

# Optical investigation of room-temperature chain ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We have investigated the near-infrared (0.5–1.5 eV) optical response of quenched  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples with intermediate oxygen content as a function of the time  $\tau$  the samples spent at room temperature. In a previous experiment, we determined the dielectric function in the spectral region between 3.8 and 4.3 eV under similar conditions using spectroscopic ellipsometry. We find an increase of the concentration of  $\text{Cu(I)}^{1+}$  ions with  $\tau$ , indicating an oxygen-reordering process in the course of which Cu-O dumbbells [linearly coordinated O(IV)-Cu(I)-O(IV) complexes] are generated. The reflectance measurements in the infrared regime between 0.5 and 1.5 eV indicate that simultaneously additional carriers are generated in the  $\text{CuO}_2$  planes. Both findings are in accordance with previous explanations of the rise of  $T_c$  with  $\tau$ .

## I. INTRODUCTION

Recent investigations<sup>1</sup> of the superconducting properties of quenched  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  crystals with intermediate oxygen content show a remarkable behavior. Starting out with a rather low  $T_c$ , the samples show a considerable rise in the superconducting transition temperature with increasing  $\tau$  ( $\tau$  is the time the sample was left in ambient atmosphere at room temperature). Veal *et al.*<sup>1,2</sup> assign this effect to a reordering of the chains in a fashion that longer chain fragments are formed during this so-called *room-temperature annealing* process.

The doping mechanism can be visualized in the following way: assuming that only the linearly coordinated Cu ion is monovalent, both the dumbbell [the O(IV)-Cu(I)-O(IV) complex encountered in  $\text{YBa}_2\text{Cu}_3\text{O}_6$ ] and the threefold coordinated O(IV)-Cu(I)-O(IV) have the nominal valence 3-. (Our model splits each chain oxygen between two neighboring unit cells.) Only the complete chain O(IV)-Cu(I)-O(IV) needs one electron more, leaving a hole in the  $\text{CuO}_2$  network. In the reordering process, two threefold coordinated Cu(I) ions combine to form one fourfold coordinated Cu(I) and one twofold coordinated Cu(I) ion. The newly generated fourfold coordinated Cu(I) ion can thus dope the  $\text{CuO}_2$  network.

Both reaction products can be detected separately using spectroscopic techniques. In a previous paper<sup>3</sup> we have shown that one prominent peak in the in-plane component of the optical response (around 4.1 eV) is directly related to the presence of dumbbells [or better  $\text{Cu(I)}^{1+}$  ions] in the material. Additional evidence for this assignment can be found in the work of Kelly *et al.*<sup>4</sup> The free carriers generated in the networks, and by these means also the fourfold coordinated Cu(I) complexes, can be seen by monitoring the plasma edge between 0.5 and 1.5 eV.

In this work, we present results of both optical measurements, as well as measurements of the critical temperature as a function of  $\tau$ . We find a correlation between the increase of the  $\text{Cu(I)}^{1+}$  ions and the increase of the free carrier concentration.

## II. EXPERIMENT

Single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  were grown in a  $\text{SnO}_2$  crucible. Metastable oxygen-deficient samples were obtained by annealing these single crystals at 800 K under suitable oxygen partial pressure (calibrated beforehand using bulkier polycrystalline samples) and subsequent fast quenching to 77 K in liquid nitrogen.

One sample was used for ellipsometric measurements in the spectral region around 4 eV. For the (001) face, we obtained the pseudodielectric function, i.e., the dielectric function evaluated from the ellipsometrically determined complex reflectance ratio modeling the sample as semi-infinite, isotropic, and homogeneous with a flat interface between sample material and ambient. Although the modeling does not take into account the anisotropy of the material, the so-obtained spectrum roughly corresponds to the dielectric tensor element  $\tilde{\epsilon}^{\alpha}$  (with the  $E$  field parallel to the  $\text{CuO}_2$  planes).<sup>5</sup> Between the ellipsometric measurements, the sample was allowed to relax in laboratory atmosphere at room temperature. To avoid errors introduced by changes in the optical alignment the sample was kept in the ellipsometer for a measurement period of 2 weeks. In Fig. 1 we show two ellipsometric spectra—the initial and the final spectrum of the series.

Parallel to the ellipsometric measurement the change in  $T_c$  during the aging process was monitored on a crystal with the same history by a SQUID magnetometer. Between subsequent  $T_c$  measurements the samples were left in the magnetometer at 300 K in He atmosphere. The

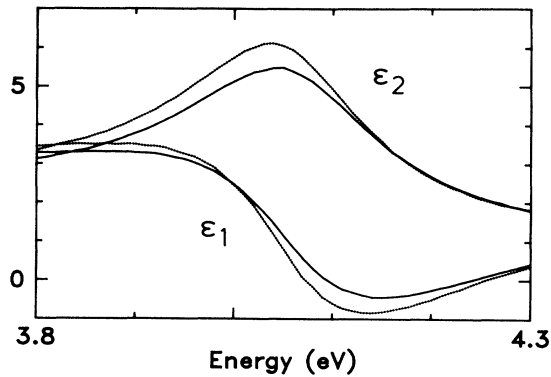


FIG. 1. Ellipsometric spectra taken at  $\tau = 0.5$  h (solid line) and  $\tau = 2$  weeks (dotted line).

results of the  $T_c$  measurements are shown in Fig. 2.

We have checked in an investigation before the actual experiment that the ambient (He or air) has no effect on the room-temperature annealing. This preparatory experiment also assured us that samples with identical history show the same annealing effects.

In another experiment we have monitored the changes in the infrared optical properties with  $\tau$ . Again several samples with the same history were used to determine, on the one hand, the changes of the infrared optical properties and, on the other, the superconducting transition temperature  $T_c$  during the aging process. This was done by repeated recording of the reflectance spectra of a (001) surface at near-normal incidence in the energy range between 0.5 and 1.5 eV. Figure 3 shows the reflectance spectrum of a shiny (001) surface of one of the investigated samples in an extended energy region between 50 meV and 6 eV in the final state of the aging. The first and the last spectrum of the series in the 0.5–1.5 eV region are compared in Fig. 4. By fitting a Drude-Lorentz model

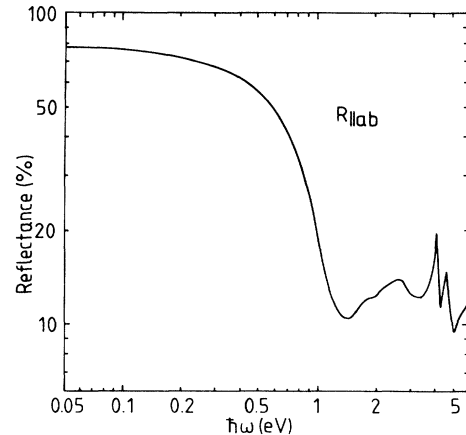


FIG. 3. Reflectance spectrum in the final state of room-temperature annealing.

to each of the curves we determined the time-dependent behavior of the transport properties.

All these investigations are greatly simplified by noting that the chain disorder can be preserved at any stage by “deep freezing” the samples in liquid nitrogen.<sup>1</sup> The reproducibility of our measurements was confirmed by repeating them on several samples from the same quench.

### III. DISCUSSION

#### A. Superconducting behavior

The transition curves displayed in Fig. 2 show a slightly steeper increase with  $\tau$  than the measurements of Veal *et al.*<sup>1</sup> One possible explanation could be the incorporation of Au in the latter samples, grown in Au crucibles. It has been reported that these impurities lead

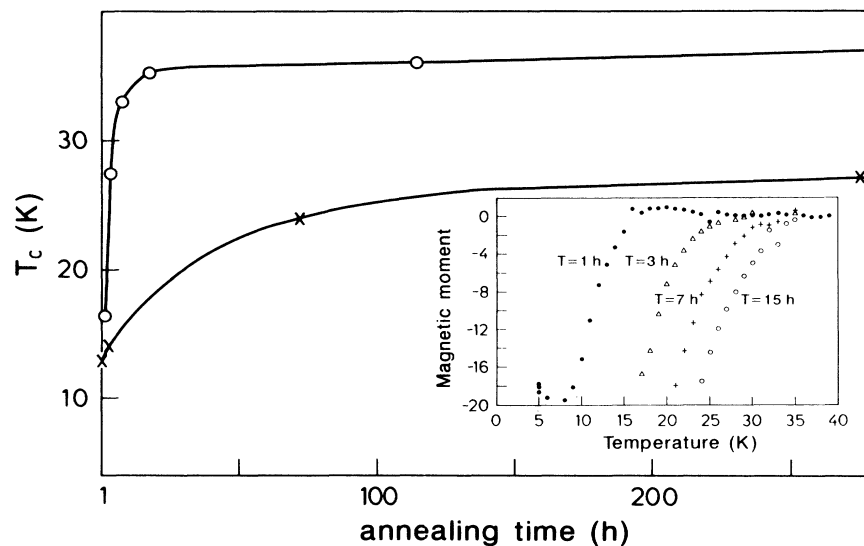


FIG. 2.  $T_c$  vs  $\tau$  as measured on our sample simultaneously with the ellipsometric measurements (circles, note that first measurement was taken at  $\tau = 1$  h) and of Veal *et al.* (crosses). Both lines are a guide to the eye and involve no fitting procedure. Inset: Susceptibility curves (shielding), taken for different  $\tau$ .

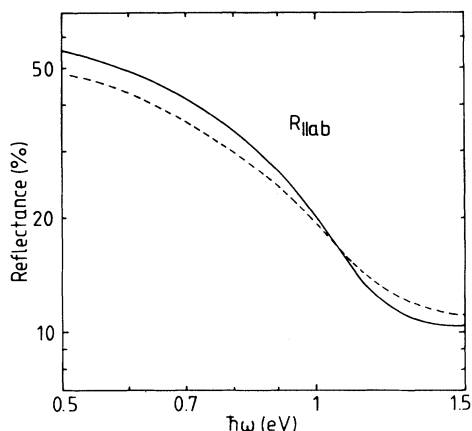


FIG. 4. Reflectance spectra taken at  $\tau = 27$  min (dashed line) and  $\tau = 121$  h (solid line).

to increased disorder in the chains<sup>6,7</sup> and it may be speculated that they also tend to preserve a larger amount of disorder even after long relaxation times. We have also found that samples that are supposedly heavily Al contaminated (and had no sharp superconducting transition) show only very weak annealing effects.

The samples used for the two optical experiments were prepared at different times and showed different oxygen content. This is indicated by the critical temperature, the critical point parameters of the 4.1 eV peak, the energy position of the plasma edge, and the position of the 500  $\text{cm}^{-1}$  mode determined by Raman scattering. All the characterization methods assign a lower oxygen content to the sample used for the ellipsometric investigations (roughly 6.35 versus 6.45 for the reflectance sample). As Veal *et al.* have reported earlier,<sup>1</sup> the relaxation effect tends to be larger if the sample has lower oxygen content (and thus starts out with a lower  $T_c$  immediately after the quench). In our case  $\Delta T_c$  was 19 K for the ellipsometry

sample (starting out at 16 K 60 min after quenching) and 8 K for the reflectance sample (starting with 47 K immediately after quenching).

## B. Ellipsometric measurements

Let us now focus on the optical spectra as displayed in Fig. 1. As shown in a previous paper,<sup>3</sup> a strong feature in  $\epsilon_2^a$  of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  at 4.1 eV has an intraionic transition within the Cu(I) ion as an origin. The initial state was assigned to a band derived from the Cu(I)  $3d_{3z^2-1}$  orbitals while the final state was assigned to a band with Cu(I)  $4p_x$  character. Upon oxidization of the Cu(I) ion, the initial state band becomes unoccupied and takes part in forming the well-known chain band in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (for a review, see, e.g., Ref. 8). Thus the 4.1 eV structure should vanish with increasing oxygen content or, more precisely, with decreasing Cu(I)<sup>1+</sup> concentration. We have fitted excitonic life shapes<sup>9</sup> to the measured spectra; the so-obtained line-shape parameters amplitude, energy position, and broadening are displayed versus  $\tau$  in Fig. 5. We clearly observe an increasing amplitude, a decreasing broadening, and a shift to lower energies of the 4.1 eV peak with  $T_c$ . This finding strongly suggests that we are not seeing an effect of incorporation of oxygen. As we have shown in a previous paper,<sup>10</sup> increasing oxygen content would result in the opposite behavior for all three parameters. In addition, we have calculated the effective number of Cu(I)<sup>1+</sup> ions,  $N_{\text{eff}}$  employing the sum rule

$$N_{\text{eff}} = \frac{2mV_{\text{cell}}\epsilon_0}{\pi e^2} \int_{\omega_1}^{\omega_2} \epsilon_2(\omega)\omega d\omega \quad (1)$$

in the range between 3.8 and 4.3 eV (see Fig. 5). Keeping in mind our assignment of the 4.1 eV peak,<sup>3</sup> this number should correspond to the concentration of Cu(I)<sup>1+</sup> ions. Our data show an increase of this concentration with  $\tau$ , in accordance with the assignments of Veal *et al.*<sup>1</sup>

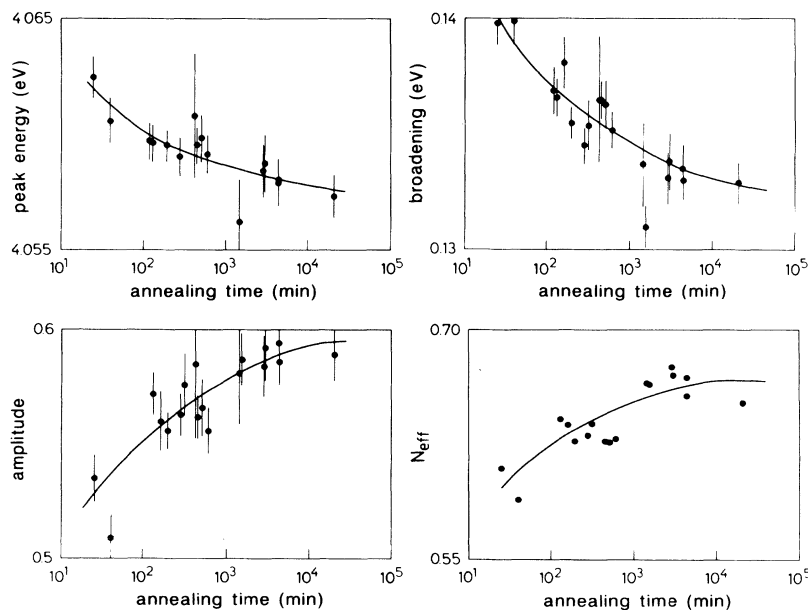


FIG. 5. Parameters of the excitonic line shapes fitted to the optical data as a function of  $\tau$ . The bars represent the errors of the fitting process. The lines are a guide to the eye. Upper left, energy position; upper right, broadening; lower left, amplitude; lower right,  $N_{\text{eff}}$  as calculated from Eq. (1).

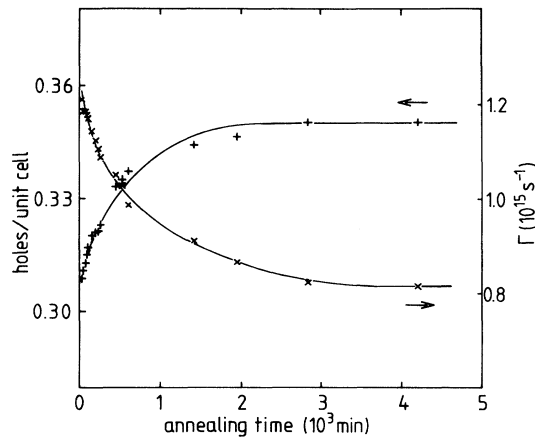


FIG. 6. Effective density and scattering rate of free carriers (i.e.,  $\omega_p^2$ ) as a function of annealing time  $\tau$ .

Numerical simulations of the reordering process at 300 K were performed by Ceder *et al.*<sup>11</sup> They predict two sorts of oxygen rearrangement processes: One has a very small time constant and involves the hopping of an oxygen ion initially occupying an O(V) site to an empty O(I) site. Another, much slower, process is the above-described combination of two threefold coordinated O(IV)-Cu(I)-O(I)-O(IV) complexes. The former one could not be seen by the neutron diffraction experiments of Jorgensen *et al.*,<sup>12</sup> however, Ceder *et al.* suggest that it might be too fast to appear during the quenching as Jorgensen *et al.* performed it. We have performed *ab initio* calculations for the optical response of perfectly ordered  $\text{YBa}_2\text{Cu}_3\text{O}_6$  (Ref. 3) as well as  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>13,14</sup> However, we have no detailed microscopic understanding of the optical response of an  $\text{O(IV)}_2\text{-Cu(I)-O(V)-O(I)}_x$  complex and thus cannot clearly detect this process in our data. Since the hopping of an oxygen ion from an O(V) site to an O(I) site does not involve any change in the number of oxygen neighbors of a given Cu(I) ion, we presume the 4.1 eV peak should be fairly insensitive to that sort of reordering (to a first approximation). Ceder *et al.* predict a  $\approx 10\%$  increase of the  $\text{Cu(I)}^{1+}$  ion concentration for  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  due to the slower process of hopping between O(I) sites. This is the same order of magnitude as suggested by our experiment (see the plot of  $N_{\text{eff}}$  in Fig. 5). We find a 14% increase in  $N_{\text{eff}}$ , but we should bear in mind that the investigated crystal had more than 50% oxygen vacancies and the increase is thus expected to be more dramatic.

### C. Reflectance measurements

Using a Drude-Lorentz model with two fixed oscillators we attempted to parametrize the reflectance spectra in the energy regime between 0.5 and 1.5 eV. The intraband contribution was fitted by a Drude term with the unscreened plasma frequency  $\omega_p^2 = \frac{Ne^2}{m^*\epsilon_0}$  where  $N$  and  $m^*$  are the concentration and the effective mass of the free charge carrier, respectively, and with the free car-

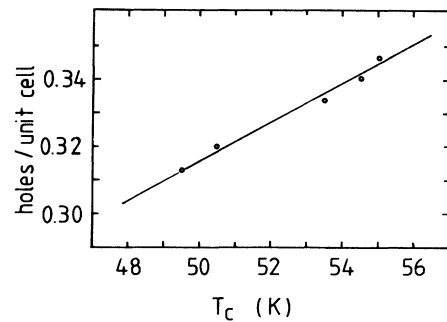


FIG. 7. Effective density of free carriers as a function of  $T_c$ .

rier scattering rate  $\Gamma$ . We have measured two samples from the same quench. Both of the investigated samples  $\text{YBa}_2\text{Cu}_3\text{O}_x$  had similar oxygen content of about  $x = 6.5$  determined by Raman measurements<sup>15</sup> and showed the same behavior during the room-temperature annealing process.

Compared to the strongly time-dependent behavior of the Drude term, the time dependence of Lorentz oscillators present in this energy range can be neglected. Figure 6 shows the effective number,  $N$ , i.e., holes per unit cell, and the scattering rate,  $\Gamma$ , of the free carriers versus  $\tau$ . The number of holes is compatible with values obtained on other samples with an oxygen content between  $x = 6.4$  and  $x = 6.5$ .<sup>16,17</sup> We observe an increase of the number of the free carriers by 13% with growing chain ordering. Simultaneously the scattering rate decreases by 33%. Since the sample is twinned, the parameters include contributions from the plane and chain carriers.

Qualitatively, this finding is consistent with the assumption that the *hole count* is crucial to the magnitude of  $T_c$ , to the explanation of the *room-temperature annealing effect* by Veal *et al.*, and with our ellipsometric data from the previous section. Quantitatively, the ellipsometric and the reflectance measurements cannot be correlated, since the two experiments were performed on samples with slightly different oxygen contents and thus different aging behavior.

It is interesting to note the changes in scattering rate with growing chain perfection (see Fig. 6). As expected the scattering rate  $\Gamma$  decreases with the increasing chain ordering.

In Fig. 7 we correlate the superconducting transition temperature  $T_c$  with the number of holes per unit cell. The experimental results suggest a linear dependence within the investigated range of oxygen chain ordering.

### IV. SUMMARY

We have presented optical data on the aging effects in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . We find that the changes in the optical properties with aging time are consistent with the model of Veal *et al.* and with our previous assignment of the microscopic origin of the 4.1 eV structure. We obtain an order-of-magnitude agreement with the numerical simulations of Ceder *et al.* for the increase in  $\text{Cu(I)}^{1+}$  concentration with aging time  $\tau$ .

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<sup>1</sup>B.W. Veal, H. You, A.P. Paulikas, H. Shi, Y. Fang, and J.W. Downey, *Phys. Rev. B* **42**, 4770 (1990).

<sup>2</sup>B.W. Veal, A.P. Paulikas, H. You, H. Shi, Y. Fang, and J.W. Downey, *Phys. Rev. B* **42**, 6305 (1990).

<sup>3</sup>J. Kircher, M. Alouani, M. Garriga, P. Murugaraj, J. Maier, C. Thomsen, M. Cardona, O.K. Andersen, and O. Jepsen, *Phys. Rev. B* **40**, 7368 (1989).

<sup>4</sup>M.K. Kelly, P. Barboux, J.-M. Tarascon, and D.E. Aspnes, *Phys. Rev. B* **40**, 6797 (1989).

<sup>5</sup>D.E. Aspnes, *J. Opt. Soc. Am.* **70**, 1275 (1980).

<sup>6</sup>M. Cieplack, Gang Xiao, L.L. Chien, A. Bakhshai, D. Artymowitz, W. Bryden, J.K. Stalick, and J.J. Rhyne, *Phys. Rev. B* **42**, 6200 (1990).

<sup>7</sup>U. Welp (private communication).

<sup>8</sup>W.E. Pickett, *Rev. Mod. Phys.* **61**, 433 (1989).

<sup>9</sup>D.E. Aspnes, in *Handbook on Semiconductors*, edited by T. Moss and M. Balkanski (North-Holland, Amsterdam, 1980), Vol. II.

<sup>10</sup>J. Kircher, M.K. Kelly, S. Rashkeev, M. Alouani, D. Fuchs, and M. Cardona, *Phys. Rev. B* **44**, 217 (1991).

<sup>11</sup>G. Ceder, R. McCormack, and D. de Fontaine, *Phys. Rev. B* **44**, 2377 (1991).

<sup>12</sup>J.D. Jorgensen, Shiyu Pei, P. Lightfoot, Hao Shi, A.P. Paulikas, and B.W. Veal, *Physica C* **167**, 571 (1990).

<sup>13</sup>Sudha Gopalan, J. Kircher, O.K. Andersen, O. Jepsen, M. Alouani, and M. Cardona, *Physica C* **185-189**, 1473 (1992).

<sup>14</sup>J. Kircher, Sudha Gopalan, and M. Cardona, *Thin Solid Films* (to be published).

<sup>15</sup>V. Hadjiev, C. Thomsen, J. Kircher, and M. Cardona, *Phys. Rev. B* **47**, 9148 (1993).

<sup>16</sup>M. Dürbler, A. Zibold, K. Widder, H.P. Geserich, Th. Wolf, G. Roth, G. Bräuchle, A. Erb, G. Müller-Vogt, and J. Kircher, in *Electronic Properties of High-T<sub>c</sub> Superconductors*, edited by H. Kuzmany, M. Mehring, and J. Fink (Springer, Berlin, 1993).

<sup>17</sup>A. Zibold, M. Dürbler, H.P. Geserich, A. Erb, and G. Müller-Vogt, *Physica C* **171**, 151 (1990).