

Raman-Study of Photoinduced Chain-Oxygen Ordering in $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$

S. Bahrs, A. R. Goñi, B. Maiorov, G. Nieva, A. Fainstein, and C. Thomsen

Abstract—We investigated Raman-forbidden signals in $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $R = \text{Y}$ or Pr , which lose intensity under illumination at low temperatures. These defect-induced peaks are only visible in oxygen-deficient material and for light polarized parallel to the copper-oxygen chains along the material's b -axis. In a first, two-laser based experiment we established that the bleaching effect of the light is polarization dependent as well. From this and other known properties we conclude that the signal is connected to the copper-oxygen chains, reflecting their state of disorder, and is thus closely related to aging and to the persistent photoconductivity effect in the material. In a second set of experiments we followed the temperature dependence of the Raman spectra and the intensity decrease.

Index Terms—Oxygen-defects, Raman, superconductivity, YBCO.

I. INTRODUCTION

THE STRUCTURAL and electric properties of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are known to depend sensitively on oxygen content. The defects in the oxygen-deficient material are located in the plane containing copper-oxygen chains along one axis and define the difference between the crystallographic a and b -axis. Therefore, the oxygen loss results in a structural change from orthorhombic to tetragonal structure ($\delta \approx 0.6$), where the latter does not show superconductivity anymore. Aging of the material at room temperature results in ordering of defects in superstructures with alternating long and completely empty chains and an increased orthorhombicity [1]. Interestingly, this causes an increase in conductivity and critical temperature, because the average valence of the copper atoms changes such that the hole doping level of the superconducting planes is increased [2]. The reordering of defects in the chain plane freezes out below room temperature, but is thought to be responsible for the persistent photoconductivity effect at low temperatures [3], [4]. Illumination has the same effect on conductivity as aging, the change is stable at low temperatures, but recovers at room temperature.

The Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and all other materials of the $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ -family [5]–[7] that have been

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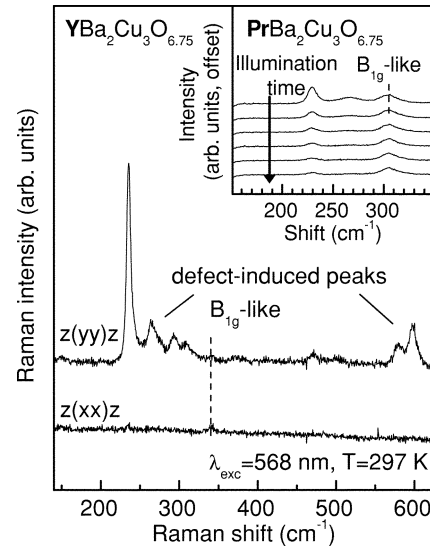


Fig. 1. Selection rules of defect-induced peaks in an untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ single crystal. The spectra were taken at $T = 80$ K with resonant excitation ($\lambda = 568$ nm). The polarization is given in Porto's notation. The inset shows the loss of intensity of defect peak under illumination in a twinned $\text{PrBa}_2\text{Cu}_3\text{O}_{6.75}$ crystal. The illumination time is one hour in total and increases from top to bottom. The mode marked B_{1g} is a Raman-active phonon and remains unperturbed. The spectra have been offset for clarity.

investigated show Raman-forbidden signals with the unusual property of losing intensity under illumination [8]. There are several peaks in two groups around 240 cm^{-1} and 600 cm^{-1} , which are not assigned to any of the Raman-active phonons and are exclusively seen in oxygen deficient material (maximum intensity at $\delta \approx 0.3$ [7]). In $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ they are resonant for an excitation energy of 2.2 eV, dominating the Raman spectra [8]. Their selection rules are illustrated in the spectra of an $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ untwinned single crystal in Fig. 1: In backscattering geometry along the crystallographic c -axis they are present for incoming and outgoing light polarized along the b -axis [$z(yy)z$ in Porto's notation], that is, parallel to the copper-oxygen chains, but absent in perpendicular polarization [$z(xx)z$]. Their relation to the orthorhombic properties of the material is evident [7]. The Raman-allowed B_{1g} -like mode coming from the superconducting copper-oxygen plane, which is weak but present in both setups, has been marked for comparison. The inset in Fig. 1 shows sequential Raman spectra of equal integration time taken on a twinned $\text{PrBa}_2\text{Cu}_3\text{O}_{6.75}$ crystal at a temperature of 80 K, starting at the top. In this material the defect-induced peaks are less pronounced, so that the B_{1g} -like mode is clearly visible in resonant spectra. Its intensity remains constant, whereas the defect peak at 229 cm^{-1} diminishes under the influence of the laser light used for

Raman excitation, i.e., it “bleaches.” Like the persistent photoconductivity the intensity loss is stable at low temperatures, but recovers to its original value at room temperature. Another similarity is the time dependence of the two effects: neither follow a simple exponential rule, but can be described using a stretched exponential function [5]. Taking these similarities into account we have proposed [5] that the two effects have the same origin, namely the light-induced reordering of the oxygen atoms into patterns with longer chains. On the one hand, the longer chains change the average valence of the copper atoms and thus the hole doping level of the superconducting planes. On the other hand, the Raman signal decreases in intensity proportional to the defect-density.

We conducted two sets of experiments in order to find further evidence for this model. First we analyzed the light-induced ordering and the Raman intensity in a two-color experiment on single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ and $\text{PrBa}_2\text{Cu}_3\text{O}_{6.75}$, changing the polarization of the second color without altering the Raman part of the experiment. This is to determine whether not only the Raman signal, but the bleaching effect as well is polarization dependent, as Wake *et al.* have mentioned briefly [8]. In the second set we investigated the bleaching rate as a function of temperature on an $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ ceramic sample. In a previous experiment Panfilov *et al.* [7] reported that the decay is slow for low temperatures, fast in an intermediate range and then slow again approaching room temperature. This, however, would contradict the oxygen-hopping assumption, which should speed up for higher temperatures that make movement of oxygen more probable. In fact, in our experiments the speed of bleaching increases monotonously with temperature.

II. EXPERIMENTAL DETAILS

The $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ and $\text{PrBa}_2\text{Cu}_3\text{O}_{6.75}$ crystals were prepared using the flux-growth technique with Ytria stabilized ZrO_2 trays, using the same method and proportion of $R = \text{Y, Pr}$ in the starting composition materials as that described in Ref. [9]. No impurities were found in the crystals using energy dispersive spectroscopy with a scanning electron microscope. Special care was taken to choose $\text{PrBa}_2\text{Cu}_3\text{O}_{6.75}$ single crystals with no Y contamination from the trays. A detwinning process was performed in the $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ crystal as described in Ref. [6]. With our growth method the pure $\text{PrBa}_2\text{Cu}_3\text{O}_{6.75}$ crystals are normally smaller than those of $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ and non-suitable for the detwinning process. Our ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ sample for the temperature dependent bleaching experiment was prepared by a solid state reaction of stoichiometrically mixed powders as described in Ref. [3]. The oxygen content reduction was performed at 507°C in an oxygen atmosphere of 14.5 mbar followed by a controlled cooling down process [10].

The samples were kept at room temperature in the dark for several weeks and then quenched from 293 K to the various low temperatures with a cooling rate of 20 K/min using an Oxford cryostat. All bleaching measurements were recorded on a previously unilluminated spot of the sample using a triple Dilor spectrometer in backscattering geometry with a nitrogen cooled Charge Coupled Device-detector. For Raman excitation the 568

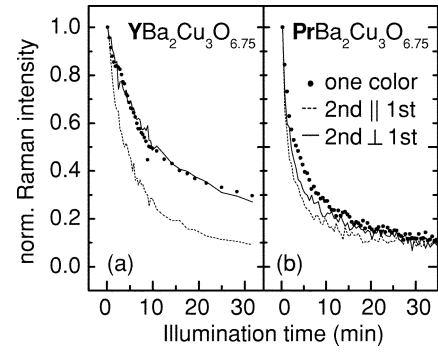


Fig. 2. Decrease of the intensity of the largest defect-induced peak [(a) $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ untwinned single crystal at 234 cm^{-1} , (b) $\text{PrBa}_2\text{Cu}_3\text{O}_{6.75}$ twinned crystal at 229 cm^{-1}] over illumination time at 80 K. The data has been normalized to the first data point. Raman excitation occurred with $\lambda = 568\text{ nm}$, $P = 5\text{ mW}$ in all curves. Filled circles represent data taken with that single line. Solid lines show data taken with additional illumination with $\lambda = 488\text{ nm}$ and $P = 5\text{ mW}$ in polarization perpendicular to that of the Raman excitation line (i.e., polarization along a in $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$), dashed lines are used for both colors in parallel polarization (i.e., along b in $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$, the chain direction).

nm line ($P = 5\text{ mW}$ in the two-color experiment, 6 mW in the temperature series) of an $\text{Ar}^+ - \text{Kr}^+$ laser was focused on a spot of about $100\ \mu\text{m}$ in diameter. The laser light served as excitation as well as for bleaching the samples. Additional bleaching in the two color experiments was provided by the 488 nm line of an Ar^+ laser (5 mW) focused on the same spot. The bleaching was observed by sequentially taking spectra with accumulation times of 20, 30, 100 and 200 s in the two-color experiments, and of 5 and 10 min for a total illumination period of two hours in the temperature experiments.

III. POLARIZATION DEPENDENT BLEACHING

In Raman spectroscopy the effect the light has on the material cannot, in principle, be distinguished from the observation. It is impossible to see the peaks without the Raman excitation line bleaching them at the same time. Furthermore, the Raman excitation laser line cannot be varied in polarization in a bleaching experiment, as the peaks are only visible for polarization parallel to the chains. In order to circumvent this we introduced a second laser with an independently variable polarization in our experiment. We set up the same Raman experiment with the resonant excitation with $\lambda = 568\text{ nm}$ at $T = 80\text{ K}$ three times, once with the Raman excitation alone, once with a second laser line (488 nm) focused on the same spot with polarization parallel to the first laser, and once with perpendicular polarization. The second color was not detected in the Raman-experiment. As the decrease of intensity becomes faster for higher illumination intensities, the two lasers together should bleach the peaks faster than one alone [8]. As can be seen in Fig. 2(a), where the corresponding curves are shown for an untwinned single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$, this is true for both lines in the same polarization. However, polarizing the second color perpendicular to the chains results in the same development as that of the single color experiment. So at least for the part of the effect that can be sensed by Raman, we conclude that the excitation of the oxygen atoms, enabling them to hop to neighboring places, is

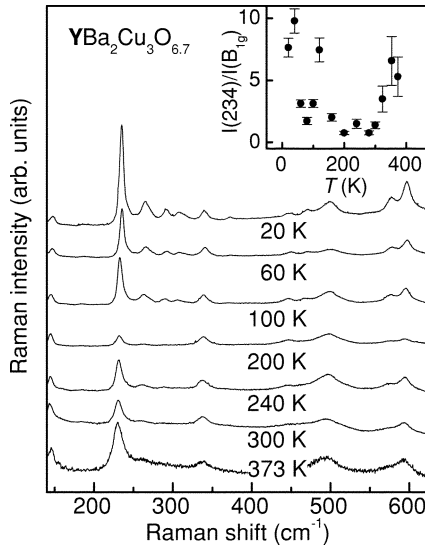


Fig. 3. Resonant Raman spectra of an $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ ceramic sample at various temperatures. The excitation was $P = 6$ mW at 568 nm, the integration time 2 h for all spectra except the one at 373 K (5 min). The data has been normalized to the intensity of the Raman-allowed B_{1g} -mode at 340 cm^{-1} and offset for clarity. The inset shows the intensity of the largest defect-induced peak at 234 cm^{-1} versus temperature in the same normalization, but corrected for the energy dependence of the Bose-factor.

itself dependent on polarization. It would be interesting to find out whether the persistent photoconductivity effect shows the same property.

For the twinned $\text{PrBa}_2\text{Cu}_3\text{O}_{6.75}$ -crystal in Fig. 2(b) the situation is different: The same setup results in three very similar curves, with much smaller differences than in the untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ sample. Again the single color curve is slightly slower than the decay obtained with both lasers polarized parallel to each other, but the perpendicular bleaching lies in between. We think that the principle reason for this difference is that the sample was twinned, so there is no macroscopic distinction between the two directions. In both directions light can cause reordering by enabling oxygen atoms to change site. In a twinned crystal both two-color curves should then fall below the single color one, which they do, although the difference in our measurements is rather small and vanishes for long illumination times. So part of the explanation is certainly that the bleaching in the more tetragonal material with $R = \text{Pr}$ is almost one order of magnitude faster than in $R = \text{Y}$, while the overall signal is smaller [5]. Precise observation of the fast change in the beginning is hampered by the fact that the signal quality requires a minimum integration time.

IV. TEMPERATURE DEPENDENT BLEACHING

Spectra taken at various temperatures on an $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ ceramic sample under resonant excitation are shown in Fig. 3. The two groups of defect peaks around 240 cm^{-1} and 600 cm^{-1} (for $T = 80\text{ K}$ at $234, 265, 291, 308, 579$ and 597 cm^{-1}) are so intense that they dominate each entire spectrum, making the Raman-allowed modes at 340 and 501 cm^{-1} (80 K) appear small in comparison. This is especially true for the low temperature spectra, where the defect-induced peaks are narrow and intense and a large number of them can be distinguished. With

increasing temperature they lose intensity and become broader, making a distinction of the smaller peaks impossible. Above room temperature the tendency changes for the intensity, and an increase in comparison to the Raman-allowed modes is observed, reaching almost the low-temperature values. Raman-allowed signals from the active phonons show temperature dependent broadening, which is why they lose amplitude in the high temperature spectra. The intensity of the largest defect induced peak (234 cm^{-1} at 80 K) normalized to that of a Raman-allowed mode (B_{1g} -like at 340 cm^{-1} at 80 K) versus temperature is plotted in the inset to Fig. 3.

Before discussing the temperature dependence of the bleaching, we would like to comment on the observed change in overall intensity at low temperatures of all defect-induced peaks in Fig. 3. One reason for this behavior could lie in the temperature dependence of the resonance profile for the Raman scattering by the defect modes. As we show below, the hopping of the oxygen atoms after photoexcitation is a thermally activated process. At higher temperatures the movement of oxygen atoms could lead to a lifetime reduction for the intermediate electronic states participating in the resonance at 2.2 eV , which could then become quenched. Similar processes have been observed in multiple quantum wells [11]. Another important part of the intensity development is due to the bleaching itself. Within a fixed integration time different stages of bleaching are viewed for varying decay constants. We took this into account by extrapolating time dependent measurements back to the beginning of illumination using a stretched exponential function as is described in the next paragraph. We obtained roughly equal values for the initial intensity, confirming that the bleaching is largely responsible for the temperature dependence of the intensity up to ambient temperature. Above 330 K , bleaching is not detectable anymore, either because it is too fast to be observed, or because the thermal oxygen ordering and the relaxation of the bleaching are so fast that it becomes impossible to move the oxygen atoms to a nonequilibrium state (see Ref. [12] for a comparison of time constants of relaxation). Within the model of oxygen reordering the renewed increase in intensity of the defect modes above 300 K can be interpreted as more disorder at higher temperatures due to increased entropy in the chains.

Fig. 4 shows the time dependent intensity of the largest defect-peak taken from sequential Raman-spectra. According to our previous work we describe the intensity decay with a stretched exponential function as was used for persistent photoconductivity data already [5]:

$$I(t) = I_0 \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] + \text{const.}$$

where τ is a decay constant and β reflects the distribution of different decay times in a heavily disordered system. By evaluating the data using these parameters, we find that the decay times decrease monotonously from 90 ± 20 min for 20 K to about 8 ± 2 min for 280 K with increasing temperature. The parameter β reflects the change in curve shape, yielding a different value for two separate regions (below 100 K $\beta \approx 0.7$, above 200 K $\beta \approx 0.4$).

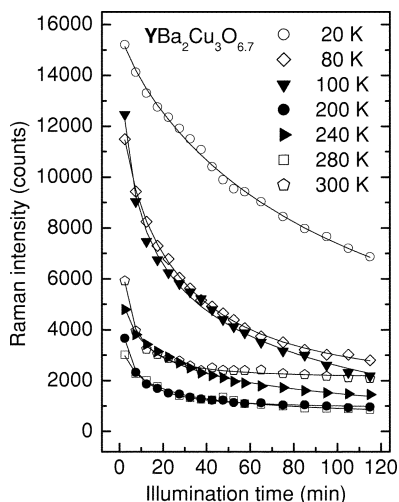


Fig. 4. Decrease of intensity in absolute counts of the peak at 234 cm^{-1} under illumination with 568 nm ($P = 6\text{ mW}$) in an $YBa_2Cu_3O_{6.7}$ ceramic sample for various temperatures. The curves correspond to some of the spectra in Fig. 3. The lines represent fits using a stretched exponential function.

An interesting result of this work concerns the strong reduction of the decay time τ with increasing temperature. This dependence, which is in discrepancy with that reported in Ref. [7], points to a thermally activated behavior for the photoexcited oxygen atoms. From an Arrhenius plot of τ versus T^{-1} in the high temperature range we obtain an activation energy of $(15 \pm 5)\text{ meV}$, i.e., $\approx 170\text{ K}$, in agreement with the temperature interval separating the two regions of high and low β -values. The activation energy determined from photoconductivity relaxation above room temperature was determined to be about 0.9 eV , almost two orders of magnitude higher than in the photoexcited data presented here [4]. Nevertheless, there is obviously a strong influence of temperature on the bleaching effect. In order to investigate this further, we are carrying out measurements on single crystals.

V. CONCLUSIONS

The bleaching of the defect-induced Raman signal at about 230 cm^{-1} in $RBa_2Cu_3O_{7-\delta}$ for different polarizations and temperatures was observed. The loss in intensity is caused exclusively by light polarized parallel to the copper-oxygen chains in an untwinned crystal, supporting the close connection between the defect-peaks and the chains. The intensity decay

becomes faster for higher temperatures. It can be described using a stretched exponential function, which yields a high and a low temperature region with a different parameter β reflecting the shape of the decay. We relate the oxygen reordering effects of aging and persistent photoconductivity in the material to the Raman signal, the bleaching reflecting reordering of the oxygen defects in the chain-planes into higher symmetry superstructures, which are characterized by longer chains.

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