Cu_3O_{7-x}$ single crystals

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A remarkable resonance-Raman effect has been observed for some ''defect oxygen'' modes in underdoped $YBa_2Cu_3O_{7-x}$ single crystals. In resonant conditions, we have studied the temperature dependence of frequencies for these originally Raman-forbidden modes as well as for the Raman-active ones. It has been found that, similar to the B_{1g}-like mode, the yy-polarized ''Raman-forbidden'' modes soften below T_c, while the A_{1g}-like modes dominating in the zz-polarized spectra do not. This difference in the phonon behaviors indicates a peculiarity of the interaction between the phonons and quasi-two-dimensional electron system in high-T_c superconductors. Above T_c, no clear phonon anomaly relevant to a pseudogap has been observed. [S0163-1829(98)50910-1]

Recently, the electronic state in the underdoped regime of high-T_c superconductors has attracted much attention. In addition to a number of anomalous normal-state properties of these unconventional metals, the so-called pseudogap phenomena have been observed well above T_c.[1] At present, it is a hot topic whether the origin of the pseudogap is the same as that of the superconducting gap. Concerning the gap problem, it is well known that Raman-active vibrations show unusual temperature behavior below T_c owing to the superconductivity-induced phonon self-energy effect.[2] This means that one can study the electronic state by using a phonon probe. Phonon-Raman studies have provided rich information about the superconducting gap in the systematic studies of $YBa_2Cu_3O_{7-x}$.[3–5] A similar study is expected for the pseudogap problem.

With decreasing oxygen content, the superconductivity-related anomalies in Raman spectra become unclear presumably because of the reduction of the electron-phonon interaction.[3–5] Additional information about the electronic states in oxygen-deficient $YBa_2Cu_3O_{7-x}$ can be obtained by studying not only originally Raman-active modes but also ''forbidden'' ones, which appear in the Raman spectra of $YBa_2Cu_3O_{7-x}$ owing to the oxygen nonstoichiometry. The additional lines are usually weak, and this makes it difficult to study their temperature behaviors. One of the ways to solve this problem is to study the Raman spectra in resonant conditions.

It has been reported[6–8] that the resonant profiles for the A_g Raman modes strongly depend on the oxygen content in $YBa_2Cu_3O_{7-x}$ and dramatically change when going from the metallic, fully oxygenated $YBa_2Cu_3O_7$ to insulating $YBa_2Cu_3O_6$. There is no clear study of the resonant Raman scattering in the crystals with intermediate oxygen contents except for the study[9] using an inhomogeneous single crystal containing clusters of three phases with $T_c = 90$ K, 60 K, and 0 K. For the fully oxygenated $YBa_2Cu_3O_7$ crystal, resonant behavior of two additional lines in the Raman spectra was found by Wake *et al.*[10]

Additional lines in the Raman spectra may also appear as a result of the high incident-laser power, about 10^2 W/cm^2, that leads to nonlinearly rising defect oxygen modes in the Raman spectra,[11] presumably because of local structural disordering under laser excitation.[12] Paying attention to the problems of both the crystal inhomogeneity and nonlinearity at strong laser powers, we have investigated the temperature dependence of phonon Raman scattering in the resonant conditions.

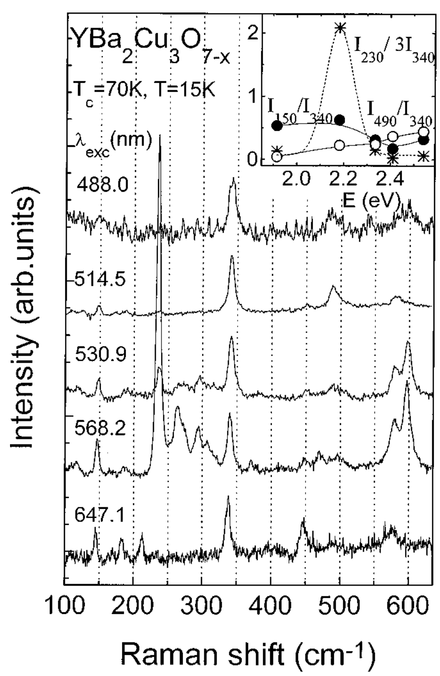

FIG. 1. The yy polarized Raman spectra of the detwinned $YBa_2Cu_3O_{7-x}$ single crystal for different laser-wavelength excitations. Inset shows the ratios of several line intensities to that of the B_{1g}-like mode as functions of the excitation energy.

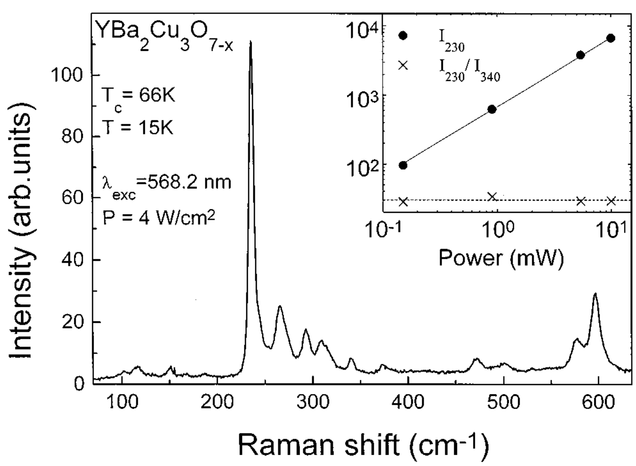

FIG. 2. The Raman spectrum of the twinned $YBa_2Cu_3O_{7-x}$ single crystal in the $xx+yy$ polarization under the resonant excitation $\lambda_{exc}=568.2$ nm. Inset shows the dependence on the laser power for the 230 cm^{-1} line intensity (circles) and for its ratio to the 340 cm^{-1} line intensity (crosses). The dashed line corresponds to the constant ratio=30, and the solid line is the linear dependence $I_{230}=A\times$Power.

In our experiments, the incident laser power was usually 2 W/cm^2 on the sample surface (5 mW with a 0.4×0.8 mm^2 laser spot on a crystal), with local overheating by no more than 5–10 K, which was controlled by recording anti-Stokes spectra. Since some phonon lines lose their intensities with the laser irradiation and recover them when switching off the irradiation as was first reported by Wake *et al.*,[10] we measured the spectra with long enough intervals to avoid this time-dependent bleaching effect. Lines of Ar-Kr laser were used for the excitation. The spectra were studied in the pseudobackscattering configuration with use of a T64000 Jobin-Ivon triple spectrometer with a liquid-nitrogen cooled charge-coupled device detector. The spectral resolution was 1–3 cm^{-1}. Several underdoped $YBa_2Cu_3O_{7-x}$ ($x=0.2$–0.4, $T_c=60$–80 K, $\Delta T_c=2$–5 K) crystals under study had been grown and some of them were detwinned as described in Ref. 13, and the homogeneity of the samples was carefully checked. Only the freshly cleft crystals were studied to eliminate the effects of both the polishing and crystal degradation. The spectra were obtained at 15 K, except for studying the temperature dependencies. At low temperatures, the closed-cycle UHV cryostat was used with temperature stability better than 1 K.

Figure 1 presents yy-polarized Raman spectra of the detwinned $YBa_2Cu_3O_{7-x}$ crystal with $T_c=70$ K for five different laser wavelengths. The spectra are normalized to the intensity of the B_{1g}-like mode at 340 cm^{-1}. One can see that some ''forbidden'' lines are noticeably enhanced at the 568.2 nm (2.2 eV) excitation. In the inset of Fig. 1, the normalized intensities of several yy-polarized lines are plotted as a function of the excitation energy. Compared with the behaviors of the 150 and 490 cm^{-1} lines, which are well-observed at the standard 514.5 nm excitation, the 230 cm^{-1} line exhibits an extremely sharp resonance effect at 568.2 nm, suggesting the existence of a narrow electron band with the width less than 0.2 eV. A similar resonance profile is also seen in other ''forbidden'' lines.

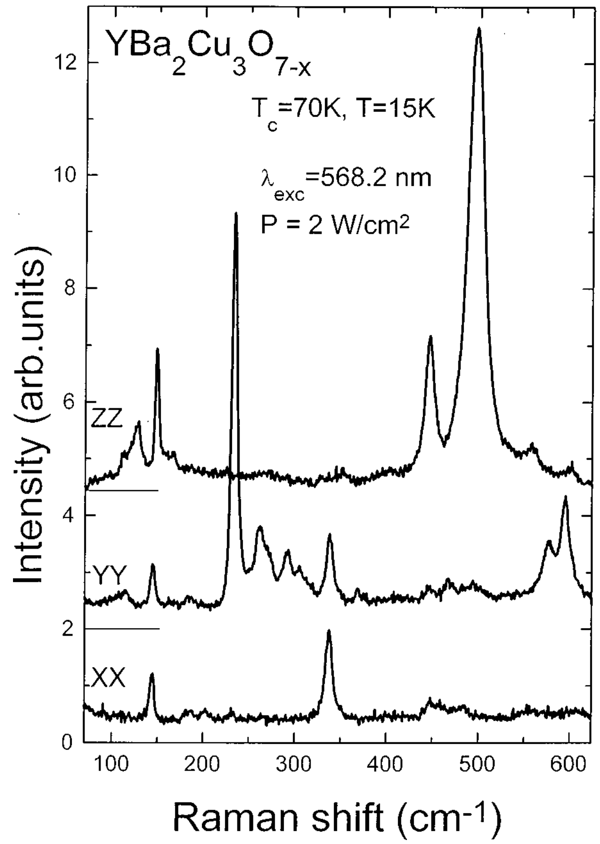

FIG. 3. The Raman spectra of the $YBa_2Cu_3O_{7-x}$ single crystal in different polarizations under the resonant excitation $\lambda_{exc}=568.2$ nm.

This resonance effect is also observed in the other oxygen-deficient $YBa_2Cu_3O_{7-x}$ crystals. In our experiments, the resonance was most pronounced for the $YBa_2Cu_3O_{7-x}$ crystal with $T_c=66\pm2$ K, the intensity ratio for the 230 and 340 cm^{-1} lines becoming as large as 30 (see Fig. 2). For other crystals under study, with higher and lower T_c, this ratio was less than 10 (cf. Fig. 1). For comparison, for a crystal with $T_c=91$ K,[10] the intensity of the 230 cm^{-1} line did not exceed that of the 340 cm^{-1} line at any excitation. Note that the phonon line intensities linearly depend on the excitation power, as is shown in the inset of Fig. 2. It implies that we can rule out the possibility of nonlinear effects, which do take place at higher excitations.[11] Therefore, the observed resonant enhancement of the ''forbidden'' lines can be regarded as an intrinsic effect.

These ''forbidden'' lines are well polarized. Figure 3 shows the polarized spectra at the resonant 568.2 nm excitation. In the zz polarization, four well-known A_{1g}-like modes are observed at about 115, 150, 440, and 490 cm^{-1}. As for in-plane polarizations, in addition to the B_{1g}-like 340 cm^{-1} mode, the strongly enhanced additional lines are observed at about 230, 260, 290, 305, 365, 575, and 595 cm^{-1} in the yy spectrum, while very weak additional modes are seen at 200, 560, and 610 cm^{-1} in the xx spectrum.

Such a strong polarization dependence of the resonance effect as well as its sharpness and correlation with the oxygen nonstoichiometry indicate the resonance of the chain-oxygen-induced mode with a narrow electron band related to oxygen defects in the CuO chains.[14] The existence of such a

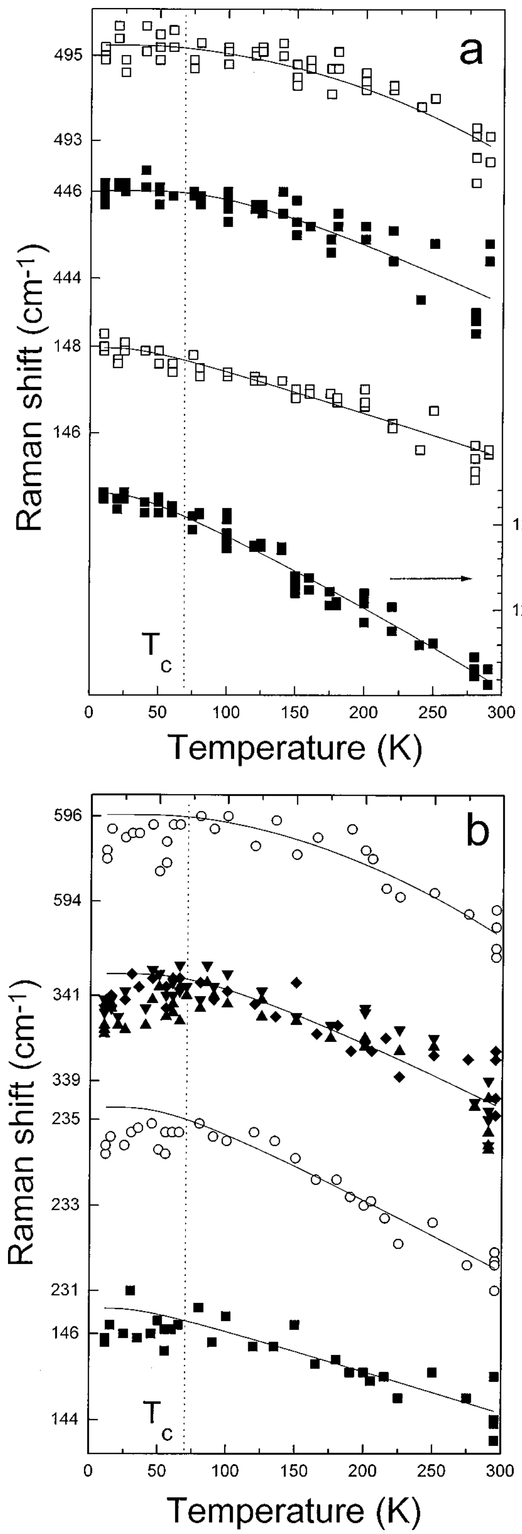

FIG. 4. The temperature dependencies of the frequencies of the most intense lines in Raman spectra of the $YBa_2Cu_3O_{7-x}$ single crystal obtained at the $\lambda_{exc}=568.2$ nm excitation: (a) zz polarization: the A_{1g}-like modes (squares); (b) yy polarization: the 150 cm^{-1} mode (squares); the 230 and 595 cm^{-1} defect-oxygen modes (circles), the 340 cm^{-1} B_{1g}-like mode (diamonds). The results of the Fano fitting analysis at the 514.5 nm excitation for the 340 cm^{-1} B_{1g}-like mode are shown by down triangles (the yy polarization) and up triangles (the xx polarization). Solid lines are results of multi-phonon-decay fitting (see text). Note the compressed scale for the lowest-frequency mode.

band is consistent with the cathodoluminescence studies of underdoped $YBa_2Cu_3O_{7-x}$, which show the presence of several bands located at 2.0–3.4 eV and attributed to defects in the oxygen sublattice.[16,17]

Next, we present the temperature behavior of the most intense additional lines at 230 and 595 cm^{-1} together with the main lines. The linewidths of all lines for all underdoped crystals under study have shown no peculiar T dependencies in the range between 15 and 290 K. The temperature dependencies of the frequencies of the lines for the same crystal as in Fig. 1 are presented in Fig. 4. Owing to practically symmetric line shapes, the mode frequencies could be determined by the positions of the line maxima. The Fano analysis, which was made for the 340 cm^{-1} line, gave a merely systematic shift within 0.5 cm^{-1}.

As one can see in Fig. 4(a), the frequencies of the A_{1g}-like modes in the zz-polarized spectra do not show any peculiar behavior in a whole temperature region, exhibiting a usual saturation at low temperatures, which can be described in a framework of a simple two-phonon-decay anharmonicity.[18] There is a deviation from such a simple temperature behavior for the highest-frequency zz-polarized mode (490 cm^{-1}) at $T^* \approx 150-200$ K. Since other modes do not show such a deviation, it can be associated with an increasing probability of processes involving the decay of this high-frequency phonon into three, though we cannot rule out the possibility of a pseudogap opening. The same explanation may be valid for a similar change in the slope of the temperature dependence for the highest-frequency yy-polarized line at 595 cm^{-1}. For the two lines, the three-phonon-decay fittings[18] are shown in Fig. 4. The behavior of the zz-polarized mode at 490 cm^{-1} is well described by the calculated curve.

In contrast, the temperature dependencies of frequencies of additional yy-polarized lines are quite different from those of the A_{1g}-like modes dominating in the zz-polarized spectra, but are rather similar to the behavior of the B_{1g}-like mode at 340 cm^{-1} [Fig. 4(b)]. The B_{1g}-like mode is observed in xx- and yy-polarized spectra and exhibits a softening below T_c. Even the mode at 150 cm^{-1} demonstrates such a softening tendency, which indicates that this line is not a simple polarization leakage because of the inexact geometry[19] but is some mixture with the B_{1g}-like in-plane polarized mode.

The observed difference in phonon behaviors can be attributed to the quasi-two-dimensional nature of the electron system in high-T_c superconductors, which results in a different character of its coupling to the Raman-active phonons. The interaction of the electron system with in-plane polarized phonons (such as the B_{1g}-like mode and the yy-polarized additional modes) must be stronger than the interaction with the out-of-plane polarized phonons (such as A_{1g}-like modes).[20] As a result, the opening of the superconducting gap causes preferentially the softening of the in-plane polarized phonons, whereas no clear softening is observed for the out-of-plane phonons. From this point of view, the behavior of the 150 cm^{-1} mode is very indicative. This mode softens below T_c in the yy spectrum but does not in the zz one. Since the phonon frequency is the same in all polarization, the difference in the Raman line frequencies must originate from the anisotropy of the electronic continuum[21] interacting with this mode. In fact, the electronic scattering in the zz polarization is very weak, whereas there exists rather strong electronic background in the yy polarization.

The observed phonon-softening effect is smaller than that in the highly-oxygenated $YBa_2Cu_3O_7$,[22] which may be a result of the decrease in the strength of the electron-phonon interaction.[3–5] Furthermore, according to the phonon-self-energy theories,[23–25] in which a phonon softens if it has the energy lower than the superconducting gap 2Δ, our observation of the 595 cm^{-1} mode softening turns out to indicate the possible ratio $2\Delta/k_BT_c$ more than 15. The anomalously large gap value has also been reported in other experiments.[11,26]

In relation to the so-called pseudogap phenomenon, clear softening of some Raman modes below 150 K has been reported for $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{15-x}$ polycrystals.[27] However, for the underdoped $YBa_2Cu_3O_{7-x}$ crystals, we have observed no clear phonon softening in the normal state, whereas the superconductivity-induced softening is obvious for the in-plane-polarized modes. Since the phonon softening originates from the reduction of the electron density of states (DOS), the present result may indicate that, in the normal state, there is no suppression of the DOS around the phonon energies, or that the nature of the pseudogap, if it exists, must be different from that of the superconducting gap.

In summary, we have found a strong resonant enhancement of defect-oxygen-induced lines in the underdoped $YBa_2Cu_3O_{7-x}$. The studies of the temperature dependencies of their frequencies in the resonant conditions have demonstrated their softening below T_c, which is similar to the behavior of the in-plane-polarized B_{1g}-like mode but different from that of the zz-polarized A_{1g}-like modes. This indicates a peculiar electron-phonon coupling for a two-dimensional electronic state in high-T_c superconductors. The maximum gap value is suggested to be larger than 600 cm^{-1}. No clear phonon anomaly is observed above T_c.

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[14] In this paper, we do not discuss in detail the origin of the additional lines. However, we note that the appearance of additional modes in Raman spectra is unlikely due to conversion of odd-parity infrared modes as a result of an energy resonance of the laser excitation with an electric dipole transition as was suggested by Wake *et al.* (Ref. 10), since the yy polarized spectra taken from the (ab) and (bc) crystal planes are almost identical. For example, the spectrum in Fig. 2 was taken from the plane containing the z axis, whereas the spectra in Figs. 1 and 3 are from the (ab) plane. Instead, we propose that these modes are induced by the particular oxygen distribution (Ref. 15), similar to that proposed for the orthorhombic-II $YBa_2Cu_3O_{6.5}$ phase with empty and full chains alternating along the a axis. In a simpler case of the ortho-II phase, the doubling of a unit cell results in the folding of the Brillouin zone. Consequently, the phonon states from the zone boundary, which belong originally to the IR-active branches, become the even-parity Γ-point states, showing up in Raman spectra. However, we cannot rule out the possibility of the Fröhlich electron-phonon interaction in resonant conditions, which was suggested by Heyen *et al.* (Ref. 8) for the Raman spectra of $YBa_2Cu_3O_6$, where several forbidden modes are seen at a red-laser excitation. Further studies of the origin of the additional Raman modes are thus required.

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