Raman scattering of $YBa_2Cu_3O_x$ single crystals with different oxygen contents at high pressures

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The Raman spectra of $YBa_2Cu_3O_x$ single crystals ($x = 6.25, 6.75, 7.0$) were measured at pressures up to 22 GPa (35 GPa for $x = 6.25$) at room temperature under nearly hydrostatic conditions. The frequency-volume curves for the most Raman-active fundamental vibrations were derived from the present data making use of the previous high-pressure study of the equations of state of $YBa_2Cu_3O_x$ compound.

It is widely known that variation of the oxygen content in a $YBa_2Cu_3O_x$ compound strongly influences its many important physical properties. The high sensitivity of the ν_5 Raman frequency corresponding to the axial symmetrical vibrations of the "bridging" oxygen atom O4 to the oxygen content x was repeatedly pointed out and studied in detail in Ref. 1. Change of x leads to a significant variation of the frequency of the ν_2 and ν_4 modes, which are related to the axial symmetrical vibrations of Cu2 and O2 + O3 atoms, but influences little the frequency of the ν_3 deformation mode, corresponding to the out-of-phase vibrations of O2 and O3 atoms in the CuO_2 plane. As was shown in Ref. 1, the frequency of the ν_5 mode depends on the oxygen concentration in the same way as the superconducting critical temperature T_c does. It was tempting to suggest that the observed T_c and ν_5 correlation is connected with the free carrier concentration, which might affect T_c and ν_5 in the similar way. On the other hand, an important point was missed in those speculations: the variation of the oxygen content appreciably influences the unit cell parameters[2] and the compressibility[3] of $YBa_2Cu_3O_x$ compound; the most drastic changes occur along the **c** axis. Obviously, the change of the unit cell parameters alone affects the Raman frequencies (see high-pressure experiments[4,5]), and, to make certain conclusions whether and how much free carriers contribute to the O4 mode, one must take into account the volume dependence of ν_5. This can be readily done by studying the volume dependence of the Raman spectra of $YBa_2Cu_3O_x$ compounds with various oxygen contents.

In the present paper we describe the results of a high-pressure study of the Raman spectra of $YBa_2Cu_3O_x$ single crystals with the oxygen contents $x = 6.25$, 6.75, and 7.0. These results, when combined with our previous data[3] of the x-ray diffraction studies of $YBa_2Cu_3O_x$ single crystals at high pressures, yield all the information that we need. Surprisingly, it turns out that the frequency-volume curves for the ν_5 mode do not reveal a noticeable dependence on the oxygen content.

The $YBa_2Cu_3O_x$ single crystals were grown from nonstoichiometric melt, as described in Ref. 6. The selected samples were subsequently treated at elevated temperatures in oxygen and helium atmosphere.[2] The oxygen-rich samples (R 1 and R 2) had orthorhombic symmetry and the following lattice parameters: $R\,1$—$a = 3.820(2)$, $b = 3.888(2)$, $c = 11.680(6)$ and $R\,2$—$a = 3.828(2)$, $b = 3.880(2)$, $c = 11.725(5)$. The oxygen-deficient crystal (T) had tetragonal symmetry with $= 3.862(2)$ and $c = 11.825(6)$. According to the data of Ref. 2, the oxygen content in our samples is estimated to be $x = 7.00(5)$, 6.75(5), and 6.25(5). A diamond-anvil cell was used to generate high pressures. Condensed helium was used as a pressure-transmitting medium which provided nearly hydrostatic conditions in the high-pressure chamber. The Raman spectra were excited by an ion–argon laser ($\lambda_{ex} = 488$ nm) and were measured in the 135° geometry employing a laser microscope and a triple polychromator with a multichannel detector.[7] Small chips of $YBa_2Cu_3O_x$ single crystals $40\times20\times20$ μm in size were placed in the cell, where the orientation of the c axis was perpendicular to the cell axis. The laser beam was focused into the spot of approximately 15 μm diameter. The pressure in the cell was measured by the ruby fluorescence technique with use of the pressure scale.[8] All measurements were performed at room temperature.

Figure 1 shows the Raman spectra of an orthorhombic crystal with $x = 7$ ($R\,1$) at various pressures. For this sample we could trace the change of the frequency for all the Raman-active modes, including the low-frequency ν_1 mode, which is related to the symmetrical axial vibrations of Ba atoms. For the crystals with $x = 6.75$ ($R\,2$) and $x = 6.25$ (T) we have measured the spectral positions of the three high-frequency modes ν_3, ν_4, ν_5 and the ν_2, ν_3, ν_5 modes, respectively. The frequencies of all the modes

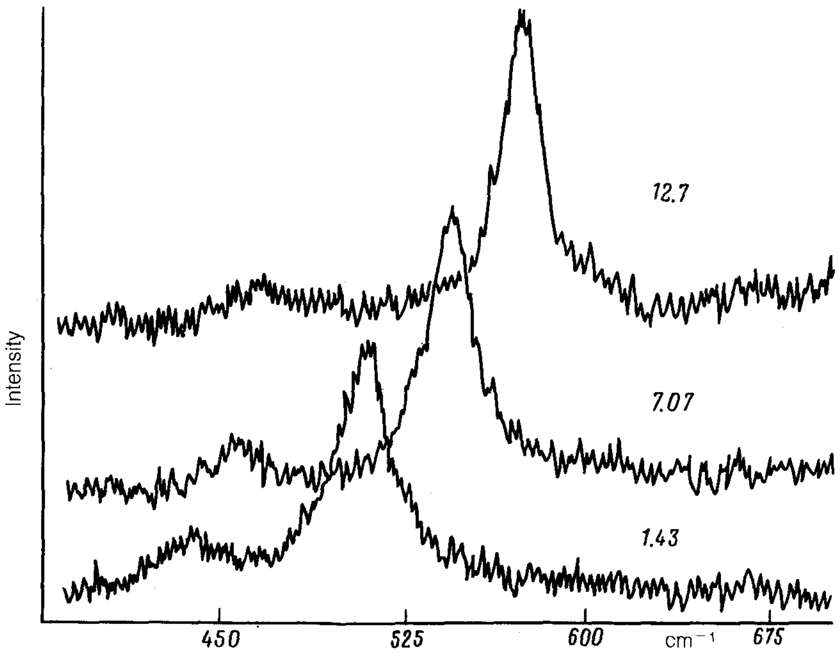

FIG. 1. Raman spectra of $YBa_2Cu_3O_7$ single crystals at various pressures (GPa).

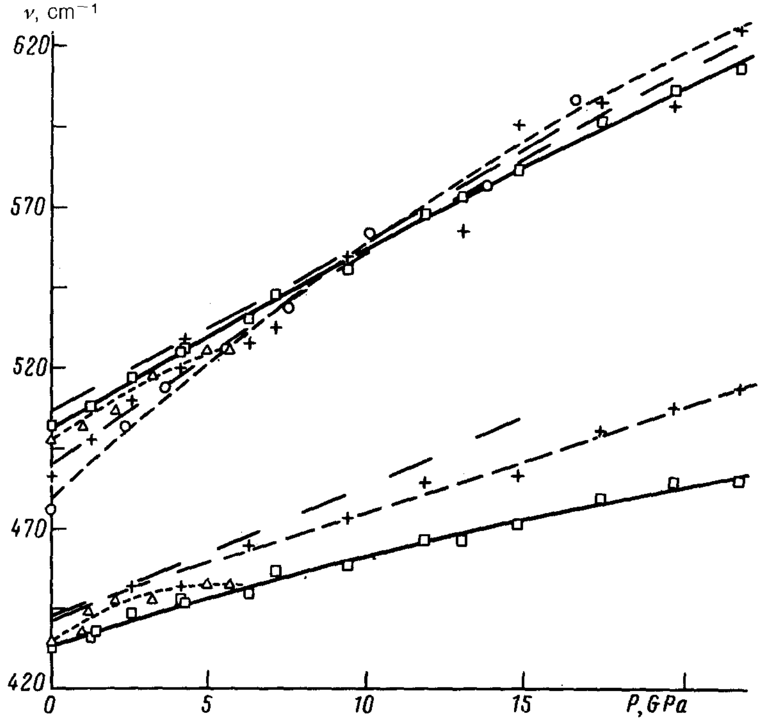

FIG. 2. Pressure dependences of the Raman frequencies for ν_4 and ν_5 modes -□—-$x = 7$; -- + -- —$x = 6.75$; --○-- —$x = 6.25$; --- —$x = 7$ (Ref. 4); --△-- —$x = 7$ (Ref. 5).

measured smoothly increase with pressure. We have not observed the appearance of a new band under pressure. It can be concluded, therefore, that the initial structures remain stable to the highest pressures achieved. Figure 2 shows the pressure dependence of the frequencies for the high-frequency modes ν_4 and ν_5 for all the crystals studied in comparison with the corresponding data of Refs. 4 and 5. We see that there is a fair agreement between these data and our results for R 1 sample, with the exception of the ν_4 mode, measured in Ref. 4. As for the samples with different oxygen contents, we see in Fig. 2 that the behavior of the ν_5 mode at high pressures clearly depends on x. The slope of the $\nu(P)$ curve decreases with increasing value of x. Finally, all the curves are crossed at the pressure near 10 GPa. This picture is reminiscent of the behavior of the compression curves of the crystals with similar oxygen content.[3] Plotting the frequencies ν_2, ν_3, ν_4, and ν_5 as a function of volume (Fig. 3), we obtain a rather unexpected result. The frequency of the ν_5 mode seems to depend on the volume only, whereas the ν_2, ν_3, and ν_4 modes depend on both the volume and the oxygen content. It should be emphasized that ν_2, ν_3, and ν_4 modes are attributed to the vibrations of atoms which are situated in the CuO_2 plane, although the ν_4 and ν_5 modes are assumed to be coupled.[9] The bridging O4 oxygen is strongly bound to the Cu1 atom. At first sight, it seems incredible that the frequency of the ν_5 mode is not sensitive to a lack of oxygen at the (0,1/2,0) site at high pressures. This circumstance

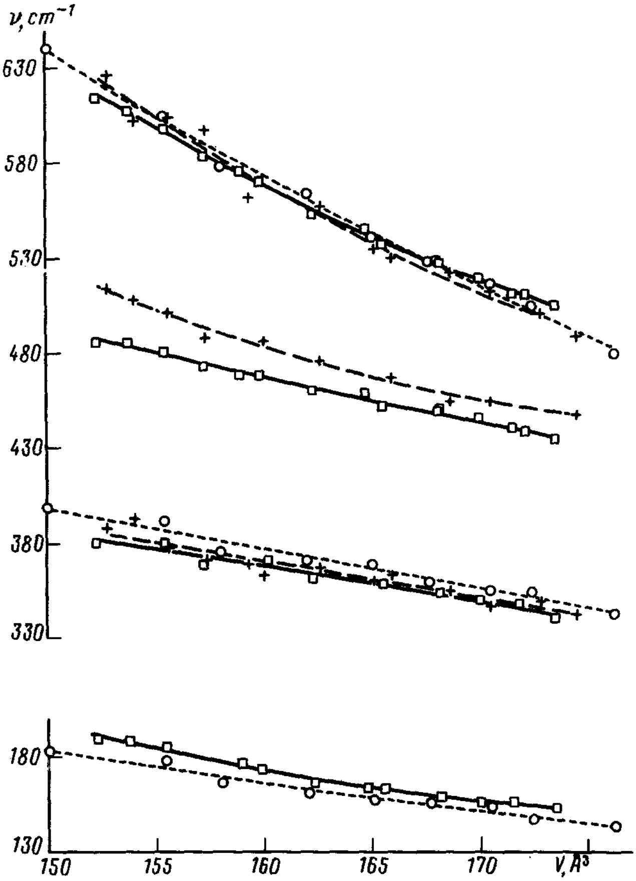

FIG. 3. Volume dependences of the Raman frequencies. The symbols are the same as in Fig. 2. The necessary *P-V* data for $YBa_2Cu_3O_x$ compound were taken from Ref. 3.

suggests that the O1 atom does not interact strongly with the Cu1 and O4 atoms. In other words, the electronic orbitals of the Cu1–O4 complex and O1 atom are not hybridized or are hybridized only slightly.[1)] This conclusion might explain why the superconducting properties of two substances, $YBa_2Cu_3O_x$ and $CaBa_2TlCu_2O_7$, whose crystal structures are very similar, differ so little, despite the substitution Cu1 and *Y* for Tl and Ca.

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[1)] This possibility was mentioned briefly in Ref. 3 on the basis of an x-ray study of the equation of state of $YBa_2Cu_3O_x$ at high pressures.

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