

# RAMAN SCATTERING OF $\text{YBa}_2\text{Cu}_3\text{O}_x$ SINGLE CRYSTALS WITH DIFFERENT OXYGEN CONTENT AT HIGH PRESSURES

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The Raman spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  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 in nearly hydrostatic conditions. The frequency-volume curves for the most Raman-active fundamental vibrations were derived from the present data making use the previous high-pressure study of the equations of state of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  compound.

It is widely known that variation of the oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  compound strongly influences its many important physical properties. The high sensitivity of the  $\nu_5$  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 details in <sup>1</sup>. Change of  $x$  leads also to the significant variation of the frequency of the  $\nu_2$  and  $\nu_4$  modes, related to the axial symmetrical vibrations of Cu2 and O2+O3 atoms, but influences little the frequency of the  $\nu_3$  deformation mode, corresponding to the out-of-phase vibrations of O2 and O3 atoms in the  $\text{CuO}_2$  plane. As was shown in <sup>1</sup>, the frequency of the  $\nu_5$  mode depends on the oxygen concentration in the same way like the superconducting critical temperature  $T_c$  does. It was tempting to suggest, that the observed  $T_c$  and  $\nu_5$  correlation is connected with the free carriers concentration, which might affect  $T_c$  and  $\nu_5$  in the similar way. On the other hand an important point was missed at those speculations. The thing is that the variation of the oxygen content appreciably influences the unit cell parameters <sup>2</sup> and the compressibility <sup>3</sup> of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  compound, the most drastic changes occurring along the  $c$  axis. Obviously, the change of the unit cell parameters alone affect the Raman frequencies (see high-pressure experiments <sup>4,5</sup>), and, to make certain conclusions whether and how much free carriers contribute to the O4 mode, one has to take into account the volume dependence of  $\nu_5$ . It can be readily done by studying the volume dependence of Raman spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  compounds with various oxygen content.

In the present paper we describe the results of high-pressure study of the Raman spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  single crystals with the oxygen content  $x = 6,25; 6,75; 7,0$ . Those results when combined with our previous data <sup>3</sup> of the X-ray diffraction studies of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  single crystals at high pressures yield all the information we need. Surprisingly, it turns out that the frequency-volume curves for the  $\nu_5$  mode do not reveal any noticeable dependence on the oxygen content.

The  $\text{YBa}_2\text{Cu}_3\text{O}_x$  single crystals were grown from nonstoichiometric melt as it was described in <sup>6</sup>. The selected samples were subsequently treated at elevated temperatures in oxygen and helium atmosphere <sup>2</sup>. The oxygen-rich samples (*R1* and *R2*) had orthorhombic symmetry and the following lattice parameters: *R1* -  $a = 3,820(2)$ ;  $b = 3,888(2)$ ;  $c = 11,680(6)$  and *R2* -  $a = 3,828(2)$ ;  $b = 3,880(2)$ ;  $c = 11,725(5)$ . The oxygen-deficient crystal (*T*) had tetragonal symmetry with  $a = 3,862(2)$ ;  $c = 11,825(6)$ . According to the data <sup>2</sup> the oxygen content in our samples should be estimated as  $x = 7,00(5)$ ;  $6.75(5)$ ;  $6.25(5)$ . A diamond-anvil cell was used to generate high pressures. Condensed helium was used as a pressure transmitting medium providing almost hydrostatic conditions in the high pressure chamber. The Raman spectra were excited by an ion-argon laser ( $\lambda_{ex} = 488\text{nm}$ ) and were measured in the  $135^\circ$ -geometry employing a laser microscope and a triple polychromator with a multichannel detector <sup>7</sup>. Small chips of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  single crystals  $40 \times 20 \times 20\mu\text{m}$  were placed into the cell, the orientation of the *c*-axis being perpendicular to the cell axis. The laser beam was focused into the spot of approximately  $15\mu\text{m}$  diameter. The pressure in the cell was measured by the ruby fluorescence technique with the use of the pressure scale <sup>8</sup>. All measurements were performed at room temperature.

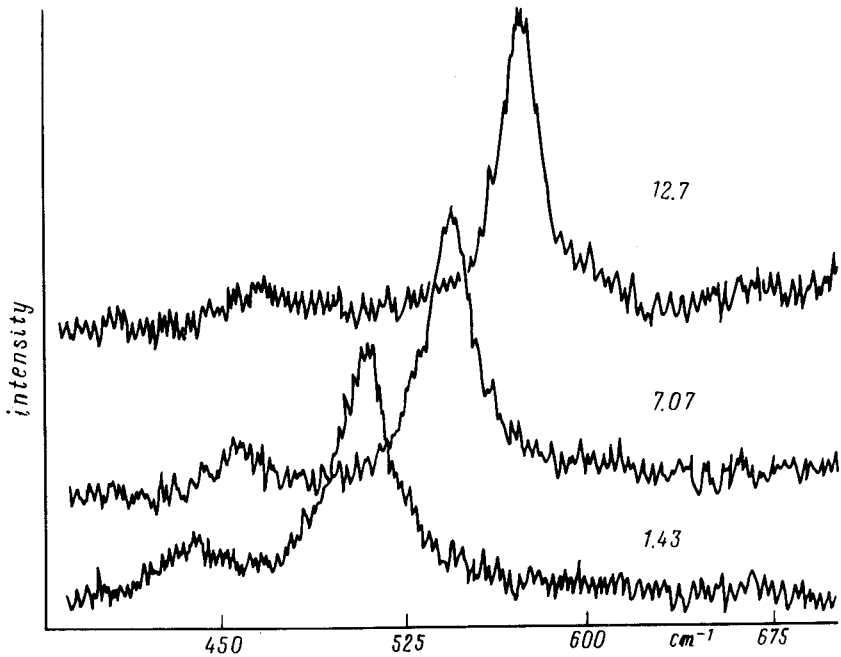


Fig.1. Raman spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  single crystals at various pressures (GPa).

Fig.1 presents the Raman spectra of the orthorhombic crystal with  $x = 7$  (*R1*) at various pressures. For this sample we could trace the change of the frequency for all the Raman active modes, including the low-frequency  $\nu_1$  mode,

related with the symmetrical axial vibrations of Ba atoms. For the crystals with  $x = 6,75$  (*R2*) and  $x = 6,25$  (*T*) we have measured the spectral positions of the three high-frequency modes  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$  and  $\nu_2$ ,  $\nu_3$ ,  $\nu_5$  modes respectively. The frequencies of all the modes measured smoothly increase with pressure. We have not also observed the appearance of any new band under pressure. That is why one may conclude that the initial structures remain stable up to the highest

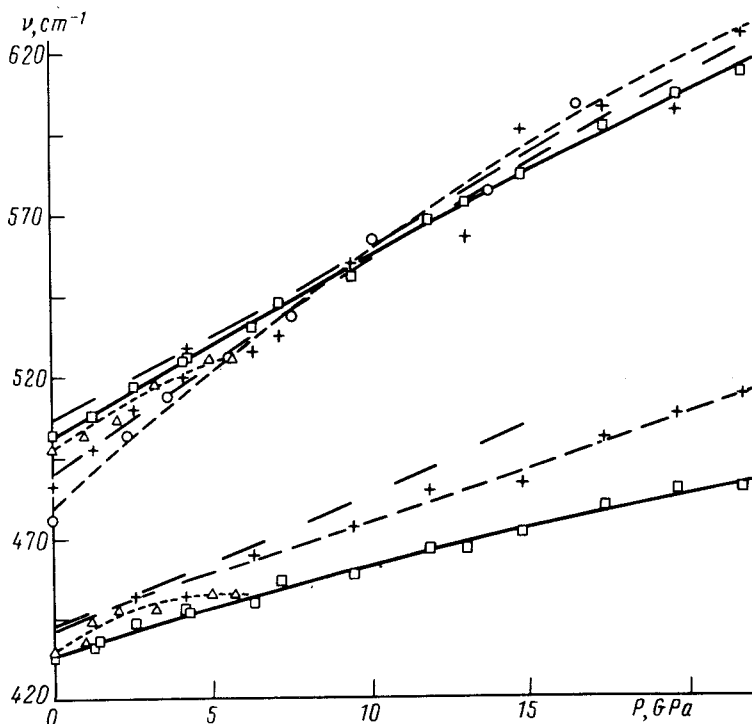


Fig.2. Pressure dependences of the Raman frequencies for  $\nu_4$  and  $\nu_5$  modes —□—  $x = 7$ ; —+—  $x = 6,75$ ; —○—  $x = 6,25$ ; —×—  $x = 7^4$ ; —△—  $x = 7^5$ .

pressures achieved. Fig.2 shows the pressure dependence of the frequencies for the high-frequency modes  $\nu_4$  and  $\nu_5$  for all the crystals studied in comparison with the corresponding data of <sup>4,5</sup>. One can see, that there is a fair agreement between those sets of data and our results for *R1* sample with the exception of the  $\nu_4$  mode, measured in <sup>4</sup>. As for the samples with different oxygen content it is seen in fig.2 that the behavior of the  $\nu_5$  mode at high pressures clearly depends on  $x$ . The higher is  $x$  the less steeper is the slope of the  $\nu(P)$  curve. Finally, all the curves are crossed at the pressure near 10 GPa. This picture reminds us the behavior of the compression curves of the crystals with similar oxygen content

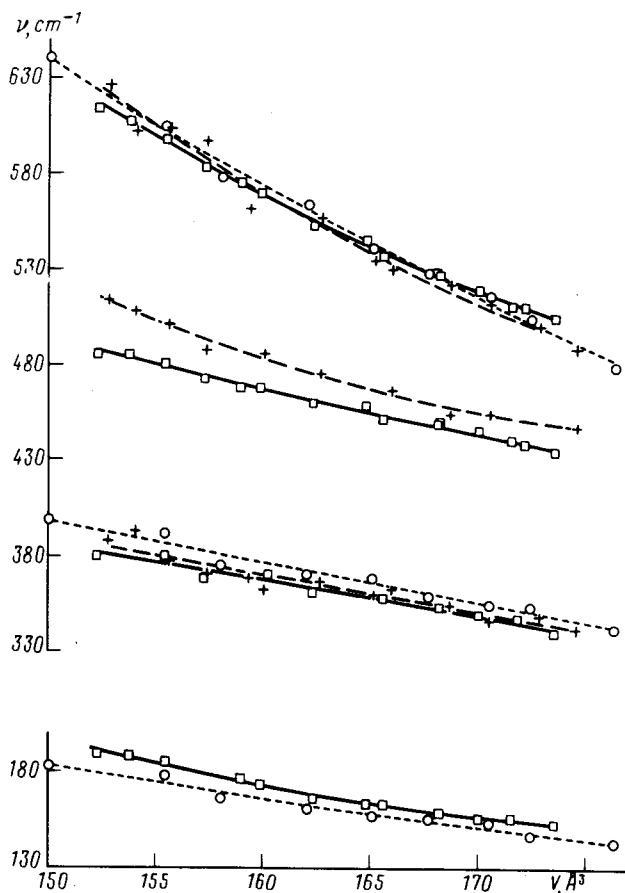


Fig.3. Volume dependences of the Raman frequencies. Symbols are the same as in Fig.2. The necessary  $P - V$  data for  $\text{YBa}_2\text{Cu}_3\text{O}_x$  compound were borrowed from <sup>3</sup>.

<sup>3</sup>. Plotting the frequencies  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$  as a function of volume (Fig.3) we get quite an unexpected result. The frequency of the  $\nu_5$  mode seems to depend on the volume only, whereas the  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$  ones depend on both, volume and oxygen content. It should be emphasized that  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  modes belong to the vibrations of atoms, which are situated in the  $\text{CuO}_2$  plane, though  $\nu_4$  and  $\nu_5$  modes are assumed to be coupled <sup>9</sup>. The "bridging" oxygen O4 is strongly bound to Cu1 atom and at the first sight it looks amazing that the frequency of the  $\nu_5$  mode does not feel a lack of oxygen in the (0,1/2,0) position at high pressures. This situation could only mean, that O1 atom does not interact strongly with Cu1 and O4 atoms. In other words the electronic orbitals of Cu1 - O4 complex and O1 atom are not hybridized or hybridized slightly <sup>1</sup>. This conclusion might

<sup>1</sup>This possibility was mentioned briefly in <sup>3</sup> on a basis of the X-ray study of the equation of state of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  at high pressures.

explain why the superconducting properties of two substances,  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and  $\text{CaBa}_2\text{TlCu}_2\text{O}_7$ , which crystal structures are very similar, differ so little despite of the substitution Cu1 and Y for Tl and Ca.

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1. Goncharov A.F., Denisov V.N., Zibrov I.P. et al. *Pis'ma ZhETF*, 1988, Vol.47, P.453.
  2. Aleksandrov I.V., Bykov A.B., Zibrov I.P. et al. *Pis'ma ZhETF*, 1988, Vol.48, P.449.
  3. Aleksandrov I.V., Goncharov A.F., Stishov S.M.. *Pis'ma ZhETF*, 1988, Vol.47, P.357.
  4. Syassen K., Hanfland M., Strossner K. et al. *Physica C*, 1988, Vol.153-155, P.264.
  5. Kulakovskiy V.D., Misochko O.V., Timofeev V.B. et al. *Pis'ma ZhETF*, 1988, Vol.47, P.536.
  6. Bykov A.B., Demianets L.N., Zibrov I.P. et al. *Journal of Crystal Growth*, 1988, Vol.91, P.302.
  7. Goncharov A.F.. *Pis'ma ZhETF*, 1990, Vol.51, P.368.
  8. Aleksandrov I.V., Goncharov A.F., Zisman A.N., Stishov S.M.. *ZhETF*, 1987, Vol.91, P.680.
  9. Misochko O.V., Rashba E.I., Sherman E.Ya., Timofeev V.B. *Phys.Reports*, 1990, Vol.194, P.387.