

Raman scattering by phonons in orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals

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The Raman scattering spectra of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals have been measured in all polarizations and for various crystallographic directions. The observed vibrations are classified.

The phonon spectrum is a pertinent topic for research on the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. In this letter we are reporting studies of long-wave optical phonons in single crystals of this superconductor, carried out by the Raman scattering method. This method can reveal the reference frequencies of the even modes at the center of the Brillouin zone. Spectra of the Raman scattering by phonons in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were obtained previously from polycrystalline samples.^{1–4} Since it is not possible to determine the symmetry of vibrations in polycrystalline samples, the interpretation of the observed modes was of basically a hypothetical nature. By working with single crystals we have been able to resolve more modes in the Raman spectra and to classify them on the basis of symmetry considerations and also on the basis of the existing calculations on vibrations in the rigid-bond approximation.⁴

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were grown by slowly cooling a molten mixture of the oxides Y_2O_3 , BaO , and CuO in air with compositions on the CuO -rich side of the stoichiometry of the compound (1:2:3). The samples were rectangular plates with mirror-finish faces with dimensions up to $2 \times 2 \times 0.2$ mm³. They exhibited a

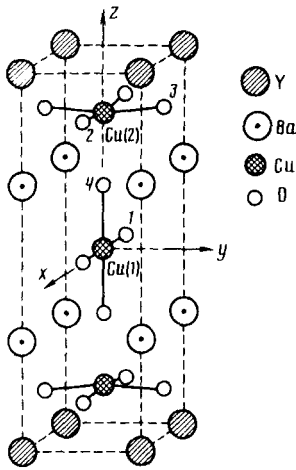


FIG. 1. Unit cell of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystals.

transition to the superconducting state at $T = 90 \pm 3$ K. The single crystals were of orthorhombic symmetry [the group $D_{2h}(P_{mmm})$; $a = 3.86 \text{ \AA}$, $b = 3.92 \text{ \AA}$, $c = 11.59 \text{ \AA}$] and contained a large number of twins with a transverse dimension less than $0.1 \mu\text{m}$ and a $\langle 110 \rangle$ twinning axis.⁵

Raman scattering spectra were measured for various faces of the single crystals in the "backscattering" geometry at 300 K on a spectrometer with a microscope attachment. The laser beam ($\lambda = 4880 \text{ \AA}$ or 5145 \AA) was focused onto the sample in a spot $3\text{--}10 \mu\text{m}$ in size. We kept the power of the laser beam at the sample from exceeding 10 mW in order to avoid a pronounced heating of the excited region. From the ratio of the intensities of the Stokes and anti-Stokes components of the Raman spectrum we found that the heating did not exceed 40° .

The $\text{YBa}_2\text{Cu}_3\text{O}_7$ unit cell contains 13 atoms (Fig. 1).^{6,7} In it there are two Cu(2)-(2,3) plane layers, which form a two-dimensional rectangular lattice, and a linear chain Cu(1)-O(1)-Cu(1)-O(1). The oxygen O(4) forms a bridge between Cu(1) and Cu(2). The vibrational spectrum has 36 optical and three acoustic modes. The vibrations of the atoms Y, Cu(1), and O(1), which have a local symmetry D_{2h} , are active only in the IR absorption: $[3(B_{1u} + B_{2u} + B_{3u})]$. The positional symmetry for the O(2), O(3), O(4), Cu(2) and Ba atoms, which are positioned symmetrically with respect to the (xy) plane, is C_{2v} . Their vibrations each contribute three active modes to the IR absorption $[5(B_{1u} + B_{2u} + B_{3u})]$ and to the Raman scattering $[5(A_g + B_{2g} + B_{3g})]$. The completely symmetric vibrations of these atoms are active in the Raman spectra in the (zz) polarization. These are valence vibrations of O(4) and deformation vibrations of the atoms of the Cu(2)-O(2)-O(3) layer and of the Ba atoms. The B_{2g} and B_{3g} vibrations are active in the (zx) and (zy) polarizations, respectively. Consequently, five vibrations are allowed in each of the polarizations (zz) , (zx) , and (zy) in the Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystals with orthorhombic symmetry D_{2h}^1 , and there are no allowed vibrations in the other polarizations.

Figure 2 shows experimental Raman spectra in the (zz) , (zx) , and (zy) polariza-

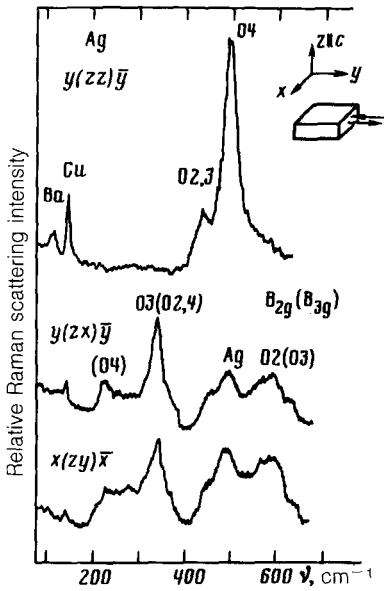


FIG. 2. Raman spectra (Stokes components) of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ single crystals in the (zz) , (zx) , and (zy) polarizations at $T = 300$ K. The $y(zx)\bar{y}$ and $x(zy)\bar{x}$ spectra were recorded at an amplification four times that used in the recording of the $y(zz)\bar{y}$ spectrum.

tions. The most intense spectrum of Raman scattering by phonons, which corresponds to a diagonal component of the polarizability tensor, is observed in the (zz) polarization. In this polarization, we see four lines: 113 , 145 , 435 , and 495 cm^{-1} . The lines in the (zx) and (zy) polarizations are of noticeably lower intensity (lower by about an order of magnitude) and have a greater half-width. It is interesting to note that the spectra recorded in these polarizations are the same. We believe that the reason for this agreement is a microtwinning of the single crystals, which has the consequence that the excited region, with a size of $3\text{--}5$ μm , always contains twins with Ox and Oy axes.

In order to classify the observed vibrations, we need to consider, in addition to the symmetry, the differences among the masses of the vibrating atoms. The lowest-frequency vibrations in the (zz) spectrum (113 and 145 cm^{-1}) should be assigned to A_g vibrations of the heavy atoms Ba and Cu(2), respectively. In a previous interpretation of the Raman spectra of ceramic samples, in which the weak line at 113 cm^{-1} was not spectrally allowed, the line at 145 cm^{-1} was associated with Ba vibrations.³ The incompletely symmetric (B_{2g} and B_{3g}) vibrations of the heavy atoms, which are allowed in the (xz) and (yz) polarizations, respectively, should have even lower frequencies.⁴ Because of the low efficiency of these modes, we were not able to detect them in the spectrum.

The highest-frequency vibrations among the vibrations of oxygen are the Cu-O valence vibrations. Included in this group are the completely symmetric A_g vibrations of O(4) along the z axis and the B_{2g} vibrations of the O(2)-Cu(2) bond and the B_{3g} vibrations of the O(3)-Cu(2) bond. On this basis we assign the line at 495 cm^{-1} in the (zz) spectrum to O(4) valence vibrations, and we assign the wide line at 585 cm^{-1} in the (zx) and (zy) spectra to valence vibrations of O(2) and O(3). The high intensi-

ty of the line at 495 cm^{-1} in the (zz) spectrum agrees with the expected large polarizability of the unit cell for the A_g vibrations of O(4). Furthermore, the frequency ratio ($\approx 5:6$) of the valence vibrations of O(4) and O(2,3) agrees well with the ratio estimated in Ref. 4 on the basis of the rigid-bond model and the interparticle distances.

The remaining vibrations of the oxygen atoms are in the deformation category. According to estimates of the frequencies of these vibrations carried out⁴ on the basis of the rigid-bond model, we would expect the frequencies of the incompletely symmetric deformation vibrations of the oxygen atoms O(2) and O(3) in the Cu(2)-O(2,3) plane (the B_{2g} and B_{3g} modes) and of the oxygen atoms O(4) along the Cu(1)-O(1)-Cu(1) chain (the B_{2g} mode) to be approximately equal to each other and lower by a factor of about 1.5–2 than the frequencies of the valence vibrations. The frequency of the O(2) vibrations of the B_{3g} type [perpendicular to the Cu(1)-O(1)-Cu(1)-O(1) chain] should be substantially lower. Taking these estimates into account, we assign the wide line at 335 cm^{-1} in the (zx) and (zy) spectra to the spectrally unresolved B_{2g} (B_{3g}) modes for O(2) [O(3)] and the B_{2g} mode for O(4). We assign the lower-frequency line at 220 cm^{-1} to B_{2g} vibrations of O(4). The reason for the manifestation of the B_{3g} vibrations in the (zx) spectrum is that the measured (zx) spectra [like the (zy) spectra] consist of a mixture of (zx) and (zy) polarizations, because of a microtwinning of the single crystals. The faint lines at 495 and 145 cm^{-1} in the (zx) and (zy) spectra, which coincide in position with intense lines in the (zz) spectrum, should probably be assigned to A_g vibrations. They are manifested in these spectra because of the use of a large-aperture objective.

The two completely symmetric deformation vibrations of oxygen, O(2) and O(3), along the z axis, with frequencies which are expected to be close together because of the small difference between the lengths of the Cu–O bonds, should be seen in the (zz) spectrum. We associate these vibrations with the line at 435 cm^{-1} . This frequency is greater than that estimated in Ref. 4 ($\approx 350\text{ cm}^{-1}$). The reason for this discrepancy is not clear to us.

We note in conclusion that in the Raman spectra recorded in the (xx) and (xy) polarizations we also detected two faint lines (at frequencies ~ 330 and $\sim 135\text{ cm}^{-1}$) with intensities which varied wildly from sample to sample and from one observation point to another in a given sample. We observed these lines, with a higher intensity, in the Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals of tetragonal symmetry, with a greater oxygen deficiency. We therefore suggest that these lines are due to microscopic inclusions of a tetragonal phase in the single crystals, because of the inhomogeneous distribution of oxygen in the samples.

In summary, of the 15 vibrational modes of $\text{YBa}_2\text{Cu}_3\text{O}_7$ which are active in the Raman spectra, we have classified five completely symmetric and six incompletely symmetric vibrations. These are valence vibrations of oxygen atoms O(4) (A_g) with $\nu = 495\text{ cm}^{-1}$ and O(2) (B_{2g}) and O(3) (B_{3g}) with $\nu \approx 585\text{ cm}^{-1}$; deformation vibrations of oxygen atoms O(2) and O(3) (A_g) with $\nu \approx 435\text{ cm}^{-1}$, of O(2) (B_{3g}), O(3) and O(4) (B_{2g}) with $\nu \approx 335\text{ cm}^{-1}$, and of O(4) (B_{3g}) with $\nu \approx 220\text{ cm}^{-1}$; and also A_g vibrations of Ba with $\nu = 113\text{ cm}^{-1}$ and of Cu(2) with $\nu = 145\text{ cm}^{-1}$.

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