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Photoinduced chain-oxygen ordering in detwinned $YBa_2Cu_3O_{6.7}$ single crystals studied by reflectance-anisotropy spectroscopy

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We present a reflectance-anisotropy spectroscopy (RAS) investigation of photoexcitation and annealing effects in oxygen deficient detwinned $YBa_2Cu_3O_{6.7}$ single crystals. Well-resolved RAS spectral features are either bleached or enhanced on a time scale of hours upon laser illumination with polarization parallel to the Cu(1)-O(1) chains. These photoinduced effects recover with room temperature annealing in the dark. Based on previous ellipsometric studies and on cluster models for the oxygen Cu-O(1) chain-fragments we are able to assign the RAS peaks that depend on illumination to optical transitions involving copper atoms located either on short chain-fragments or in isolated Cu-O$(4)_2$ sites. This provides strong evidence that photoinduced chain-oxygen ordering is indeed at the origin of persistent photoconductivity and Raman vibrational mode bleaching in these materials.

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A great effort has been devoted to understand the critical dependence on the oxygen content of the structural and transport properties of the high-T_c superconductors $YBa_2Cu_3O_{7-\delta}$ $(0 \leqslant \delta \leqslant 1)$. For nonstoichiometric materials, a decrease in the superconducting critical temperature (T_c) with increasing oxygen deficiency (δ) has been found. Oxygen deficiency manifests itself as a vacancy-defect in the Cu(1)-O(1) chains of the corresponding fully oxygenated material $(\delta=0)$. These chains play an important role in the carrier-doping of the CuO_2-planes. In fact, the location and distribution of the vacancies, or equivalently the length of the remaining chain-fragments, are determinant for the superconducting properties, particularly for the transition temperature T_c.

Under illumination with visible or UV light, transport measurements in oxygen-deficient samples display an increment in conductivity and T_c. These effects of *persistent photoconductivity* (PPC) (Refs. 1 and 2) were attributed to photoassisted oxygen ordering.[3] In this model, the chain order is altered due to light-activated diffusion of the chain-oxygen atoms, increasing the length of the chain fragments. Basal planes with longer chains are known to be better hole dopants than those with shorter ones, thus explaining the increase in T_c.[4] This behavior is reversible and the initial state is recovered by annealing at room temperature in the dark.[2] Results of Raman experiments, in which so-called defect-induced modes attributed to Cu-O(1) chain-fragments and their bleaching under photoexcitation are investigated, have shown to be compatible with the oxygen-ordering model.[5–9] These particular phonon modes exhibit a strong resonance for laser excitation around 2.2 eV.[10]

The structural *a-b* anisotropy of $YBa_2Cu_3O_{7-\delta}$ crystals, evidenced e.g., in ellipsometric measurements of the dielectric properties,[11,12] comes from the basal chain planes due to the presence of Cu(1)-O(1) chains aligned along the *b*-axis. Hence, if oxygen-ordering is induced through photoexcitation, as PPC and Raman experiments suggest, it must be accompanied by structural changes. Most notably, it has to produce a modification in the optical anisotropy. In this work we present for the first time a reflectance-anisotropy spectroscopy (RAS) investigation applied to detwinned $YBa_2Cu_3O_{6.7}$ crystals. RAS is a particularly suitable technique for the detection and study of subtle changes in the anisotropy of crystalline samples.[13,14] Our results give strong support for the chain-oxygen ordering model, providing further microscopic insight into the persistent photoconductivity phenomena in these materials.

We used an $YBa_2Cu_3O_{6.7}$ single crystal $1.0 \times 0.5 \times 0.1$ mm^3 (*a*, *b*, and *c* axis, respectively) in size. The crystal was prepared following the same method and proportions as those reported in Refs. 15 and 16, and was subsequently detwinned under uniaxial stress as described in Ref. 8. The sample was characterized by x rays and Raman spectroscopy establishing the excellent quality and complete detwinning. The RAS spectra were obtained at room temperature in the spectral range from 1 to 6 eV using a Xe-lamp as white light source, which was focused onto the (001) surface of the crystal at near normal incidence. The state of linearly polarized light was modulated with a photoelastic modulator to probe the reflectance difference $r_b - r_a$ between the *b* and *a* crystalline axis of the sample. The average reflectance as well as the amplitude of the periodic changes of the reflection were measured. By normalizing the periodic change with the average reflectance, the so-called "RAS signal" is obtained,

$$\frac{\Delta r}{r} = \frac{r_b - r_a}{\frac{1}{2}(r_b + r_a)}.$$

Only the second harmonic of the signal was detected, which corresponds to the real part of this complex quantity. Further details concerning the method as well as the equipment are described elsewhere.[13,14]

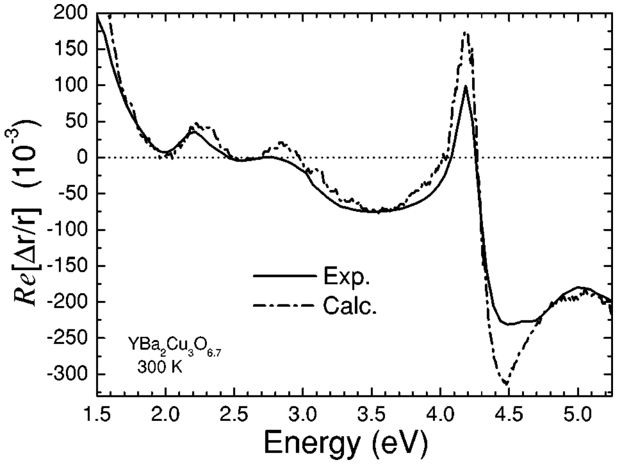

FIG. 1. RAS spectrum of a detwinned $YBa_2Cu_3O_{6.7}$ single crystal measured at room temperature (solid line). The dashed line represents the calculated RAS spectrum derived from the ellipsometric data of Ref. 11, where a similar sample with oxygen deficiency of T_c=66 K and $\delta\sim 0.3$ was measured. We note that the calculated RAS spectrum has been shifted down by ~130 units to coincide with the experimental curve.

The penetration depth for the visible and UV light of $YBa_2Cu_3O_{7-\delta}$ lies typically between 30 and 150 nm. Thus, we expect the signal to originate from the bulk of the material. This expectation is supported by experiments performed in air and in vacuum ($\sim 10^{-7}$ Torr) which gave identical results. For this case the RAS signal can be directly related to the bulk dielectic function:[13,17]

$$\frac{\Delta r}{r} = \frac{\varepsilon_b - \varepsilon_a}{\left(\frac{\varepsilon_b + \varepsilon_a}{2} - 1\right)\cdot\sqrt{\frac{\varepsilon_b + \varepsilon_a}{2}}}. \tag{1}$$

As mentioned above, RAS is a technique extremely sensitive to small variations of the optical anisotropy. In addition, the acquisition of a full spectrum is very fast (typically 2–5 min), implying that it can be used to monitor *in situ* the variations induced by illumination and/or annealing. For photoexcitation the red line (632.8 nm) of a He-Ne laser was used with a power-density of $\sim 1.4\ \mathrm{W/cm^2}$.

Figure 1 shows a typical RAS spectrum (solid line) of a $YBa_2Cu_3O_{6.7}$ detwinned crystal at room temperature. We concentrate on the peaklike features at 2.2 eV and 4.1 eV, and the dip at around 4.5 eV, which as we will show change under illumination. Features at these energies have been previously observed and discussed in several ellipsometry studies on $YBa_2Cu_3O_{7-\delta}$. Kotz *et al.*[11] measured all three crystal components of the dielectric tensor ϵ (real and imaginary part of each component) for three different oxygen contents ranging from $\delta=1$ to $\delta=0$. Using the data from Ref. 11 and Eq. (1) we have calculated the RAS signal, as represented by the dashed curve in Fig. 1. The matching with the experiment is excellent, reproducing the main spectral features of the RAS spectrum in position and relative intensity.

We make use of this excellent agreement between RAS and ellipsometry to identify the main features of the RAS spectrum. The peak at 2.2 eV arises from an absorption which is present for light polarized along *b* but is completely absent in the ϵ_2^a component.[11] In contrast, the peak at 4.1 eV is observed in ellipsometry for polarization parallel to *b*, whereas at 4.5 eV the dielectric tensor exhibits mainly a broad feature in ϵ_2^a.[11] Since the RAS signal is proportional to the difference of the reflectivity between both directions $\Delta r = r_b - r_a$, the feature at 4.1 eV appears as a peak, while the one at 4.5 eV appears as a dip.

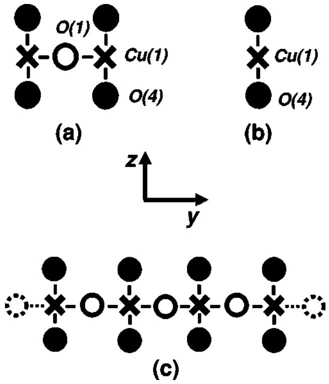

FIG. 2. Scheme of the considered Cu-O configurations: (a) exactly solved Cu_2O_5 cluster, (b) isolated CuO_2 cluster, and (c) longer chain consisting of four Cu atoms, forming a Cu_4O_{11} cluster. Crosses indicate Cu(1) ions, and empty (full) circles O(1)(O(4)) oxygen ions. The dashed circles indicate the "dressing" of the cluster by two additional O(1) atoms (see text for details).

Not being aware of any definitive assignment for the origin of the small peak at 2.2 eV and to help in the interpretation of the data, we have solved exactly a Cu_2O_5 cluster which corresponds to a short chain with two Cu atoms. The cluster consists of two neighboring Cu atoms of the chain, the O(1) atom between them and the four nearest neighbors apex O(4) atoms, as shown in Fig. 2(a). Such a cluster is the simplest possible model for describing the electronic states and optical transitions involving oxygen chain fragments. We have also compared the result with previous calculations for a chain with four Cu atoms [see Fig. 2(c)].[18]

The cluster calculation is performed using the four-band Hubbard Hamiltonian appropriate for the $CuO_{3-\delta}$ subsystem, which has been modified to take into account the effect on the on-site energies of Cu atoms at the chain ends due to the lack of nearest-neighbor Cu-O(1) repulsion, when O vacancies are introduced.[4] As basis functions the model considers the $3d_{z^2-y^2}$ orbitals of the copper atoms within a chain, the $2p_y$ orbitals of the chain O(1) atoms, and the $2p_z$ orbitals of the apex O(4) atoms. Based on the literature data for the cuprates,[19] in general, and of $YBa_2Cu_3O_{7-\delta}$,[20] in particular, we used the following set of parameters: U_d=10 eV and U_p=5 eV for the Cu and O on-site repulsion, respectively, U_{pd}=1.5 eV for the Cu-O interatomic repulsion, t_y=1.5 eV for the Cu-O(1) hopping energy along the chain, $t_z=1.3t_y$ (Ref. 4) and $t_{pp}=-0.6$ eV for the Cu-apex O(4) and the O(1)-O(4) hopping, Δ=2 eV and $\Delta_a=\Delta+0.5$ eV for the Cu-O(1) and the Cu-O(4) transfer energy, respectively.

With the chosen parameters we obtain an excitation energy of E_{C_3}=2.49 eV for the lowest optical transition in the

Cu_2O_5 cluster[21] with two holes, which is dipole allowed with the electric field $\mathbf{E}\|\hat{y}$ (i.e., parallel to *b*). The subindex notation follows the assignment explained below. This transition corresponds to the one from the ground state to the lowest-excited state which is even under reflection about the $z=0$ plane and odd under reflection onto the $y=0$ plane (the origin is at the O(1) atom). Small variations of the parameters within reasonable bounds lead to changes in E_{C_3} of up to ±0.5 eV. For similar parameters as ours but considering a longer chain with four Cu atoms (a Cu_4O_{11} cluster, see Fig. 2(c)) and one hole per Cu, a transition energy of around 1.9 eV has been previously obtained by solving the system using the Lanczos method.[18] This indicates that the fundamental optical transition of the cluster redshifts with increasing size. In fact, the fully oxygenated material shows no optical absorption in the energy region around 2.2 eV.[11] This transition is clearly related with the ends of the 4-atom chain, since its energy shifts to ~3 eV if the chain is "dressed" by two additional O atoms at the ends,[18] as shown with dashed circles in Fig. 2(c). We therefore ascribe the peak observed at 2.2 eV to *b*-polarized optical transitions involving electronic states of Cu(1) ions with threefold coordination (C_3) corresponding to short chain-fragments with one hole per Cu atom. We point out that our assignment is also consistent with the fact that Raman scattering by the chain-related defect modes exhibits a strong resonance at 2.2 eV for light linearly polarized along the *b* axis.[7,9,10]

We now address the RAS features observed above 4 eV. For $YBa_2Cu_3O_{7-\delta}$ with $\delta>0$, if the chains were perfectly ordered, there should be δ Cu ions per unit cell belonging to empty chains. These Cu ions do not have O(1) nearest neighbors and therefore build isolated CuO_2 clusters, as illustrated in Fig. 2(b). The allowed optical transitions for $\mathbf{E}\|\hat{x}$ or $\mathbf{E}\|\hat{y}$ for such clusters are beyond the reach of our multiband Hubbard-model calculation.[22] However the assignment of the electronic transitions responsible for these absorptions above 4 eV have been extensively addressed in the past.[11,12] They are related to Cu intraionic transitions $3d_{3z^2-r^2}\rightarrow 4p_x$, $4p_y$. For deoxygenated samples ($\delta\simeq 1$), where CuO_2 clusters are dominant, this transition is very strong.[11,12] Since the $4p_x$ orbitals should sense the presence of O(1) atoms of neighboring full chains differently than the $4p_y$ orbitals, it is natural to expect a splitting of the energy of the transitions in the $\hat{x}$ and $\hat{y}$ direction as δ decreases. Note that these transitions are not present in the fully oxygenated materials. In view of these arguments, we interpret coincident with previous work the peaks at 4.1 eV and 4.5 eV as due to intraionic transitions polarized along *b* or *a*, respectively, of isolated CuO_2 clusters, i.e., Cu(1) atoms with twofold coordination (C_2).

In Fig. 3(a) we show what happens to the RAS spectra under photoexcitation with the red line of a He-Ne laser polarized parallel to the chain axis *b*. The spectra are equally spaced in time and were taken during a total exposure interval of 280 min. The general shape remains basically unaltered. However, important changes are apparent for the 2.2, 4.1, and 4.5 eV features. The peak at 2.2 eV (labeled C_3 in the figure) loses intensity, whereas the other two features at 4.1 eV (C_2^b) and 4.5 eV (C_2^a) become more pronounced. This is better seen in Fig. 3(b), where the difference between the first RAS spectrum and those acquired at three selected intervals of time are shown. This demonstrates that the photoinduced changes in the optical anisotropy occur for the optical transitions involving Cu(1) electronic states. Based on the peak assignment discussed above the interpretation of the photoinduced RAS variations is quite straightforward: upon illumination the oscillator strength of isolated Cu-O_2 clusters (C_2) increases, whereas the number of O(1)-Cu(1)-$O(4)_2$ clusters (C_3 short chain-fragments) decreases with time. This result is fully consistent with the model of photoinduced chain ordering, in which, on the average, the length of the chains increases by the hopping of isolated O(1) atoms from energetically less favorable sites in *a* or *b*-aligned "monomers" [short Cu-O(1)-Cu fragments]. These O(1) atoms can enlarge another chain fragment either by adding at its end, or by filling a vacancy between two fragments. In both cases isolated Cu(1)-atoms are generated while the number of short fragments is reduced. In such process the 2.2 eV RAS signal should bleach, while the absolute intensity of the 4.1 and 4.5 eV peaks should increase, in complete agreement with the experiment.

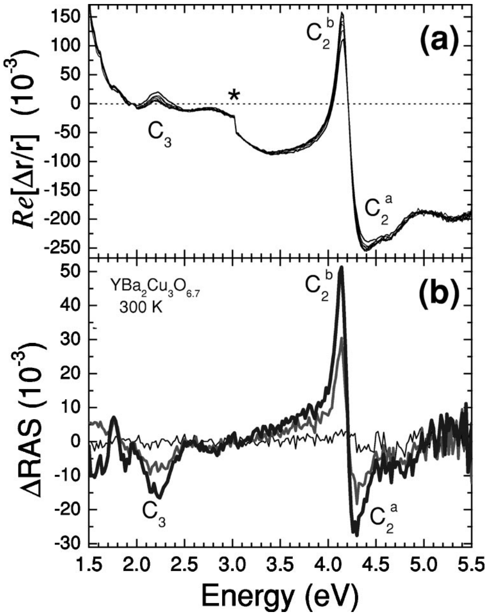

FIG. 3. (a) RAS spectra taken under photoexcitation with light polarization parallel to the Cu-O(1) chains (*b*-axis). The asterisk (*) marks a jump in the spectrum due to a change of detector. (b) Difference RAS spectra between the first two scans (3 min), the first and one taken after 64 min, and the first and last spectrum (280 min). Clear changes are apparent for the 2.2 eV, 4.1 eV, and 4.5 eV features.

Figure 4 displays the transients corresponding to the time evolution of the intensity of the RAS peaks at 2.2 and 4.1 eV for the following sequence: (i) photoexcitation with red light polarized parallel to the chains, (ii) room temperature annealing with laser excitation turned off, (iii) photoexcitation performed with polarization perpendicular to the chains, and finally, (iv) photoexcitation with polarization again parallel to *b*-axis. Two results should be highlighted. First, the bleaching of the RAS signal under photoexcitation and its recovery upon annealing at room temperature displays a

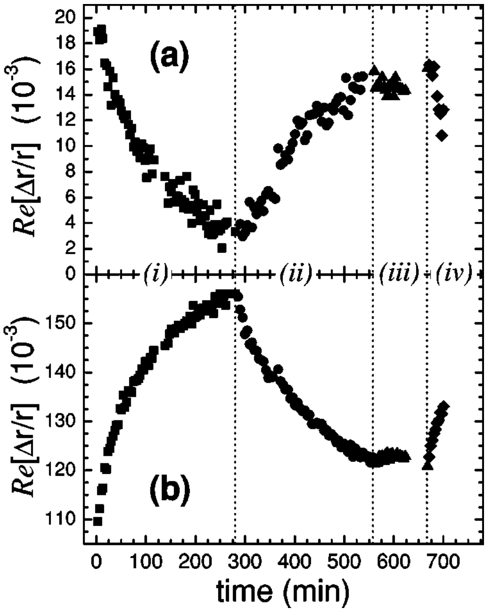

FIG. 4. Time dependence of (a) the 2.2 eV and (b) 4.1 eV peak for the following continuous sequence: (i) photoexcitation polarized parallel to the chains (full squares), (ii) room temperature annealing with laser excitation turned off (full circles), (iii) photoexcitation performed with polarization perpendicular to the chains (triangles), and (iv) photoexcitation with polarization again parallel to the chains (rhombus).

similar time dependence as the PPC (Ref. 23) and the defect-induced Raman modes.[5–9] In all cases, it can be well described by a stretched exponential function.[6] Second, the photoinduced effects on the RAS signal are totally polarized along the chains, exactly as observed for the bleaching of the defect-induced Raman modes.[6,7,10] We find that practically no changes in the RAS spectra take place if the light is polarized along the *a* axis. An understanding of this polarization dependence would require a detailed model of the complete photoexcitation phenomena, which is lacking so far. However, a plausible explanation can be given as follows. It is known that steric effects are very important in the perovskites[24] and therefore, core-core repulsion provides an energy barrier for the introduction of an O atom in a vacant place in a chain, between two Cu atoms. Due to the important electron-phonon interaction, any optical transition along the chain direction *b* should excite phonons vibrating along the chains. Such vibrations near the chain ends should make it easier for O atoms to enter vacant places and enlarge the CuO chains. The observed RAS features and their assignments to electronic transitions at Cu(1) chain atoms, their change under illumination, the time scale and polarization dependence, and the recovery at room temperature point to the intimate connection between the anisotropy in the optical constants, the transport properties and the lattice vibrations in high-T_c superconductors.

In summary, we have presented the first experiments of reflectance-anisotropy spectroscopy in $YBa_2Cu_3O_{6.7}$ detwinned single crystals under photoexcitation. Strong changes of the optical anisotropy are observed upon illumination or annealing. Using literature data of the dielectric tensor and the results of a cluster calculation within the Hubbard model for short chain-fragments we have identified the origin of the peaks observed in the RAS spectra that depend on photoexcitation and annealing. Since the optical anisotropy of the studied crystals primarily depends on the chain formation in the Cu-O chain planes, from the effects of photoexcitation and annealing on the RAS spectra we are able to monitor the time evolution of the number of Cu atoms belonging either to isolated Cu-O_2 clusters (transitions at 4.1 and 4.5 eV) or to O(1)-Cu-O(4)$_2$ short chain-fragments (transition at 2.2 eV). In this way, we have provided important microscopic information about the photoinduced oxygen-ordering mechanism and its fundamental role in the phenomena of persistent photoconductivity and Raman-mode bleaching in oxygen deficient cuprates.

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