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Phonon Raman scattering of $NbBa_2Cu_3O_y$ and $Nd_{1.6}Ba_{1.4}Cu_3O_y$

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Polarized Raman scattering from $NdBa_2Cu_3O_y$ and $Nd_{1.6}Ba_{1.4}Cu_3O_y$ single crystals is reported. Single-phonon peaks have been observed in $NdBa_2Cu_3O_y$ at 136, 168, 316, 448, 508, and 580 cm^{-1} at room temperature where the 316- and 580-cm^{-1} peaks are strong in the (x,x) while the 448- and 508-cm^{-1} peaks are strong in the (z,z) configurations. The 316-cm^{-1} peak is found to separate into two peaks at 290 and 323 cm^{-1} at 4 K, which are assigned as in-phase and out-of-phase vibration of oxygen atoms in the Cu-O plane, respectively. The polarization dependence of the scattering peaks has been explained on the basis of the characteristics of the electronic transitions. The energy shift of peaks when Ba is substituted by Nd has also been discussed.

The recent discovery of high-T_c oxide superconductors[1,2] has led to a plenitude of theoretical models for an attractive electron-electron interaction[3] among which is the conventional electron-phonon coupling model. Weber[4] has shown that a T_c of 40 K is attainable in $La_{2-x}Sr_xCuO_4$ by the electron-phonon coupling model due to the strong coupling of a hole with the stretching vibration of oxygen atoms in the Cu-O plane. On the other hand, in $YBa_2Cu_3O_x$ (Y-Ba-Cu-O), it has been shown that it is difficult to explain the T_c of 90 K by the electron-phonon coupling model.[5]

Intensive studies of Raman spectra of Y-Ba-Cu-O have been performed to understand the role of phonons in the superconductivity. Strongly anisotropic spectra of Y-Ba-Cu-O single crystals have been obtained.[6-8] Five Ag mode phonons are identified[6,7] and the behavior of these modes has been measured under the change of oxygen contents or the substitution of constituent atoms.[9] However, polarization dependence of the scattering lines cannot be explained by the group-theoretical considerations.[6] Also, only a little information has been obtained concerning the stretching mode of oxygen in the Cu-O plane which is expected to have an important role in the superconductivity.[4,5]

$NdBa_2Cu_3O_y$ is a superconductor with T_c of around 90 K and the Y-Ba-Cu-O-type crystal structure. In this compound a solid solution is formed with a formula $Nd_{1+x}Ba_{2-x}Cu_3O_y$ where $0 < x < 0.8$.[10] The concentration of holes can be controlled in this system by changing the composition x.[11] Thus, this system is attractive for investigating the electron-phonon interaction through the renormalization of the phonon energy due to electron-phonon interaction.[4,5]

In the present study we have investigated the Raman spectra of $NdBa_2Cu_3O_y$ and $Nd_{1.6}Ba_{1.4}Cu_3O_y$ single crystals. Anisotropic spectra have been obtained between the polarizations of light along the x and z directions. Scattering lines due to oxygen vibration modes including the stretching mode in the Cu-O plane have been identified. It has been pointed out that the polarization dependence of the scattering lines can be explained by considering the characteristics of the electronic transitions in the Raman-scattering process.

Single crystals of $NdBa_2Cu_3O_y$ were obtained by heating the sintered $NdBa_2Cu_3O_y$ samples at 1150 °C in air for 24 h. The crystals were thin platelets presenting (001) face, as confirmed by x-ray diffraction, with typical dimensions of $1 \times 1 \times 0.1$ mm^3. Superconductive transition temperature 60 K in the zero-field cooled magnetic susceptibility were achieved by annealing the crystals at 400 °C in O_2 environment for 4 d. Single crystals of $Nd_{1.6}Ba_{1.4}Cu_3O_y$, which were semiconductors, were obtained from the liquid phase by cooling equal amounts of $NdBa_2Cu_3O_y$ and CuO powders from 1300 to 900 °C by the rate of 5 °C/h. Compositions of the samples were analyzed by the energy-dispersive x-ray analysis method. The Raman-scattering measurements were carried out using 5145-A light from an argon laser, which was focused onto the ac plane of the sample with a diameter of about 0.1 mm. The incident laser power was maintained below 50 mW to avoid damaging samples. The scattered light was detected with a Jobin Yvon U-1000 double monochromator and the photon-counting detection system.

In Figs. 1(a) and 1(b) the Raman spectra of $NdBa_2Cu_3O_y$ are shown at room temperature in the backscattering geometry in the (z,z) and (x,x) configurations, respectively, where (z,z) $[(x,x)]$ means that the polarization of both the incident and scattered lights are parallel to the crystallographic c axis (a axis). Because of twinning in the a-b plane, we cannot distinguish between (x,x) and (y,y) Raman polarization. There is no detectable depolarization (z,x) or (x,z) scattering to within noise. In the (z,z) configuration peaks are seen at 136, 168, 448, and 508 cm^{-1} and broad structures at around 780 and 1000 cm^{-1}. The 508-cm^{-1} peak is shifted to the lower-energy side in comparison with the 513 cm^{-1} of sintered samples.[12] This fact implies that our sample has oxygen deficiency[13] which is consistent with the T_c of 60 K. The Raman shift of the 1000 cm^{-1} structure is about twice that of the 508-cm^{-1} peak. Thus, it is supposed that the 1000-cm^{-1} structure is caused by the two-phonon scattering of the 508-cm^{-1} phonon. In the (x,x) configuration peaks are seen at 136, 316, and 580 cm^{-1} and a broad structure at around 1160 cm^{-1}. Sharp peaks around 100 cm^{-1} are caused by the rotational vibration of oxygen molecules in the air. The 1160-cm^{-1} structure

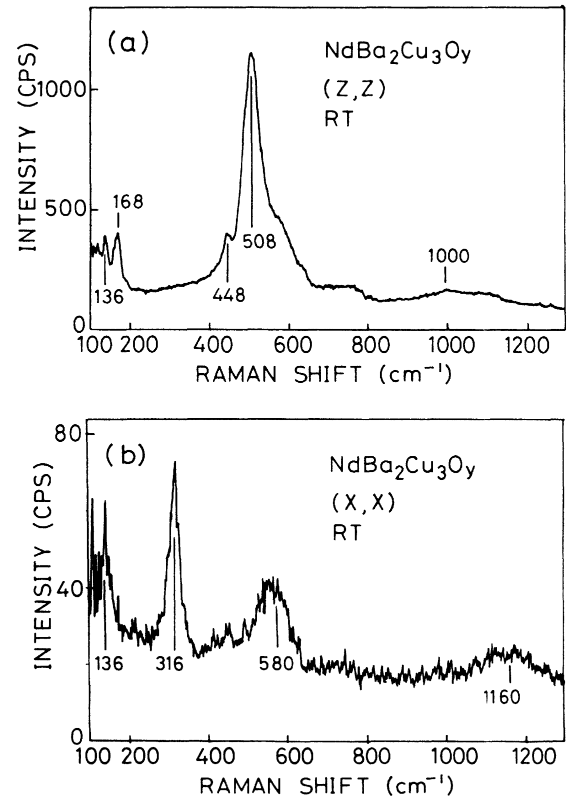

FIG. 1. Raman spectra from the a-c plane of the $NdBa_2Cu_3O_y$ single crystal at room temperature with polarization configurations of (a) (z,z) and (b) (x,x).

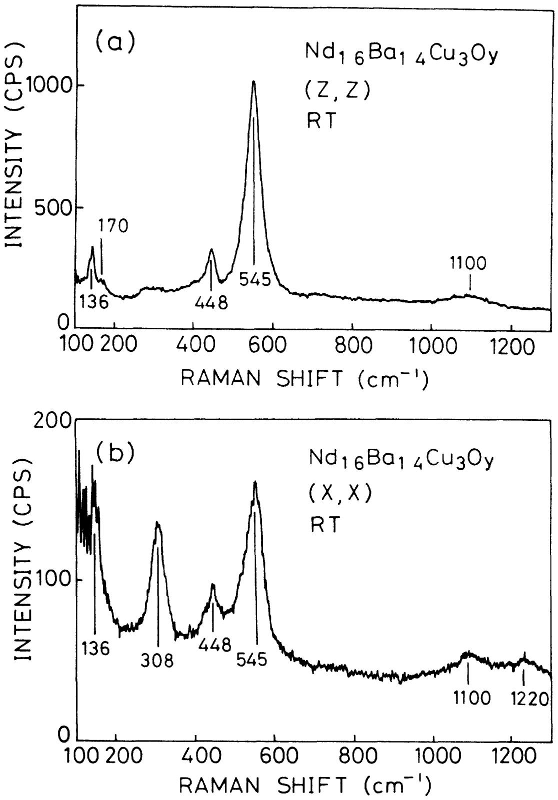

FIG. 3. Raman spectra from the a-c plane of the $Nd_{1.6}Ba_{1.4}Cu_3O_y$ single crystal at room temperature with polarization configurations of (a) (z,z) and (b) (x,x).

can be ascribed to the two-phonon scattering of the 580-cm^{-1} phonon.

It has been found that the 316-cm^{-1} peak in Fig. 1(b) is constructed by two peaks. In Fig. 2 the Raman spectrum of $NdBa_2Cu_3O_y$ is shown at 4 K in the (x,x) configuration. It is shown that the 316-cm^{-1} peak in Fig. 1(b) separates into two peaks at 323 and 290 cm^{-1}. The origin of these peaks will be described later.

In Figs. 3(a) and 3(b) the Raman spectra of $Nd_{1.6}Ba_{1.4}Cu_3O_y$ are shown at room temperature in the (z,z) and (x,x) configurations, respectively. In Fig. 3(a) peaks are observed at 136, 170, 448, 545, and 1100 cm^{-1}. It has been found that, by the subtitution of Ba by Nd, the 508-cm^{-1} peak of $NdBa_2Cu_3O_y$ shift considerably to the higher-energy side while the positions of 136-, 168-, and 448-cm^{-1} peaks hardly change. The two-phonon scattering lines are observed at 1100 cm^{-1} in Fig. 3(a) in accord with the single-phonon energy of 545 cm^{-1}. In Fig. 3(b) peaks are observed at 136, 308, 448, 545, 1100, and 1220 cm^{-1}. Peaks at 448, 545, and 1100 cm^{-1} are seen both in (x,x) as well as in (z,z) configurations. The 316 cm^{-1} peak in Fig. 1(b) shifts to the lower-energy side to 308 cm^{-1} in Fig. 3(b). On the other hand, the 1160-cm^{-1} peak in Fig. 1(b) shifts to the higher-energy side to 1220 cm^{-1}, which implies that the single-phonon energy increases from 580 to 610 cm^{-1}.

Anisotropic phonon features have been obtained in Figs. 1 and 3. We consider the identification of these features below. The crystal structure of $NdBa_2Cu_3O_y$ is shown in Fig. 4, which is similar to that of Y-Ba-Cu-O. There are five Ag mode phonons in this structure. In the Raman spectra of Y-Ba-Cu-O Ag symmetry peaks are observed at 116, 150, 340, 440, and 500 cm^{-1}, where the 340-cm^{-1} peak is strong in the (x,x) and the 440- and 500-cm^{-1} peaks are strong in the (z,z) configurations.[6,7] Liu *et al.*[7] gave the assignments of these peaks on the basis of their phonon-energy calculation. According to

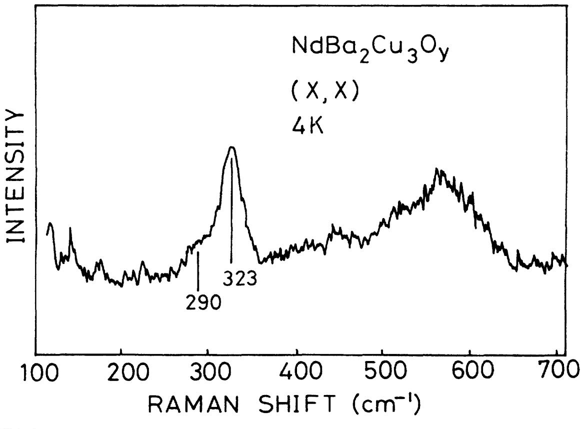

FIG. 2. Raman spectrum from the a-b plane of the $NdBa_2Cu_3O_y$ single crystal at 4 K with configuration (x,x).

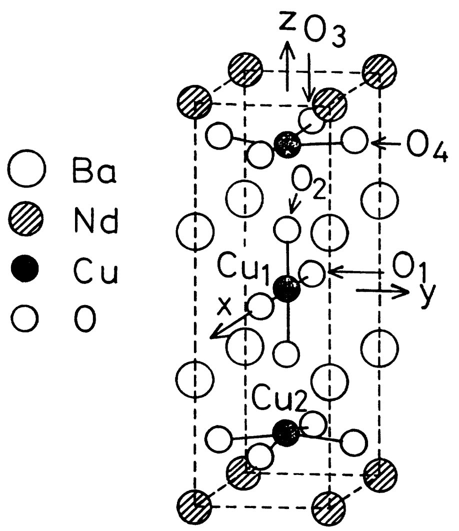

FIG. 4. Crystal structure of $\mathrm{NdBa_2Cu_3O_y}$.

them, the two lower-energy peaks are due to the vibration of Ba (116 cm^{-1}) and Cu (150 cm^{-1}). The three higher-energy peaks are due to the vibration of oxygen atoms where the 340- and 440-cm^{-1} peaks are assigned to the out-of-phase and in-phase vibration of O(3) and O(4) atoms along the c axis, respectively, and the 500-cm^{-1} peak the vibration of the O(2) atom along the c axis. However, the energy difference of 100 cm^{-1} between the 340- and 440-cm^{-1} peaks is too large in comparison with the expected value of about 20 cm^{-1} as the difference between the in-phase and out-of-phase vibration of the O(3) and O(4) atoms.[7] Also, the polarization dependence of these two peaks, that the in-phase vibration is strong in the (x,x) configuration while the out-of-phase vibration is strong in the (z,z) configuration, could not be explained. In the present experiment, it has been found that the 316-cm^{-1} peak in $\mathrm{NdBa_2Cu_3O_y}$ is constructed by two components. We ascribe the peak at 290 and 323 cm^{-1} in Fig. 2 to the in-phase and out-of-phase vibrations of the O(3) and O(4) atoms, respectively. Both of these scatterings are strong in the (x,x) configuration. On the other hand, scattering due to the vibration of the O(2) atom [508-cm^{-1} peak in Fig. 1(a)] is strong in the (z,z) configuration. These polarization dependences cannot be explained by group-theoretical consideration since these scatterings are allowed both in (x,x) and (z,z) configurations. However, they can be explained by considering the characteristics of the electronic transition as follows.

The Raman scattering is the third-order perturbation process which consists of (i) virtual creation of the electron-hole pair by the absorption of light, (ii) scattering of the electron or hole by phonons, and (iii) radiative annihilation of the electron-hole pair.[14] The polarization of light has a crucial role in determining the electron and the hole which take part in the Raman scattering.

According to the band-structure calculation of Y-Ba-Cu-O by Mattheiss and Hamann[15] it is conjectured that the valence bands of Y-Ba-Cu-O are constructed by antibonding Cu—O bonds. They contain $3d_{x^2-y^2}$ of Cu(2), $3d_{x^2-z^2}$ of Cu(1), $2p_x$ of O(3), $2p_y$ of O(4), $2p_z$ of O(2), and $2p_x$ of O(1) orbitals, among which $2p_x$ of O(3) and $2p_y$ of O(4) orbitals are the highest in energy and holes are doped in these bands by doping.[16] The conduction bands where electrons are excited by the absorption of light is supposed to be the upper Hubbard band[17] of Cu $3d$ states. Thus, according to the selection rule of the dipole transition, the radiative transtion occurs mainly between $2p_x$ $(2p_y)$ of the O(3) [O(4)] atom and $3d_{x^2-y^2}$ of Cu(2) for the x-polarized (y-polarized) light and between $2p_z$ of O(2) and $3d_{x^2-z^2}$ of Cu(1) for the z-polarized light. Thus, holes are created on the O(2) atom in the (z,z) configuration and the O(3) [O(4)] atom in the (x,x) $[(y,y)]$ configuration. Holes on the O(2) atom [O(3) or O(4) atoms] are expected to couple strongly with the vibration of the O(2) atom [O(3) or O(4) atoms] unless the coupling is forbidden by the symmetry condition.

The fact that the 508-cm^{-1} peak (316-cm^{-1} peak) is not observed in the (x,x) $[(z,z)]$ configuration implies that the holes are localized on the O(2) cite [O(3) and O(4) cites] near perfectly and the tight-binding picture holds well in this compound. On the other hand, this picture does not hold in $\mathrm{Nd_{1.6}Ba_{1.4}Cu_3O_y}$ since in the Raman spectra of $\mathrm{Nd_{1.6}Ba_{1.4}Cu_3O_y}$ [Figs. 3(a) and 3(b)], the 545-cm^{-1} peak which we ascribe to the same origin as the 508-cm^{-1} peak in $\mathrm{NdBa_2Cu_3O_y}$, is seen in the (x,x) as well as in the (z,z) configurations. This is probably because the lattice constant of $\mathrm{NdBa_2Cu_3O_y}$ along the c axis becomes small as Ba is substituted by Nd (Ref. 18) so that the distance between O(2) and O(3) [O(2) and O(4)] atoms becomes small and the interaction of holes on O(3) [O(4)] with the vibration of the O(2) atom becomes strong.

Next, we consider the origin of the 448-cm^{-1} peak in $\mathrm{NdBa_2Cu_3O_y}$. This peak is strong in the (z,z) configuration as shown in Figs. 1(a) and (b). Thus, it is supposed that the 448-cm^{-1} peak is associated with the vibration of the O(2) atom. According to the calculation of Y-Ba-Cu-O by Liu *et al.*, the bending modes of O(2) atoms with B_{2u} or B_{3u} symmetries are expected to have energies around 400 cm^{-1} (TO modes, 361 and 429 cm^{-1}; LO modes, 454 and 485 cm^{-1}). These modes have large TO-LO splittings implying large effective charges. Thus, it is expected that these modes have a strong Frohlich-type interaction.[19] We ascribe the 448-cm^{-1} peak (440-cm^{-1} peak in Y-Ba-Cu-O) to the bending vibration of O(2) atoms which becomes Raman allowed in the (z,z) configuration due to the intraband scattering of the $2p_z$ hole on O(2) through the Frohlich-type interaction.

In Fig. 1(b) peaks have been observed at 580 and 1160 cm^{-1}. These peaks can be associated with the vibration of O(3) and/or O(4) atoms by their polarization dependence. We assign these peaks to the stretching vibration of O(3) or O(4) atoms along the x or y direction (B_{2u} or B_{3u}) since these modes are expected to have energies around 580 cm^{-1}.[7] Intensity of the 580-cm^{-1} peak changes from sample to sample suggesting a defect-induced nature. In the spectrum of $\mathrm{Nd_{1.6}Ba_{1.4}Cu_3O_y}$, first-order scattering peak of the 610-cm^{-1} phonon has not been observed [Fig. 3(b)]. This fact also suggests the defect-induced mechanism of the 580-cm^{-1} peak in $NdBa_2Cu_3O_y$.

By the substitution of Ba with Nd, the 508- and 580-cm^{-1} peaks in $NdBa_2Cu_3O_y$ are found to shift to the higher-energy side. The lattice constant along the c axis becomes considerably small by the substitution, as described above. Thus, the frequency of the 508-cm^{-1} mode [vibration of O(2) along the z axis] is expected to increase, which agree with the experimental results. The crystal structure changes from orthorhombic to tetragonal at $x = 0.3$. However, the average of the lattice constants along the a and b axis is nearly constant.[18] Weber has pointed out that the energy of the stretching mode of O(3) and O(4) in $YBa_2Cu_3O_y$ decreases considerably when holes are introduced by doping through the strong coupling of this vibration mode with holes.[4] Since by the replacement of Ba by Nd the concentration of the hole becomes small, the decrease of the energy of the stretching mode of O(3) and O(4) atoms in $NdBa_2Cu_3O_y$ in comparison with $Nd_{1.6}Ba_{1.4}Cu_3O_y$ may be explained by the renormalization of the phonon energy by the strong coupling of this mode with holes.

In summary, anisotropic Raman spectra of $NdBa_2Cu_3O_y$ and $Nd_{1.6}Ba_{1.4}Cu_3O_y$ have been obtained between the polarization configurations (x,x) and (z,z). Scattering due to the vibration of the O(2) atom is strong in the (z,z) configuration while that of O(3) and O(4) atoms in the (x,x) configuration. This polarization dependence has been explained by the fact that holes are created on the O(2) atom in the (z,z) configuration and on the O(3) and O(4) atoms in the (x,x) configuration. The 316-cm^{-1} peak in $NdBa_2Cu_3O_y$ is found to be constructed by two components, which are assigned as the in-phase and out-of-phase vibration of O(3) and O(4) atoms. The 448-cm^{-1} peak is assigned to the bending vibration of the O(2) atom being different from the previous assignment as the in-phase vibration of O(3) and O(4) atoms. The scattering peak, due to the stretching vibration of O(3) and O(4) atoms, has also been identified, which shifts to the higher-energy side when Ba is substituted by Nd.

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