Superconducting gap anisotropy and phonon anomalies in single crystal $NdBa_2Cu_3O_{7-x}$

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The temperature dependence of the low-frequency part of electronic Raman scattering was investigated in single crystal $NdBa_2Cu_3O_{7-x}$ with light polarized within the CuO_2 planes and along the c axis. From the electronic continuum redistribution below T_c, the pair-breaking energy is derived and is shown to depend on polarization. The in-plane pair-breaking 2Δ peaks are located at 330 cm^{-1} for the A_{1g} symmetry and around 580 cm^{-1} for B_{1g}. If we assume that the pair-breaking peak position is a measure of the superconducting gap, these values are almost the same, as in $YBa_2Cu_3O_{7-x}$, $2\Delta/T_c$ ratios being roughly 5.2 and 8.5. For the c-axis response we detect the pair-breaking peak between 400 and 500 cm^{-1} and there is also a small decrease in the intensity at frequencies below 200 cm^{-1}. We also discuss some phonon anomalies probably caused by the substitution of Ba^{2+} by Nd^{3+}. [S0163-1829(97)02537-X]

I. INTRODUCTION

A great deal of interest has been focused on the energy gap of high- T_c superconductors. Several experimental techniques can be used for its determination, Raman scattering being one of them. The effectiveness of the Raman scattering to probe the superconducting gap has been demonstrated in almost all high-T_c cuprate superconductors.[1] While the dispute about s-wave or d-wave superconductivity still continues, some features revealed by the Raman scattering, for instance, anisotropic nature of the pairing and a more clean gap at the B_{1g} symmetry have received substantial verification.[1] All high- T_c superconductors have unusual optical properties in both the normal and superconducting states. In the normal state for light polarized within the CuO_2 planes, there are electronic continua that are nearly energy independent. Below the superconducting transition, the continua redistribute—the intensity at low frequencies is decreased and there is an increase in intensity at high frequencies. As the intensity peaks at a position which depends on the specific scattering geometry, it has been argued that, from the polarization dependence of the spectra, one can infer the symmetry of the superconducting gap.[1] It is now evident from the in-plane Raman scattering that the superconducting gap is not clearly visible (i.e., there is no threshold). A complete understanding of the threshold absence will help elucidate the order-parameter symmetry. However, any full study of the pairing symmetry should also address charge dynamics perpendicular to the planes. Raman data on the electronic scattering along the c axis are scarce: It is known, for instance, that there is quite strong electronic continuum for light polarized along the c axis,[2] but superconductivity-induced redistribution has been reported for $Bi_2Sr_2CaCu_2O_{8+x}$ crystals only.[3] The present study extends the electronic Raman-scattering results to the $NdBa_2Cu_3O_{7-x}$ system allowing us to compare the data obtained with those for the isostructural compound $YBa_2Cu_3O_{7-x}$.

In this paper, we report the inelastic light-scattering study of the superconducting order parameter in single crystal $NdBa_2Cu_3O_{7-x}$ using electronic Raman scattering. We find that the electronic continuum distribution below T_c appears to be intrinsic to superconducting behavior of the $RE123$ system (RE=rare earth). The positions of the in-plane pair-breaking peak for different symmetries, a linear contribution to the low-energy scattering in the superconducting state, coincide independent of the rare-earth ion in the structure. For the c-axis superconducting response we detect a pair-breaking peak together with a small decrease in intensity at frequencies below 200 cm^{-1}. We also briefly discuss the phonon spectra and mention a possible explanation of a few phonon anomalies in $NdBa_2Cu_3O_{7-x}$ crystals.

II. EXPERIMENTAL DETAILS

The crystals used in this study were grown by the traveling solvent floating-zone method, described elsewhere.[4] The as-grown crystals were annealed in flowing O_2 gas at 400 °C for three weeks. This resulted in crystals with T_c=95 K as determined through dc magnetization. The high critical temperature indicated that the crystals were optimally doped. The Raman-scattering measurements were taken in a pseudo-backscattering geometry with the blue (458 nm) line of an Ar^+/Kr^+ laser using the Raman JY6400 triple spectrometer and a nitrogen-cooled CCD multichannel detector. The polished twinned crystals were mounted on the cold finger of a He-flow UHV cryostat. Prior to mounting in the cryostat the sample was washed in methanol for about 3 min to remove any potential surface impurities. The zz, $x'x'$, and $x'y'$ polarizations were checked (the x' and y' refer to diagonals to the crystallographic axes). Considered within the tetragonal representation, the mentioned polarizations couple to excitations of A_{1g}, $A_{1g}+B_{2g}$, and B_{1g} symmetry, respectively.

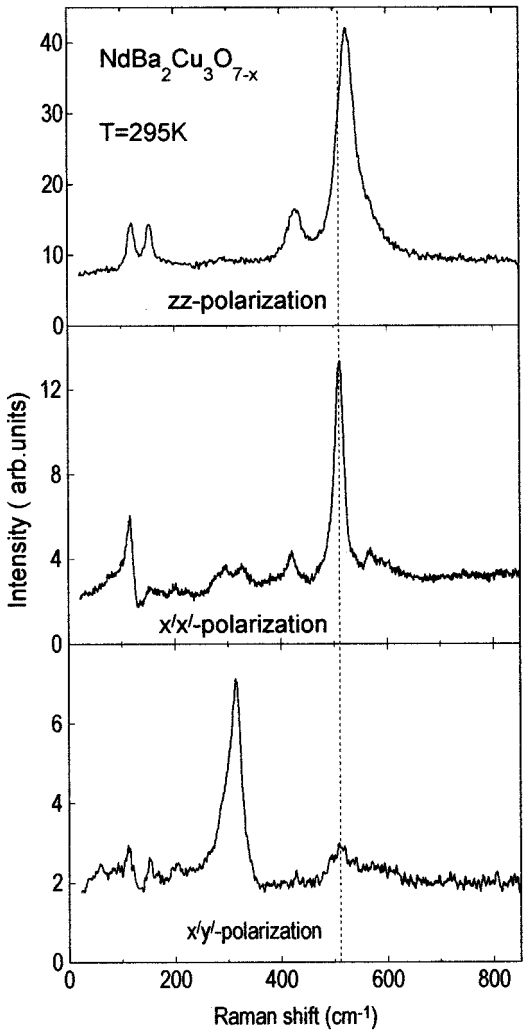

FIG. 1. Room-temperature Raman spectra of single-crystal $NdBa_2Cu_3O_{7-x}$ for various polarizations: zz (A_{1g}), $x'x'$ (A_{1g}), and $x'y'$ (B_{1g}). Dashed line serves to indicate a disparity in frequency for the apical oxygen mode in different polarizations.

Due to twinning we could not separate the xx and the yy contributions. The laser beam was precisely located in order to probe the same crystal point after changing the temperature or the scattering geometry. The laser power density did not exceed 5–10 W/cm^2 and all spectra were corrected for the optical system response.

III. SUPERCONDUCTIVITY INDUCED CHANGES OF THE ELECTRONIC SCATTERING IN $NdBa_2Cu_3O_{7-x}$

Figure 1 illustrates the room-temperature spectra of single crystal $NdBa_2Cu_3O_{7-x}$ in various polarizations. Each spectrum demonstrates a number of optical phonons superimposed on an intense electronic continuum. The in-plane electronic continuum with A_{1g} symmetry strongly interferes with the Ba mode centered at 117 cm^{-1} which is reflected in its asymmetric line shape. The overall structure of the phonon spectra observed in different polarizations is similar to that of the $YBa_2Cu_3O_{7-x}$ crystal,[5] however, some deviations will be discussed later.

Figure 2 shows the $x'x'$ and the $x'y'$ spectra at about

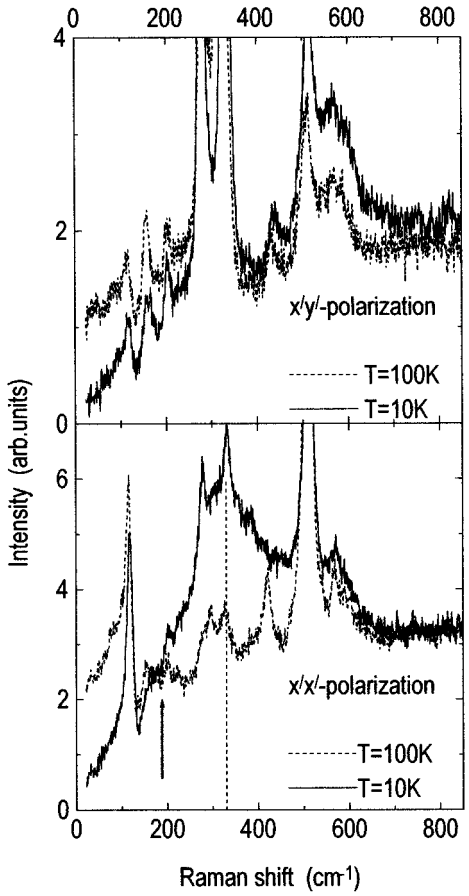

FIG. 2. Polarized $[x'x'$ $(A_{1g})]$ and depolarized $[x'y'$ $(B_{1g})]$ spectra in $NdBa_2Cu_3O_{7-x}$ at temperatures above ($T=100$ K) and well below ($T=10$ K) $T_c=95$ K. The arrow and dashed line in the bottom panel indicate the intersection point and maximum of the pair-breaking peak, respectively.

(100 K) and well below T_c (10 K), allowing us to examine separately the A_{1g} and B_{1g} components of the superconducting gap (we assume here that the B_{2g} contribution is negligible to the $x'x'$ spectrum and most of the contribution comes from A_{1g}). In the two symmetries the electronic continua lose scattering strength at low frequencies in the superconducting state, as the scattering below gap is suppressed by the opening gap.[6] This suppression is, however, incomplete—there exists residual electronic scattering at the lowest detected energy (no threshold). The low-energy portion of the low-temperature spectra in both scattering configurations is quite linear in frequency, though in the B_{1g} symmetry there is more of a suggestion of a higher power law in frequency. In addition to the suppression at low frequencies, a broad peak in the continua developed at low temperature, which is believed to arise from pair breaking of the Copper pairs. From comparison of the $x'x'$ and the $x'y'$ spectra, it is evident that the pair-breaking peak for the former case is located at lower energy than for the latter case. To be precise, the A_{1g} continuum is observed to peak at 330 cm^{-1}, while the B_{1g} continuum peaks around 580 cm^{-1}. Furthermore, the B_{1g} peak seems to appear at a temperature well above the transition temperature, as evident in Figs. 1 and 2. There is a remnant of the peak at room temperature and just

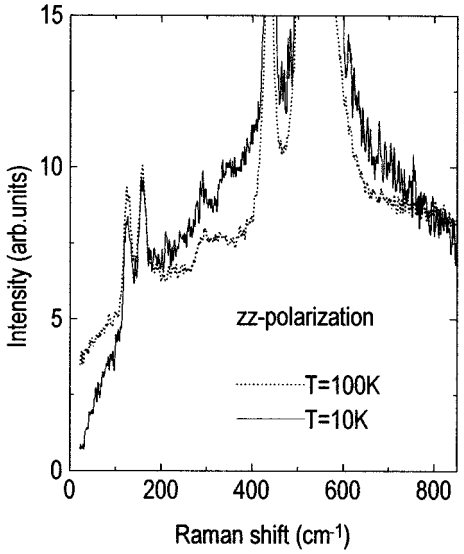

FIG. 3. Temperature dependence of the polarized c-axis response, zz (A_{1g}), illustrating the continuum redistribution into a pair-breaking peak.

above T_c the peak is well formed, though separating out electronic continuum from phonon features to prove this statement is difficult. We note that this observation complicates the interpretation of the B_{1g} symmetry peak as a superconducting gap. Additionally, in the B_{1g} spectrum suppression of the low-energy continuum occurs at much higher energies than for the A_{1g} continuum (the intersection point, where the scattering in the normal state coincides with that in the superconducting state, is located for the parallel and the cross-polarization geometries at 300–350 and 200 cm^{-1}, respectively).

A precise estimate of the superconducting gap anisotropy in $NdBa_2Cu_3O_{7-x}$ is difficult to obtain due to the absence of a well-defined gap. Following the reasoning of Cooper *et al.*[7] for $YBa_2Cu_3O_{7-x}$, where there is also no clean gap, we can estimate the in-plane anisotropy from the pair-breaking peak positions. This gives almost the same, as $YBa_2Cu_3O_{7-x}$, $2\Delta/T_c$ ratios of 5.2 and 8.5 for the polarized and depolarized scattering, respectively. A superconducting gap denotes a region of excitation energies where there is no density of states, and its existence stabilizes the superconducting state. If the excitation density is reduced but not all the way to zero, as it is observed in the Raman scattering, the suppression of excited states may also stabilize the superconducting phase with respect to the normal one. Therefore, the energy region where the suppression takes place is to some extent a measure of the gap. If the intersection point does characterize the superconducting gap, the gap in the B_{1g} channel would be located around 300–350 cm^{-1}, instead of 580 cm^{-1} as determined from the pair-breaking peak position. For the A_{1g} symmetry we would have in this case $2\Delta = 200$ cm^{-1}, instead of 330 cm^{-1}. We also note that the determination of the superconducting gap from the intersection point does not strongly affect the in-plane anisotropy of the order parameter which remains almost unchanged.

The continuum in the zz polarization upon entering the superconducting state also demonstrates a similar redistribution as for the in-plane polarizations. This is shown in Fig. 3 for two different temperatures, above and well below T_c. It can be seen that for the zz spectrum there is also a loss of scattering strength at low energies which redistributes into the weak and broad pair-breaking peak at higher energies. This peak is apparent in either the raw data (Fig. 3) or in the normalized spectra shown in Fig. 4. Given the strong phonons in this polarizations, to determine the exact position of the pair-breaking peak, which is relatively weak, is not easy. Therefore, in Fig. 4 we present the change between the normal and superconducting spectra in an enhanced manner, where the low-temperature spectrum is normalized by (1) dividing (bottom panel) by the normal state spectrum at 100 K and (2) subtracting the normal-state spectrum (upper panel). As can be seen from the results, the pair-breaking peak is very broad, starting from 200 and extending up to 800 cm^{-1}, with a maximum located between 400 and 500 cm^{-1}. While the change between the normal state and the superconducting state is small, it was reproducibly observed from different crystals. We note in passing that the characteristic energy (200 cm^{-1}) indicated by the dashed line in Fig. 4, where the scattering in the superconducting state shows a deviation from the scattering in the normal state, coincides with the c-axis superconducting gap suggested for $YBa_2Cu_3O_{7-x}$ by McCarty *et al.*[2]

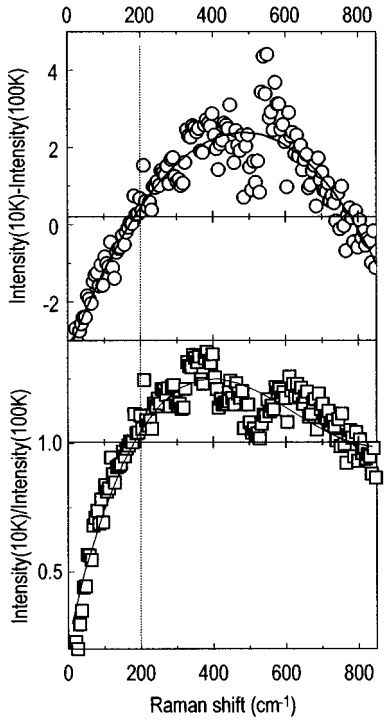

FIG. 4. Normalized superconducting spectra with c-axis polarization obtained by (1) dividing by a normal-state spectrum (upper panel) and (2) subtracting the normal-state spectrum (bottom panel). Solid line in each panel is a guide to the eye. Dashed line indicates the position of the intersection point.

As there are no previously reported electronic Raman-scattering studies on $NdBa_2Cu_3O_{7-x}$, we can compare our superconducting energy gap values only with those obtained from tunneling and far-infrared spectroscopy data.[8,9] In the

tunneling measurements Kasiviswanathan and Rangarajan detected the superconducting gap at 165 cm^{-1} ($2\Delta/T_c \approx 5.3$), and Crawford *et al.*[9] observed an appreciable drop around 400 cm^{-1}, which was interpreted as the manifestation of a superconducting gap.[8] Since the tunneling measurements give us an average gap, the tunneling data correspond better to the A_{1g} Raman contribution to the superconducting gap, representing an average over the Fermi surface. On the other hand, the B_{1g} contribution to the gap comes from particular parts of the Fermi surface. The difference between the two contributions is believed to reflect the in-plane anisotropy of the superconducting gap. Furthermore, we can make a comparison with the Raman data on the isostructural compound $YBa_2Cu_3O_{7-x}$ at similar doping, where for the same in-plane polarizations similar gap anisotropy has been reported.[7,10,11] Moreover, low-frequency behavior and relative intensities in different channels in $NdBa_2Cu_3O_{7-x}$ are consistent with those in $YBa_2Cu_3O_{7-x}$.[5,7,10,11]

While important, the charge dynamics perpendicular to the CuO_2 planes are not well investigated since most superconducting crystals are very thin along the c axis. However, based on analysis of the electronic continuum obtained by a Raman microprobe, McCarty *et al.*[2] placed the superconducting gap in $YBa_2Cu_3O_{7-x}$, measured in the zz polarization, at 200 cm^{-1}, which is very close to our observation when we measure the gap from the intersection point. However, unlike the result of McCarty *et al.*,[2] where no piling up of the electronic states was detected, in our $NdBa_2Cu_3O_{7-x}$ crystals such a redistribution was observed. We note that our crystals in the same polarization showed the linewidth anomaly for the 520 cm^{-1} apical oxygen mode—the linewidth being smaller above the superconducting transition than below. The increased damping inferred from the larger linewidth allows us to guess that there is an increased electronic density of states due to the superconducting gap formation around this energy region. We should mention that a redistribution of the c-axis continuum has been reported by Boekholt, Hoffman, and Guentherodt in $Bi_2Sr_2CaCu_2O_{8+x}$ crystals.[3] In sharp contrast to the data of Boekholt, Hoffman, and Guentherodt, where the c-axis pair-breaking peak was almost half that of the A_{1g} in-plane pair-breaking peak, in our crystals we have larger (or at least equal) superconducting gaps for the A_{1g} c-axis and in-plane responses as seen from comparison of Figs. 2 and 4. On the other hand, if we measure the superconducting gap from the intersection point, there is no difference between the gaps along the c axis and perpendicular to it. The origin of this discrepancy may be caused by different doping conditions (the crystal studied by Boekholt, Hoffmann, and Guentherodt was underdoped as we can judge from the quoted T_c), crystal anisotropy (Bi-based crystals are more two dimensional than $RE123$ crystals), or from other factors affecting the interlayer interactions.

To conclude with this part, we can state that our data on $NdBa_2Cu_3O_{7-x}$ reproduces the main features of electronic scattering in the $YBa_2Cu_3O_{7-x}$ crystal at the same doping, with (i) a reduced scattering at low frequencies being roughly linear in the frequency shift, and (ii) an additional scattering at higher frequency, attributed to a pair-breaking peak whose location differs for the polarized and depolarized spectra.

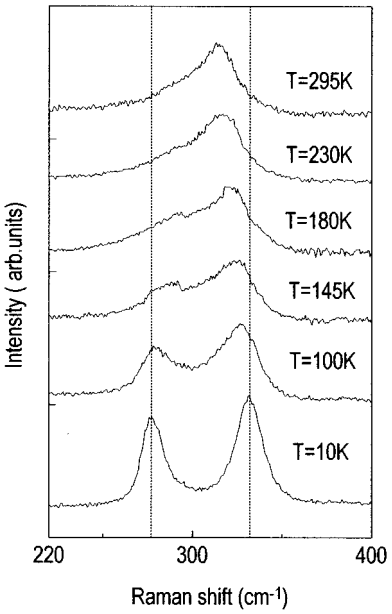

FIG. 5. Temperature dependence of the doubled peak of B_{1g} symmetry.

IV. PHONON RAMAN SCATTERING

Though the superconducting gap had never been studied in the $NdBa_2Cu_3O_{7-x}$ system by electronic Raman scattering before we started our work, the phonon spectrum was the subject of intense study.[12,13] In spite of overall agreement with the spectra of isostructural $YBa_2Cu_3O_{7-x}$, the measurements reported by Yoshida *et al.*[13] reveal at low temperature an additional peak near 290 cm^{-1}. This feature was later ascribed by Heyen *et al.*[12] to crystal-field excitation of the Nd^{3+} $4f$ electrons mixed with the B_{1g} phonon at 320 cm^{-1}. Heyen *et al.*[12] also mentioned other peculiarities such as (i) the relatively high frequencies of metal ions vibrations [Ba (A_{1g}) 142 cm^{-1} and Cu (A_{1g}) 172 cm^{-1}] of the single-crystal $NdBa_2Cu_3O_7$ and (ii) different frequencies for the apical oxygen vibration in the zz and the xx spectra. In our crystal we also observed the double peak around 300 cm^{-1}, which was most pronounced in the $x'y'$ scattering geometry, and the disparity in frequency for the apical oxygen vibration measured in different polarizations which is evident in the spectra shown in Fig. 1.

Figure 5 shows the temperature dependence of the double-peak structure near 300 cm^{-1}. When the temperature decreases, the upper mode shifts to higher frequencies, while the lower mode softens, while strongly gaining in intensity. We note that the softening starts well above T_c. In the isostructural $YBa_2Cu_3O_{7-x}$ system, anomalies of physical properties are sometimes observed above the transition temperature and interpreted as being related to either superconducting fluctuations, or a coupling of the phonons to the spins[14] and the opening of a pseudogap at $T > T_c$. For optimally doped crystals, the softening was reported to start slightly above T_c, though for the underdoped crystals and the crystals with impurities much more pronounced effect is observed with the softening starting 40 K above T_c.[14] The softening starting from room temperature, revealed by our

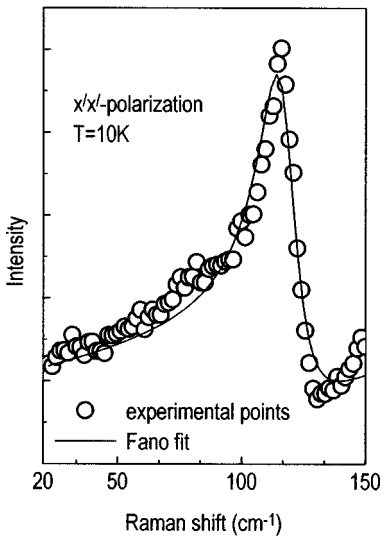

FIG. 6. Illustration of the coupling of the Ba mode to electronic continuum. The phonon has been fit to a Fano profile (solid line) as described in the text.

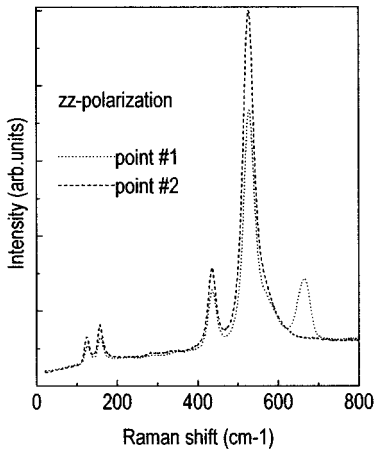

FIG. 7. Illustration of two types of the zz spectrum. Note that the integrated intensity of the high-energy mode for the spectrum presented by the dashed line roughly coincides with that of the two modes for the spectrum presented by the dotted line.

data, is unlikely to be related to superconducting fluctuations. What is also interesting is that the integrated intensity of the double-peak structure strongly deviates from the expected Bose dependence on temperature. Instead of the continuous decrease with temperature expected for the first-order Raman scattering, the integrated intensity increases. It may happen that phonon anomalies observed in this polarization are related to persistence of the B_{1g} symmetry peak in the electronic continuum well above T_c.

While our phonon spectra seem to be consistent at high energies (region of oxygen vibrations), with previous works,[12,13] the low-energy part (related to metal ion modes) is substantially different. In fact, we observe the Ba mode at 117 cm^{-1} and the Cu mode at 154 cm^{-1}, approximately the same values as reported in $YBa_2Cu_3O_{7-x}$.[5] Moreover, the Ba mode demonstrates a well formed antiresonance, evident on the high-energy side, which has not been observed before in previous studies.[12,13] The interference effect due to coupling of the phonon to the electronic continuum is demonstrated in Fig. 6. The coupling is illustrated by fit to a Fano line shape in Fig. 6 (solid line):

$$I(\omega) \propto 2\Gamma\omega(\omega_a^2-\omega^2)^2/(\omega_0^2-\omega^2)^2+4\Gamma^2\omega^2, \qquad (1)$$

where I is the phonon intensity, ω_a and ω_0 are antiresonance and renormalized frequencies, and Γ is the phonon linewidth. Thus, the low-energy part of the $NdBa_2Cu_3O_{7-x}$ spectrum exactly coincides with that of $YBa_2Cu_3O_{7-x}$ and at the point of the interference effect.[15]

Checking the ab plane by a Raman microprobe (spatial resolution better than 2 μm), we found that for the zz polarization not all phonons (relative intensities and frequencies) were reproducible at different points of the sample, indicating inhomogeneity of the crystals. Apart from the spectrum presented in Fig. 1, few points of our crystals provide a spectrum with an additional high-energy mode centered at 665 cm^{-1}. This is illustrated by Fig. 7 where the two different spectra are shown together. As can be seen from Fig. 7, the appearance of the additional high-energy mode is accompanied by a decrease in intensity of the apical oxygen mode. This might be an indication that the two modes are generated by the same ion in different environments. Since the ionic radii of Nd^{3+} and Ba^{2+} are very close, it is known[16] that Nd can occupy the position of Ba. The apical oxygen with a Nd^{3+} ion nearby can, therefore have a different frequency, as observed in our experiment. Additionally, the occupational disorder can reduce the symmetry of the CuO_2 plane, making one of the IR-active modes Raman active, which may be an alternative explanation for the presence of a double-peak structure in the B_{1g} spectrum. Note that the disorder-induced nature of the doubled peak does not explain the temperature anomaly, and at present stage hardly can be considered as a substitute to the well documented crystal-field excitation model.[12]

V. CONCLUSION

In summary, the polarization-dependent measurements of electronic Raman scattering in single-crystal $NdBa_2Cu_3O_{7-x}$ demonstrate substantial in-plane anisotropy in the superconducting gap. This anisotropy is revealed through both the pair-breaking peak position and suppression of scattering in the superconducting state. Specifically, the B_{1g} pair-breaking peak and loss of scattering strength occur at roughly 40% higher energy than those of the A_{1g} symmetry. For the c-axis response, we observed the pair-breaking peak centered between 400 and 500 cm^{-1}. There have been claims of superconducting gap anisotropy in $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$ crystals[2,3] with different gap values parallel and perpendicular to the copper-oxygen planes. Thus, the gap anisotropy studied by us may be a common feature for all high-T_c materials, though its origin remains still unclear.

We have also demonstrated that there is no superconductivity induced renormalization effect for the B_{1g} phonon mode in $NdBa_2Cu_3O_{7-x}$, though one of the modes of the double-peak structure near 300 cm^{-1} shows a substantial

softening starting from room temperature. The integrated intensity of the whole structure does not follow the temperature dependence expected for the first-order Raman scattering. The metal ion vibrations in $NdBa_2Cu_3O_{7-x}$ coincide with those in $YBa_2Cu_3O_{7-x}$ including the Fano interference of the Ba mode for in-plane polarization.

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