Bulk Superconductivity at 91 K in Single-Phase Oxygen-Deficient Perovskite $Ba_2YCu_3O_{9-\delta}$

R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika,
E. A. Rietman, S. Zahurak, and G. P. Espinosa

AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 5 March 1987)

We have prepared and identified as a single phase the high-temperature superconducting compound in the chemical system Y-Ba-Cu-O, an orthorhombic, distorted, oxygen-deficient perovskite of stoichiometry $Ba_2YCu_3O_{9-\delta}$ ($\delta \approx 2.1$). Samples exhibit zero resistance at 91 K, with a transition width of 1.5 K. The Meissner effect attains a value of 76% of the independently measured diamagnetic susceptibility. We estimate parameters that characterize this superconductor, e.g., $\gamma \approx 3-5$ mJ (mole Cu)$^{-1}$ K^{-2}. The critical current density at 77 K and $H = 0$ exceeds 1100 A/cm^2.

PACS numbers: 74.70.Ya, 74.30.Ci

The investigation of the properties of high-temperature superconductors has increased in pace in recent months since the announcement of possible high-T_c superconductivity in the La-Ba-Cu-O chemical system,[1] and subsequent studies on that and related systems showing the superconductivity to be a bulk effect.[2-5] Recent reports of superconductivity at temperatures of 90-95 K in the chemical system Y-Ba-Cu-O have dramatically demonstrated that T_c's higher than those generally considered attainable can be achieved[6] in oxide systems. The very high T_c's in the Y-Ba-Cu-O system were obtained in polycrystalline material with optimal formulation $Y_{1.2}Ba_{0.8}CuO_{4-y}$, which was actually a mixture of several phases.[6] It was suggested that superconductivity might even arise from interfacial interactions between phases.

In this Letter we present the results of a study in which we have identified and prepared as a pure phase the superconducting compound in this chemical system, and examined its properties employing single-phase polycrystalline samples. We find that the composition originally reported actually contains predominantly a green semiconducting phase, Y_2BaCuO_5, when prepared as described in those reports. The superconducting phase is $Ba_2YCu_3O_{9-\delta}$ ($\delta = 2.1 \pm 0.05$) which can be described as a distorted, oxygen-deficient perovskite. As in the K_2NiF_4-structure-type $La_{2-x}M_xCuO_{4-\delta}$ compounds,[1-4] the transport properties are critically dependent on the partial oxidation of Cu^{2+}. In $Ba_2YCu_3O_{9-\delta}$ oxidation is controlled almost exclusively by oxygen deficiency. The bulk polycrystalline material demonstrates zero resistance at 91 K and a Meissner effect at low temperatures of 76% of the independently measured diamagnetic signal. The lower critical field at 20 K is 500 ± 50 Oe, and the resistivity above T_c is ∼200-250 $\mu\Omega$ cm. From these data and reported[6] $H_{c2}(T)$ values we derive some material parameters and estimate a density of electronic states at E_F of ∼3-5 mJ (mole Cu)$^{-1}$ K^{-2}, a value considerably smaller than in $La_{1.85}Sr_{0.15}CuO_{4-y}$.

The superconducting compound was identified through a phase-equilibrium study of the ternary system BaO-CuO-Y_2O_3 at temperatures of 950 and 1050°C, in both air and oxygen. The composition reported by Wu et al.[6] consists of a mixture of semiconducting[7] Y_2BaCuO_5 ($\sim \frac{2}{3}$) and superconducting $Ba_2YCu_3O_{9-\delta}$ ($\sim \frac{1}{3}$), a previously unidentified (to our knowledge) compound, although several other Cu-based perovskites are known.[8,9] In oxygen ambients, the latter phase is stable to 1050°C, where dense polycrystalline pellets can be made. The superconductivity is lost on annealing in argon. A third ternary phase, with a perovskitelike composition, is also present under some synthetic conditions, but as it is not superconducting, we did not study its crystal chemistry further.

Single-phase $Ba_2YCu_3O_{9-\delta}$ was prepared by our mixing $BaCO_3$, Y_2O_3, and CuO, grinding, and heating at 950°C in air for 1 d. This material was then pressed into pellets, sintered in flowing O_2 for 16 h, and then cooled to 200°C in O_2 before removal from the furnace. Additional overnight treatment in O_2 at 700°C was found to improve the observed properties. The oxygen content for this material was determined by our heating a sample in H_2 at 900°C for 2 h and measuring the weight loss on reduction to Cu metal and Ba/Y oxides, yielding the value $\delta = 2.1 \pm 0.05$. The oxygen content of the material depends critically on the synthetic conditions. Prepared as described, $Ba_2YCu_3O_{9-\delta}$ is an orthorhombically distorted perovskite. All observed x-ray powder diffraction peaks can be accounted for by a crystallographic unit cell of $a = 3.822$ Å, $b = 3.891$ Å, and $c = 11.677$ Å ($\sim 3a_{perov}$). The cell volume is 3 times the standard perovskite cell, and contains one formula unit of $Ba_2YCu_3O_{6.9}$. Materials prepared for Ba:Y ratios different from 2:1 show the presence of either $BaCuO_2$ or $Y_2Cu_2O_5$, indicating that the A site (see below) has a well-defined stoichiometry. This suggests ordering of the Ba and Y atoms, which is also indicated by the tripled perovskite unit-cell volume. With the possible ordering of oxygen vacancies, the true crystallographic unit cell may be larger in volume than that reported here. Further crystallographic study will resolve this issue.

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The powder x-ray diffraction pattern of this new compound is presented in Table I for purposes of identification. For material with lower oxygen content (e.g., prepared in air at 950°C) the distortion from tetragonal symmetry is smaller.

Compounds with the perovskite structure generally have stoichiometry ABO_3. The A atoms (in this case Ba and Y) occupy sites in large cavities within the BO_3 framework (in this case CuO_3). The BO_3 framework is an infinitely connected three-dimensional array of BO_6

TABLE I. Powder x-ray diffraction pattern for $Ba_2YCu_3O_{6.9}$. Orthorhombic unit cell, $a = 3.8218(7)$ Å, $b = 3.8913(7)$ Å, $c = 11.677(2)$ Å.

h	k	l	d_{OBS} (Å)	I/I_0 (%)
0	0	2	5.844	2
0	0	3	3.893	11
1	0	0	3.822	3
0	1	2	3.235	3
1	0	2	3.198	5
0	1	3	2.750	60
1	0	3	2.726	100
1	1	0		
1	1	1	2.653	2
1	1	2	2.469	3
0	0	5	2.336	11
1	0	4	2.321	3
1	1	3	2.232	13
0	2	0	1.946	23
0	0	6		
2	0	0	1.911	10
1	1	5	1.775	3
0	1	6	1.741	2
0	2	3		
1	0	6	1.734	2
1	2	0		
2	0	3		
2	1	0	1.716	2
1	2	1		
1	2	2	1.662	1
1	2	3	1.584	24
1	1	6		
2	1	3	1.569	11

octahedra exclusively sharing corners. In most compounds of this type, oxygen deficiency is not tolerated in significant amounts without the creation of crystallographic shear. However, in Cu perovskites[8,9] considerable oxygen vacancies are tolerated because of the stability of square-planar and square-pyramidal Cu coordination. The crystallographic unit-cell parameters of $Ba_2YCu_3O_{9-\delta}$ suggest that the atomic arrangement is of a simple perovskite type. We suggest that the structure consists of alternating CuO_2-(Ba,Y)O planes perpendicular to c. The CuO_2 planes would contain copper in square-planar coordination (Cu-O distances near 1.9 Å), corner shared as in $La_{2-x}M_xCuO_4$. The YO, BaO planes would be of the 100 rocksalt type, again as in $La_{2-x}M_xCuO_4$. Oxygen deficiency, up to $\delta = 3$ in $Ba_2YCu_3O_{9-\delta}$, could easily occur in the YO,BaO planes without resulting in an unfavorable coordination for any of the cations. For an oxygen stoichiometry corresponding to $\delta = 2.1$ the formal copper valence is $+2.27$, which is higher than that for the K_2NiF_4-type superconducting compounds (2.15).

Some parameters for this superconductor can be estimated from measurements of the resistivity, the susceptibility, and the lower and upper critical fields. The temperature dependence of the resistivity of a sintered pellet is shown in Fig. 1. At room temperature ρ is 600–700 $\mu\Omega$ cm and decreases to 200–250 $\mu\Omega$ cm at 100 K. Particularly interesting is the approximate linearity in $\rho(T)$ ($d\rho/dT = 1.7$–2.5 $\mu\Omega$ cm/K), which is also characteristic[3,10] for $(La,Sr)_2CuO_4$ and $Ba(Pb,Bi)O_3$. Seebeck measurements at room temperature indicate that the samples are p type. A lower limit for the inverse of the Hall coefficient is 1.1×10^{23} cm^{-3}. The critical current density (j_c) was measured on a sample which was necked down to a cross-sectional area of 2×10^{-3} cm^2. When immersed in liquid nitrogen, at zero field, the sample remained superconducting at current densities at least up to 1100 A/cm^2, limited by the contacting technique. This is substantially higher than the reported[11] j_c
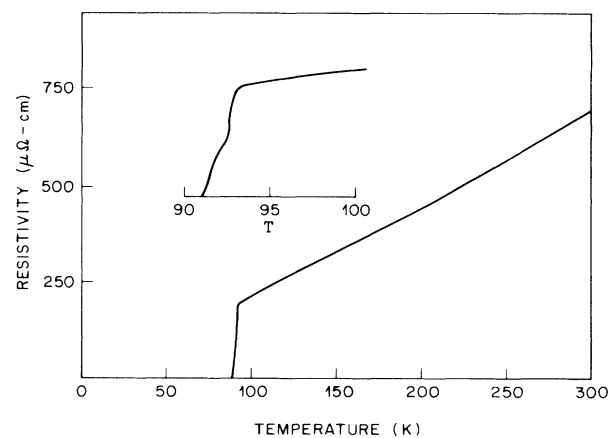

FIG. 1. Temperature dependence of the electrical resistivity.

TABLE II. Material parameters for $Ba_2YCu_3O_{6.9}$. "GL" denotes Ginzburg-Landau.

Measured parameters	
Transition temperature midpoint	$T_c = 92.5$ K
Resistivity in the normal state	$\rho_{300} = 600-700$ $\mu\Omega$ cm
	$\rho_{95} = 200-250$ $\mu\Omega$ cm
Lower critical field slope	$dH_{c1}/dT = -7$ Oe K^{-1}
Upper critical field slope[a]	$dH_{c2}/dT = -13$ kOe K^{-1}
Critical current density (77 K, $H=0$)	$j_c > 1100$ A cm^{-2}
Dominant carrier type (300 K)	p type
Derived parameters	
Sommerfeld parameter	$\gamma = 3-5$ mJ (mole Cu)$^{-1}$ K^{-2}
GL coherence length	$\xi(0) \sim 22$ Å
GL penetration depth	$\lambda(0) \sim 1400$ Å
GL κ	$\kappa \sim 62$
Thermodynamic critical field	$H_c(0) = 10 \pm 2$ kOe

[a]Reference 6.

in $(La,Sr)_2CuO_4$ at comparable T/T_c.

Magnetic measurements, including dc magnetization and Meissner effect, were performed in a SQUID magnetometer (S.H.E. model 905). Magnetization measurements at 20 K and up to 1 kOe yield a value for H_{c1} of 500 ± 50 Oe, and $dH_{c1}/dT = -7$ Oe K^{-1}. For dH_{c2}/dT we use data from Ref. 6. Analyzing these experimental results within the standard framework for type II superconductors, we deduce the various parameters given in Table II. Note that the Sommerfeld parameter γ is evaluated in two different ways (within the weak-coupling limit): either from the Rutgers relationship (dH_c/dT from dH_{c2}/dT and dH_{c1}/dT) or from dH_{c2}/dT and ρ. Both values agree within 5% to give $\gamma \sim 4$ mJ (mole Cu)$^{-1}$ K^{-2}. In Fig. 2 we present the results for the flux-exclusion (Meissner effect) measurement, in which

the sample is stationary in one of the two pickup coils and cooled in a field of 18.5 Oe. The sharp onset is noteworthy. The low-temperature signal is 61% of the value expected for a similarly shaped ideal diamagnet of the same solid volume, or 76% of the diamagnetic susceptibility derived from $M(H)$ measurements used to determine H_{c1} on this sample. Flux trapping makes this a conservative lower limit for the superconducting volume fraction; a Meissner effect of this magnitude is only rarely seen even in good superconducting single crystals. The magnetic susceptibility above T_c, shown in Fig. 3, is well described by a Curie-Weiss law added to a constant background χ_0. After correction for core diamagnetism, χ_0 can be used to estimate γ within the free-electron model to yield $\simeq 3$ mJ (mole Cu)$^{-1}$ K^2, a value in good agreement with our other estimates. The Curie constant corresponds to $p_{\text{eff}} = 0.3\mu_B/Cu$ if the same moment is assigned to every Cu atom, but further studies will have to test this assumption.
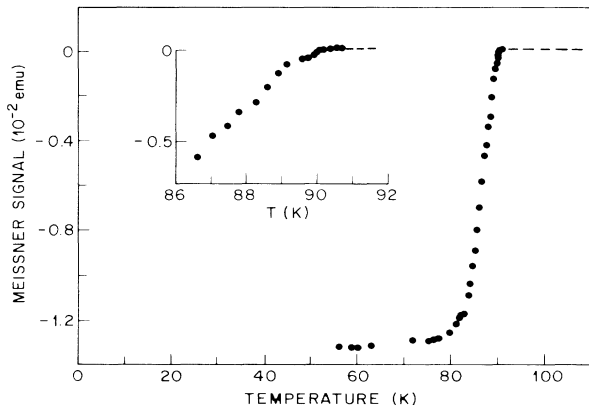

FIG. 2. Flux-expulsion (Meissner effect) measurements in a field of 18.5 Oe. The signal at 60 K corresponds to 76% of the diamagnetic value derived from $M(H)$ data on the same sample, thus giving a conservative lower limit for the superconducting volume fraction.
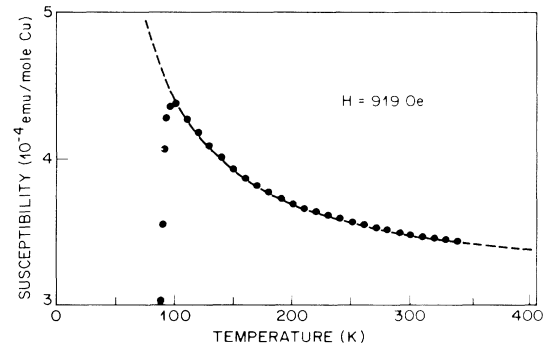

FIG. 3. Temperature dependence of the normal-state susceptibility. The dashed line is a fit to the data of the form $\chi(T) = \chi_0 + c/(T+\Theta)$, with $\chi_0 = 3.07 \times 10^{-4}$ emu (mole Cu)$^{-1}$, $C = 11.84 \times 10^{-3}$ emu K (mole Cu)$^{-1}$, and $\Theta = -11.3$ K.

In summary, we have identified the superconducting compound in the chemical system Y-Ba-Cu-O. Single-phase polycrystalline samples of the new perovskite-type compound $Ba_2YCu_3O_{9-\delta}$ have been prepared and their electronic properties have been characterized. The density of electronic states at E_F is substantially smaller than in $(La,Sr)_2CuO_4$,[12,13] and as T_c is more than twice that in those materials, it remains to be studied in detail if the superconductivity is of the ordinary phonon-mediated type.[14-16]

Note added.—Upon completion of this work, we received a preprint from Tarascon, Green, McKinnon, and Hull,[17] confirming the results of Ref. 6 in a mixture of phases in the Ba-Y-Cu-O system.

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