Superconductivity and Raman scattering of light in $YBa_2Cu_3O_x$ single crystals

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The Raman-scattering frequency of a completely symmetric mode corresponding to the vibrations of the "bridge" O4-ν oxygen and to the superconducting transition temperature T_c of $YBa_2Cu_3O_x$ single crystals with various oxygen concentrations has been measured. The $\nu(x)$ curve was found to have a plateau, similar to that found on the $T_c(x)$ curve, at concentrations in the range $6.5 < x < 6.8$.

It has been established that the superconducting properties of the compound $YBa_2Cu_3O_x$ depend essentially on the total oxygen concentration and that they are sensitive to the method of fabrication of the samples. Using a special technology for fabricating samples with various oxygen concentrations, Cava *et al.*[1] found that the curve of $T_c(x)$ has a 60° plateau (T_c is the critical temperature). In contrast, the high-temperature quenching method usually does not lead to the development of structural features in the function $T_c(x)$. The ambiguity observed in the function $T_c(x)$ would seem to suggest that the critical temperature of $YBa_2Cu_3O_x$ is sensitive to the distribution of oxygen in the *x,y* plane. This situation creates, as we will see below, favorable conditions for conducting a search for the nontrivial properties of high-temperature superconductors which are genetically related to the formation of the superconducting state.

In the present letter we report the results of the measurement of the frequency of the optical phonon mode which corresponds to the out-of-phase displacement of atoms of the "bridge" O4 oxygen in the **c** direction (the O4 mode) and to the superconducting transition temperature in $YBa_2Cu_3O_x$ single crystals with various oxygen concentrations $6 < x < 7$. The model in question, which is the dominant mode in Ra-

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man-scattering spectra,[2–9] must be sensitive to the oxygen distribution with respect to the positions (1/2, 0, 0) and (0, 1/2, 0) (this condition also holds for the infrared mode, which corresponds to the displacement of the Cu1 atoms with respct to the in-phase motion of the O4 atoms).

The $YBa_2Cu_3O_x$ single crystals which we have studied were grown from a non-stoichiometric melt. The samples with the required oxygen concentration were synthesized with the help of a thermogravimetric device in oxygen and helium atmospheres.[10] The absolute error of the values of x which we have measured was no greater than ± 0.05.

The Raman scattering spectra were recorded from freshly cleaved surfaces of crystals in the *zz* geometry, using a multichannel triple spectrometer.[5,6,11] The spectral position of the test mode was determined within ± 2 cm^{-1}.

The superconducting properties of crystals were studied by a contactless method using an LC oscillator operating in the megahertz frequency range. An abrupt shift in the oscillator frequency in one, sufficiently narrow temperature interval or the other was identified with the transition of the sample of the superconducting state.[10]

Figure 1 shows the Raman-scattering spectra for $YBa_2Cu_3O_x$ single crystals. The spectra clearly show two bands ($\nu = 500$ cm^{-1} and $\nu' = 435$ cm^{-1}) which experience a noticeable energy shift as a result of the variation of x. The low-frequency mode with respect to the low intensity, $\nu' = 435$ cm^{-1}, is linked primarily with the vibrations of the O2 and O3 atoms and will no longer be considered. It is interesting to note that the principal band broadens significantly with decreasing x. This mode remains nonetheless a well-define collective excitation at any value of x, which quite definitely suggests that the interaction of O1 oxygen with the quasimolecular O4-Cu1-O4 complex is

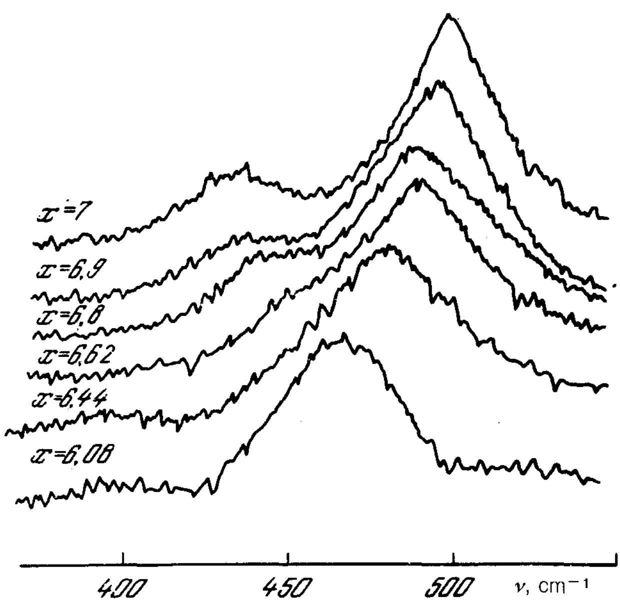

FIG. 1. Raman-scattering spectra of $YBa_2Cu_3O_x$ single crystals with various oxygen concentrations x. $x > 6.5$—Orthorhombic crystals; $x < 6.5$—tetragonal crystals; *zz* geometry; $\lambda_i = 514.5$ nm.

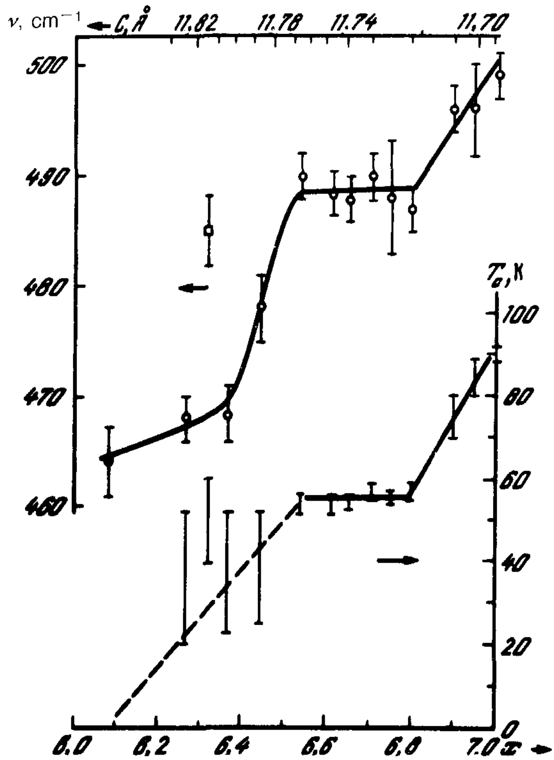

FIG. 2. Raman-scattering frequency of O4 mode and the superconducting transition temperature versus the oxygen concentration. The vertical bars represent the range within which the frequency of the LC oscillator varies sharply (see the text proper). Shown for comparison are the data for annealed tetragonal sample (□).

rather weak (see Ref. 12 for further discussion of this problem). Figure 2 is a plot of the frequency of the O4 mode and of the superconducting transition temperature as a function of the oxygen concentration x. The striking similarity between the functional dependences $\nu(x)$ and $T_c(x)$ does not raise any doubt. We wish to point out that the Raman-scattering band does not contract in the region $6.5 < x < 6.8$, suggesting that there is no global ordering of any sort (see Refs. 13 and 14).

We also had access to the results of the measurements of ν and T_c for samples with various oxygen concentrations, which were obtained as a result of annealing and quenching in flowing helium. Judging from the available data, the use of this method does not account for the plateau on the $T_c(x)$ and $\nu(x)$ curves.[5,6] These results are compared in Fig. 3 with the data of our measurements. Despite the discrepancy at low temperatures ($x < 6.5$), which is quite natural because of the extreme inhomogeneity of the samples, a one-to-one correspondence very likely exists between ν and T_c, regardless of the method used to synthesize the crystals and regardless of their symmetry (see the data in Fig. 2 on the quenched tetragonal sample).

The first question that arises in the analysis of the results concerns the nature of the 60° plateaus. Since there is no evidence in favor of the existence of true superstruc-

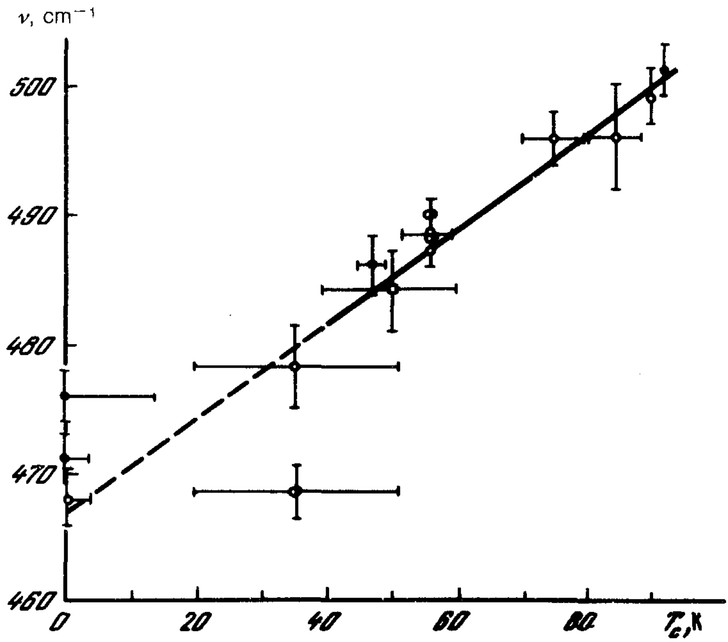

FIG. 3. Relationship between the Raman-scattering frequency of the O4 mode and the superconducting transition temperature. The notation is the same as in Fig. 2. ●—Data for the orthorhombic crystals obtained by annealing (see the text proper).

tural order near the plateau, we must assume that subcrystalline or quasimolecular organization of particles is essential if superconductivity is to occur. In this case the pseudoquadratic Cu1-O1–O4 complex requires first consideration. In the limiting case $x = 7$, the Cu1-O1-O4 "squares," which are linked by vertices, form continuous ribbons which extend in the **b** direction. If we make the natural assumption that the energy of the hybrid orbitals corresponding to the square complex Cu1-O1-O4 is slightly lower than the energy of other probable atomic and electronic configurations, we will see that the states with virtually constant density of the square complex can occur in the region of the intermediate values of x. Such arguments can explain the existence of a plateau on the $\nu(x)$ curve but shed no light on how ν is related to T_c.

It can be assumed, without specifying the nature of pairing, that the superconductivity of $YBa_2Cu_3O_x$ is associated with only a particular group of carriers which are linked with the Cu1-O1-O4 orbitals. The relationship between ν and T_c would then be quite natural. This assumption, however, generally leads to a one-dimensional nature of superconductivity and sets $YBa_2Cu_3O_x$ apart from the other superconducting cuprates.

On the other hand, it is tempting to assume that the pairing mechanism is governed by the exchange of optical phonons which are associated with the motion of the bridge O4 oxygen. A reasonable value of the dimensionless coupling constant, $g \approx 0.5$, can be obtained by directly substituting in the basic BCS equation the experimental values of the frequency of the O4 mode ($500\ cm^{-1} \approx 720$ K) and the critical temperature. The plot of the critical temperature T_c as a function of the oxygen concentration to within $x \approx 6.5$ can be explained on the basis of the band calculations[15,16] which suggest that the electron state density is quite sensitive to the oxygen concentrations and distribution. In this case it must be assumed, that the single-electron calculations are inadequate for $YBa_2Cu_3O_x$ when $x < 6.5$. The observable superconductivity is not an intrinsic superconductivity in this range of compositions and is associated with fluctuations in the oxygen concentration, consistent with experimental data.

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