

## Effect of light on the reflectance anisotropy and chain-oxygen related Raman signal in untwinned, underdoped crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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### Abstract

Recent studies of the optical anisotropy of a detwinned, underdoped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -crystal showed that illumination-induced change and recovery in the surface reflectance can be traced on a time scale of hours. This effect of light is also known from Raman bleaching and electrical transport and shares features of the oxygen reordering processes above room temperature. We report temperature-dependent studies of the optical anisotropy using reflectance anisotropy spectroscopy and present time-dependent data for the optical transitions at 2.2 and 4.4 eV. We compare our results to Raman bleaching and discuss them within the picture of superstructure patterns and oxygen-defect reordering in underdoped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

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$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  displays a number of effects particularly connected to oxygen defect sites in the underdoped material. Among them, the illumination-induced effects of persistent photoconductivity and Raman defect-peak bleaching have been repeatedly investigated in the past [1–5]. They are attributed to light-induced reordering of oxygen atoms in the chain plane, or partly to carrier trapping in defect sites in the current discussion. Spontaneous reordering into superstructure patterns which affects the conducting properties is known from room-temperature ageing. In a recent study, we documented that the light-induced effects can also be traced in the  $a$ – $b$  components of the dielectric function using reflectance anisotropy spectroscopy (RAS), which is very sensitive to differences in the dielectric properties along two alternating directions of polarization [6]. A RAS peak around 2.2 eV, matching the Raman resonance profile of the photobleaching peaks, decreases upon illumination, while a large feature above

4 eV increases. Ab initio and Hubbard-model calculations attribute the features to different structural elements in the copper–oxygen chain plane [7,6]. The effect shares properties with Raman photobleaching regarding the long time scale, the polarization dependence, and the recovery on a similarly slow time scale at room temperature. Here, we report on low-temperature properties of the RAS spectra, showing that the illumination-induced effect also occurs below room temperature. We discuss its properties in comparison to the known temperature dependence of Raman photobleaching, and within the picture of oxygen reordering.

We used  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  detwinned single crystals with an oxygen content of 6.7 and 6.65. Their size was approximately  $1.0 \times 0.5 \times 0.1 \text{ mm}^3$  ( $a \times b \times c$ ). Their preparation followed the method and proportions as described in Refs. [9,10], and detwinning under uniaxial stress was done as described in Ref. [3]. X-ray diffraction and Raman spectroscopy characterization showed excellent detwinning.

The RAS spectra were obtained in the spectral range from 1 to 6 eV using a Xe-lamp as white-light source, which was focussed onto the  $a$ – $b$  surface of the crystal at near normal incidence. A photoelastic modulator was used to probe the reflectance difference  $r_b - r_a$  between the  $b$  and  $a$  crystalline

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axes of the sample. The RAS signal was taken as the real part of the amplitude of the periodic changes normalized to the average reflectance, corresponding to

$$\text{Re}\left(\frac{\Delta r}{r}\right) = \text{Re}\left(\frac{r_b - r_a}{0.5(r_b + r_a)}\right).$$

This difference in reflectance relates to the difference between the  $a$  and  $b$  components of the dielectric function [6]. Further details of the RAS method are described elsewhere [11,12]. For additional excitation the 442 nm line of a HeCd Laser was used with a power density of 10 mW/mm<sup>2</sup>. The samples were cooled in a temperature regulated flow cryostat with a sapphire optical window.

Fig. 1 shows reflectance anisotropy spectra taken at room temperature from two samples with slightly differing oxygen concentration, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.65</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.7</sub>. Comparison to ellipsometry data from Kotz et al. [7] showed that the RAS peak centered at 2.2 eV is due to a peak in the  $b$ -components of the dielectric function, which is absent in the  $a$ -components [6]. Cluster calculations in the Hubbard model yield an electronic transition with suitable selection rules near this energy associated with states of short fragments of copper oxygen chains in the chain plane of the underdoped material [6]. The peak is more pronounced in the sample with higher oxygen doping, as would be the qualitative expectation for the case of more oxygen distributed in the chain plane. An X-ray diffraction experiment on the crystals (to be reported in detail elsewhere [13]) yielded two different oxygen superstructure patterns. While the structural phase diagram in this range of oxygen concentrations is very complex and much depends on the details of preparation and annealing, our finding matches recent work on the oxygen ordering phase diagram, which is placing samples with oxygen concentrations 6.65 and 6.7 into different phases [14]. Our sample with O<sub>6.65</sub> displayed ortho-II ordering, while the superstructure peak positions for the O<sub>6.7</sub>

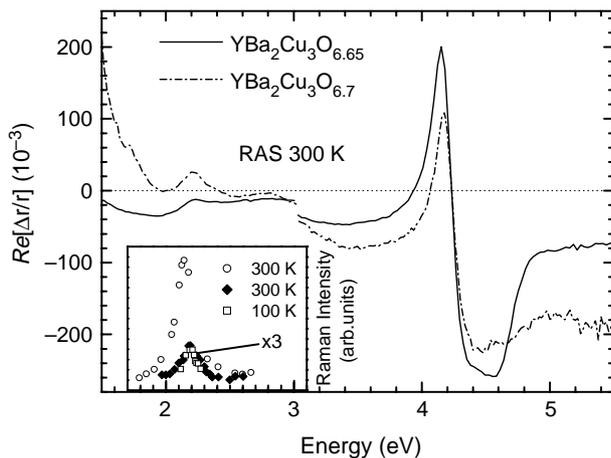


Fig. 1. Reflectance anisotropy spectra of two detwinned single crystals of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  with slightly different oxygen content at room temperature. The data for the 6.7-sample is reproduced from Ref. [6]. Zero anisotropy is set using an isotropic Si(111) reference sample surface. The discontinuity in the data at 3 eV occurs for technical reasons, on detector change. For comparison, resonant Raman data is depicted in the inset on the same energy scale (from Wake et al. [2], (multiplied by 3) and Käll et al. [8]).

sample are consistent with the ortho-VIII phase suggested in Ref. [14]. RAS thus proves to be very sensitive to the oxygen content and the superstructure phase.

The inset of Fig. 1 displays literature data of the Raman resonance profile taken from Wake et al. [2] (300 and 100 K,  $\delta \approx 0$ ) and Käll et al. [8] (room temperature,  $\delta \approx 0.23$ ). Centered at 2.19 and 2.15 eV, respectively, and with a width of 160 meV it is similar, though not identical to the dielectric peak. Both resonances occur only for light polarized along the chain direction and provide evidence for a common microscopic origin of the dielectric response and the Raman resonance.

The large, first positive and then negative RAS feature above 4.1 eV results from a peak in the dielectric function, which is slightly shifted in energy in the  $a$  and  $b$  components. It is attributed to copper atoms without in-plane oxygen atom neighbors [7,6], consistent with the fact that it is more pronounced in the sample with lower oxygen content.

The development of the RAS spectra on cooling is shown in Fig. 2. The most clearly seen effect is the shift of spectral weight towards lower energy. The reflection of the sample surface turned visibly from white to red. It also became weaker as the average reflectance in the visible range went down. Note that the overall vertical shift of the spectra had opposite direction for the two samples investigated. Considering the different oxygen ordering phases, differences in response to

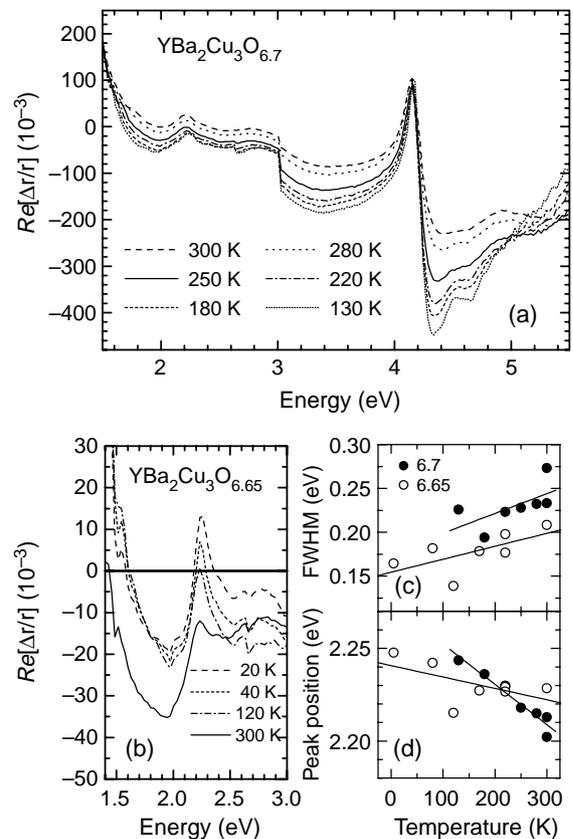


Fig. 2. Temperature-dependent reflectance anisotropy spectra of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> . (a) Spectra between 300 and 130 K of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.7</sub>. At low temperatures two features at 4.3 and 4.6 eV evolve. (b) The 2.2 eV peak in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.65</sub> at various temperatures. (c) Width and (d) position of the 2.2 eV peak versus temperature. Full symbols correspond to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.7</sub>, open symbols to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.65</sub>.

temperature changes or to illumination can be expected, the nature of this relation is subject to further investigation. Two separate, negative peaks at 4.3 and 4.6 eV develop from the one at room temperature at 4.4 eV, and the overall anisotropy increases. The peak at 2.2 eV was fitted using a Lorentzian lineshape. Fig. 2(c) depicts its slight shift in position towards higher energies at low temperatures, as well as its sharpening. The change in width of 20% between 100 and 300 K matches the sharpening of the Raman resonance observed by Wake et al. as depicted in Fig. 1 [2].

Illumination-induced changes of the RAS spectra are not restricted to the room temperature range of spontaneous oxygen mobility. Fig. 3 shows spectra taken during a 1 h period of additional laser illumination, with the 2 and 4 eV regions magnified in (a) and (b), and the differences between spectra depicted in (d). Like in the room temperature series, the 2 eV feature decreases in intensity, while the anisotropy at the 4 eV feature increases upon illumination. This is consistent with the oxygen ordering picture, as less short fragments but more two-fold coordinated chain coppers and a more pronounced orthorhombicity should develop during superstructure pattern formation [5].

The changes in the spectral ranges of interest are traced versus time for series at 300, 200 and 170 K in Fig. 4. The 200 K series was continued at constant temperature after

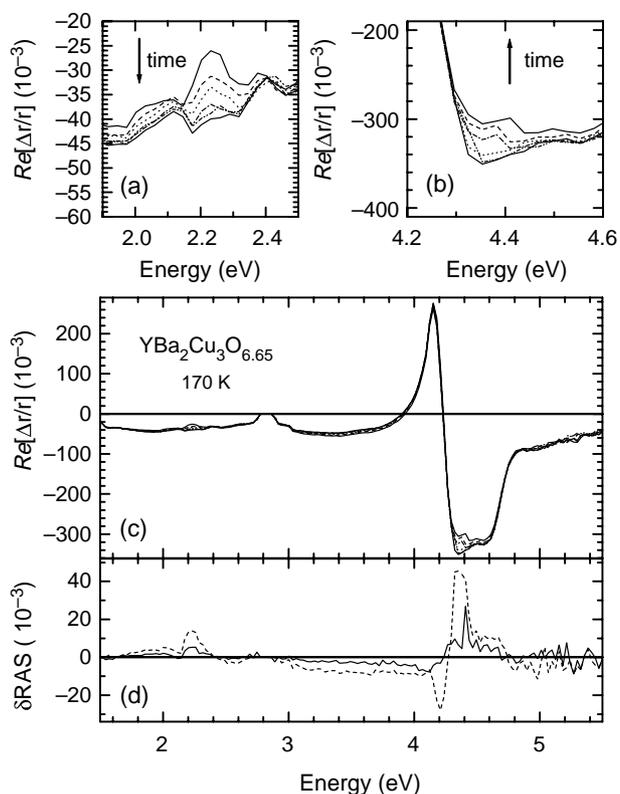


Fig. 3. The change in the reflectance difference of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.65}$  upon additional illumination at 170 K. (a) and (b) magnified the areas around 2.2 eV and 4.4 eV where changes occur upon illumination; (c) entire RAS spectra during illumination; (d) displays the differences between the first two and between the first and the last spectrum in a series. The spectra were taken at regular intervals during a time span of 1 h.

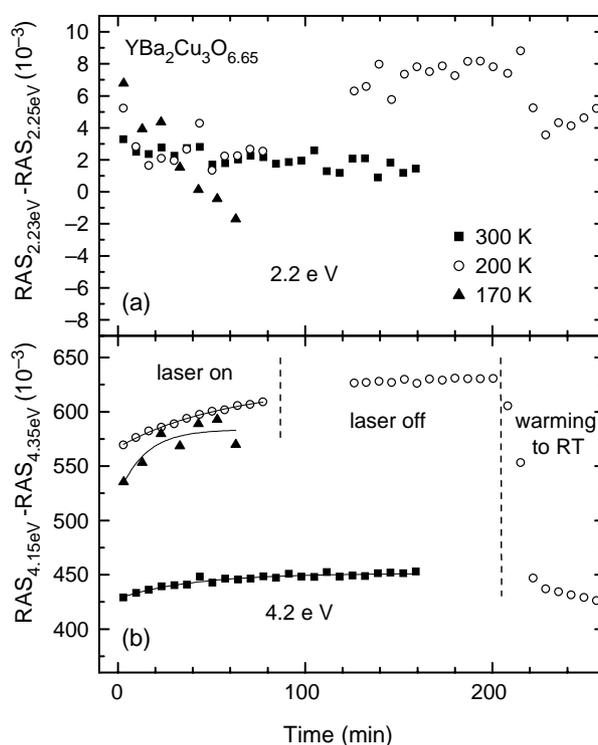


Fig. 4. Time dependence of the RAS signal of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.65}$  at 2.2 eV (a) and 4.3 eV (b) under additional laser illumination at 300, 200 and 170 K. The 2.2 eV RAS signal is depicted as the signal at 2.23 eV minus the one at 2.35 eV. The 4.3 eV signal is shown as the difference between the maximum at 4.15 eV and the minimum at 4.35 eV. The lines represent fits with a stretched exponential function. The 200 K series was continued after the additional illumination was switched off, first at 200 K with laser off (92–200 min), then during warming to room temperature (after 200 min).

the additional illumination was turned off. Apart from an immediate offset without laser, the light-induced change remains stable at 200 K, a property which is typical for Raman bleaching and persistent photoconductivity at low temperatures as well. Likewise, it recovers rapidly on heating to room temperature. To take the comparison one step further, the series were fitted with a stretched exponential function (see Ref. [5] for more information) in the case of the 4 eV curves, resulting in the exponent  $\beta = 0.7 \pm 0.1$ , and the time constant  $\tau = (40 \pm 5)$  min and  $(200 \pm 20)$  min for the room temperature and the 200 K experiment, respectively. These values are combined with a small initial amplitude and high background for the room temperature curve, where the change is initially fast and soon saturating. At 200 K, the initial amplitude is larger and the constant background smaller, so despite being slower, the relative change in anisotropy increases on cooling. A time and temperature-dependent Raman photobleaching study showed that at room temperature the change is also initially fast and quickly saturating, while it is slow and producing larger differences at low temperature, with the most efficient bleaching occurring in between, at around 190 K [5]. The RAS curves show the same tendency on moving from room temperature to 200 and 170 K, supporting the conclusion that the electronic transitions involving RAS and Raman resonance are connected to the same structural change, or even

have an identical origin. However, RAS measurements at very low temperatures, have not yet been performed because the sample reflectivity became very low. It would also be interesting to exploit the methods sensitivity to the superstructure phase for sample characterization.

In conclusion, we observed reflectance anisotropy in the  $a$ - $b$ -plane of detwinned single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{6-\delta}$  at various temperatures. Peaks at 2.2 and 4.4 eV are attributed to chain-plane structural elements and become more or less pronounced according to slight changes in the oxygen content, reflecting different superstructure phases in the samples. On cooling, the overall reflectivity undergoes a notable red shift, the anisotropy increases, and the peaks sharpen, with two separate peaks evolving above 4 eV. Under illumination at 200 K, a decrease in the anisotropy is observed at the 2.2 eV and an increase at the 4.4 eV peak. The changes remain stable in the dark at low temperatures, but recover on warming to room temperature, displaying similar properties as Raman bleaching and persistent photoconductivity. Similar to Raman, bleaching is more efficient at low temperatures, supporting the connection between the two effects.

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