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Time-dependent superconducting behavior of oxygen-deficient $YBa_2Cu_3O_x$: Possible annealing of oxygen vacancies at 300 K

B. W. Veal, H. You, A. P. Paulikas, H. Shi, Y. Fang, and J. W. Downey
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

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Oxygen stoichiometries in single crystals of $YBa_2Cu_3O_x$ are controlled by quenching from an O_2-N_2 atmosphere at 520 °C to liquid nitrogen. After quenching, the superconducting behavior and lattice parameters are found to be time dependent. T_c increases as much as 15 K in a period of several days. Apparently, annealing, with increasing oxygen vacancy order, occurs at room temperature.

In the $YBa_2Cu_3O_x$ (Y 1:2:3) high-temperature superconductor, the oxygen stoichiometry can be varied over a wide range ($6 < x < 7$). The metastable, oxygen deficient samples can be produced using a variety of procedures (for discussion and citations, see Refs. 1–3). As oxygen is removed, superconducting transition temperatures fall systematically from ~90 K to zero. In near coincidence with the loss of superconductivity, the material transforms from an orthorhombic to tetragonal crystal structure as oxygen is depleted. The tetragonal phase does not show superconductivity. When fully oxygenated, the structure is characterized by the presence of both "planes" and "chains," both constructed from copper atoms in four-planar coordination to neighboring oxygen atoms. The chains, which result from the ordering of oxygen vacancies, appear only in the orthorhombic phase. In the superconducting region, transition temperatures plotted versus oxygen stoichiometry usually exhibit two plateaus, one near 90 K and one near 60 K.[1–3] The plateaus are commonly attributed to vacancy ordered structures believed to appear in a complex phase field.[1–6] The definition of the plateaus apparently depends on the method of preparing the metastable samples.

In this paper, we report the observation of time-dependent behavior in the superconducting and structural properties of Y 1:2:3 (Ref. 7) when stoichiometries are controlled in the range $6.3 < x < 6.6$. Metastable samples were prepared by quenching from 520 °C, where they were equilibrated in a controlled O_2-N_2 atmosphere, to liquid nitrogen. For samples stored in air at room temperature, superconducting transition temperatures rise, as much as 15 K, in a period of several days after the quench. Structural changes, representing increased orthorhombicity, simultaneously occur. We believe that these annealing results are a consequence of oxygen vacancy ordering that occurs at 300 K during this aging process. In a profoundly simple experiment, this work demonstrates that T_c can be varied by as much as 15 K (or varied between nonsuperconducting and superconducting behavior) by simply permitting the material to spontaneously alter its structure and internal charge distribution in a sample of constant composition. This may be the simplest possible way to obtain a direct, and controllable, link between superconductivity, structure, and internal charge distribution in $YBa_2Cu_3O_x$.

With room temperature annealing, the plateau in T_c vs x becomes more clearly defined showing that the plateau depends on equilibration temperature, quench rate, and/or low-temperature annealing. Possibly room-temperature annealing rates are also sample dependent.

All samples used in this study were single crystals (0.2–2 mg) taken from the same batch. The crystals were grown from a CuO-rich melt using a procedure similar to that described by Kaiser *et al.* and Schneemeyer *et al.*[8] To fix its oxygen stoichiometry, a crystal was placed in a closed container made of ceramic Y 1:2:3 (weighing ~0.5 g). This assembly was then placed in a loosely capped Pt cup in a flowing O_2-N_2 mixture where it was held at 520 °C for at least 20 h. During heat treatment, the oxygen partial pressure was controlled using a zirconia cell oxygen pressure indicator (Ametek, Inc.). After equilibration, the sample (including Pt cup and ceramic container), was quenched to liquid nitrogen. Oxygen stoichiometries were determined from the equation

$$\ln(P_{O_2}) = A + Bx ,$$

where $A = -96.26$ and $B = 13.96$. Oxygen pressure is expressed in atmospheres. This relationship was found[3,9] to accurately characterize the equilibrium stoichiometry as a function of oxygen pressure at 520 °C for $6.3 < x < 6.6$.

With this preparation procedure, relatively sharp superconducting transitions could be obtained at all levels of oxygenation for $x > 6.4$. Magnetization data were taken with a superconducting quantum interference device (SQUID) magnetometer on samples cooled in zero field (shielding). Measuring fields were 5 Oe or less. For a fully oxygenated sample (annealed at 450 °C for 24 h in O_2), $T_c = 93.1$ K and the width (10% and 90% of complete transition) is no more than 0.2 K. For the reduced samples, at stoichiometries where T_c changes rapidly with x, transition widths are about 1.5 K. For quenched samples in the lower plateau, transition widths are ~0.3 K. Within demagnetization correction uncertainties, the magnitude of the shielding signal for all samples with $T_c > 10$ K (where the transition was complete) is equal to that expected from a fully superconducting bulk material.

In Fig. 1 we show magnetization measurements for a quenched sample with stoichiometry $x = 6.45$. Typical sample aging results are also shown in Fig. 1. The first measurement (lowest T_c) was made within 10 min of

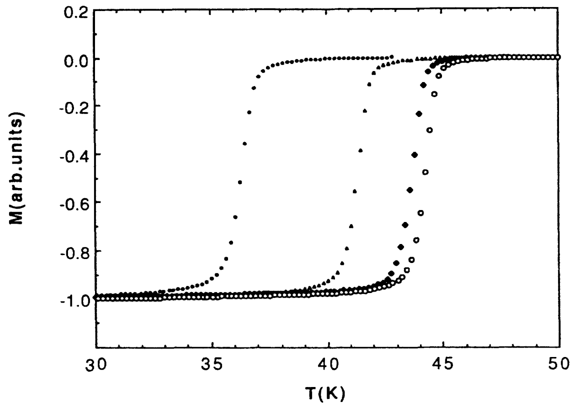

FIG. 1. Magnetization vs temperature showing T_c's for a quenched sample of $YBa_2Cu_3O_{6.45}$. The low-T_c curve was obtained immediately after quenching. As the sample is aged in air at room temperature (1, 2, and 16 days), T_c systematically rises to a saturation value.

quenching (i.e., sample was transferred from liquid-nitrogen bath to SQUID and was cooled below 77 K within 10 min—no sample aging is observed when samples are maintained at 77 K). The T_c measurements were repeated after 1, 2, and 16 days. With aging, the initial 37 K transition temperature systematically shifts to higher temperatures, reaching an apparent saturation value of 45 K after several days. Transition temperatures for all measurements remain relatively sharp (~1.5 K) with remarkably uniform transition widths. The same aging behavior (and comparable transition width) was seen in samples prepared with stoichiometries of 6.35 and 6.38. However, these samples were initially *nonsuperconducting* (for $T > 5$ K) and developed superconductivity after aging for several hours or days at room temperature in ambient atmosphere.

Figure 2 shows aging results for three of the samples investigated. The samples show changes as large as 15 K which occur in a period of several days. The samples show different saturation temperatures depending on their initial stoichiometries. After saturation, transition temperatures are remarkably stable, showing no observable change in a period of weeks.

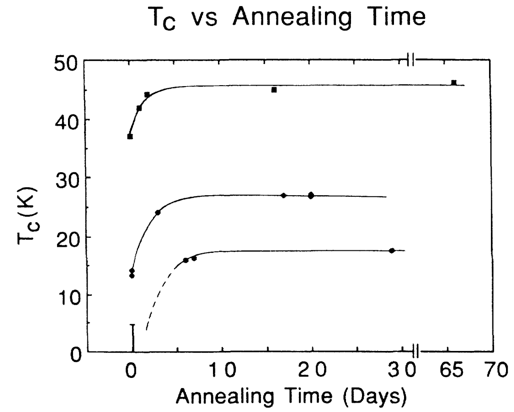

FIG. 2. Transition temperatures of quenched $YBa_2Cu_3O_x$ plotted vs annealing time at room temperature. Samples (bottom to top) have oxygen stoichiometries $x = 6.38$, 6.41, and 6.45, respectively. Both initial and saturation values of T_c depend on x.

Figure 3 shows high resolution x-ray-diffraction scans[10] for three different quenched samples with stoichiometries between 6.30–6.41. We show radial scans of the (400) and (040) diffraction peaks (from twin domains) which are sensitive to the a and b lattice parameters, respectively. The effect of aging on lattice parameters is monitored. The top (solid dots) spectrum for the $x = 6.30$ sample, was taken within 2 h of the quench. It shows only a single peak indicating that a and b are equivalent and the structure is tetragonal. Within 40 h, this peak has broadeded dramatically indicating the onset of a structural transition to orthorhombic symmetry. The second sample with $x = 6.35$ shows orthorhombic symmetry (and relatively broad peaks) within 2 h of the quench. After 44 h, the orthorhombic splitting has significantly increased. The third sample ($x = 6.41$) shows a larger orthorhombic splitting, very sharp peaks, and a small but clearly discernable increase in orthorhombicity with aging.

Figure 4 summarizes the transition temperature and structural results for the quenched Y1:2:3 samples with varied oxygen contents. We observe that (for both newly quenched and aged samples) there is a small region of oxygen stoichiometries where the samples are orthorhombic and nonsuperconducting (for $T > 5$ K). This result also has been reported previously.[1] Aged samples show superconductivity and orthorhombic symmetry persisting to lower stoichiometries than the freshly quenched samples.

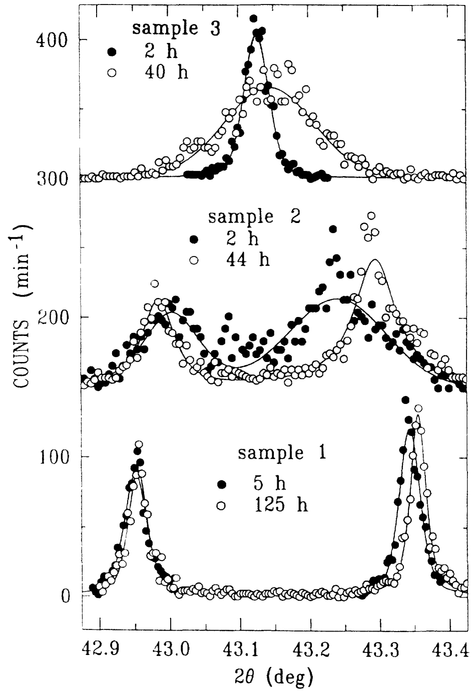

FIG. 3. X-ray diffractometer spectra showing (400) and (040) peaks for samples with oxygen stoichiometries (top to bottom) $x = 6.30$, 6.35, and 6.41. Spectra were acquired after aging (as indicated) in air at room temperature. Increased orthorhombicity appears with aging. (Spectra for samples No. 2 and No. 3 were offset by 150 and 300 counts, respectively.)

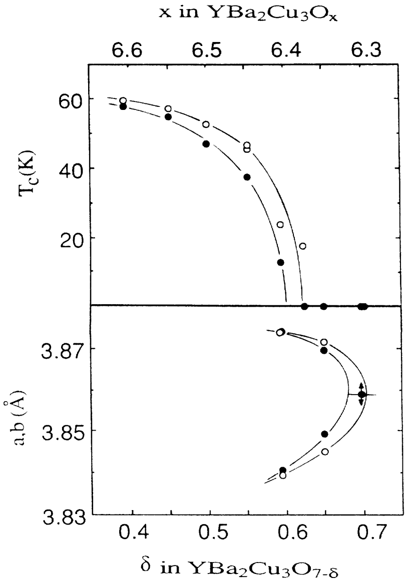

FIG. 4. Transition temperatures and (a,b) lattice parameters plotted vs oxygen stoichiometry for quenched samples of $YBa_2Cu_3O_x$. Solid dots designate measurements taken immediately after the quench. Open circles are data recorded after samples had aged to near saturation. With aging, T_c rises and orthorhombicity increases. For the tetragonal sample $(a=b)$, arrows indicate time-dependent broadening, the onset of an orthorhombic distortion.

While the directions of change of both T_c and lattice parameters are consistent with oxygen uptake in the samples during aging, we will show that oxygen uptake is an extremely unlikely explanation for the aging behavior. The possibility of oxygen uptake requires serious consideration, particularly since a very thin outer shell of oxygen-rich material might give the observed magnetization results. Absorption and subsequent diffusion of atomic oxygen through the sample at room temperature would appear to be far too slow a process[11] to account for this behavior. Further, we observe that the T_c's saturate at different final values depending on the as-quenched stoichiometry. If the samples were absorbing oxygen during aging, then it is likely that the saturation condition would not depend on the starting point of the aging process. Also, the x-ray measurements probe at least 10 μm (Mo $K\alpha$ radiation) into the sample. In general, with aging, the samples show increased orthorhombicity without additional line broadening. If oxygen were slowly absorbing at the surface, one would expect broadening or an additional pair of diffraction peaks with a larger separation.

To test for the possibility of oxygen uptake, several additional experiments were performed.

(i) Sample weights were monitored immediately after quenching and after aging. No weight gains were detected. However, because of the small sample masses, detectable (uniform) changes in oxygen stoichiometry were limited to about ±0.04.

(ii) A sample with initial $T_c \sim 12$ K was permitted to age until T_c saturated at 23 K. The aged sample was then crushed to a powder, quickly placed in a gelatin capsule and cooled to 10 K. Then the magnetization was remeasured. Though broadened slightly, the transition temperature of the powder was unchanged (within 0.5 K) from the result for the unbroken crystal. A shell effect resulting from surface absorbed oxygen would have shown a residual 12-K superconducting transition from the exposed sample interior.

(iii) An aged sample with $x=6.45$ was soaked overnight at 100 °C in flowing N_2 (containing about 35-ppm O_2), quenched to liquid nitrogen, and T_c was measured. The sample was then soaked at 100 °C overnight in flowing O_2 and quenched to liquid nitrogen. T_c's measured after these two heat treatment steps were the same (although both T_c's were shifted about 6° lower than the T_c for the room-temperature anneal). If oxygen was being absorbed at room temperature, the process should be accelerated at 100 °C in flowing O_2 and T_c would rise. (Normally stoichiometry changes become observable when soak temperatures exceed approximately 300 °C.) Alternatively, treatment in flowing N_2 would tend to reduce the sample, lowering T_c.

Thus it appears that the room-temperature aging behavior is associated with an annealing process that occurs in the absence of a composition change. The most likely explanation is that oxygen vacancies are dynamically ordering. In the orthorhombic structure(s), an ordered chain (or chains) of oxygen vacancies appears.[1] This ordering does not exist in the tetragonal phase.[12] As the orthorhombic-tetragonal transition is approached from the orthorhombic side (e.g., by reducing x or by increasing temperature), the (normally vacant) O(5) site occupancy[13] increases. Some O(5) occupancy may be preserved in the quench.

Our first interpretation of the low-temperature annealing behavior[7] was that oxygens, quenched into O(5) sites, move to neighboring O(1) (chain) sites thus enhancing the order in the O(5) oxygen vacancy array. An obvious test of this model is to measure site occupancy changes, with aging, using neutron-diffraction measurements. Since the initial submission of this paper, such measurements were made on ceramic samples.[14] Large time-dependent changes in T_c and lattice parameters were observed. However, no significant site repopulations between O(5) and O(1) were observed with aging. An alternative model was proposed[14,15] suggesting that ordering associated with the low-temperature anneals (for $x=6.5$) likely involves the formation of alternating full and empty (oxygen free) chains, consistent with many theoretical descriptions.[5,6]

In the ordering process, orthorhombicity increases, lattice parameters change and charge is redistributed in the structure without changing the O(5) population. These observations are consistent with the formation of alternating rows of oxygen vacancy chains, an ordering process that can be accomplished by very short diffusion paths, i.e., one or two atomic jumps. While annealing, oxygens move between adjacent O(1) (chain) sites. This process occurs over several days at 300 K but apparently is inhibited to the point of undetectability at 77 K. The vacancy ordering results in correlated changes in superconductivity and structure.

We note that $YBa_2Cu_3O_x$ is known to have a remarkably high oxygen mobility. Data of Rothman, Routbort, and Baker[11] show that, in a day, the diffusion length $2(Dt)^{1/2}$, at 300 K, may be as much as 10 Å. Also, disordering and twin boundary motion has been observed in electron microscopy for samples nominally at room temperature, though the effects may be radiation assisted.[16] Further, Bagley *et al.*[17] have observed that oxygen stoichiometry could be increased using a plasma oxidation technique, with several days of treatment, at temperatures near 80 °C.

It is now widely believed that superconductivity predominately occurs in the planes of the Y 1:2:3 structure. However, T_c can be modulated by composition variations in the chains (e.g., by adding oxygen vacancies or cation substitutions) that produce charge redistributions in the structure.[18] A common view[2,3,19,20] is that these composition variations alter the hole concentration in the planes which, in turn, controls the superconductivity. Variation of the oxygen content does, of course, change the overall hole content with consequent variation of T_c. However, the distribution of holes between planes and chains is unknown. Increased hole counts normally result in higher T_c's for the Y 1:2:3 system. Since T_c rises with increased oxygen vacancy order in the chains, we might infer that a charge redistribution occurs within the structure such that the hole count in the planes increases with this improved order. This inference is consistent with results of tight binding calculations recently reported by Lambin.[21]

While prior studies have shown correlated behavior between superconductivity and structure, accompanying composition changes, with unknown effect, were also present. However, in the annealing process reported here, structural changes occur with corresponding changes in T_c but with *no change* in sample composition. In addition to demonstrating a remarkable low-temperature annealing effect in Y 1:2:3, these discoveries provide the opportunity to investigate, with simple and direct experiments, the relationship between superconductivity, structure, and correlated electronic properties.

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