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Effect of compositional variation and annealing in oxygen on superconducting properties of $Y_1Ba_2Cu_3O_{8-y}$

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Changes in the ratios of cations by ~10% off the $Y_1Ba_2Cu_3O_{8-y}$ composition demonstrated that a range of solid solutions exists in this material. The critical temperature within this range is strongly composition dependent and falls off from above 90 to ~70 K. Annealing stoichiometric samples in 1 bar of oxygen at 700 °C for 36 and 108 h resulted in a narrowing of the magnetic susceptibility transition and significant increases in the critical current density J_c, p-type effective carrier concentration n^*, and upper critical field H_{c2}. After annealing, J_c between 5 and 60 kOe was $(3-1.5)\times10^4$ A/cm^2 at 4.2 K and $(2-0.5)\times10^2$ A/cm^2 at 77 K. The value of n^* after annealing was 4.2×10^{21} cm^{-3}. An extrapolated value of $H_{c2}(T=0)=1.2$ MOe was obtained from $|dH_{c2}/dT|=19$ kOe/K. A set of microscopic superconducting parameters was derived from results of resistive measurements made on a single, annealed specimen.

The observation of a superconducting transition above 90 K in phase mixtures of nominal composition $Y_{1.2}Ba_{0.8}CuO_{4-y}$ and $Y_{0.6}Ba_{0.4}CuO_{4-y}$ was first reported by Wu *et al.*[1] and Chu *et al.*[2] This discovery was promptly followed by the identification of the superconducting compound $Y_1Ba_2Cu_3O_{8-y}$ (hereafter called the 1:2:3 compound) having a perovskite-related orthorhombic structure.[3-8] In our case, as in Ref. 5, the identification was based on the scanning electron microscope (SEM) and the x-ray energy dispersive spectroscopy (EDS) analysis of phases in the first of the Wu and Chu multiphase compositions. Grains of two major phases present had distinctly different growth habits and compositions which made the identification possible. These two phases were then prepared in pure form and examined. Magnetic susceptibility χ and x-ray diffraction data confirmed that the black phase responsible for superconductivity at 90–95 K was $Y_1Ba_2Cu_3O_{8-y}$, having an orthorhombic crystal structure.

In this Rapid Communication, we show the effect of deviation from the ideal 1:2:3 composition on the superconducting transition and examine the effect of annealing in oxygen on the transition width, carrier density, and critical current density in sintered specimens of Y-Ba-Cu-O. Upper critical field and resistivity data obtained near the superconducting transition temperature T_c are used to estimate several pertinent parameters of the superconducting phase and to compare results with those of Cava *et al.*[3] No determination of the number of oxygen vacancies y was made, although the effects of annealing in oxygen indicated that $y\neq0$.

Samples were prepared from reagent grade Y_2O_3, $BaCO_3$, and CuO by mixing the constituents and reacting at 940 °C for 16 h in flowing oxygen at atmospheric pressure. After cooling in oxygen, the reaction mixture was reground, the same heat treatment repeated, and the product reground again. The resulting powder was pressed into 1-mm-thick pellets, 13 mm in diameter, which were sintered at 940 °C and cooled in oxygen. The pellet density was 87% of the pycnometric powder density.

The dependence of resistance upon temperature T and magnetic field intensity H and the magnetic moment $M(T,H)$ have been determined, as in an earlier Letter where experimental details were described and discussed.[9] The critical current density was derived, as before, from magnetization hysteresis loops.

Figure 1 shows the effect of deviations from the composition with 1:2:3 stoichiometry on magnetic susceptibility $\chi(T)$. The magnetometer samples were powders that were prepared in oxygen but not subjected to any additional annealing before the magnetic moment measurements. The results of the susceptibility measurements are

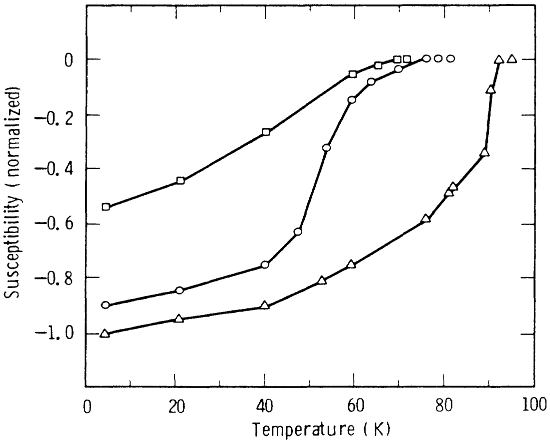

FIG. 1. Magnetic susceptibility, normalized to the diamagnetic signal at 4.2 K from the $Y_1Ba_2Cu_3O_{8-y}$ sample, plotted as a function of temperature for samples with different cation compositions. The T_c onset and superconducting volume fraction for $Y_1Ba_2Cu_3O_{8-y}$ (open triangles), $Y_{1.05}Ba_{1.8}Cu_{3.0}O_{8-y}$ (open circles), and $Y_{1.0}Ba_{2.2}Cu_{3.0}O_{8-y}$ (open squares) are shown in Table I.

TABLE I. Effect of deviation from the $Y_1Ba_2Cu_3O_{8-y}$ stoichiometry on T_c and the superconducting-phase content derived from diamagnetic susceptibility of powders. Resistive T_c and resistivity ρ in sintered unannealed pellets are also given.

Composition, cations only	T_c (K) onset from susceptibility	Superconducting volume (%)	T_c (K) 5%–95% resistive	$\rho_{120\,K}$ ($\mu\Omega$ cm)	$\rho_{300\,K}/\rho_{120\,K}$
$Y_{1.0}Ba_{2.0}Cu_{2.0}$	91	100	95–90	730	1.9
$Y_{1.05}Ba_{1.8}Cu_{3.0}$	70	90	81–60	1580	2.3
$Y_{1.0}Ba_{2.2}Cu_{3.0}$	70	55	94–88	10700	1.1

summarized in Table I, along with the results of resistive measurements on unannealed pellets. The critical temperature and the relative volume fraction of a superconductor determined from $\chi(T)$ (Fig. 1) decreased when the ratios, (Ba+Y)/Cu and Ba/Y, were lower or higher than 1 and 2, respectively. The superconducting fraction of the $Y_{1.05}Ba_{1.8}Cu_{3.0}O_{8-y}$ sample was relatively homogeneous since the resistive T_c was comparable to that from χ. In $Y_{1.0}Ba_{2.2}Cu_{3.0}O_{8-y}$, the resistive T_c did not decrease relative to the 1:2:3 sample, the resistivity at 120 K, $\rho_{120\,K}$, increased by a factor of 15, and the resistivity ratio $\rho_{300\,K}/\rho_{120\,K}$ decreased. Therefore, a small concentration of the 90-K composition was present in a matrix of higher-resistivity and lower-T_c material.

The x-ray diffraction patterns were indexed in all three specimens listed in Table I to the same orthorhombic structure with some line broadening observed in the off-stoichiometric powders. The unit cell dimensions were $a = 3.817 \pm 0.010$ Å, $b = 3.888 \pm 0.010$ Å, and $c = 11.652 \pm 0.010$ Å. Differences observed in the lattice parameters of samples of the three compositions were within the estimate of lattice constant error. Within the limitation imposed by the intensity of our x-ray source, no evidence for a second crystallographic phase was found in the off-stoichiometric samples.

It is generally believed that $Y_1Ba_2Cu_3O_{8-y}$ is a line compound based on the fact that the high-T_c phase was observed in multiphase samples as far off stoichiometry as $Y_{1.75}Ba_{0.25}CuO_x$.[10] In contrast, our data suggest that a range of solid solutions with Y, Ba, and Cu exists and that $Y_1Ba_2Cu_3O_{8-y}$ is not strictly a line compound. Our x-ray data for samples prepared in oxygen are in contrast to the crystallographic data of samples prepared in air, presented in Ref. 6, where a second phase was detected in samples with similar deviations from ideal stoichiometry.

The reduction in superconductor volume fraction and the decrease in T_c of most of the superconducting fraction indicate that the composition range for superconductivity is very narrow. The insensitivity to slight off-stoichiometry variations reported by Engler *et al.*, based on resistive T_c measurement, can be explained by the presence of small amounts of the stoichiometric phase in their off-stoichiometric preparations,[11] such as we observed in our Ba-rich samples. Considerable accuracy in the formulation of the material is thus required to obtain properties fully representative of the 1:2:3 superconductor.

We measured the dc susceptibility as a function of temperature for a sintered disk of $Y_1Ba_2Cu_3O_{8-y}$, 3 mm in diameter and 1 mm thick, which was annealed at 700 °C in flowing O_2 successively for the total time of 0, 36, and 108 h followed by cooling in O_2 to below 400 °C. The susceptibility at 4.2 K was in all cases comparable to that in a geometrically identical Nb disk. Table II summarizes the effect of annealing time on the T_c onset (defined as 5% of the diamagnetism at 4.2 K), on the 5–95% superconducting transition width ΔT_c, from magnetic moment measurements, and on the resistive properties discussed below. As shown in Table II, the susceptibility transition sharpened upon annealing for 36 h but further annealing had no effect. The transition in the as-sintered disk was much broader than in the starting powder which indicated that filling of oxygen vacancies was occurring at temperatures lower than the sintering temperature. During cooling, the oxygen diffusion into the pellet was more difficult than into the powder. A direct determination of the vacancy content before and after annealing in oxygen remains to be done.

The critical current density J_c increased significantly due to annealing in oxygen. Figure 2 compares $J_c(H)$ in magnetic fields between 5 and 60 kOe at several temperatures, before and after annealing for 36 h. The J_c increase was observed at all temperatures of measurement. It was

TABLE II. Effect of annealing in oxygen on superconducting and normal properties of $Y_1Ba_2Cu_3O_{8-y}$. Magnetic moment data and resistive data were obtained on two different samples.

	Magnetic moment data		Resistive measurements			
Annealing time (total hours)	T_c (K) 5% onset	ΔT_c (K) 5%–95%	T_c (K) 5%–95%	$\rho_{120\,K}$ ($\mu\Omega$ cm)	$\rho_{300\,K}/\rho_{120\,K}$	n^* (cm^{-3})
0	87	67	95–90	760	2.1	1.4×10^{21}
36	91	~21	· · ·	· · ·	· · ·	· · ·
72	· · ·	· · ·	95–93	400	2.3	4.2×10^{21}
108	91	~21	· · ·	· · ·	· · ·	· · ·

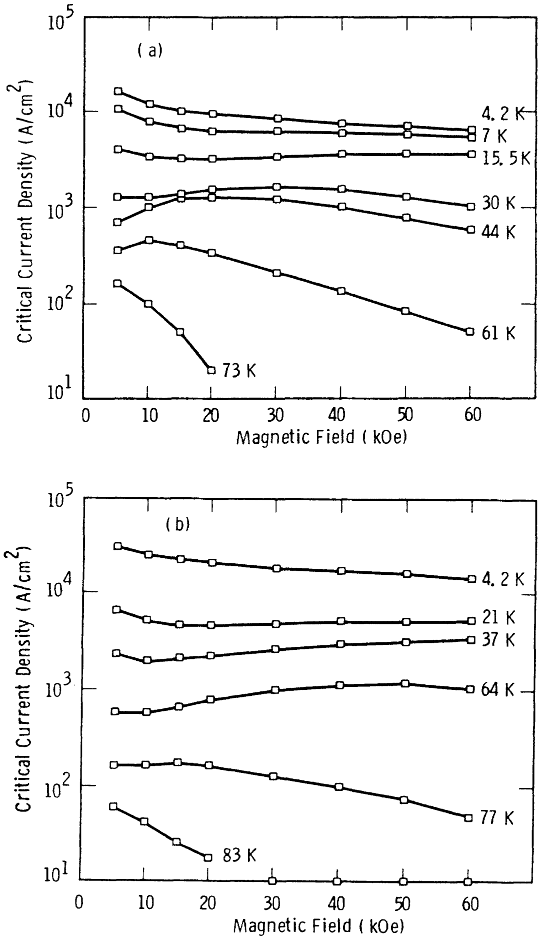

FIG. 2. Critical current densities from magnetic moment hysteresis loops. (a) Before annealing and (b) after 36 h in O_2 at 700 °C.

especially noticeable above 60 K where annealing made J_c less dependent upon H, thus indicating that the increase of J_c was primarily due to an increase in the upper critical field H_{c2}. At lower temperatures, the J_c's were almost independent of H reflecting the fact that the measurement fields were much smaller than the very high upper critical field.

Upon annealing for an additional 72 h (108 h total time) the J_c's remained almost unchanged or decreased slightly. This is an indication that a prolonged heat treatment reduces the number or strength of flux pinning sites of a yet unspecified nature. The SEM observation of the sample surface did not reveal any noticeable grain growth. We are aware of only one J_c data point reported by others for the 1:2:3 compound: the self-field $J_c = 1.1 \times 10^3$ A/cm^2 at 77 K determined from transport data by Cava *et al.*[3] This value is higher than our data obtained in the annealed sample at $H = 5$ kOe and 77 K. However, since J_c at 5 kOe could be several times smaller than self-field values, their data point is consistent with our measurements. At comparable reduced temperatures T/T_c, the J_c's were an order of magnitude higher than those which we reported for the $La_{1.8}Sr_{0.2}CuO_4$ superconducting oxide.[9] In the case of both high-T_c oxides, an unexplained maximum in J_c was observed at some magnetic field greater than zero but much less than H_{c2}.

Hall constant measurements were made at 103 K by the dc van der Pauw technique, as described before.[9] The Hall voltage was linear in field up to 50 kOe and its sign was indicative of hole conduction. The effective carrier density was $n^* = 1.4 \times 10^{21}$ cm^{-3} before annealing, and increased by a factor of 3 to 4.2×10^{21} cm^{-3} after 72 h of annealing. The resistivity at 120 K decreased from $\rho = 760$ to 400 $\mu\Omega$ cm. Cava *et al.* also observed that their samples were p type (from the Seebeck voltage) but found the Hall constant too low to measure, leading to a lower limit of $n^* = 1.1 \times 10^{23}$ cm^{-3} in samples having a residual resistivity of 200–250 $\mu\Omega$ cm.[3] It is important to determine whether the changes in the Hall constant and normal-state resistivity were due to deviations from the ideal cation stoichiometry, less than optimum oxygen contents, or perhaps they were due to other causes.

An extrapolation of the upper critical field in the sample annealed for 72 h was obtained from $|dH_{c2}/dT| = 19 \pm 2$ kOe/K near T_c. This value was obtained from resistive transition midpoint values measured in magnetic fields up to 60 kOe. The value $H_{c2}(0) = 1.2$ MOe, was calculated in the dirty limit assuming zero paramagnetic limiting.[12] The slope of the upper critical field and the resulting H_{c2} extrapolation are higher than those derived from transition midpoints in phase mixtures.[2,13,14] We are not aware of other H_{c2} data reported for the single phase material.

From the slope of the upper critical field and other resistive properties of one specimen, we calculated several pertinent parameters of the 1:2:3 compound which are given in Table III.[15,16] Also listed are parameters calcu-

TABLE III. Superconducting parameters derived from T_c, $|dH_{c2}/dT|$, $\rho_{120\,K}$, and n.

		$n = 4.2 \times 10^{21}$	$n = 10^{23}$	Ref. 3
Electronic specific-heat coefficient	γ [erg/(K^2-cm^3)]	450	1050	750
	γ [mJ/(K^2-molf.u.^{a})]	5	11	8
Ginzburg-Landau coherence length	$\xi(0)$ (Å)	14	14	22
Ginzburg-Landau penetration depth	$\lambda(0)$ (Å)	2000	1300	1000
Ginzburg-Landau κ	κ	150	100	45
Thermodynamic critical field	$H_c(0)$ (kOe)	8	13	10
Depairing critical current density	$J_d(0)$ (A/cm^2)	3×10^6	7×10^6	8×10^6

[a] f.u. is the formula unit defined as $Y_1Ba_2Cu_3O_{8-y}$.

lated in the dirty limit to show the largest discrepancy that could result if the carrier density of Cava *et al.* were assumed.[3] The parameters from Ref. 3, given in the last column to permit comparison, were based on $\rho_{120\,\mathrm{K}}$ and T_c from one sample, and dH_{c2}/dT from Ref. 1 for a sample with a different composition.

The derived values of γ, the electronic specific-heat coefficient, fit the qualitative pattern noted by Batlogg *et al.*[17] Specifically, $Y_1Ba_2Cu_3O_{8-y}$ joins $(La,Sr)_2CuO_4$ and $Ba(Pb,Bi)O_3$ as part of a distinct class of superconductors with high T_c and relatively low γ. The depairing critical current density is higher than for $(La,Sr)_2CuO_4$ because the thermodynamic critical field $H_c(0)$ is larger.[9] The coherence length is not much larger than the size of the unit cell. The use of $\rho_{120\,\mathrm{K}}$ in these calculations probably overestimated the normal-state resistivity that would be obtained at low temperature in high magnetic fields, so γ, $H_c(0)$, and $J_d(0)$ were correspondingly underestimated.

In conclusion, the superconducting properties of $Y_1Ba_2Cu_3O_{8-y}$ are very strongly dependent upon the concentration of oxygen vacancies and also upon deviations from the 1:2:3 stoichiometry. The measured critical current densities, although low, show a better promise of technical applicability than those observed in Sr-substituted La_2CuO_4. The calculated depairing current is also much higher in the present case.

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