

Effect of hydrostatic compression on oxygen vibrations in orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals

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The Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta \sim 0.1$) have been measured in the zz polarization during hydrostatic compression over the range 0–65 kbar. The results show that the A_g valence vibrations of the O4 oxygen correspond to a frequency of 498 cm^{-1} , while the A_g deformation vibrations of O2–O3 correspond to a frequency of 435 cm^{-1} . The Grüneisen parameters of these vibrations have been determined.

Measurements of the Raman spectra of ceramic samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with various oxygen concentrations¹ have shown that the frequencies of certain vibrations ($\nu = 498 \text{ cm}^{-1}$) soften with increasing oxygen deficiency, while the frequencies of others increase ($\nu = 435 \text{ cm}^{-1}$). It may now be regarded as an established fact that the line at 498 cm^{-1} corresponds to A_g vibrations of the Cu1-O4 bond, while the line at 435 cm^{-1} corresponds to in-phase A_g vibrations of oxygen atoms O2 and O3, which lie in the Cu2-O2, O3 plane.^{2–6} The softening of the frequency of the 498-cm^{-1} vibrations can be explained qualitatively by taking account of the increase in the lattice constant upon an increase in the oxygen deficiency.⁷ Working from the data of x-ray measurements for the parameter c , Thomsen *et al.*¹ estimated the Grüneisen constant to be $\gamma = -(1/3)d \ln \nu / d \ln c$ for the Cu1-O4 vibrations, and they found $\gamma = 1.9$.

In this letter we are reporting direct measurements of the Grüneisen parameters for these two oxygen vibrations, on the basis of measurements of the Raman spectra of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals in the zz polarization.

The Raman spectra were measured in a backscattering geometry on a Raman spectrometer with a microscope attachment. We used the 488-nm line from an Ar^+ laser at room temperature. The laser beam was focused into a spot a few microns in diameter on the sample. The power of the radiation at the sample was kept below 10 mW to avoid heating. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were grown by slow cooling a molten mixture of the oxides Y_2O_3 , CuO and BaO in air in a composition region on the CuO-rich side of the stoichiometric composition (1:2:3). The samples were rectangular wafers with dimensions $\sim 1\text{--}2 \text{ mm}$ in the basal plane and a thickness of 20–100 μm . The lattice symmetry of the resulting crystals was monitored by x-ray diffraction. The orthorhombic crystals [symmetry group $D_{2h}^1(P_{mmm})$] usually contained twins with a [110] twinning axis and a typical size of the twinning region less than 1 μm . The critical temperature of the superconducting transition was $\sim 90 \text{ K}$. We used a diamond-anvil cell to impose a hydrostatic (omnidirectional) compression on the

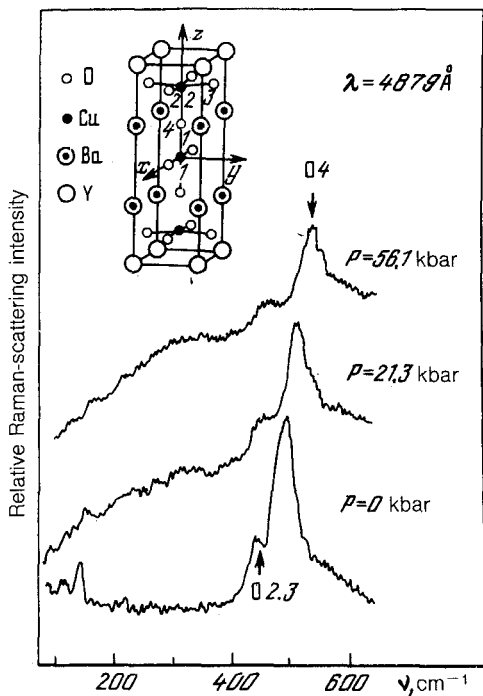


FIG. 1. The zz Raman spectra of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta \sim 0.1$) single crystals during hydrostatic compression at 0, 21.3, and 56.1 kbar ($\lambda = 4879 \text{ \AA}$, $T = 300 \text{ K}$). The unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is shown at the top.

crystals. The medium which transmitted the pressure was a mixture of ethanol and methanol. Samples with dimensions of $50 \times 50 \times 20 \mu\text{m}$ were prepared from the single-crystal wafers by cleavage. To minimize the background radiation from the diamond windows and the alcohol mixture, we selected diamonds among crystals of the I4 and I2 types, and we used highly pure ethanol and methanol. Furthermore, the sample was placed as close as possible to the diamond anvil which served as a window. The design of the laser made it possible to work with an objective with a working distance of 8 mm and a numerical aperture of 0.55. The pressure in the diamond chamber was monitored on the basis of the R_1 fluorescence line of ruby.

Figure 1 shows the measured Raman spectra zz polarization of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at several pressures. We see that the pressure, in contrast with a variation in the oxygen concentration, leads to an increase in both the frequencies of the O4 valence vibrations (ν_4) and those of the O2 and O3 deformation vibrations ($\nu_{2,3}$) (Fig. 2). This result is not surprising, since the hydrostatic compression reduces all the bond lengths in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ unit cell. Consequently, the increase in the frequency $\nu_{2,3}$, which is observed upon a decrease in the oxygen concentration in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ref. 1), indicates a decrease in the lengths of the corresponding bonds, despite the increase in the overall lattice constant c . This interpretation agrees with neutron-scattering data,⁸ according to which the distance ($d_{2,3}$) between the O2 and O3 atoms decreases slightly upon an increase in the oxygen deficiency, in contrast with the distance (d_4) between two O4 atoms. We can thus explain the increase in $\nu_{2,3}$ as we go from the orthorhombic phase to the tetragonal phase.

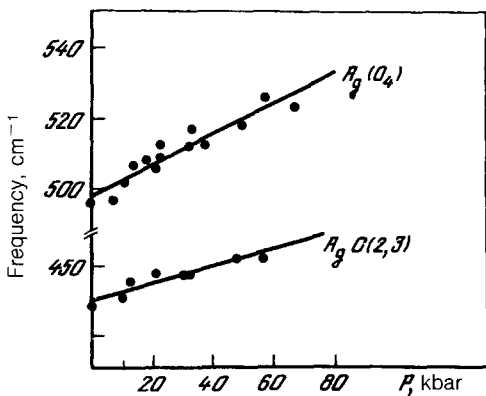


FIG. 2. Frequencies of the A_g valence vibrations of O4 and of the A_g deformation vibrations of O2 and O3 versus the hydrostatic compression.

Comparing the results found on the behavior of the frequencies of the 498-cm^{-1} and 435-cm^{-1} lines as functions of the pressure and the oxygen concentration with the particular features of the behavior of the interatomic distances between O4 atoms and O2 and O3 atoms, we can resolve the disagreement in the literature regarding the assignment of these vibrations. For example, Crimsditch *et al.*⁹ have linked the 435-cm^{-1} line with vibrations of the O4 oxygen. It follows unambiguously from the analysis above that this interpretation does not bear up under criticism, since it requires an identical dependence on P and δ for $\nu_{2,3} = 435\text{ cm}^{-1}$ and a different dependence for $\nu_4 = 498\text{ cm}^{-1}$, in contradiction of experiment. Working from the experimental results on the behavior $\nu_4(P)$ and $\nu_{2,3}(P)$, we determined the coefficients $d \ln \nu_i / dP$ and the Grüneisen parameters for the valence-vibration frequencies of the O4 atoms, $\gamma = 1.55$ and $d \ln \nu_4 / dP = 0.93 \times 10^{-3}$, and the deformation-vibration frequencies of the O2 and O3 atoms, $\gamma_{2,3} = 1.05$ and $d \ln \nu_{2,3} / dP = 0.62 \times 10^{-3}$. In calculating the Grüneisen parameters we used the value $\beta = 1700\text{ kbar}^{-1}$ for the bulk modulus.¹⁰

The bulk Grüneisen parameter $\gamma_i = d \ln \nu_i / dP$ is not very informative for substances with a unit cell of complex structure, since a change in a specific frequency ν_i under pressure results primarily from changes in the lengths and angles of the bonds which determine the given vibration. A more detailed analysis will become possible when we have data from a neutron structural analysis or x-ray-structural analysis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ under pressure. Such data are presently not available.

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