

# Isotopic effect in the Raman spectra of orthorhombic and tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals

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The spectra of the Raman scattering of light by phonons have been studied for various polarizations and various crystallographic directions in orthorhombic and tetragonal single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta < 0.7$ ) containing the isotopes  $^{16}\text{O}$  and  $^{18}\text{O}$ . The vibrations associated with oxygen are classified. The isotopic shifts of the frequencies upon the replacement of  $^{16}\text{O}$  by  $^{18}\text{O}$  are determined.

We have studied the isotopic effect which occurs in the spectra of the Raman scattering of light by phonons in orthorhombic and tetragonal single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta < 0.7$ ) upon the replacement of the oxygen isotope  $^{16}\text{O}$  by  $^{18}\text{O}$ . We have utilized this effect to find a more reliable classification of the oxygen vibrations in these crystals.

The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single crystals are grown by slowly cooling a molten mixture of the oxides  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{BaO}$  on the  $\text{CuO}$ -rich side of the stoichiometric composition (1:2:3). The samples are rectangular wafers with dimensions of  $2 \times 2$  mm in the basal plane and a thickness of 0.03–0.1 mm (Ref. 1). The lattice symmetry of the resulting single crystals is monitored by x-ray diffraction. The original crystals were present in two modifications: orthorhombic (with a small oxygen deficiency  $\delta < 0.3$ ) and tetragonal (with  $\delta \sim 0.5$ ). The orthorhombic single crystals of symmetry group  $D_{2h}^1 (P_{mmm})$  contain a large number of twins (with a thickness  $< 0.1 \mu\text{m}$ ), oriented along the  $\langle 111 \rangle$  axis. The tetragonal crystals are of symmetry  $D_{4h}^1$ . The superconducting transition temperature depends on the oxygen concentration, lying in the range 92–80 K for the orthorhombic single crystals and not exceeding 60 K for the tetragonal crystals.

To enrich the crystals with the oxygen isotope  $^{18}\text{O}$ , we used the technique which was used in Ref. 2 for ceramic samples. Specifically, the samples are first annealed in vacuum at 400 °C for 3 h. They are then annealed in an  $^{18}\text{O}$  atmosphere at 900 °C for 12 h. The subsequent cooling to 500 °C is carried out at a rate of 150 deg/h. At 500 °C, the samples are held for 4 h and then cooled to room temperature at a rate of 200 deg/h. As a result of this annealing, the crystals become enriched to  $\sim 80\%$  in the isotope  $^{18}\text{O}$ . However, the samples are not adequately homogeneous in terms of oxygen concentration, and regardless of their initial state, they contain regions of both the orthorhombic and the tetragonal phases.

We measure the Raman spectra on various faces of the single crystals in the backscattering geometry at room temperature, using a spectrometer with a microscope attachment. A laser beam ( $\lambda \approx 4880$  or  $5145 \text{ \AA}$ ), with a power up to 10 mW (at the

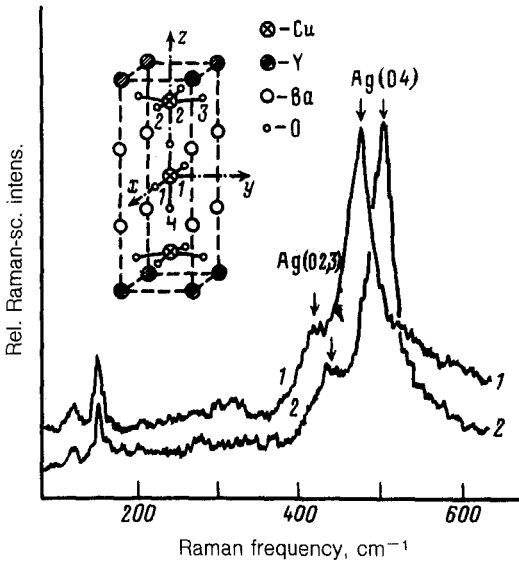


FIG. 1. Raman spectra (Stokes components) or orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta < 0.3$ ) single crystals containing (line 1) the oxygen isotope  $^{18}\text{O}$  and (line 2)  $^{16}\text{O}$ . These spectra were recorded in the polarizations  $x(zz)\bar{x}$  at 300 K. The inset shows the unit cell of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

sample), is focused into a spot 3–5  $\mu\text{m}$  in size. The beam can thus be scanned over the sample, and regions with various oxygen concentration can be selected.

The primitive cell of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (see the inset in Fig. 1) contains 13 atoms.<sup>3,4</sup> The active vibrations in the Raman spectra are the Ba atoms, Cu(2), and three oxygen atoms, O(2, 3, 4), which are positioned symmetrically with respect to the  $xy$  plane and which have a local symmetry  $C_{2v}$ . Each of their vibrations contributes three modes which are active in the Raman scattering:  $A_g + B_{2g} + B_{3g}$ . The  $B_{2g}$  and  $B_{3g}$  vibrations are active in the polarizations  $(xz)$  and  $(yz)$ , respectively; the completely symmetric  $A_g$  vibrations are predominately active in the  $zz$  polarization.

The primitive cell of tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$  (see the inset in Fig. 2) differs from that of the orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in that it does not contain the oxygen atom O(1), whose vibrations are inactive in the Raman scattering. Accordingly, the total number of vibrations active in the Raman scattering remains the same. When we go from the orthorhombic symmetry to the tetragonal symmetry, the vibrations transform in the following way. All of the  $B_{2g}$  and  $B_{3g}$  vibrations become doubly degenerate  $E_g$  vibrations; the  $A_g$  vibrations of the Ba, Cu(2), and O(4) atoms convert into  $A_{1g}$  vibrations. The only radical changes are those in the  $A_g$  vibrations of the O(2) and O(3) atoms ( $2A_g \rightarrow A_{1g} + B_{1g}$ ). The reason for these changes is that in the tetragonal crystals these atoms become equivalent. The  $B_{1g}$  mode corresponds to a diagonal polarizability tensor of O with a zero trace,

$$\begin{pmatrix} C & \cdot & \cdot \\ \cdot & -C & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$$

and it is active in the Raman spectra for the  $xx$  and  $yy$  polarizations.

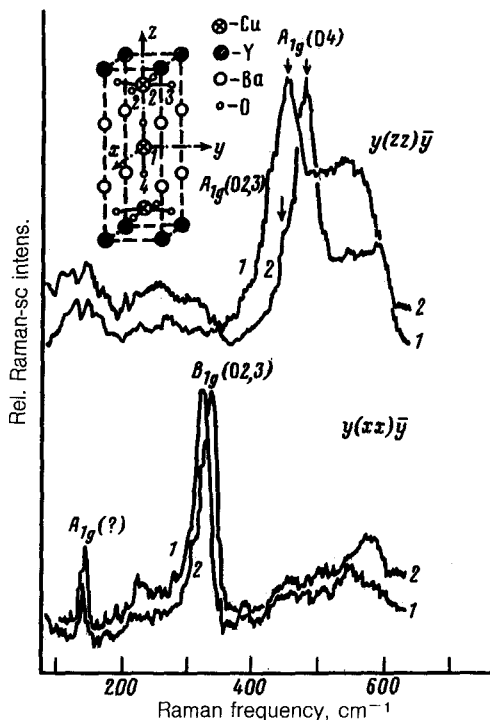


FIG. 2. Raman spectra (Stokes components) of tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \sim 0.5$ ) single crystals containing (line 1) the oxygen isotope  $^{18}\text{O}$  and (line 2)  $^{16}\text{O}$ . The spectra were recorded in the polarizations  $y(zz)\bar{y}$  and  $y(xx)\bar{y}$  at 300 K. The inset shows the unit cell of  $\text{YBa}_2\text{Cu}_3\text{O}_6$ .

Figure 1 shows the Raman spectra of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single crystals containing  $^{16}\text{O}$  and  $^{18}\text{O}$ , recorded in the  $zz$  polarization. The replacement of  $^{16}\text{O}$  by  $^{18}\text{O}$  is seen to cause a softening of the two high-frequency modes ( $435$  and  $498\text{ cm}^{-1}$ ), of about 4%. This figure is slightly lower than that which would be expected on the basis of the ratio of the masses of  $^{16}\text{O}$  and  $^{18}\text{O}$  ( $\sim 5.5\%$ ). The reason for the discrepancy may be the incomplete ( $\sim 80\%$ ) replacement of  $^{16}\text{O}$  by  $^{18}\text{O}$  in these crystals. The lines at  $435$  and  $498\text{ cm}^{-1}$  thus belong to oxygen vibrations, in agreement with the earlier assignment of the  $498\text{-cm}^{-1}$  line to valence vibrations of the  $\text{C}(1)\text{-O}(4)$  bond.<sup>1,5,6</sup> The line at  $435\text{ cm}^{-1}$  belongs to deformation vibrations of  $^{1,5}\text{O}(2)$  and  $\text{O}(3)$ , whose frequencies are expected to be nearly the same because of the small difference in the lattice constants  $a$  and  $b$  ( $\sim 1.5\%$ ).

As the oxygen deficiency in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  increases, we observe a softening of the  $498\text{-cm}^{-1}$  mode, while the  $435\text{-cm}^{-1}$  mode becomes harder. In the  $zz$  spectrum of the tetragonal single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \sim 0.5$ ) the Raman line associated with  $\text{Cu}(1)\text{-O}(4)$  vibrations corresponds to a frequency of  $472\text{ cm}^{-1}$ . The mode corresponding to the  $A_{1g}$  vibrations of the equivalent atoms  $\text{O}(2, 3)$  is seen as a slight shoulder ( $\sim 440\text{ cm}^{-1}$ ) on the low-frequency edge of the  $472\text{-cm}^{-1}$  line. This behavior of the vibration frequencies of the  $\text{O}(4)$  and  $\text{O}(2, 3)$  atoms correlates well with the changes which occur in the unit cell as the oxygen concentration decreases: The  $\text{Cu}(1)\text{-O}(4)$  bond becomes longer, and the distance between the  $\text{Ba}$  and  $\text{Y}$  atoms

becomes slightly smaller.<sup>3,4</sup> The relationship between the 472-cm<sup>-1</sup> line and the vibrations of oxygen in the tetragonal crystals is confirmed by the observed 4% decrease in the frequency of this mode in the Raman spectrum upon the replacement of <sup>16</sup>O by <sup>18</sup>O (Fig. 2).

In the tetragonal crystals the vibrations of the equivalent oxygen atoms O(2) and O(3) have, in addition to the  $A_{1g}$  mode, which is manifested in the  $zz$  polarization ( $\sim 440$  cm<sup>-1</sup>), a  $B_{1g}$  mode, which is active in only the  $xx$  or  $yy$  polarization. It can be seen from Fig. 2 that the  $xx$  spectrum of the tetragonal crystals has two lines: at 137 and 332 cm<sup>-1</sup>. Enrichment with the isotope <sup>18</sup>O does not cause a significant shift of the 137-cm<sup>-1</sup> line, while the line at 332 cm<sup>-1</sup>, like the line at 472 cm<sup>-1</sup>, shifts to an energy about 4% lower, indicating that this line is associated with vibrations of oxygen atoms. To check the symmetry of the 332-cm<sup>-1</sup> mode, we studied the behavior of the corresponding Raman-scattering line in the  $xx$ ,  $xy$ ,  $x'x'$ , and  $x'y'$  polarizations (Fig. 3) (the  $x'$  and  $y'$  axes are rotated 45° from the  $x$  and  $y$  axes). The presence of the 332-cm<sup>-1</sup> line in the  $xx$  and  $x'y'$  polarizations, on the one hand, and the disappearance of this line in the  $xy$  and  $x'x'$  polarizations, on the other, constitute evidence that this line corresponds to a mode with symmetry  $B_{1g}$ . It can thus be suggested that the two  $A_g$  deformation vibrations of the O(2) and O(3) atoms, with the frequency  $\nu \sim 435$  cm<sup>-1</sup> in the orthorhombic crystals, convert into a single  $A_{1g}$  vibration with a frequency of 440 cm<sup>-1</sup>, and one  $B_{1g}$  vibration, with a frequency of 332 cm<sup>-1</sup>, in the tetragonal

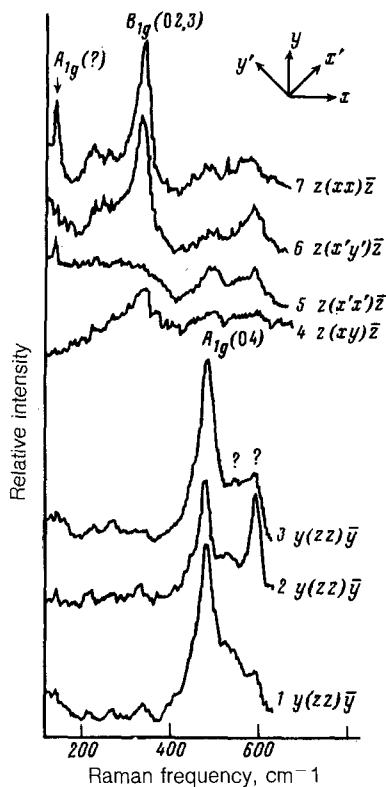


FIG. 3. Raman spectra of tetragonal single crystals containing the isotope <sup>16</sup>O recorded in various polarizations. 1-3—For the polarization  $y(zz)\bar{y}$ , from various points in the sample. The  $x'$  and  $y'$  axes are rotated 45° from the  $x$  and  $y$  axes.

crystals. It should be noted, however, that for the  $B_{1g}$  vibrations of the oxygen atoms O(2) and O(3) there are no displacement of the atoms in the  $xy$  plane. Consequently, the observation of these vibrations in the Raman spectrum in the  $xx$  polarization may be a consequence of a strong electron-phonon interaction.

Comparison of Figs. 1 and 2 shows that two additional high-frequency modes, at  $\sim 540 \text{ cm}^{-1}$  and  $\sim 590 \text{ cm}^{-1}$ , appear in the Raman spectra of the tetragonal crystals in the  $zz$  polarization. Each of these lines undergoes a significant shift down the energy scale when the  $^{16}\text{O}$  is replaced by the  $^{18}\text{O}$ ; these lines are therefore related to oxygen vibrations. The intensities of these lines vary markedly from one point in the sample to another, as is shown by curves 1–3 in Fig. 3. It can thus be suggested that these lines result from the presence of a large number of defects in the tetragonal crystals.

Finally, we consider the mode with  $\nu \sim 137 \text{ cm}^{-1}$  in the  $xx$  spectra of the Raman scattering; this mode is seen in the tetragonal crystals (Fig. 2 and 3). This is a completely symmetric mode (active in the  $xx$  and  $x'x'$  polarizations but absent from the  $xy$  and  $x'y'$  polarizations), and it cannot be explained in terms of single-phonon, dipole-allowed transitions. We do not rule out the possibility that the appearance of this mode, as well as the high efficiency in the Raman spectra of the  $B_{1g}$  vibrations of oxygen, is due to the formation of a superstructure in the crystals, which gives rise to additional modes.

In summary, we have classified several Raman-active modes in orthorhombic and tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta < 0.7$ ) crystals. Our classification is confirmed by the observation of an isotopic shift in the Raman spectra when the crystals are enriched in the oxygen isotope  $^{18}\text{O}$ . We have also observed Raman lines which cannot be explained in terms of single-phonon, dipole-allowed transitions. The magnitude of the isotopic shift of the critical temperature  $T_c$  remains an open question. Solving it will require improving the technique for isotopic enrichment to eliminate variations in the oxygen concentration over the sample.

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