

Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_x$ superconductors with different oxygen content

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The Raman spectra of high-purity samples of $\text{YBa}_2\text{Cu}_3\text{O}_x$ were studied as a function of oxygen content $6 < x < 7$. The most important changes occurred in the spectral range corresponding to the stretching vibrations of Cu—O bonds. At the transition from the superconducting orthorhombic to the semiconducting tetragonal phase, $x = 6.5$, the intensity of the highest-frequency mode at 632 cm^{-1} drops drastically as oxygen is removed from the Cu(1)—O(1) chains. The two Raman modes at 440 and 500 cm^{-1} merge into a single mode at 472 cm^{-1} . The correlation between the phase transition and changes in the spectra is discussed.

Knowledge of the phonon spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_x$ superconductors is of primary importance for understanding the mechanism of superconductivity in these high T_c materials. Interpretation of the infrared reflection spectra is difficult due to low surface quality of the materials and strong coupling between infrared-active modes and free carriers. On the other hand, Raman scattering is less sensitive to surface morphology and information on phonon energies can be obtained directly from the scattering spectrum without fitting procedures. The Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_x$ superconductors have been presented in several publications.¹⁻⁵ The published spectra are different from each other. Our own measurements on a number of $\text{YBa}_2\text{Cu}_3\text{O}_x$ superconductors prepared in different laboratories also showed the variety of the spectra. A possible explanation of these variations is that Raman spectra of high-temperature superconductors depend strongly on the method of preparation of samples, oxygen content, structural defects, domain structure, free-carrier concentration and, possibly, sizes of microcrystals in pellets. Very often several impurity phases are present in the samples which complicates the analysis significantly. In the present study we carefully prepared a series of single-phase $\text{YBa}_2\text{Cu}_3\text{O}_x$ sintered pellet samples with controlled oxygen content. We measured their Raman spectra and tried to find a correlation between phonon spectra, oxygen content, and superconductivity.

A large batch of fully oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_7$ was prepared utilizing standard ceramic techniques.⁶ Dry powders (99.999%) of Y_2O_3 , BaCO_3 , and CuO were first mixed in the proper stoichiometry. The mixture was placed in an Al_2O_3 boat and heated in air at 900°C for a period of 48 h during which time the powder was reground several times. The material was then formed into 650 mg pellets which were sintered at 900°C for a period of 6 h. The sintered pellets were annealed under a flow of oxygen at 550°C for 12 h followed by a slow cooling to room temperature (several hours). In the above procedure, care

was taken to avoid extensive melting of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ which might lead to differences in purity and oxygen content between the surface and the bulk region of the pellets. Oxygen content was measured gravimetrically. Oxygen deficient samples, $x < 7$, were prepared by heating the fully oxygenated samples in a tube furnace under an argon flow until the desired oxygen content was achieved.⁷ The samples were then slowly cooled to room temperature while maintaining the inert atmosphere. All samples were examined by x-ray powder diffraction on a Rigaku x-ray diffractometer using $\text{Cu } K_\alpha$ radiation. Resistivity measurements were made employing a standard four-point probe technique.

X-ray powder diffraction spectra showed that the samples were at least 99% pure. Primitive cell parameters were determined and agreed with previous works.⁷⁻¹⁰ In going from $x = 7$ to $x = 6$, the structure changed from orthorhombic (space group D_{2h}^1) to tetragonal (space group D_{4h}^1) at $x = 6.5$ due to removal of oxygen from the Cu—O chains along the b axis and consequent disordering of positions of remaining O(1) atoms.¹⁰ The two phases were present simultaneously in the transition region. Concomitant to the structural changes were changes in the electrical properties. As shown in Fig. 1, the fully oxygenated sample displayed the highest superconducting critical temperature, $T_c = 92 \text{ K}$, whereas for $x = 6.7$, T_c dropped to 50 K. When x was lowered to 6.4, hints of a superconducting phase below 10 K were evident, but the sample never became fully superconducting. Samples with x less than 6.3 displayed no signs of superconductivity and were all semiconductors. Similar results have been reported previously.¹¹

Raman spectra were taken in a backscattering geometry using the 5145 \AA argon-ion laser line as an excitation source and a Spex triple-scanning spectrometer. Laser light was focused by a cylindrical lens to reduce heating. Laser power was 200 mW which did not introduce any distortion in the spectra. The samples were in a He gas

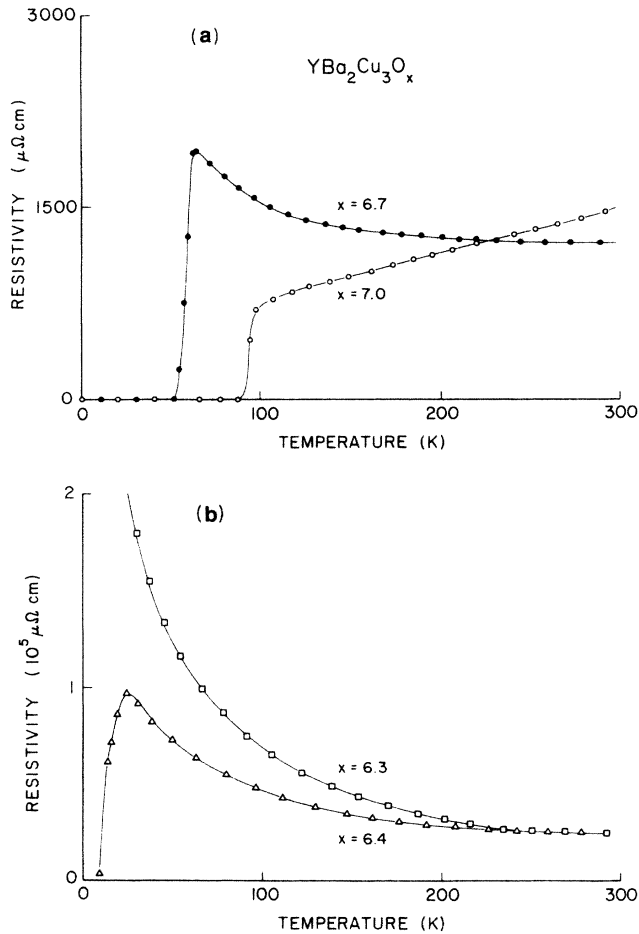


FIG. 1. Temperature dependence of the resistivity of selected $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples with different oxygen content.

environment in order to eliminate spectral lines in the low-energy region due to scattering in the air. The spectra which we obtained are presented in Fig. 2. The corresponding values of x are shown. Every spectrum contains two components: a phonon line spectrum and a continuous electronic background spectrum. This background scattering is not laser light background often observed when samples with rough surfaces are studied. In our case the triple-scanning spectrometer with holographic gratings allowed us to filter away effectively the elastically scattered light. The comparatively strong electronic continuum spectrum is therefore the inherent component of these superconductors. We attribute it to the scattering by low-mobility quasi-free charge carriers.

The spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $x = 7$ is shown in Fig. 2. The samples of this composition had the best superconducting properties and we may consider this spectrum as a typical spectrum of a good superconductor. The best superconducting films with critical current densities in the range of 10^8 A/cm^2 at 4.2 K have very similar spectra.¹² When the oxygen content is decreased, noticeable changes in the spectra are observed, Fig. 2. First of all, the intensity of the highest energy phonon at 632 cm^{-1} starts to decrease accompanied by small energy shift. It

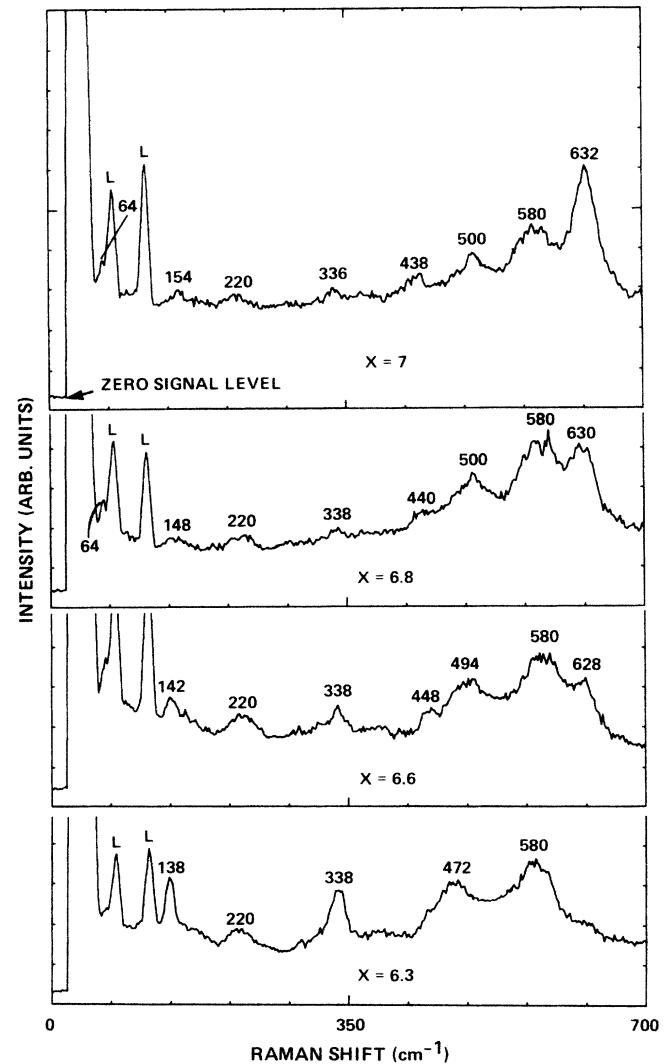


FIG. 2. Raman spectra of selected $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples with different oxygen content. L: laser plasma lines.

practically disappears in samples with $x = 6.4$, when the material becomes tetragonal and nonsuperconducting. The other pronounced effects related to the phase transformation are intensity growth of lines at 154 and 336 cm^{-1} , frequency shift of the line at 154 to 138 cm^{-1} and merging of the two lines at 500 and 438 cm^{-1} in the orthorhombic phase into one line at 472 cm^{-1} in the tetragonal phase. Our Raman data are summarized in Fig. 3, in which frequencies of the main phonon peaks as functions of oxygen content are presented. In the range of the phase transition at $x = 6.4$ – 6.5 the orthorhombic and tetragonal phases coexist in the samples. Traces of mixed phases could also be seen at other values of x close to this range.

It is difficult at present to give reliable interpretation of these changes due to unusual variety of Raman spectra observed in these materials. Dipole moment selection rules arguments must be used with caution because the spectra are always obtained in resonance with broad band electronic transitions and materials contain large number of defects. Due to a complicated crystallographic struc-

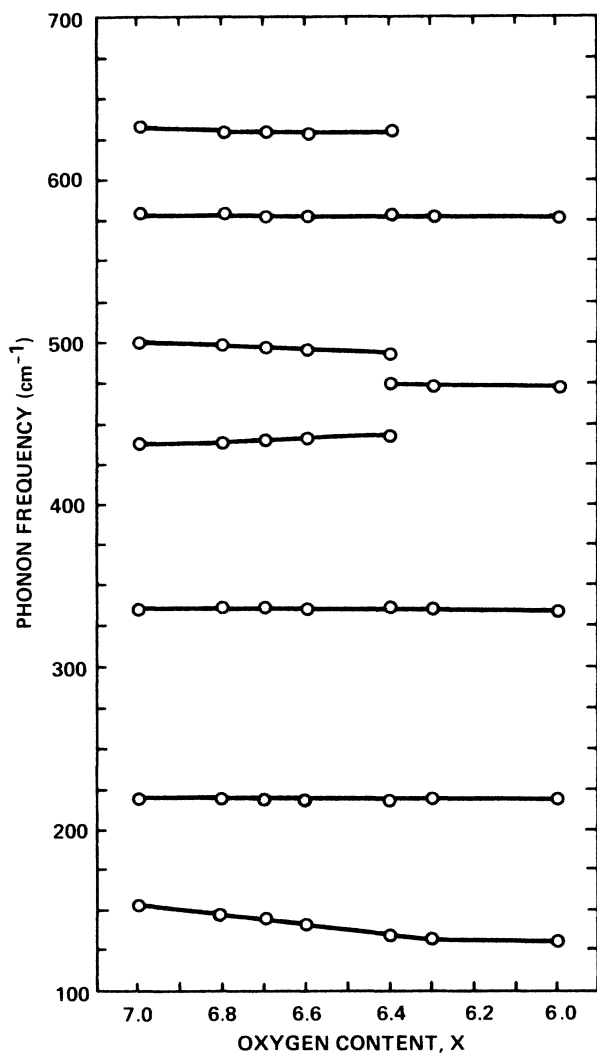


FIG. 3. Frequency of main phonon lines in Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples as a function of oxygen content. Note the coexistence of orthorhombic and tetragonal phases in the sample with $x = 6.4$.

ture, reliable lattice dynamic calculations are difficult to make. We shall try here to give a tentative interpretation of our results based mostly on structural changes at the phase transition. Most of the changes caused by removal of oxygen occur in the spectral range above 400 cm^{-1} . This spectral range corresponds to stretching vibrations of Cu—O bonds. As follows from the group theoretical and normal mode analysis, one would expect three Raman-active Cu—O stretching modes: $Q_1(B_{2g})$, bond Cu(2)—O(2) along a axis; $Q_2(B_{3g})$, bond Cu(2)—O(3) along b axis; $Q_3(A_g)$, bond Cu(1)—O(4) along c axis. Here we use the same numbering of atoms as in Ref. 10. Since the Cu—O bond lengths for the Q_1 and Q_2 vibrations are quite similar ($R = 1.93 \text{ \AA}$ for Q_1 mode and $R = 1.96 \text{ \AA}$ for Q_2 mode⁷⁻¹⁰), they are expected to have similar frequencies, with the frequency somewhat smaller for the Q_2 mode. When the structure changes upon oxygen depletion from orthorhombic to tetragonal, these modes should

merge into one E_g mode of the lattice which now has D_{4h} space group symmetry. All this favors the assignment of Q_2 and Q_1 to the observed lines at 440 and 500 cm^{-1} , respectively, which merge into one line at 472 cm^{-1} for $x < 6.4$. We may note here that this interpretation is not consistent with lattice dynamic calculations,² which give smaller splitting between Q_1 and Q_2 modes in the orthorhombic phase. Since the Cu(1)—O(4) bond lengths for the Q_3 vibration are 1.85 and 2.3 \AA (they are not equal to each other as in the cases of Q_1 and Q_2 vibrations), one would expect the Q_3 mode to be somewhat higher in frequency than Q_1 and Q_2 modes. The likely candidate for this vibration is the line at 580 cm^{-1} , whose frequency does not change at the phase transition.

The highest frequency mode at 632 cm^{-1} is most sensitive to the reduction of oxygen content. As can be seen from Fig. 2, its intensity drops sharply with even a small change in oxygen content (compare spectra for $x = 7$ and $x = 6.8$). Studies of the structure transformation due to oxygen reduction¹⁰ show that O(1) atoms are removed from the chains Cu(1)—O(1)—Cu(1) along b axis. Stretching vibrations Q_4 along the Cu(1)—O(1) bonds are expected to have the highest frequency in the lattice due to short bond lengths. The above considerations allow us to assume that phonons at 632 cm^{-1} correspond to Cu(1)—O(1) stretching vibrations. It is important to note that the irreducible representation of D_{4h} symmetry group for this phonon mode at the center of the Brillouin zone is B_{1u} which shows that according to the dipole-moment-type selection rules it is normally not active in Raman scattering and active in infrared absorption as a transverse optical mode. However, resonance effects in scattering may introduce different selection rules. Another cause of the change of selection rules may be the formation of the ordered superstructure of microdomains in the a - b plane of the material changing the symmetry of the crystal. These regular microdomains are always observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Ref. 13) and their order and size may depend strongly on the method used in the preparation of the material. Variations in the domain structure may thus explain why this phonon line is sometimes weak in superconducting materials with value of x close to 7 and is so unusually strong in the best epitaxial superconducting films grown on SrTiO_3 substrates.¹²

The interpretation of the 632 cm^{-1} mode has been discussed in previous studies. It was considered intrinsic for a superconducting phase,^{3,5} though not allowed by ordinary selection rules for Raman scattering. It was proposed,³ that removal of the oxygen from the Cu(1)—O(1) chains made this mode active in Raman scattering. Our measurements on samples with variable oxygen content lead us to the opposite conclusion. The removal of oxygen causes an abrupt decrease in the intensity of the 632 cm^{-1} mode. The 632 cm^{-1} mode was also considered as a longitudinal component of the Cu(2)—O(3) infrared active stretching mode⁵ which becomes active in Raman scattering due to resonance conditions. Our data contradict this interpretation because this mode disappears at the transition to the tetragonal phase while Cu(2) and O(3) atoms are only weakly disturbed at the transition. In another study¹ the 632 cm^{-1} mode was considered to

be an impurity mode due to the presence of BaCuO_2 phase in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples. Our measurements on BaCuO_2 pellets and thin films showed that there was no 632 cm^{-1} line in BaCuO_2 and the spectrum of this compound was different from that of presented in Ref. 1.

In conclusion, we measured the variation of the Raman spectra of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_x$ with change in oxygen content. Great care was taken to prepare high purity samples, which were characterized by x-ray diffraction and resistivity measurements. We established the spectrum of the sample with $x=7$, which corresponds to the best superconductor. With a decrease in the oxygen content, major changes occurred in the high-energy part of the spectrum corresponding to

stretching vibrations involving Cu-O bonds. The intensity of the highest energy phonon line at 632 cm^{-1} decreased, reflecting the disappearance of oxygen from the $\text{Cu}(1)\text{-O}(1)$ chains and disordering in the positions of the remaining $\text{O}(1)$ atoms. At the phase transition from orthorhombic to tetragonal phase at $x=6.5$, in addition to disappearance of the 632 cm^{-1} mode, the 438 and 500 cm^{-1} modes of the orthorhombic phase merged into one mode at 472 cm^{-1} .

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