RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 46, NUMBER 1 1 JULY 1992-I

Room-temperature annealing of $YBa_2Cu_3O_{7-\delta}$ observed by optical measurements

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(Received 21 February 1992)

Using rotating-analyzer ellipsometry we have measured the dielectric function of quenched $YBa_2Cu_3O_{7-\delta}$ samples (with intermediate oxygen content) as a function of the time τ the samples spent in laboratory atmosphere. We find an increasing concentration of $Cu(I)^+$ ions with τ, in accordance with previous explanations of the rise of T_c with τ.

I. INTRODUCTION

Recent investigations[1] of the superconducting properties of quenched $YBa_2Cu_3O_{7-\delta}$ 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 τ (τ is the time the sample was left in ambient atmosphere at room temperature). Veal *et al.*[1,2] assign this effect to a reordering of the chains in a fashion that 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 CuO_2 plane.

In a previous paper[3] we have shown that $Cu(I)^+$ ions can be directly observed by optical means. In the present work we show that indeed the $Cu(I)^+$ concentration increases with increasing τ.

II. EXPERIMENT

Single crystals of $YBa_2Cu_3O_{7-\delta}$ were grown in a SnO_2 crucible. Metastable oxygen-deficient samples were obtained by annealing these single crystals at 800 K under suitable oxygen partial pressure and subsequent quenching to 77 K in liquid nitrogen. The samples were allowed to relax at room temperature. On one sample the superconducting properties were monitored using an MPMS Quantum Design SQUID magnetometer. Between subsequent T_c measurements the samples were left in the magnetometer and aged at 300 K in He atmosphere. On the (001) face of another sample we continuously measured 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. This spectrum roughly corresponds to the dielectric tensor element $\tilde{\varepsilon}^a$ (with the E field parallel to the CuO_2 planes). The relaxation of the sample for the optical measurements took place in laboratory atmosphere at room temperature. To avoid errors introduced by changes in the optical alignment the sample was kept undisturbed in the ellipsometer for the measurement period of 2 weeks. We have checked in an investigation before the actual experiment that the ambient (He or air) has no effect on the room-temperature annealing. We show the result of the T_c measurements in Fig. 1 and the initial and final optical spectra in the 3.8 – 4.2-eV region in Fig. 2.

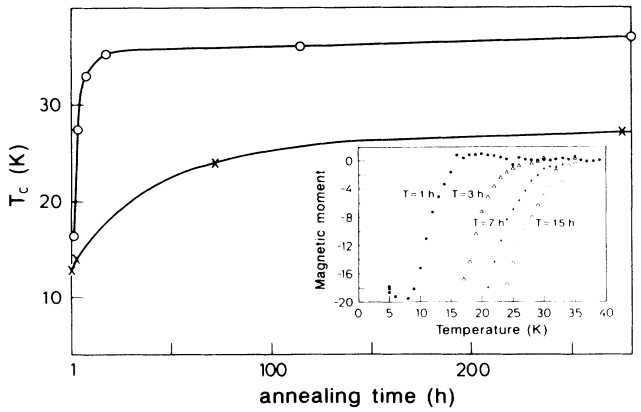

FIG. 1. T_c vs τ as measured on our sample (circles, note that first measurement was taken at $\tau = 1$ h) and of Veal *et al.* (crosses). Both lines are a guide to the eye and involve no fitting procedure. Inset: Susceptibility curves (shielding), taken for different τ.

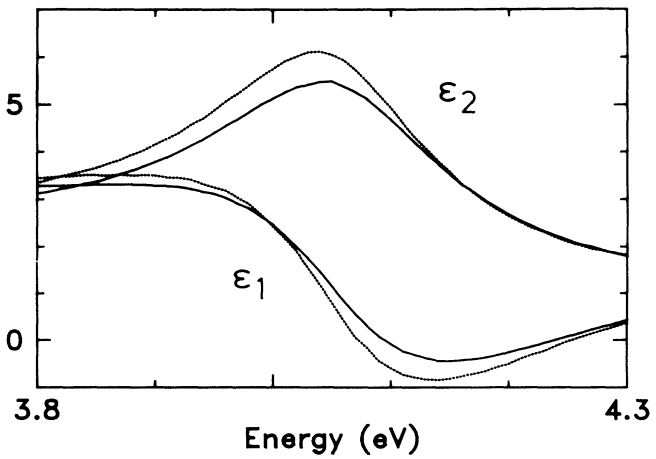

FIG. 2. Ellipsometric spectra taken at $\tau = 0.5$ h (solid line) and $\tau = 2$ weeks (dotted line).

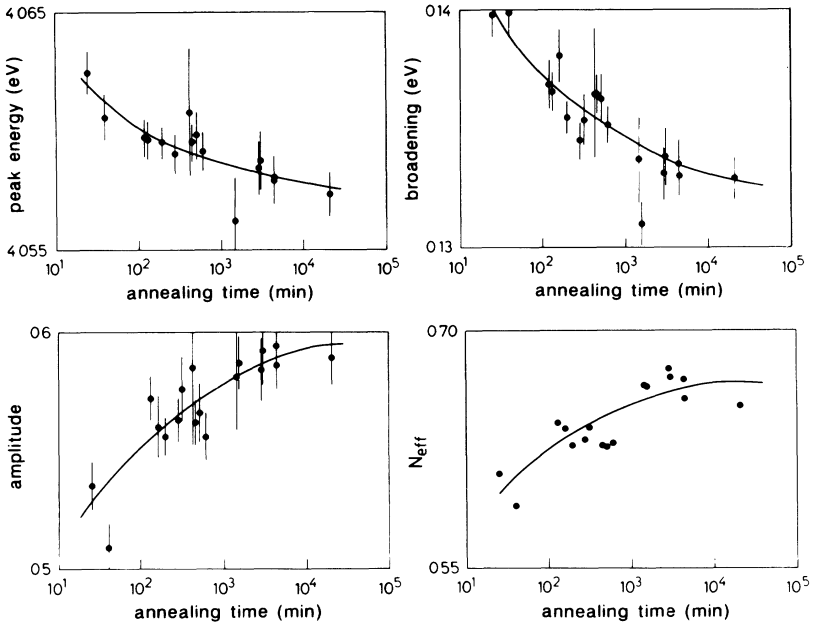

FIG. 3. Parameters of the excitonic line shapes fitted to the optical data as a function of τ. The bars represent the errors of the fitting process. The lines are a guide to the eye. Upper left: energy position, upper right: broadening, lower left: amplitude, lower right: N_{eff} as calculated from Eq. (1).

III. DISCUSSION

The transition curves displayed in Fig. 1 show a slightly larger increase with τ than the measurements of Veal *et al.*[1] One possible explanation could be the incorporation of Au in samples grown in Au crucibles. It has been reported that these impurities lead to increased disorder in the chains[4,5] and it may be speculated that they also tend to preserve a larger amount of disorder even after long relaxation times.

Let us now focus on the optical spectra as displayed in Fig. 2. As we have shown in a previous paper,[3] a strong feature in ε_2^a of $YBa_2Cu_3O_6$ at 4.1 eV has an intraionic transition within the Cu(I) ion as 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 $YBa_2Cu_3O_7$ (for a review, see, e.g., Ref. 6). Thus the 4.1-eV structure should vanish with increasing oxygen content, or, more precisely, with decreasing $Cu(I)^+$ concentration. We have fitted excitonic line shapes[7] to the measured spectra; the so-obtained line-shape parameters amplitude, energy position, and broadening are displayed in Fig. 3. 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 very strongly suggests that we are not watching an effect of oxygen uptake. As we have shown in a previous work[8] an increasing oxygen content would result in the opposite behavior for all three parameters. In addition, we have calculated the effective number of carriers, N_{eff} employing the sum rule:

$$N_{\text{eff}} = \frac{2mV_{\text{cell}}\varepsilon_0}{\pi e^2} \int_{\omega_1}^{\omega_2} \varepsilon_2(\omega)\omega \, d\omega \qquad (1)$$

in the range between 3.8 and 4.3 eV (see Fig. 3). Keeping in mind our assignment of the 4.1-eV peak,[3] this number should correspond to the concentration of $Cu(I)^+$ ions. Our data show an increase of this concentration with τ, in accordance with the assignments of Veal *et al.*[1]

Numerical simulations of the reordering process at 300 K were performed by Ceder *et al.*[9] 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.*,[10] however, Ceder *et al.* suggest that it might be fast enough to appear during the quenching as Jorgensen *et al.* performed it. We have no microscopical understanding of the optical response of a $O(IV)_2$-Cu(I)-O(V)-$O(I)_x$ complex and thus cannot clearly detect this process in our data. Due to the slower process Ceder *et al.* predict a $\approx$10% increase of the $Cu(I)^+$-ion concentration for $YBa_2Cu_3O_{6.5}$. This is the same order of magnitude as suggested by our experiment (see the plot of N_{eff} in Fig. 3).

In summary, we have presented optical data on the aging effects in $YBa_2Cu_3O_{7-\delta}$. 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 assigment 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 $Cu(I)^+$ concentration with aging time τ.

ACKNOWLEDGMENTS

We enjoyed stimulating discussions with G. Crabtree and V. Hadjiev. We also acknowledge the expert technical help of H. Hirt, M. Siemers, and P. Wurster.

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