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Resonant Raman scattering of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$: Evidence for the coexistence of ortho-I, ortho-II, and tetragonal microstructures

M. Iliev,* C. Thomsen, V. Hadjiev,† and M. Cardona
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Germany

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The polarized Raman spectra of a single crystal of $YBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0.6$) at 15 K were studied using the 647.1, 568.2, 530.9, and 482.5-nm Kr^+ laser lines. The results give clear evidence for a multiphase scattering volume with the main microstructure phases corresponding to $YBa_2Cu_3O_7$ (OI), $YBa_2Cu_3O_{6.5}$ (OII), and $YBa_2Cu_3O_6$ (T). Significant differences in the frequencies of the OI-, T-, and OII-related modes, as well as variations of the mode intensities with $\hbar\omega_L$ and scattering geometry, result in apparent shifts of the Ba, Cu(2), and O(4) lines.

Unlike the case of orthorhombic $YBa_2Cu_3O_7$ and tetragonal $YBa_2Cu_3O_6$ the structure of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ ($0 < \delta < 1$) is quite complex and far from being understood in detail. While there is a consensus that the structural changes with variation of δ occur in the Cu(1)-O(1) (basal) planes, the description of the local oxygen ordering as a function of δ, T, and the prehistory of the samples is still controversial. It is commonly accepted[1] that there are three main stable phases characterizing the oxygen ordering. At high temperatures the oxygen atoms in the basal planes are statistically distributed between the Cu(1) atoms on the O(1) and O(5) positions [the high-temperature tetragonal (T') phase]. Upon slow cooling the oxygen atoms tend to align forming parallel chains, which define the [010] direction (b axis) and, hence, the local symmetry becomes orthorhombic. A local oxygen arrangement of parallel full chains (like in $YBa_2Cu_3O_7$) corresponds to the ortho-I (OI) phase, whereas that of contiguous full and empty chains to the ortho-II (OII) phase. It is further assumed that the OI and OII phases are responsible for the 90 K and 60 K critical temperatures, respectively.

The oxygen ordering in $YBa_2Cu_3O_{7-\delta}$ was discussed in a number of mainly theoretical works (see, e.g., Refs. 2–6). The proposed models have been examined by computer simulation experiments, and the results differ mainly in their conclusions concerning the length of the oxygen (vacancy) chains. It follows from these models that other stable or metastable ordered phases [such as $3a\times b\times c$ (OIII), $2a\times 2b\times c$, $2\sqrt{2}a\times 2\sqrt{2}b\times c$ (O'), etc.] could also exist and experimental evidence for such superstructures have been reported in several experimental studies.[7–11]

A recent investigation of the oxygen arrangement in a superconducting $YBa_2Cu_3O_{6.4}$ crystal ($T_c = 27$ K) by means of ultrahigh-resolution high-voltage electron microscopy[12] has revealed that the actual distribution of oxygen atoms in the basal planes could be more complex. It was concluded from the experimental observations that the oxygen atoms do not distribute homogeneously but are mostly concentrated in areas smaller than 100 Å in diameter in which clusters of 8–30 Å are closely packed with an oxygen arrangement similar to that of $YBa_2Cu_3O_{6.9}$ or even $YBa_2Cu_3O_{7.7}$.[13] In areas of comparable size the chain oxygen atoms (O(1),O(5)) are totally absent, and the local structure is that of the $YBa_2Cu_3O_6$ T phase. An important result of Ref. 12 is that there is only a partial correlation between oxygen distributions in adjacent basal planes.

Raman scattering is among the few experimental techniques which are sensitive to the local atomic-site coordination. Indeed, the frequency of a particular Raman mode involving vibrations of mainly one type of atoms is determined to a great extent by the interaction of these atoms with their nearest neighbors (usually 2–6) and to a lesser extent by the next-nearest-neighbor interactions. A change of the atomic-site coordination results in significant *discrete* changes of the Raman frequency and the violation of some selection rules, thus allowing otherwise forbidden Raman processes.

Since the discovery of the $YBa_2Cu_3O_{7-\delta}$ system Raman scattering in the limiting cases of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ has been intensively studied both experimentally and by lattice-dynamical calculations.[14,15] There is a great deal of information on the dependence of Raman-phonon parameters as a function of scattering geometry, temperature, excitation wavelength, cation substitution, etc.[14–21] With few exceptions [restricted either to room temperature[23] or to a narrow range of δ (Ref. 24)], there have been to our knowledge, however, no detailed analyses of polarized Raman scattering data from oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ ($0 < \delta < 1$), in particular, of variations of phonon line shapes and intensities with T and $\hbar\omega_L$. The dependence of phonon-mode frequencies on δ was measured by several groups, the results exhibiting some discrepancies. For example, while in Refs. 25–27 an almost linear decrease of the O(4)-mode frequencies with δ was established, Goncharov *et al.*[23] reported a more complex dependence, exhibiting a plateau with $\omega_{O(4)} \approx 490$ cm^{-1} for $0.2 < \delta < 0.5$, almost identical to the plateau found in T_c vs δ. In spite of these discrepancies, the one-mode behavior of the phonon lines of $YBa_2Cu_3O_{7-\delta}$ has not been put into question and the frequency of the O(4) mode was often used as a measure of the oxygen content.

A one-mode behavior of the atomic vibrations in oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ would not be expected if one accepts the above-mentioned findings concerning the real structure of the Cu(1)-O(1) planes. If the excited volume contains relatively large inhomogeneously distributed fragments corresponding to orthorhombic $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.5}$, tetragonal $YBa_2Cu_3O_6$ and/or other less stable phases, it should act also Raman spectroscopically as a multiphase rather than a homogeneous system. The spectra in this case should be a superposition of spectra of the coexisting phases, their relative weight being determined by their abundance and Raman cross sections. It is then plausible to expect information on the multiphase structure by analyzing the line shape and intensity of the O(4) mode vs $\hbar\omega_L$, as both the frequencies and resonant excitation curves of this mode are significantly different for at least two of the main phases under consideration ($YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$). The coexistence of different phases could also be demonstrated by comparing the phonon mode frequencies in different scattering configurations. For example, the Cu(2) mode in $YBa_2Cu_3O_7$ is mainly ZZ polarized and of higher frequency than in $YBa_2Cu_3O_6$ where the corresponding mode is mainly XX polarized. Therefore, the observation of a shift of the Cu(2) line towards lower wave numbers in the XX spectra would provide a signature of the phase coexistence.

In this work we present a detailed study of the polarized Raman spectra (recorded with a triple-subtractive monochromator in macro configuration and a charge coupled device detector) of an oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ single crystal δ ~0.6 ($T_c = 35$ K by a superconducting quantum interference device) and their variations with $\hbar\omega_L$ and T. We demonstrate that the O(4) band is a superposition of at least three Lorentzians centered near 474, 488, and 500 cm^{-1}, which we assign to apex-oxygen vibrations within microstructures corresponding to the $YBa_2Cu_3O_6$, $YBa_2Cu_3O_{6.5}$, and $YBa_2Cu_3O_7$, respectively. Due to significant differences in the resonance excitation curves, the maximum of the O(4) line in the spectra shifts with excitation wavelength and, hence, its position cannot be simply used as a measure of the oxygen content. Additional evidence for the multiphase nature of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ is provided by the ZZ-XX shift of some of the Raman lines for spectra taken on the same spot on an ac face of the crystal. Different spots on the same face all gave equivalent spectra. Similar results were obtained on several specimens with similar oxygen concentrations.

Figure 1 shows the polarized Raman spectra obtained with 530.9-nm (2.34 eV) excitation at 15 K. The spectra are more complicated than those of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ both concerning the appearance of new Raman lines and also the unusual variations of some features with scattering geometry and excitation wavelength. Only five ($5A_g$ or $4A_{1g} + B_{1g}$) Raman lines are expected in the XX/YY and ZZ spectra of $YBa_2Cu_3O_7$ ($YBa_2Cu_3O_6$) at 118 (112), 149 (140), 335 (340), 435 (440), and 502 (472) cm^{-1}, respectively. One observes in Fig. 1 Raman lines close to these wave numbers and additional lines at 131 (ZZ), 190, 231 (XX), 270 (XX), 303 (XX), ~560 (ZZ), and ~580 (XX) cm^{-1}. The most remarkable finding, however, is the difference in the positions of the Ba, Cu(2), and O(4) (apex oxygen) Raman lines in the ZZ and XX spectra. The shift of the O(4) band is most pronounced (from 474 cm^{-1} in the ZZ to 497 cm^{-1} in the XX spectrum) and is obviously due to strong variations of the relative intensities of its components with scattering configurations.

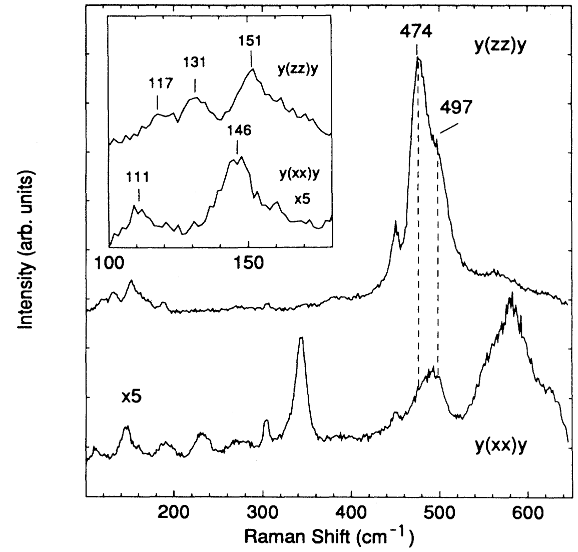

FIG. 1. Raman spectra of $YBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0.5$) as obtained with 530.9-nm (2.34 eV) excitation at 15 K. The inset shows an expanded portion of the low-frequency spectra.

The complex structure of the O(4) band and its variation with $\hbar\omega_L$ is illustrated in Fig. 2 for the ZZ spectra. Due to differences in the variation of the intensity vs $\hbar\omega_L$

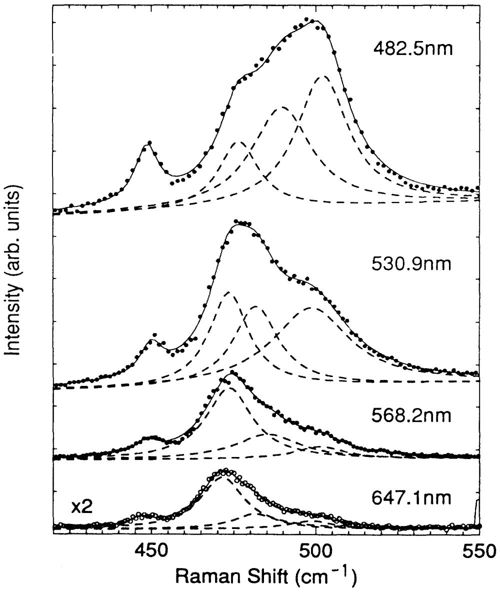

FIG. 2. Decomposition of the complex O(4) band of the $Y(ZZ)\bar{Y}$ spectra ($T = 15$ K) into three Lorentzians and variations of their relative intensity with $\hbar\omega_L$.

of the spectral components the position of the maximum shifts at 15 K from 472 cm^{-1} for 647.1-nm (1.92 eV) excitation to 499 cm^{-1} for 482.5-nm (2.57 eV) excitation. The Raman line shapes of the O(4) modes could easily be fitted with two or with three Lorentzians. With two Lorentzians, however, we obtained for different $\hbar\omega_L$ significant variations of the center frequency and linewidth, which have no simple physical meaning. The fit with three Lorentzians gave close values of the fit parameters frequency (474, 488, and 500 cm^{-1}) and linewidth (16, 20, and 21 cm^{-1}) with variations only in the relative amplitude for all four $\hbar\omega_L$'s.

Provided the O(4)-mode frequencies of $\mathrm{YBa_2Cu_3O_6}$ and $\mathrm{YBa_2Cu_3O_7}$ are 472 cm^{-1} and 502 cm^{-1}, respectively, it is plausible to accept that the corresponding contributions in the complex O(4) band of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ with a reduced average oxygen content come from domains of similar oxygen arrangements. This is further supported by the variations of the relative intensities of the 474- and 500-cm^{-1} substructures with $\hbar\omega_L$. Following the results of Misochko, Sherman, and Timofeev[19] and Heyen, Kircher, and Cardona[18] the intensity of the O(4) mode increases with $\hbar\omega_L$ (1.92 eV $\leq \hbar\omega_L \leq$ 2.57 eV) for samples with $\delta = 0$ and decreases with $\hbar\omega_L$ for samples with $0.8 < \delta < 1$. In addition, since the O(4) peak in the T phase has negligible intensity for the XX spectra,[18,22] the O(4) (XX) maximum of a multiphase system should appear shifted to higher wave numbers compared to the O(4) (ZZ) one; this is actually the case (Fig. 1).

The third component (near 488 cm^{-1}) can be tentatively assigned to scattering from domains with a structure close to that of the OII phase ($2a \times b \times c$ supercell). Recently Hadjiev *et al.*[28] monitored oxygen reordering processes in a room-temperature annealing experiment using a crystal with $\delta \sim 0.5$. Based on the ideas presented here, it was demonstrated that the intensity of the 490-cm^{-1} spectral component of the complex O(4) Raman band increases during the aging process at the expense of the less intense components at 473, 482, 496, and 503 cm^{-1}. Such an evolution shows that our assignment of the $\sim$490 cm^{-1} is the only one consistent with earlier experimental observations[29,30] and predictions of Monte Carlo simulation[31] for the increasing amount of the OII phase during the aging process in $\delta \sim 0.5$ samples.

The multiphase nature of the oxygen-deficient sample studied in this work is further established by the XX-ZZ shift of the Ba (A_g) and Cu(2) (A_g) modes as can be explained consistently only within a multiphase model. Indeed, most of the numerous reports[14–19,22,25–27,32,33] containing information about the line shapes and frequencies of the Ba and Cu(2) modes of the OI and T phases, excited in the photon-energy range under consideration, are consistent with the following observations.

(i) For the OI phase the Ba and Cu(2) modes are represented in the ZZ spectra by symmetrical lines centered at 116–118 cm^{-1} and 147–150 cm^{-1}, respectively. In the YY and to a lesser extent in the XX spectra the Ba line is of comparable intensity but of asymmetric (Fano) shape, with a maximum shifted down to 113–116 cm^{-1} (the "bare" frequency remains the same). The XX or YY intensity of the Cu(2) line, however, is strongly reduced, being at least an order of magnitude weaker than for ZZ polarization.

(ii) For the T phase the ZZ intensities of the Ba and Cu(2) lines are very weak (often not detectable) and shifted to lower wave numbers, 110–115 cm^{-1} and 140–145 cm^{-1}, respectively. A report where ZZ lines of significant intensities have been observed at 125–127 and 141 cm^{-1} (Ref. 17) for nonsuperconducting $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (δ = 0.7 and 1.0) has not been confirmed by other groups. As to the XX spectra, the Ba line is usually too weak to be observed, whereas the Cu(2) line is strong and often of comparable intensity to that of the B_{1g} mode at 340–345 cm^{-1}.

In the complex band of the ZZ spectra between 100 and 180 cm^{-1} (Fig. 1) we distinguish spectral components at 117 and 151 cm^{-1}, which could be assigned to the Ba and Cu(2) vibrations of the OI phase. No Fano shape for the Ba component, expected in the XX/YY spectra at 113–116 cm^{-1} could, however, be detected. Its absence may have the same (still unclear) cause as in the cases of slightly doped $\mathrm{YBa_2Cu_{3-x}Fe_xO_{7+\delta}}$ (Ref. 34) and $\mathrm{Y_{1-x}Pr_xBa_2Cu_3O_7}$ (Ref. 35): although the materials are both oxygen rich and superconducting, no Ba line is observed in the XX spectra.

The 111- and 146-cm^{-1} lines, pronounced in the XX spectra, cannot be related to the OI phase. Although the frequencies of these lines and their resonant behavior (not illustrated here) correspond to the T phase, such an assignment can be questioned in particular for the Ba line: both lines are of comparable intensity, while a much stronger Cu(2) line is expected for the T phase. If they do not arise from the T phase the line at 111 cm^{-1}, or even both lines, could be attributed to the OII phase expected to be dominant in this material. We will not discuss here the possible assignment of the additional lines at 131, 190, 231, 270, 303, $\sim$560, and $\sim$580 cm^{-1}. A detailed analysis of their variations with T, $\hbar\omega_L$, and δ for several oxygen-deficient crystals will be given elsewhere.[36]

In conclusion, the Raman studies presented in this work provide strong evidence that, at a microscopic level, oxygen-deficient $\mathrm{YBa_2Cu_3O_{7-\delta}}$ is a multiphase rather than a single-phase system. Raman-allowed modes of the OI, OII, and T phases plus some defect-induced modes are superimposed in the polarized spectra of partially oxygenated crystals. The different mode frequencies and dependences of the Raman intensities of each particular phase on scattering configuration and $\hbar\omega_L$, result in apparent ZZ-XX shifts and variations of the line shapes as well as the position of the maximum with $\hbar\omega_L$, arising from the superposition of the three spectral components. It becomes obvious from these findings that in such crystals the position of the O(4) mode cannot simply be used as a measure of the average oxygen content of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ without specifying the laser excitation energy and the scattering geometry. Systematic Raman studies of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ at several $\hbar\omega_L$ should make Raman spectroscopy a useful tool for qualitative and quantitative characterization of microstructures and their formations in oxygen-deficient samples.

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*Permanent address: Faculty of Physics, University of Sofia, BG 1126 Sofia, Bulgaria.

†Present address: Faculty of Physics, University of Sofia, BG 1126 Sofia, Bulgaria.

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