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Observation of temperature-dependent site disorder in $YBa_2Cu_3O_{7-\delta}$ below 150 °C

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

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We have observed annealing effects in both single-crystal and ceramic samples of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ that occur at temperatures as low as 0 °C. Oxygen stoichiometries were controlled by quenching, from 520 °C, samples equilibrated in a controlled O_2-N_2 atmosphere. For single crystals, transition temperatures with any desired value between 0 and 92 K, and transition widths less than 2 K, were readily obtained with appropriate variation of δ. After quenching, superconducting transition temperatures of the reduced samples rise, as much as 15 K, when aged in ambient atmosphere for several days; the sample composition does not change with aging. With low-temperature aging, structural changes also occur; e.g., orthorhombicity increases. These effects are attributed to oxygen-vacancy ordering that occurs in the chain region of the structure. The rise in T_c with aging (ordering) is attributed to increased hole doping in the planes that results from an increased population of two-coordinated (monovalent) copper atoms. For samples with reduced stoichiometries, the degree of disorder can be reversibly controlled with secondary quenches in the temperature range 0–120 °C. For stoichiometries $7-\delta \simeq 6.5$, an approximate activation energy of 0.96 eV was obtained for the annealing process. This low-temperature annealing behavior, occurring in samples of constant composition, provides a remarkably simple and effective way to study the relationship between superconductivity, structure, and associated electronic properties.

I. INTRODUCTION

Recently, it was discovered that annealing can be observed at room temperature in oxygen-deficient single-crystal samples of $YBa_2Cu_3O_{7-\delta}$ (Y 1:2:3) when the samples are produced by quenching from elevated temperatures.[1] The superconducting transition temperature was found to increase by as much as 15 K when the sample was permitted to age at 296 K. The orthorhombic splitting also increased with aging. This remarkable result showed that significant atomic motion occurs in this material even at very reduced temperatures and that, under these conditions, internal ordering occurs that directly influences the superconducting behavior. In Ref. 1, measurements were performed on single crystals with oxygen stoichiometries in the range $6.3<x<6.6$ where $x=7-\delta$. It was observed that, for as-quenched samples, T_c's were substantially lower than the values they realized after aging for a period of several days at ambient conditions. It was argued that the change in T_c was controlled by the degree of disorder in the basal plane (i.e., the Cu-O "chains"). The annealing behavior was subsequently found in ceramic samples; changes in both structure and superconducting properties were monitored as samples annealed at room temperature.[2] With annealing, a,b and c lattice parameters contracted, orthorhombicity increased and T_c rose. However, very little, if any, change was observed in O(1) (chain) and O(5) (apical) site occupancies. (Atomic sites are identified as in Ref. 3.) It was proposed[2] that the annealing phenomena result from an ordering process where oxygens form alternating occupied and vacant chains in the basal plane.

In this paper, we extend the study to include a wider oxygen stoichiometry range ($6.3<x<6.9$). The aging phenomenon is observed at all stoichiometries where T_c is reduced below 92 K. In addition, we have more extensively studied the temperature dependence of site disorder at the composition $YBa_2Cu_3O_{6.45}$. We observe that the disorder is strongly temperature dependent and reversible in the temperature range $0<T<150$ °C. The disorder can be (reversibly) controlled in this temperature range without composition change.

We also report low-temperature annealing results in ceramic samples. In ceramics, transition temperatures are considerably broader than for single crystals but shifts in T_c, are, nonetheless, clearly discernable with aging and are comparable in magnitude to single-crystal shifts. It is argued that the broadening is an intrinsic property of ceramics, resulting from internal strains introduced during the sinter-oxygenation process.

As oxygen is removed from $YBa_2Cu_3O_{7-\delta}$, superconducting transition temperatures fall systematically from ~92 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. In a plot of T_c versus x, two plateaus are generally observed even when a variety of procedures are used to prepare these metastable oxygen-deficient materials.[4–16] A similar dependence of T_c on x is observed when rare earths are substituted for Y.[17–23] (However, T_c versus x shows an ion size dependence;[17–19] as the ion size increases, the orthorhombic phase becomes less stable). The plateaus in T_c versus x are sometimes attributed to distinct superconducting phases that have different oxygen concentrations and different vacancy-ordered structures.[6,12–16]

The phase diagram has also been the object of intense theoretical study.[24–29] The more recent work suggests that, as oxygen stoichiometry is varied, the material acquires a variety of complex ordered arrangements of oxygen-vacancy chains in the basal plane.[28,29] In support of these calculations, a number of vacancy-ordered structures have been reported, mostly from electron-diffraction studies.[30–38]

In this work, very sharp superconducting transitions, free of composite structure, are observed for single crystals at all x where the samples are superconducting. With annealing at temperatures below 150 °C, the transitions of reduced stoichiometry samples shift without change in the transition width. Thus, atoms can be significantly redistributed in samples of constant composition by varying the sample temperature in the range 0–150 °C. Results appear to be consistent with the occurrence of chain-vacancy ordering, the degree of which can be reversibly modified with temperature. Probably, a variety of ordered arrangements occur depending on stoichiometry. No evidence is seen that the material separates into discrete phases with different transition temperatures.

II. EXPERIMENTAL

Single-crystal samples were prepared using a "self-flux" procedure similar to those described by Kaiser *et al.*[39] and Schneemeyer *et al.*[40]. The crystals were three dimensional (rather than very thin flakes, as often studied) weighing approximately 0.5–2 mg. The crystals were cooled from 475 to 415 °C in a period of 11 days to "fully oxygenate" them before fixing the stoichiometries. (Subsequent tests showed these crystals could be oxygenated in much less time, however.)

Stoichiometries were controlled by quenching, from 520 °C to liquid nitrogen, samples that were equilibrated in a predetermined (flowing) O_2-N_2 atmosphere.[1,5] For the 520 °C heat treatment, single-crystal samples were placed in a small container made of ceramic Y 1:2:3 weighing about 0.5 g. The container was capped with a small plug of Y 1:2:3. This container (holding single crystals) and added ceramic specimens, were placed in a capped Pt cup and suspended in a vertical tube furnace. After equilibration (at least 24 h), the Pt cup and contents were quenched to liquid nitrogen. This procedure for fixing oxygen stoichiometries was calibrated using ceramic Y 1:2:3.[1,5] Weight changes of standard samples were recorded to monitor final stoichiometries. It was assumed that single crystals have the same stoichiometric dependence on temperature and oxygen pressure as the ceramic samples. The equilibration temperature was held constant (520°±10 °C) for all heat treatments. The temperature and oxygen pressure are very stable; stoichiometries are readily reproduced with better than 0.01 precision in x. Thus, relative stoichiometries are very precise. The accuracy of x is dependent on iodometric titration measurements.[5]

The ceramic samples were produced using conventional sinter-processing procedures.[5] Oxygen stoichiometries were fixed, in the presence of single-crystal samples, using the procedure described above.

Superconducting transition temperatures were measured using a SQUID magnetometer with measurements taken while warming, on samples cooled in zero field (shielding). Measuring fields were 0.5–5 G.

III. RESULTS

Figure 1 shows temperature-dependent magnetization data (shielding) for a "fully oxygenated" single crystal of $YBa_2Cu_3O_{7-\delta}$ with stoichiometry approximately 6.9. This transition width ΔT_c is less than 0.2 K at 92 K, as determined by 10 and 90 % values of the full diamagnetic signal. This transition is typical for all crystals, when fully oxygenated, used in this study. These crystals were subsequently heat treated to controllably reduce oxygen stoichiometries.

Though somewhat variable with x, transition widths remained sharp as stoichiometries were reduced. Figure 2 shows a number of examples of superconducting transitions occurring at various temperatures between 16 and 92 K where stoichiometries are fixed in the range $6.35 < x < 6.9$. The largest ΔT_c (10 and 90 % values) is about 2.5 K, most ΔT_c's are within 1 K.

Low-temperature annealing behavior is illustrated in Fig. 3. Transition temperatures are recorded for a sample, with stoichiometry $x = 6.45$ ($\delta = 0.55$), taken at different time intervals covering a period of several days when stored at room temperature in ambient atmosphere. We see that T_c shifts by about 9 K from the as-quenched condition to the final, saturation condition. Note that the transitions always remain sharp during the room-temperature anneals, showing no perceptible change in width or shape.

Figures 4 and 5 show examples of the 296-K annealing behavior at other extremes of oxygen stoichiometry where the material is superconducting. In Fig. 4, aging behavior is shown for a sample with stoichiometry $x = 6.38$, close to the composition where the material exhibits an orthorhombic-to-tetragonal (O-T) phase transi-

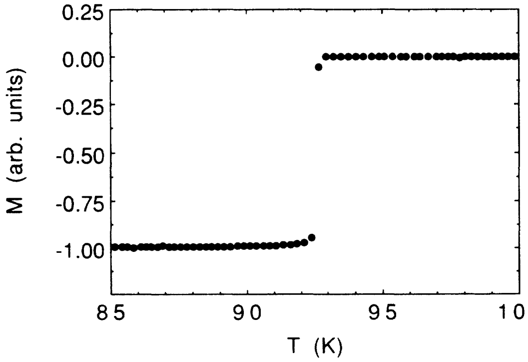

FIG. 1. Temperature dependence of diamagnetic magnetization (shielding) for a "fully oxygenated" single crystal of $YBa_2Cu_3O_{7-\delta}$ measured in a 0.5-Oe measuring field. The transition width is less than 0.2 K (10 and 90% of the full diamagnetic signal).

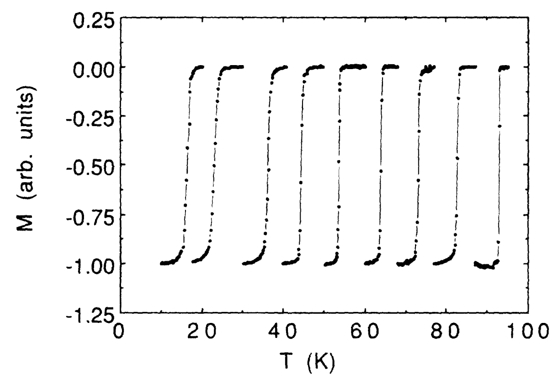

FIG. 2. Diamagnetic shielding data showing superconducting transitions for single-crystal samples whose oxygen stoichiometries are controlled at different values between 6.35 and 6.9. By quenching samples equilibrated at 520 °C in controlled O_2-N_2 environments, stoichiometries can be adjusted to produce any T_c between 0 and 92 K.

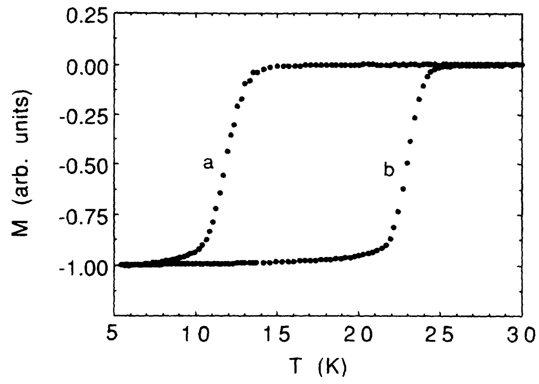

FIG. 4. Room-temperature annealing behavior of a single crystal of $YBa_2Cu_3O_{6.38}$, a sample with stoichiometry close to the composition where the orthorhombic-to-tetragonal phase transition occurs. Diamagnetic shielding is measured (*a*) immediately after the quench and (*b*) after aging at room temperature for 3 days. T_c shifts from about 13 K to nearly 24 K.

tion and becomes nonsuperconducting. The as-quenched sample shows a transition onset at about 13 K that rises to about 24 K after 3 d of aging. In Fig. 5, a sample with stoichiometry 6.75 ($\delta=0.25$) shows a transition at about 83 K when measured immediately after the quench. After aging for 4 weeks in ambient atmosphere, the transition temperature had shifted, by about 2 K, to higher temperature. This shift of T_c is rather small, but the sharp transitions make the shift very clearly discernable. Figures 3–5 illustrate that 296-K annealing behavior is easily observed at all x where $0<T_c<90$ K.

Figure 6 summarizes the results of transition-temperature measurements taken (a) immediately after quenching and (b) after aging in ambient atmosphere. In Fig. 6, transition widths are generally within the size of the dots that represent the T_c measurements. Aging is observed at all stoichiometries less than 6.85 ($\delta>0.15$) where T_c first begins to fall below 92 K. However, the effect is much larger when $\delta>0.5$ where T_c begins to fall very rapidly with increased δ.

Along with T_c versus x, Fig. 7 shows the magnitude of the observed shifts in T_c that occur with aging, plotted as a function of oxygen stoichiometry. These shifts are relatively constant, at about 2 K, for $x>6.6$ but increase rapidly as x falls below ~ 6.6, the vicinity of the lower plateau.

Figure 8 shows the aging results of Fig. 3, with T_c plotted versus annealing time at 296 K. The transition moves rapidly in the first few hours after quenching, then approaches a saturation condition in a period of several days. The solid line is Eq. (2) (see IV C) with $\tau=572$ min.

Since the annealing process was found to be relatively

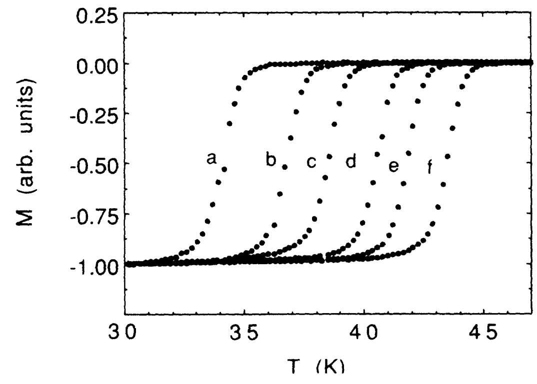

FIG. 3. Diamagnetic shielding data for a single crystal of $YBa_2Cu_3O_{6.45}$ showing the effect of room-temperature annealing on the superconducting transition temperature. The data were taken (*a*) immediately after the quench, and after aging times of (*b*) 1.75 h, (*c*) 3.5 h, (*d*) 5.75 h, (*e*) 17 h, and (*f*) 167 h. In this sample, T_c shifts by about 9 K in the annealing process with no change in the transition width.

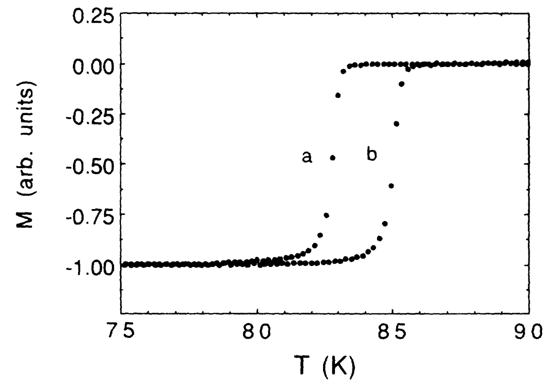

FIG. 5. Room-temperature annealing behavior of a single crystal of $YBa_2Cu_3O_{6.75}$. Transition (*a*) was taken immediately after the quench, transition (*b*) was measured 4 weeks later. A clearly discernable but smaller effect occurs here than is shown in Figs. 3 and 4.

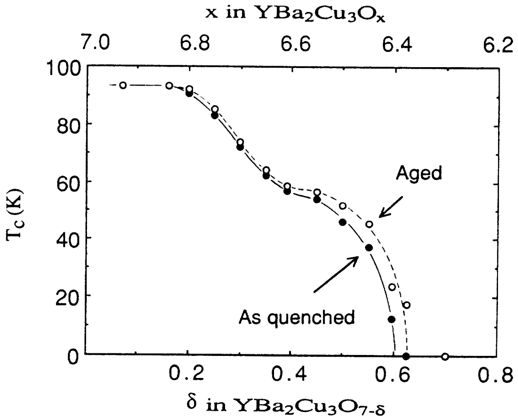

FIG. 6. Transition temperatures taken immediately after the quench (solid circles) and after aging in ambient atmosphere (open circles). Transition widths are within the size of the dots. The point at $x = 6.92$ is a "fully oxygenated" sample.

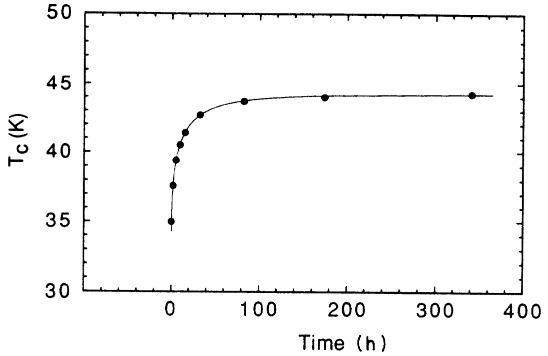

FIG. 8. The data of Fig. 3 ($YBa_2Cu_3O_{6.45}$) showing T_c plotted vs annealing time at room temperature. The transition moves rapidly in the first few hours and approaches saturation after a few days. The solid line is Eq. (2) (see text) with $\tau = 572$ min.

rapid at room temperature, the effect was also monitored (Fig. 9) in a sample aged at 0 °C. We see that saturation now requires annealing times in excess of 1 month. While the process has substantially slowed relative to the 23 °C anneal, the same type of aging behavior is observed. Different specimens were used for the measurements of Figs. 8 and 9, although both were prepared at the same time in the same container. Small differences in transition temperatures are observed in separately prepared crystals with the same nominal stoichiometries and quench conditions.

To monitor correlated structural changes, x-ray-diffraction radial scans of the (400) and (040) Bragg peaks from twin domains were simultaneously monitored to measure time dependent changes in the a,b lattice parameters.[1] Results are presented in Fig. 10 for samples with stoichiometries 6.30, 6.35, and 6.41. The 6.30 sample is seen to be tetragonal immediately after the quench; a single, sharp diffraction peak is observed showing that $a = b$. With aging, the peak broadens dramatically indicating the onset of an orthorhombic distortion. At $x = 6.35$, the sample is slightly orthorhombic after quenching, with the orthorhombic splitting increasing significantly with aging. These (6.35) peaks are quite broad, but become sharper with time. At $x = 6.41$, the crystal has a large orthorhombic splitting that increases slightly with time. In this case, peaks are again very sharp. Figure 11 shows the correspondence between T_c and a,b lattice parameters as the samples are permitted to age at 296 K. With aging, T_c rises and orthorhombicity increases. Also, these results indicate that superconductivity is lost in the orthorhombic phase, a result very similar to that reported by Pörschke *et al.*[22] Apparently, no superconductivity occurs when the material becomes tetragonal.

We point out that, in fixing stoichiometries of samples with $x \lesssim 6.55$, samples are equilibrated (at 520 °C) in the tetragonal phase or very close to the O-T phase boundary.[1,5] Yet, in Fig. 11, we find that for $x \gtrsim 6.35$,

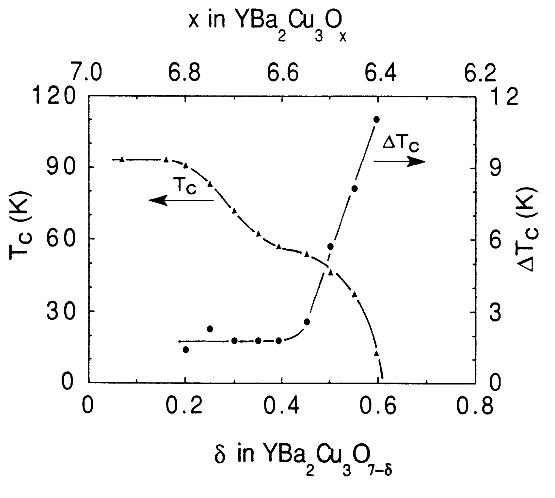

FIG. 7. ΔT_c, the total shift in T_c observed with aging at room temperature, and T_c plotted vs oxygen stoichiometry. ΔT_c rises abruptly at the falloff of the lower plateau.

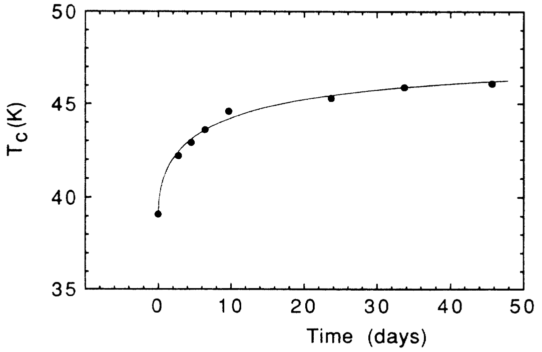

FIG. 9. T_c vs annealing time for a sample of $YBa_2Cu_3O_{6.45}$ aged at 0 °C. Kinetics are substantially slower at this temperature than they are at room temperature. The saturation T_c is approached after annealing for several weeks at 0 °C. The solid line is Eq. (2) (see text) with $\tau = 229$ h.

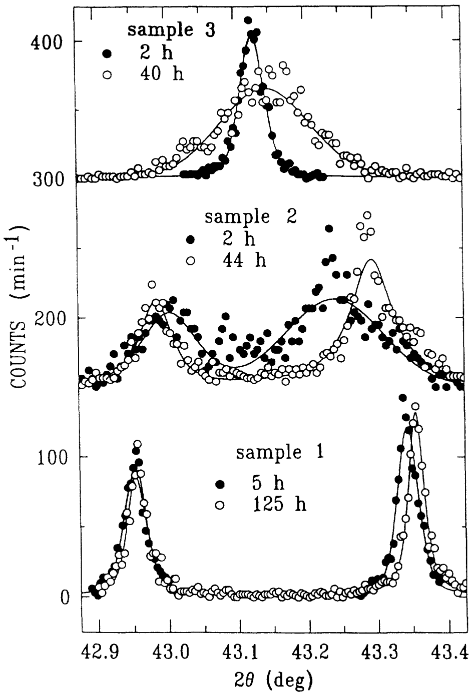

FIG. 10. X-ray-diffractometer spectra showing (400) and (040) peaks for samples with oxygen stoichiometries (top to bottom) $x=6.30$, 6.35, and 6.41. Spectra were acquired after aging (as indicated) in air at room temperature. Increased orthorhombicity appears with aging. (Spectra from samples 2 and 3 were offset by 150 and 300 counts, respectively.)

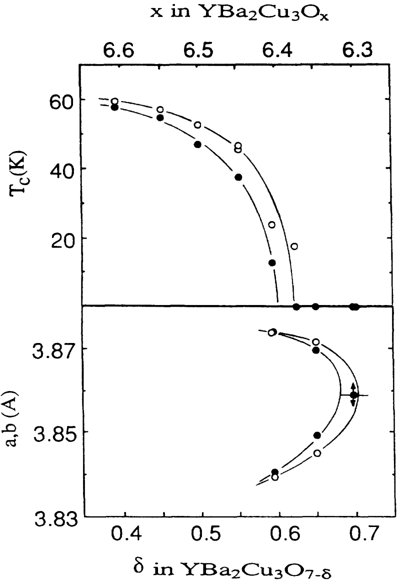

FIG. 11. Transition temperatures and (a,b) lattice parameters plotted vs oxygen stoichiometry for quenched samples of $YBa_2Cu_3O_{7-\delta}$. Solid circles designate measurements taken immediately after the quench. Open circles are data recorded after samples had aged to near saturation. With aging, T_c rises and orthorhombicity increases. For the tetragonal sample $(a=b)$, arrows indicate time-dependent broadening, the onset of an orthorhombic distortion.

quenched samples are orthorhombic. Thus, when quenching samples with stoichiometries in the approximate range 6.35–6.55, the material converts from an equilibrated tetragonal form to a metastable (oxygen-deficient) orthorhombic form.

As discussed subsequently, these results suggest that annealing results from the ordering of oxygen vacancies in the chain region of the structure. To study the temperature dependence of this vacancy ordering, a series of (secondary) quench experiments were done at temperatures below 350 °C. We observe that disorder can be reversibly controlled in this way, without observable composition change, in the oxygen-deficient samples. Recall that stoichiometries are first fixed by quenching from 520 °C (controlled atmosphere) after long (24 h or more) equilibration at temperature. With stoichiometries fixed, we now do a series of (secondary) low-temperature equilibration-and-quench experiments with T_c measured immediately after the secondary quench. Figure 12 shows T_c versus T_q, the secondary quench temperature, for two separate crystals with nominal stoichiometries $x=6.45$. T_c changes by more than 8 K when T_q is varied between 0 and 120 °C. As T_q is varied, equilibration times also vary greatly. As discussed above, the equilibration time is a month or more at 0 °C and days at 25 °C. Equilibration times become much shorter as T_q increases. As shown in Fig. 13, T_c becomes independent of T_q near 150 °C. Probably, this behavior occurs because kinetics are too fast for the quench process. Consequently, for the higher-temperature anneals, the experiment sees a 150 °C "fictive" temperature.

For the anneals above 150 °C, samples were held at temperature for 1–1.5 h before quenching. In this short time, when T_q was less than 350 °C, no detectable change in oxygen stoichiometry took place. Figure 14 shows magnetization measurements (immediately after quench) for an $x=6.45$ sample given secondary quenches

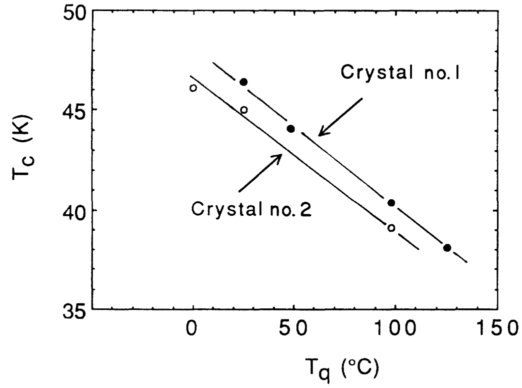

FIG. 12. Transition temperatures of two crystals with nominal stoichiometries $YBa_2Cu_3O_{6.45}$. After the compositions were fixed (by quenching from 520 °C), the samples were equilibrated at, and quenched from, temperatures T_q below 150 °C and T_c's were immediately measured. T_c changes by more than 8 K when T_q is varied between 0 and 120 °C. T_c is a reversible function of T_q indicating that T_c is responsive to an internal ordering process that depends on sample temperature.

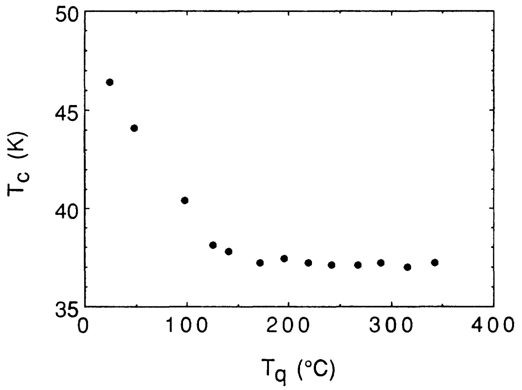

FIG. 13. T_c vs T_q (see Fig. 12) for $YBa_2Cu_3O_{6.45}$ when T_q covers the range 0–350 °C. For T_q above ~150 °C, no change is seen in the magnitude of T_c, probably because kinetics are too fast for our quench process at temperatures above 150 °C.

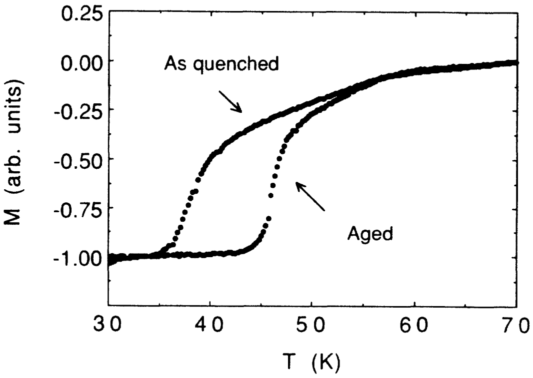

FIG. 15. Diamagnetic shielding vs temperature for the damaged sample (*d*) of Fig. 14 immediately after the quench and after 21 days aging at room temperature. With aging, the broad transition shifts to higher temperatures. The largest shift is associated with regions of the sample having the lowest as-quenched T_c's (sample interior).

$T_q = 242$, 268, and 290 °C (curves *a*, *b*, and *c*). The curves are sharp and T_c's are essentially indistinguishable. (The discernable step in the transitions near $M = -0.75$ results from a small thermometer calibration error.) *M* versus *T* is also shown (curve *d*) for the sample when $T_q = 366$ °C (at temperature for 85 min) heated in flowing oxygen. At this temperature, clearly detectable composition changes have begun to occur. The transition is noticeably broadened with a significant superconducting fraction discernable above 40 K. The sample has begun to absorb oxygen in the near-surface region and T_c increases. The very broad transition is indicative of the resulting sample inhomogeneity. With this heat treatment, the sample has been destroyed (for reversible isocomposition studies). We show, nonetheless, in Fig. 15, results of room-temperature annealing of the damaged sample. Consistent with results presented above, the broad transition shifts to higher temperatures. The largest shift is associated with regions of the sample having the lowest as-quenched T_c's (sample interior).

In addition to the single crystal-studies, we have observed low-temperature annealing in ceramic samples with reduced oxygen stoichiometries when prepared using the same equilibration-quench procedure described above. Figure 16 shows *M* versus *T* for ceramic and single-crystal (*a*) and ceramic (*b*) samples with $x = 6.45$. These samples were prepared in the same heat treatment (i.e., in close proximity in the same Pt crucible at the same time and for the same duration). For the ceramic, T_c is significantly broadened and shifted to higher temperature. Figure 17 shows aging results for this ceramic sample. T_c shifts in a manner very similar to the crystal results, rising by about 7 K in several days. Transitions

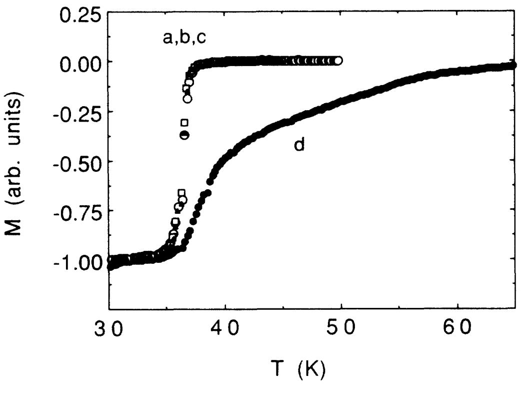

FIG. 14. Diamagnetic shielding vs temperature for $YBa_2Cu_3O_{6.45}$ when subjected to four different secondary quenches T_q. For quenches (*a*) $T_q = 242$ °C, (*b*) $T_q = 268$ °C, and (*c*) $T_q = 290$ °C, the $M(T)$ curves are indistinguishable. For curve (*d*), where $T_q = 366$ °C, the sample has begun to absorb oxygen at the sample surface and T_c rises. A significant superconducting fraction now occurs at temperatures above 40 K. After treatment (*d*) the oxygen stoichiometry in the sample has become inhomogeneous.

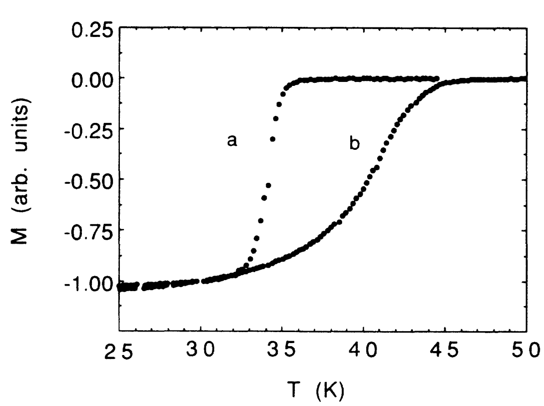

FIG. 16. Diamagnetic shielding vs temperature (*a*) for a single crystal of $YBa_2Cu_3O_{6.45}$ and (*b*) for a ceramic sample given identical heat treatment to control oxygen stoichiometry. In each case, $M(T)$ was measured immediately after the quench.

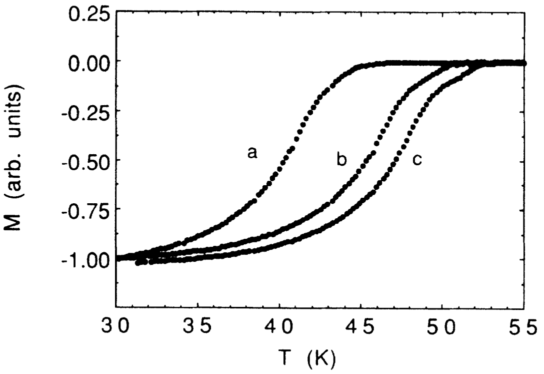

FIG. 17. Diamagnetic shielding vs temperature for the ceramic sample of Fig. 16 showing an example of room-temperature annealing behavior in ceramic Y 1:2:3. Curve (*a*) was measured immediately after quenching (from 520 °C), curve (*b*) after 19.3 h, and curve (*c*) after 116.3 h.

are comparably broad for both as-quenched and for aged samples.

Since T_c strongly depends on oxygen stoichiometry, it is necessary to firmly establish whether any composition changes occur during the low-temperature annealing experiments. We cite several tests to demonstrate that annealing behavior clearly occurs without composition change.

(1) Perhaps the strongest argument that oxygen stoichiometries do not change with the secondary low-temperature treatments is that T_c is a reversible function of the anneal temperature T_q and this reversibility occurs *independent of the annealing atmosphere.* Samples were alternately annealed in flowing O_2 and in flowing N_2 (containing ppm levels of oxygen) with no difference in the effect on T_c. Only the annealing *temperature* was effective in altering T_c. If the rise in T_c could be attributed to oxygen uptake, then annealing in flowing oxygen would enhance the rise relative to results from a nitrogen anneal.

(2) If, during low-temperature annealing, oxygen were absorbed from the ambient atmosphere on the near surface of the sample, a higher-T_c shell would be created surrounding the lower-T_c interior. This information might be lost in a shielding experiment of the kind reported here. With warming, the interior of the sample would become normal but the transition could be missed since the outer shell could prohibit flux penetration to the interior until the surface went normal at the higher temperature. To test for this possibility, 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 quickly crushed to powder, placed in a gelatin capsule, and remeasured. If the interior were different from the surface, the powder would show only a very small fraction of the high-T_c (surface) signal. We would expect to see a dominant, low-T_c (interior) signal. In fact, the powder results show that T_c is unchanged (within 0.5 K) from the higher-T_c (aged crystal sample) result. The sample does not have a low-oxygen, low-T_c interior. Note that oxygen uptake, if it were to occur at ambient conditions, must involve only the very near surface region since oxygen-diffusion rates would severely limit its motion through the sample.[41]

(3) X-ray measurements clearly show the aging phenomena. X-rays (Mo $K\alpha$ radiation) penetrate at least 10 μm into the sample. In general, with aging, the samples show increased orthorhombicity without additional line broadening. If oxygen was being slowly absorbed at the sample surface, one would expect broadening or an additional pair of diffraction peaks with a larger separation characteristic of the surface material.

Further, the aging phenomena were observed in neutron diffraction measurements[2] taken on a ceramic sample weighing ~15 g. In these measurements, the entire bulk of the sample was probed.

(4) When the secondary quench temperature was raised to a sufficiently high temperature such that oxygen uptake did occur, then the effect of the uptake was clearly seen with very substantial broadening of the superconducting transition as oxygen moved into the near surface region of the sample (Fig. 14).

IV. DISCUSSION

A. Controlled disorder experiments

These experiments show that annealing, even at temperatures as low as 0 °C, occurs in oxygen depleted $YBa_2Cu_3O_{7-\delta}$ when samples are quenched from 520 °C. Annealing is easily observed by monitoring time-dependent changes of the superconducting transition temperature in a sample stored in ambient atmosphere. The superconducting transition shifts in time to higher temperature with no discernable change in the transition width. Accompanying this aging shift of T_c are structural changes showing increasing orthorhombic distortion, a volume contraction, and bond-length changes.[1,2]

Evidence from these experiments points to the conclusion that disorder can be controllably and reversibly varied in the chain region of the structure. As temperatures of the reduced stoichiometry samples are elevated (between 0 and 150 °C), increased disorder is observed. This disorder can be quenched in and monitored using x-ray and T_c measurements.

The 1:2:3 superconductor has a remarkably high tolerance for variation of oxygen content. This variability can be attributed to the basal plane, which contains the Cu-O chains, illustrated in Fig. 18 for stoichiometric $YBa_2Cu_3O_7$. Oxygen appears only in O(1) chain sites (one such site per unit cell). The chains are separated by a string of ordered oxygen vacancies, the O(5) sites.[3] Oxygen can be easily removed from the O(1) chain sites; however, with oxygen depletion, increasing occupancy of the O(5) sites occurs.[3,5] In samples of $YBa_2Cu_3O_{7-\delta}$ with varied oxygen stoichiometries, the amount of orthorhombic distortion is closely associated with O(5) site occupancy. *Increased* O(5) occupancy is associated with *reduced* orthorhombicity and loss of oxygen-vacancy ordering that defines the chains. Since rising T_c's correlate directly with increasing orthorhombicity, in Ref. 1 it was inferrred that the annealing effect resulted from the order-

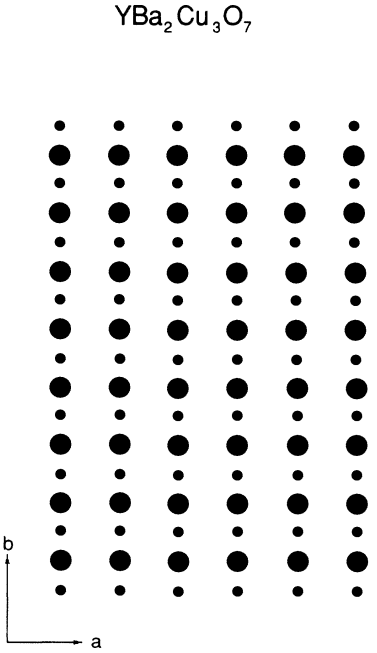

FIG. 18. A representation of the basal plane in ideal $YBa_2Cu_3O_7$. Large atoms are oxygens occupying O(1) crystallographic sites. The small atoms are coppers in Cu(1) sites. Copper-oxygen chains are formed along the *b* direction. Vacant O(5) sites, located between adjacent Cu(1) atoms in the *a* direction, separate the chains.

ing of oxygen atoms, quenched into O(5) sites, that slowly move to O(1) chain sites at room temperature. However, subsequent neutron-diffraction experiments[2] showed that the O(5) site population was low, about 0.04 at $x = 6.41$, while most basal plane oxygens (0.38) occupied the O(1) sites. Furthermore, no discernable change could be detected in the relative site populations as the sample aged, though T_c and lattice parameters changed markedly. Thus, it becomes clear that the annealing involves a different type of chain-vacancy ordering.

For stoichiometries near 6.5, it appears likely that annealing is predominantly attributable to ordering which forms the double-period $\langle \frac{1}{2},0,0 \rangle$ orthorhombic structure.[34,36,38] This ordered structure is commonly referred to as the ortho II phase. We observe that, at $x = 6.5$, one-half of the oxygens are missing from the basal plane. Yet, the material is orthorhombic with very little O(5) site occupation.[3,5] With this extreme dilution of O(1) site occupation, it is difficult to see why the material should preserve orthorhombic symmetry unless additional ordering occurs. With a random distribution of oxygens in chain sites, O(5) occupancy would appear to be as probable as O(1) occupancy. More likely, the orthorhombic distortion at these dilutions is a consequence of additional chain-vacancy ordering. The ortho II and a number of other ordered structures have been reported.[30-38] However, the ordering is observed only with difficulty, usually in electron-diffraction experiments where typically only a small fraction of the sample reveals the structure. Experimental difficulty is encountered because ordering is generally not sufficiently long range. Slip dislocations, twins, and poor coherence in the *c* direction can be expected to contribute to the difficulty. Also, it is not clear which of these structures might represent transient forms, and which might represent equilibrium forms.

Assuming that $\langle \frac{1}{2},0,0 \rangle$ ordering occurs for x near 6.5, then at elevated temperatures we expect that the degree of vacancy ordering will be diminished, with oxygen atoms increasingly occupying the chains of normally vacant O(1) sites, as illustrated in Fig. 19 for the ortho II structure. This disorder can be retained by quenching. We believe that, while annealing at reduced temperature, the oxygens move between adjacent chain sites to enhance the degree of $\langle \frac{1}{2},0,0 \rangle$ ordering. The secondary quench experiments (Fig. 12) demonstrate that the degree of disorder is a reversible function of temperature. Improved chain-vacancy ordering increases the orthorhombicity, largely because the vacant chains lead to a substantial reduction in the *a*-axis parameter.[2]

B. Superconducting transition temperature: relationship to structure

The superconducting transition temperature rises with aging. This apparently results from charge redistribution in the structure that increases the hole content in the planes. That is, the variable chain disorder directly

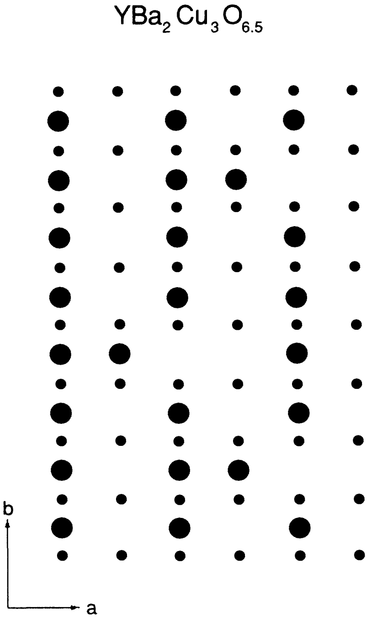

FIG. 19. A representation of the basal plane in $YBa_2Cu_3O_{6.5}$ in the ortho II structure. The ideal structure contains alternating occupied and vacant (oxygen-free) chains. The reversible behavior of T_c vs T_q shown in Fig. 12 is believed to result from a variable (temperature-dependent) disorder associated with the occupancy of O(1) sites in normally vacant chains with introduction of vacancies into the normally occupied chains (as illustrated). Low-temperature annealing, with rising T_c, results from improving ortho II order.

affects the electronic properties in the plane region of the structure. The generally accepted view is that superconductivity is most intimately associated with the planes. Variations (usually compositional) in the chains, which alter the overall charge balance in the R-1:2:3 system, are believed to produce changes in the carrier concentration in the planes with a direct effect on T_c.[5,6,42–46] In this work, we observe that T_c changes without change in composition so that charge variation in the planes must occur simply as a consequence of oxygen atom redistribution. Probably, charge redistribution occurs simply as a consequence of changes in the coordination of chain copper atoms.[29] The valence state of copper bonded to oxygen is closely associated with its coordination number.[47] Two-coordinated copper is monovalent. The shift of oxygen atoms from their normally vacant chain sites (Fig. 19) to their normally occupied chain sites increases the population of two-coordinated (monovalent) copper atoms. In becoming monovalent, these copper atoms acquire an additional electron charge which comes from the planes. The charge redistribution is reflected in the clearly observed bond-length changes.[2]

Recent theoretical results[45,46] appear to be consistent with this picture. The calculations show that, as oxygen is removed from $YBa_2Cu_3O_{7-\delta}$, the carrier concentration in the planes systematically falls. Importantly, however, when the chain region of the structure is ordered, there is a corresponding rise in the in-plane carrier concentration. These variations of the in-plane carrier concentration directly affect T_c.

The above discussion has focused on the behavior of samples with stoichiometries near 6.5 where $\langle \frac{1}{2},0,0 \rangle$ chain-vacancy ordering is expected to be most pronounced. However, fixed-composition low-temperature annealing, signaling an internal ordering process, also occurs at much higher oxygenation levels (Figs. 6 and 7). Ordering at high stoichiometries probably involves vacancy arrangements of other types, perhaps the Magneli-type structures.[28,29]

C. T_c versus aging time: Functional dependence

In Figs. 8 and 9, we have presented data showing the time (t) dependence of T_c in its approach to equilibrium during low-temperature annealing. For ceramic samples,[2] the data could be fit with high precision using either of the functional forms:

$$T_c(t)=T_c(\infty)-[T_c(\infty)-T_c(0)][\tau/(t+\tau)] \quad (1)$$

or

$$T_c(t)=T_c(\infty)-[T_c(\infty)-T_c(0)]\exp[-(t/\tau)^{1/2}] \ . \quad (2)$$

Both forms have been used extensively to analyze ionic relaxation phenomena.[48] For the single-crystal sample with $x=6.45$, we obtain characteristic times τ of 556 and 572 min for the two functional forms, respectively, when samples are aged at room temperature. These values differ somewhat from results obtained for an $x=6.41$ ceramic sample reported previously[2] where $\tau=386$ min, obtained from the exponential fit [Eq. (2)]. Differences between the crystal and ceramic samples might be attributable to variations in defect density, sample purity, slightly different stoichiometries, and to strains in the ceramic. Figure 9 shows relaxation data for a single crystal with stoichiometry 6.45 aging at 0 °C. The data are fit with the exponential form [Eq. (2)] with $\tau=229$ h.

D. Activation energy

We have noted that the dependence of T_c on the secondary quench temperature T_q (Fig. 12) is reversible. Thus, when equilibrated at temperature T_q, the material has apparently reached a stable condition representing a particular state of disorder. We expect that, after a quench, the rate at which the system relaxes to its new equilibrium condition will be a thermally activated process, i.e.,

$$\tau=A\exp(\Delta E/k_BT) \ , \quad (3)$$

where k_B is the Boltzmann constant and T is the temperature at which the sample is aged. From the relaxation rates obtained at room temperature and at 0 °C (Figs. 8 and 9), we obtain an estimate of the activation energy $\Delta E=0.96$ eV, and of the preexponential $A=1.4\times10^{-12}$ s. We have observed, in Fig. 13, that kinetics become too rapid, above about 120 °C, to stabilize the disordered condition by quenching. Consistently, from Eq. (3), we obtain $\tau=2.9$ s at 120 °C. Of course, relaxation rates become much faster as T_q increases above 120 °C.

This estimate of activation energy was obtained from a sample with stoichiometry close to 6.5. As discussed above, we expect that this process is primarily associated with thermally activated disorder in the ortho II phase, predominantly occurring in the manner suggested by Fig. 19. Nonetheless, Rothman *et al.*[41] have obtained the same value for the activation energy (0.97 ± 0.03) for oxygen diffusion in Y 1:2:3, when determined over a range of oxygen stoichiometries.

As we see in Fig. 19, ordering may involve a single hop between adjacent O(1) sites, a distance of 3.85 Å. An alternative possibility is that oxygens follow the path $O(1)\rightarrow O(5)\rightarrow O(1)$. In any case, this distance is comparable to the diffusion length, $2(Dt)^{1/2}$, of several Å (estimated from tracer diffusion data of Rothman *et al.*[41], that the atoms travel in the characteristic time at room temperature.

E. Ceramic samples

Figure 16 and Refs. 2, 5, 7, and 10–15 show that superconducting transitions, measured magnetically, are significantly broader for the ceramic samples than for the crystals reported here and in Ref. 49. We believe that this broadening is an intrinsic property of sintered ceramics that are prepared using conventional procedures. Sintering takes place at temperatures of 900 °C or higher where the material is tetragonal and highly oxygen deficient. Grains are formed and bonds between grains are established. As the sample is cooled in O_2, oxygen uptake occurs and a highly anisotropic change in lattice parameters occurs.[3,5] Since the bonded grains are randomly oriented, the cooled, oxygenated material is necessarily anisotropically stressed unless some strain relief mechanism (such as microcracking due to tensile stress) is available. Since T_c has a strong dependence on pressure at reduced stoichiometries,[50] it may be that the observed shift of T_c to a higher temperature (relative to the ceramic), with substantial broadening, is a consequence of internal strains.

We also note that the data in Fig. 16, comparing results for single-crystal and ceramic samples at $x = 6.45$, suggest that the lower plateau might be more clearly defined for ceramics than for crystals. For the as-quenched ceramic, T_c is about 8 K higher than the as-quenched crystal. As the samples age, both superconducting transitions move to a higher T_c, approaching the usual plateau value, but, at saturation, the ceramic comes much closer. It seems possible that the plateau is enhanced in ceramics by internal strain effects that are introduced in conventional ceramic sinter-processing methods and by a variable dependence of T_c on pressure.

F. Varied oxygen stoichiometry: Microstructure

From the low-temperature annealing results, it is clear that ordering occurs for all $x < 6.85$. For the 6.45 sample investigated in this study, the ordering is a reversible function of temperature indicating that equilibrium structures are being probed. In the vicinity of 6.5, it seems likely that the material orders into alternating rows of vacant and occupied chains. With increasing temperature, the material acquires increasing disorder, perhaps represented by partial occupation of normally *vacant* chains and corresponding introduction of vacancies into normally *occupied* chain sites as illustrated in Fig. 19.

As the stoichiometry deviates significantly from 6.5, the microstructure apparently becomes much more complicated. Recent theoretical work predicts the occurrence of a series of Magneli-type vacancy-ordered structures,[28,29] varying with stoichiometry. These structures have the common feature that they contain chains of oxygen vacancies aligned along the *b* direction in O(1) basal plane sites. A variety of such ordered structures, representing either transient or equilibrium phases, have been reported[30–38] using electron diffraction and microscopy measurements. From the present work we are unable to provide detailed information on the possible variety of ordered structures that might occur. If, however, the common feature of these structures is that they have vacant rows of O(1) oxygen atoms, then the same reversible temperature dependent disordering observed for the 6.45 sample might be expected to occur generally. At all x, oxygens in occupied chains will increasingly move to unoccupied chains as temperature is increased.

An important consequence to the electronic properties that results from this complex microstructure is that chain formation maximizes the number of two-coordinated, monovalent coppers which, in turn, maximizes the hole concentration in the planes. Thus, the pervasive ordering which occurs in this structure is favorable to superconductivity. The ordering may be viewed as a form of doping.[29]

In a somewhat different view, the plateaus delineate extended "60- and 90-K phase fields" that are characterized by different oxygen stoichiometries and structures with specific vacancy orderings.[6,12–16] Mixed phase behavior might occur in the composition regions between the plateaus and at the dropoff from the lower plateau.[31] In possible support of this picture, Tetenbaum *et al.*[51] have reported evidence for a miscibility gap, at temperatures below 400 °C, for x near 6.65. However, in a two-phase region, one would generally expect to see, in a shielding experiment, the (different) T_c's associated with each of the two phases.[10] Data were presented in Fig. 2 showing transition temperatures for Y 1:2:3 samples with widely varied stoichiometries. We see that samples can be fabricated that give sharp transitions, apparently at any x where the sample is superconducting, including the regions between plateaus. These data do not confirm the hypothesis that the composition region between the plateaus consists of a simple mixture of "60- K and 90-K phases." However, if the phase-separated regions were finely dispersed, it might be that proximity effects would smoothly shift T_c's in the two-phase regions.[10]

Similarly, at the dropoff of the lower plateau, the material is perceived to be a two-phase mix containing the 60-K phase and a nonsuperconducting phase.[36] In this case, only a single (constant 60-K) transition is expected as x is varied. Again, however, the systematically declining, sharp superconducting transitions that are observed for $T_c < 60$ K do not provide evidence to support the two-phase model. Further, the superconducting volume fraction should fall systematically, in this region, with increasing x. However, the single crystals examined in the current study do not show a declining superconducting volume fraction, even when T_c falls well below the 60-K plateau value. While a declining superconducting volume fraction has been reported,[6,10–14] we note that this behavior may result from oxygen inhomogeneity in the ceramic samples and from the use of excessively large measuring fields. H_{c1} is less than 1 Oe when $T_c = 10$ K.[52] If measuring fields are well above H_{c1}, the diamagnetic signal that measures the superconducting volume fraction may be severely reduced by flux penetration into the sample.

V. CONCLUSIONS

Samples of $YBa_2Cu_3O_{7-\delta}$, both single crystal and ceramic, were prepared with reduced-oxygen stoichiometries by quenching to liquid nitrogen after first equilibrating the samples in a controlled O_2-N_2 atmosphere. It was found that single-crystal samples could be prepared with any desired transition temperature between 10 and 92 K with transition widths generally being no more than 1 K. Ceramic samples showed broadened transitions somewhat shifted from the crystal values, effects believed to be associated with internal strain.

The quenched samples showed annealing behavior when stored at room temperature in ambient atmosphere. The transition temperature rose, by as much as 15–20 K, in a period of several days and the material showed increased orthorhombicity. Annealing was observed at all oxygen stoichiometries $x < 6.85$. After stoichiometries were fixed, followup quench experiments were performed in the temperature range $0 < T_q < 350\,^{\circ}\mathrm{C}$. It was found that T_c (and, by inference, disorder) could be reversibly controlled by varying T_q, again without composition change.

The low-temperature annealing apparently results from oxygen-vacancy ordering that occurs in the chain region (basal plane) of the structure. For stoichiometries near $x = 6.5$, ordering apparently involves the formation of alternating full and empty (oxygen-free) chains. At more general stoichiometries, the annealing results are consistent with proposed models which suggest that a variety of (Magneli-type) structures, containing ordered arrays of oxygen vacancies, occur as stoichiometry is varied. Thus, at any stoichiometry, as temperature is increased, the material becomes increasingly disordered by increasing the O(1) occupation on normally *vacant* chains with corresponding introduction of vacancies into normally *occupied* chains.

Chain formation maximizes the number of two-coordinated, monovalent coppers which in turn, maximizes the hole concentration in the planes. Thus, the pervasive oxygen-vacancy ordering which occurs in this structure may be viewed as a form of doping favorable to superconductivity.

These experiments offer a remarkable opportunity to examine the relationship between atomic structure, superconducting behavior, and associated electronic properties in $YBa_2Cu_3O_{7-\delta}$ without the complicating effects of composition variations. Experiments are particularly easy to perform, either in single crystals or in ceramics, with room-temperature annealing occurring on a convenient time scale.

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