

Raman-scattering probe of oxygen ordering during room-temperature annealing of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Using Raman spectroscopy we have monitored oxygen reordering processes in a room-temperature annealing experiment. We have discerned several structures corresponding to different oxygen coordination of Cu(1) in the basal plane by analyzing the line shape of the Raman band of apical-oxygen vibrations. We observed a chain-growing process with increasing annealing time followed by oxygen rearrangements in various orthorhombic superstructures.

I. INTRODUCTION

Recent experiments^{1,2} involving room-temperature annealing of quenched $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with intermediate oxygen content have demonstrated the importance of oxygen-ordered structures for efficient doping of the CuO_2 planes and hence for determining T_c . So far, the kinetics of oxygen ordering and rearrangement have been studied by x-rays,¹ neutron diffraction,² and optical ellipsometry.³ In particular, by using the latter method an increase of $\text{Cu}(1)^{1+}$ ions in the basal plane with annealing time has been observed.³ The $\text{Cu}(1)^{1+}$ ion state is characterized by an optical feature at 4.1 eV (Ref. 4) and has been attributed to a twofold oxygen coordinated Cu(1) ion in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure.^{4,5} Thus, an enhancement of $\text{Cu}(1)^{1+}$ concentration in a sample with constant oxygen content has been considered to increase the number of additional fourfold coordinated Cu(1) ions which in turn, can dope the CuO_2 planes. A recent ellipsometric study⁶ of untwinned single crystals has shown that the 4.1-eV feature is strongly *b* polarized in the range of intermediate oxygen contents. This makes it difficult to distinguish in aging experiments between twofold coordinated Cu(1) in different microstructures, e.g., in tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ -like domains and in an empty chain place in the $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ ordered superstructure. Raman spectroscopy, on the other hand, is known⁷ to be sensitive to structural changes near the apical-oxygen O(4), also including those in the vicinity of the Cu(1) site. The O(4) Raman line has measurably different positions in various super or micro structures in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

In the present work we show that changes in the line shape of the Raman band of apical-oxygen vibrations in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ monitor the reordering processes during a room-temperature annealing experiment.

II. EXPERIMENTAL

In our experiment we used several single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ taken from the same batch grown in a SnO_2 crucible.⁸ The crystals were annealed at 525 °C under suitable oxygen partial pressure¹ and subsequently quenched to 77 K in liquid nitrogen in order to fix stoichiometry δ close to 0.5. For one of the thus pre-

pared samples [superconducting quantum interference device (SQUID) sample] the superconducting properties were monitored using a Quantum Design SQUID magnetometer. Between subsequent superconducting transition temperature - T_c measurements, the sample was left in the magnetometer and aged at 300 K in He atmosphere. A second sample (RAMAN sample) was quickly mounted in a cold-finger liquid-nitrogen cryostat. Before the first Raman measurement the sample spent ≈ 2 min in air and ≈ 8 min in vacuum at 300 K and then was quenched again to 77 K. All Raman measurements were performed when the sample was at 77 K. In each annealing cycle the RAMAN sample was aged for a given time at 300 K in vacuum, then rapidly cooled down (in about 2 min) to 77 K. Previous experiments showed that the ambient (He, air, or vacuum) has no effect on the room-temperature annealing, neither as regards the structural and superconducting properties¹ nor for the optical response.³

Raman spectra were recorded by a Dilor-XY multi-channel spectrometer. The spectrometer slits were set to 3.5 cm^{-1} spectral width, which along with an absolute accuracy of 1 cm^{-1} allowed us to resolve subtle changes in Raman line shapes. The Ar^+ line at 514.5 nm was used as an excitation source. The laser beam was focussed to a spot of $\approx 30 \mu\text{m}$ in diameter on the crystal surface and the laser-power density was kept below 100 W/cm^2 . Special care was taken to focus the laser beam always on the same spot of the crystal surface. At the end of the experiment we compared the Raman spectra of the SQUID and RAMAN samples and found that they were nearly the same.

III. RESULTS AND DISCUSSION

In Fig. 1 we present the *ZZ*-polarized Raman spectra (*Z* denotes a direction parallel to the *c*-axis of the crystal under study) of the sample taken after the first and final aging procedures at 300 K. At the same annealing conditions the SQUID sample showed an increase of T_c of about 8 K (from 47 to 55 K). Generally, there is no significant shift of the Raman lines with aging time. However, some changes of the line shape of the Raman band at 490 cm^{-1} are obvious, as displayed in Fig. 2.

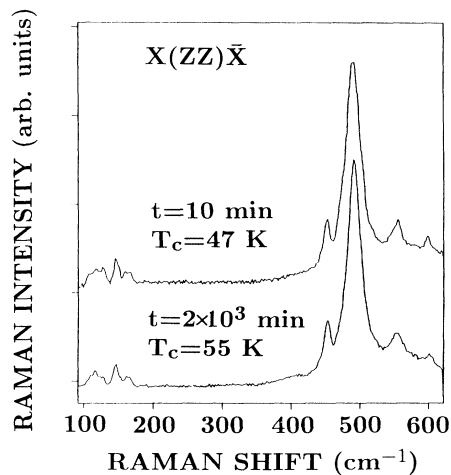


FIG. 1. Polarized Raman spectra of rapidly quenched $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (δ close to 0.5) measured after the initial and final annealing.

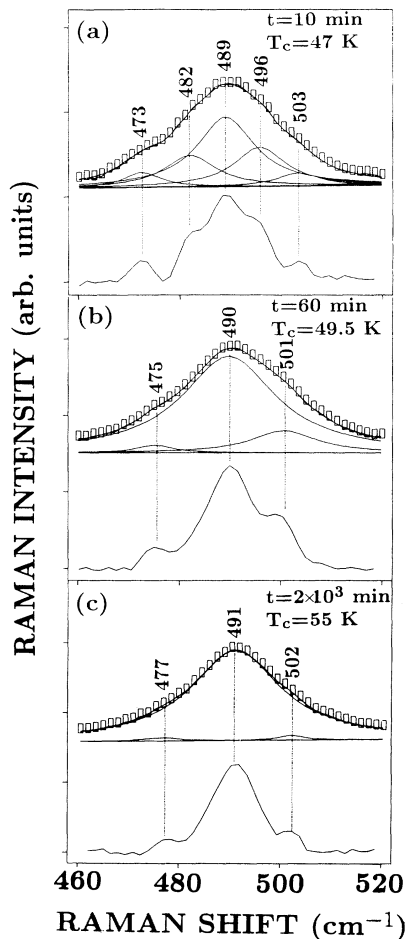


FIG. 2. Raman spectra of the sample after subsequent annealing procedures. The Lorentzians which were included in the best fit are given below the experimental spectra. The lower part of each vignette displays the FFT-filter treated spectrum (see the text). The spectra were taken after annealing of (a) 10 min; (b) 60 min; (c) ≈ 2000 min.

We focus now our attention on the complex shape of this band. It is well established that the Raman-active A_g vibration of the apical oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (with $\delta \approx 0$) has a frequency around 500 cm^{-1} (see, e.g., Ref. 7). The position of this peak has been found to depend strongly on oxygen deficiency δ . It shifts from 503 cm^{-1} for $\delta \approx 0$ down to 474 cm^{-1} for $\delta \approx 1$ for samples measured at room temperature.^{9,10} Recently, it has been shown that the A_g Raman band of the apical-oxygen atom in oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals is a superposition of Raman lines corresponding to vibrations of the O(4) atoms in various microstructures in a crystal.¹¹ Thus, the dependence of the O(4) Raman peak on oxygen content has to be regarded as a dependence on δ of the center of the average spectral weight originating from the O(4) vibrations.

Further, we exploit that Raman lines at $497\text{--}503 \text{ cm}^{-1}$ are representative for O(4) vibrations in the OI (ordered, orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure), those at $490\text{--}492 \text{ cm}^{-1}$ for vibrations in the OII (ordered, orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$) phase and those at $474\text{--}477 \text{ cm}^{-1}$ for the T phase (tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$).^{7,10} All those frequencies seem to correspond to vibrations of the O(4) atoms in ordered crystal structures. Keeping in mind these assignments we also present in Fig. 2 the best fit to the experimental spectra with basically the components just mentioned. The fit was performed by varying the number of Lorentzians and their parameters. In order to have additional confidence that the fitting procedure is reliable, we separately treated the spectra with a high-pass FFT (fast Fourier transform) filter using a method described in Ref. 12. The filter procedure consisted of a Fourier transformation of the measured Raman spectra with subsequent multiplication by an exponential decay function (exponential filter). The thus created product was smoothed (apodization filter) and then a reverse Fourier transformation was performed. Varying the parameters of the exponential filter (its Fourier transform is Lorentzian) one can synthetically narrow the spectral bandwidth features of the Raman spectrum. This procedure helped us in identifying the principal lines comprising the 490-cm^{-1} complex band. The result of such filtering is shown by the lower panels in Figs. 2(a)–2(c) and yields similar frequencies as the Lorentzian fit.

Now we discuss the intensity redistribution over the spectral components of the Raman band at 490 cm^{-1} with annealing time. Since this redistribution reflects certain structural changes, it is instructive to parallel it to the results from numerical simulations of aging experiments. Ceder, Mc Cormack, and de Fontane¹⁵ performed a Monte Carlo simulation of the room-temperature aging behavior of samples quenched from the high-temperature tetragonal phase. They predicted two types of processes for the oxygen rearrangement. The process that dominates the initial reordering involves the hopping of oxygen occupying "inter-chain" O(5) sites to the unoccupied "chain-oxygen" sites O(1). This process converts the T-phase into the OI-phase. The reordering is relatively fast because only nearest-neighbor jumps are required. The second process corresponds to the OII-superstructure formation. It consists of a rearrangement of the OI do-

mains into local regions with OII structure. The spectrum shown in Fig. 2(a) was measured after the rapidly quenched sample spent ≈ 10 min at room temperature. The Raman band is characterized by a rather complex line shape which likely reflects a significant inhomogeneity of the oxygen distribution. An analysis of the best fit for this band suggests that the oxygen was ordered in microdomains having structures similar to those of the main ordered phases in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The line at 489 cm^{-1} - OII phase is dominant. There are also spectral components at 473 and 503 cm^{-1} which are signatures of the T and OI structures, respectively. The relatively strong features at 482 and 496 cm^{-1} are likely to arise from microdomains with $\delta \approx 0.6$ - 0.8 [short-chain tetragonal phase \bar{O} (Ref. 13)] and 0.2 - 0.4 (two full and one empty chains superstructure, OIII phase¹⁴), respectively. Comparing the relative intensity of the spectral components one can conclude that orthorhombic structures are dominant in our sample. Therefore, the fast-ordering process from tetragonal to orthorhombic local symmetry had been largely accomplished after the first annealings of 10 min.

The variety of microstructures which contribute to the Raman band at 490 cm^{-1} was surprisingly reduced with 50 min of further annealing. The best fit of the Raman band, as shown in Fig. 2(b), involves only three Lorentzians. The dominant spectral component at 489 cm^{-1} is shifted upward by one wave number and the remaining spectral weight is redistributed over two bands at 475 and 501 cm^{-1} . We believe that the changes from Fig. 2(a) to 2(b) are due to a process of chain growth leading to the disappearance of the short-chain \bar{O} phase (spectral feature at 482 cm^{-1}). We also measured a number of spectra (not shown) of the sample after several subsequent annealings up to 500 min long. We found a tendency of reduction of the relative intensity of the Raman lines corresponding to the T and OI phases. The final measurement was performed after the sample was annealed for ≈ 2000 min [Fig. 1(c)]. The fit of the Raman band

shows an increase of the 490-cm^{-1} line intensity, which is shifted upwards by one cm^{-1} , and a further relative decrease of intensity of the lines at 477 and 502 cm^{-1} . Thus the relative intensity of the line at 490 cm^{-1} (OII phase) increases continuously at the expense of those at 477 cm^{-1} (T phase) and at 502 cm^{-1} (OI phase). Simultaneously the T_c of the sample increases. In terms of $\text{Cu}(1)^{1+}$ concentration this process can be related to an increase of $\text{Cu}(1)^{1+}$ ions in the OII phase. The 490-cm^{-1} line intensity increases by $\approx 10\%$ in accordance with previous experimental observation^{2,3} and with the predicted slow oxygen rearrangement.¹⁵ On the other hand, the upward shift of the position of the line at 490 cm^{-1} is consistent with a slight shortening of the average O(4)-Cu(2) distance as a result of charge-transfer processes that take place in aging experiments.² Measurements¹⁶ of bond lengths versus T_c when oxygen content is varied have shown an increase of the T_c with decreasing the O(4)-Cu(2) distance. Therefore, note that the position of the 490-cm^{-1} phonon line consistently follows the changes of the O(4)-Cu(2) bond length and the T_c .

In summary, we have demonstrated that changes in the line shape of the Raman band at 490 cm^{-1} reflect the oxygen rearrangement in the basal plane during room-temperature annealing of the sample. We have thus monitored the chain growing process and a subsequent reordering of OI into OII with time.

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