

Superconductivity in $\text{YBa}_{1.95}\text{Cs}_{0.05}\text{Cu}_3\text{O}_{7-y}$ granular ceramics

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A new compound of the high-temperature ceramic oxide superconductor family has been synthesized and analyzed, i.e., $\text{YBa}_{1.95}\text{Cs}_{0.05}\text{Cu}_3\text{O}_{7-y}$. Its crystallographic structure is given. Two well-defined "critical regimes" are observed at 86 and 90 K, respectively, on electrical resistivity measurements. Magnetoresistivity measurements are also reported for small magnetic field. No anomalous hysteresis is found. Features in these transport properties are interpreted in terms of phase mixtures. The interest of such data is emphasized.

I. INTRODUCTION

Since the discovery of high onset superconductivity temperatures, as well as related high critical and percolative temperature in ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (called "classical" 1:2:3 compound hereby), much work has been devoted to understanding the basic properties of such systems.¹⁻⁶ It has been shown that rare-earth element substitution for Y does not drastically modify the characteristic physical parameters of the compound, like the critical temperature,⁶ defined as the temperature T at which the temperature derivative of the resistivity R , dR/dT , has a maximum. In many cases, the critical temperature of the substituted compounds is lowered below the 90.5-K value of the pure 1:2:3 ceramic oxide. Moreover, under element substitution, a marked tail very often appears masking the "critical transition temperature" at which macroscopic coherence of the order parameter diverges.⁷⁻¹¹

We have attempted to substitute monovalent ions at Ba sites.¹² This has allowed us to scan the effect of different ionic masses and ionic radii on the usual superconductivity parameters.¹³ Moreover, substitution of monovalent ions for divalent Ba may lead to some relevant modification in the number of available "free" carriers in the Cu-O planes, and hence modification of properties related to the number of carriers at the Fermi level. Finally, from the technical point of view, synthesis of crystals with monovalent ion substitution for divalent cations is expected to occur at lower temperatures.

Two arguments may be given to support the idea of faster reaction in the presence of Cs_2CO_3 . The first one is that Cs_2CO_3 is not very stable and is destroyed at temperatures as low as 600°C, giving a liquid phase which is able to react much more rapidly than a solid (by contrast, BaCO_3 is by itself stable at temperatures as high as 1200°C). Secondly, after the possible disappearance of this liquid phase (by reaction with the other constituents), the process is a solid-state reaction, the rate of which is controlled by the mobility of the ions. It is evident that,

because of its lower charge, the mobility of the Cs^+ cation is *much* greater than that of Ba^{2+} . (This is clearly illustrated by the behavior of *superionic* conductors, where the conductivity is determined by the mobility of some cations: The conductivity of a Na^+ superionic conductor is reduced by 3 or 4 orders of magnitude if Na^+ is replaced by Ca^{2+} .) From a purely experimental point of view, we have noticed that, after one day at 800°C, a classical 1:2:3 mixture still contains significant amounts of uncombined BaCO_3 , whereas this amount is *considerably* reduced in the Cs-containing systems.

We have synthesized a batch of $\text{Y}(\text{Ba}_{1-x}\text{Cs}_x)_2\text{Cu}_3\text{O}_{7-y}$. We describe its preparation in Sec. II and report crystallographic data analysis. In Sec. III, we report precise measurements of the electrical resistivity and of the (weak field) magnetoresistance with the same precision as that done in our investigations of the different conductivity regimes across and near the critical temperature.^{5,14,15}

We observe a "minor phase" superconductivity fluctuations at 90.5 K. It is followed at about 4 K below by a drastic drop in resistivity which we attribute to coherent macroscopic fluctuations of the superconductivity order parameter of the major (substitution) phase. Data for the weak-field magnetoresistivity are also reported and the tail regimes are discussed. In Sec. IV, we conclude on the relevance of our observations for "shell conductivity," "intragrain Josephson," and "multiphase composition" effects and point out the interest of fine electrical resistivity measurements from which dR/dT can be extracted to obtain information on multiphase compounds.

II. CHEMICAL SYNTHESIS AND SAMPLE CRYSTALLOGRAPHIC ANALYSIS

$\text{YBa}_{2-x}\text{Cs}_x\text{Cu}_3\text{O}_{7-y}$ samples have been synthesized from stoichiometric quantities of BaCO_3 , Y_2O_3 , $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, and Cs_2CO_3 with $x=5\%$. After well

grinding and mixing these compounds under petroleum ether, the mixture has been progressively heated up to 800 °C and kept at this temperature during one day. The resulting mixture is removed from the oven to room temperature, ground again, and pressed into a pellet which is wrapped in a platinum sheet. The resulting mixture is heated up to 800 °C again in an O₂ atmosphere during one day. The temperature of the furnace is then lowered to 750 °C and the system maintained at such a temperature overnight. The furnace is turned off and the pellet withdrawn when the temperature reaches 200 °C.

The sample appears black and rather porous (estimated porosity 35%). An ir spectrum taken down to 30 cm⁻¹ indicates a wide-band spectrum as expected for free-electron systems. However, some very weak structure seems to exist in the spectrum: It indicates that the starting materials have not wholly reacted, or that another phase is present. Under microscopic examination a few blue widely dispersed microcrystals have been seen. From the density of such blue spots we can estimate that 95% of the sample is homogeneous, but contains a "dense impurity phase." The x-ray powder diagram does not show any sharp line characterizing the *starting* materials. As hinted in the Introduction, the reaction has been markedly optimized by the use of Cs₂CO₃. Furthermore, the powder diagram shows that the total amount of Cs⁺ has likely reacted, but we have no appropriate equipment (such as an electronic microprobe) to make an accurate determination of the amount nor of local variations.

The main phase is certainly characterized by an orthorhombic unit cell with $a=3.827(2)$ Å, $b=3.876(2)$ Å, $c=11.632(8)$ Å. The unit-cell volume $V=172.55(17)$ Å³ is *smaller* than that of the classical ($x=0$) ceramic oxide for which $V=173.66$ Å³. Let us recall here the $x=0$ parameters from, e.g., Beyers,¹⁶ $a=3.820$, $b=3.893$, $c=11.688$. Notice that the b/a ratio is *smaller* in the substituted compound. In Table I, we recall the ionic radius of Cs under a different coordination number, and compare it to that for Y and Ba,¹⁷ for a similar number of neighbors;¹⁸ in $x=0$ samples, made along the same technique, statistics of pore measurements have been made from nitrogen adsorption isotherms following the Brunauer-Emmett-Teller method.⁵ The pore size distribution is peaked around 35 ± 5 Å, but linear size pores larger than 600 Å cannot be seen by this method. *These* large pores induce a 35% porosity value from macroscopic (density and microphotography analysis) measurements.

The sample is a $7.0 \times 1.91 \times 1.41$ -mm bar. The cryostat and experimental setup have been described elsewhere.¹⁵

TABLE I. Ionic radius (Å) as a function of coordination number q for atomic element Z of interest (from Shannon, Ref. 17).

Z	q	8	9	10
Cs		1.74	1.78	1.81
Y		1.019		
Ba				1.52

The method for investigation is identical to that reported in Ref. 5. The electrical current intensity used was 3.2 mA.

III. EXPERIMENTAL RESULTS

The resistivity versus temperature data are reported in Fig. 1 for the case of 72, 620, and 4150 G, as well as in absence of external field, (i.e., the so-called "0-G" curve corresponds to the earth magnetic field).

In absence of field, a slow decrease from room temperature [$R(300) = 70 \times 10^{-3}$ Ω, $dR/dT \approx 0.25 \times 10^{-3}$ Ω/K] is followed by a break in slope at 90.5 K. A sigmoid curve follows, and the resistivity smoothly decreases to reach a value below 10^{-6} Ω at 78.0 K. The "large" resistance value is not relevant here for discussing the "critical region." This value reflects the "large" porosity and bad intergrain contacts.

The resistivity behavior differs from that found in classical ($x=0$) "1:2:3" granular ceramic oxide: The intermediary sigmoid curve starts at 90.5 K, i.e., *before* the sharp drop usually characterizing the critical region, where the order parameter becomes macroscopically coherent. Therefore, the "high-temperature" part of the sigmoid can be thought of resulting from the superposition of a smooth behavior "background" and a critical fluctuation regime. The background likely results from nonsuperconducting grains and intergrain contacts as usual. The critical behavior at 90.5 K observed by a peak in dR/dT (Fig. 2) indicates that (very) few grains are pure YBa₂Cu₃O_{7- δ} , i.e., are Cs free. It can be understood that superconductivity in such a system arises from the coherence of an order parameter in grain layers.¹⁹ The findings

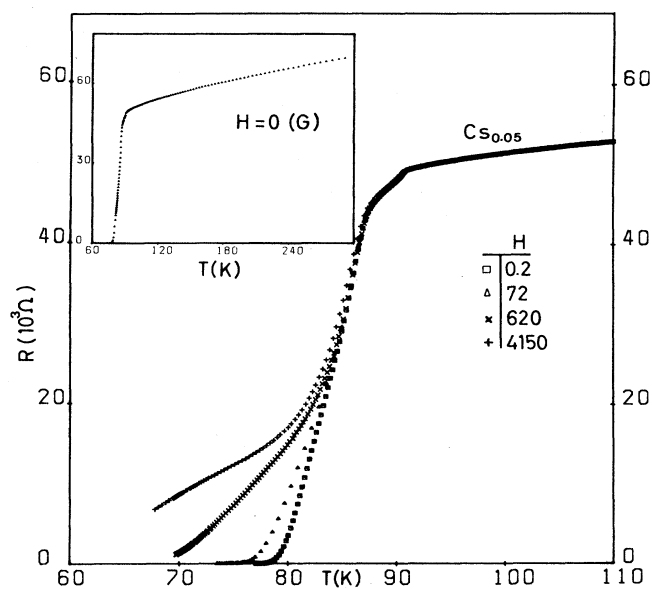


FIG. 1. Electrical resistivity R vs temperature T for YBa_{1.95}Cs_{0.05}Cu₃O_{7- δ} granular ceramics sample in the vicinity of the superconductive percolation transition with and without magnetic field H given in gauss, as indicated in inserted table. The $H=0$ case is shown in the inset for T up to 300 K.

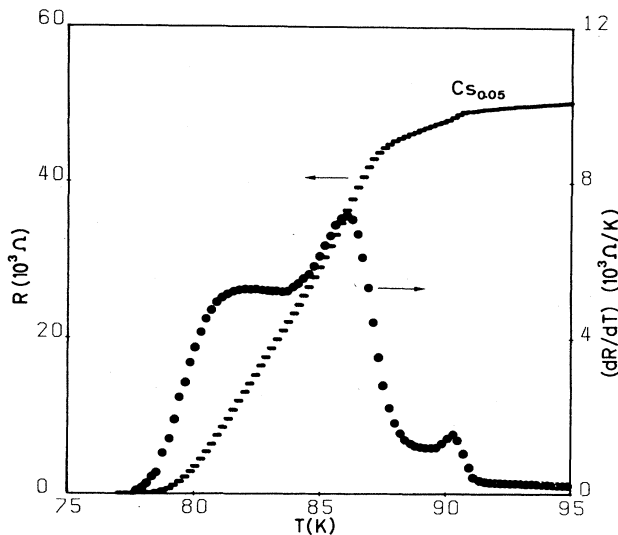


FIG. 2. Electrical resistivity R and its temperature derivative dR/dT for $\text{YBa}_{2-x}\text{Cs}_x\text{Cu}_3\text{O}_{7-y}$ granular ceramics ($x=0.05$) in the vicinity of the superconducting critical transition of the $x=0$ compound.

seem to indicate a Cs-independent surface which blocks otherwise superconducting channels.

In the lower-temperature region, the plot of dR/dT indicates that a second characteristic temperature exists, i.e., a much higher peak appears in dR/dT (i.e., $d^2R/dT^2=0$) at $T_{c,2}=85.5$ K (Fig. 2). This peak is much steeper than that corresponding to the "critical temperature" of the $x=0$ phase, and obviously characterizes another superconductivity phase. Our interpretation is that Cs has been substituted in most of the grains, giving a new stable phase.

It seems unlikely that the sample would contain just two conducting phases with very different oxygen content but with the same Cs concentration. (We recall the apparent homogeneity of the sample, disregarding the rare nonconducting phase.)

Notice also a plateau in dR/dT below $T_{c,2}$ very similar to that found at magnetic transitions below a critical temperature.²⁰⁻²² In the latter case, the plateau is interpreted as resulting from (anisotropic) phonon-spin and conduction electron-spin coupling terms renormalizing the electron-phonon interaction strength below T_c .^{21,22} It is thus interesting to use the universal (anisotropic) "order-parameter" concept to infer the importance of phonon-mediated superconducting fluctuations near the transition in such ceramics superconductors.¹² However, in view of intense controversy²³ on the role of phonons in such superconductors it may be of interest to consider an alternative interpretation of the plateau below $T_{c,2}$ in dR/dT .

Such a shoulder may be the remnant signature of weak links between grains.²⁴ In fact, the pronounced foot observed in R vs T curves in the presence of an external field (even, e.g., for "pure" Y-Ba-Cu-O) has been attributed to such links.⁵ If rather weak links exist, a small step in the resistivity curve might be observed in fields as low as the earth's field (as here). This argument is even more ap-

pealing in a two-phase material when a (e.g., lower- T_c) material separates the grains. The plateau would then measure the number of nonsuperconducting paths.

On the other hand, the plateau in dR/dT cannot be ascribed to a distribution of critical temperatures. If this is so, the "lambda peak" at the critical temperature would be rather broad. Here, the peaks are well separated. A definite conclusion on the plateau origin will be better attained when comparing materials for which microstructure is well known, for which synthesis is surely complete, and when the intergrain junction contribution to the resistivity is well monitored.

In the presence of a small (72 G) magnetic field, we observe a slight shift of the lower critical temperature $T_{c,2}$ down to 84 K. However, above 86 K the resistivity data are undistinguishable from the zero-field case. The percolation transition where $R=0$ occurs at 75.5 K in this case and is also reached through a smooth exponential.⁵

At higher field (620 and 4150 G) the $R(T)$ curve much departs from the 0-G and 72-G data in the critical region corresponding to the so-called "substituted phase." Except for the shift in "critical temperature," $R(T,H)$ has a pattern similar to that observed in the Cs-free case.⁵ The critical drop ends at a knee temperature $T_K \approx 81.8$ K. Except for a smoothly interpolating regime, below T_K the behavior of $R(T)$ is quasilinear, down to a temperature depending on the applied field and at which an exponential regime starts leading to the percolation transition.

For the range of field and electrical current which we have used we have not found any "anomalous hysteresis" as for the ($x=0$) classical (1:2:3) compound prepared in the same way^{5,25,26} as this Cs compound.

IV. CONCLUSIONS

Conclusions similar to those in Ref. 5 can be drawn. From low to high temperature a one-dimensional conductivity path is followed by a three-dimensional resistivity regime. Complications arise from the presence of two critical transitions. In the vicinity of $T_{c,2}$, the normal resistivity of the minority (1:2:3) compound competes with a (two-dimensional)¹⁴ set of short circuits in the majority compound. Above the critical temperature of the former, Cs ions act as mere normal-state impurities for the "classical" compound.

We consider that Cs ions have not been homogeneously distributed during the synthesis process. The high-conductivity, low-resistivity regimes have the same behavior as in an unsubstituted system. However, the break in $R(T)$ and small peak in dR/dT at 90.5 K indicates that a non-negligible amount of grains do not contain Cs ions. Either, we have not used enough reacting material Cs_2CO_3 , or Cs is unable to enter particular grains. In the latter case Cs ions might be unevenly distributed and create normal resistivity paths.

Notice that the ionic radius of Cs ions is rather large, and of course depends on the coordination number.¹⁷ It is clear from Table I that Cs will be more easily substituted at Ba sites than at Y ones but there is, nevertheless, an ionic size mismatch. We had indeed *a priori* used such a

guess to prepare the starting material mixture relative content. From optical data no double (superconducting) phase can however be inferred.

Finally, we do not observe any (anomalous or not) hysteresis in intermediate fields as in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ system.^{5,25-27} This hysteresis has been explained in terms of flux pinning and geometrical form factors for the supercurrent^{25,26} through grain junctions and from the ratio of the coherence length (in fact, the coherence volume). Such quantities are certainly influenced by the change in the unit-cell parameters following Cs substitution. They render the observation of such hysteresis much less likely.

The current coherent matching is more difficult due to the presence of Cs ions more likely to be found in greater density at grain interfaces than in the interior of the grains if they are unevenly distributed. The lattice distur-

tion due to a large Cs ion is indeed more energetically favorable at the grain surface. Josephson junctions^{13,19,27} would be an unlikely mechanism for current short circuits then.

The lack of reverse hysteresis, the break at 90.6 K, and the sigmoid curve centered on 88.6 K, all seem to logically agree with the interpretation of different grain compositions in the system. Therefore, electrical resistivity measurements in small magnetic fields seem to be a very interesting tool for studying biphasic or multiphase systems. Finally, by introducing a large ion as substitution element in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, we have shown how grain surfaces, hence, how intergrain resistivity, can likely be studied from electrical resistivity in small magnetic fields. We have also indicated a possible change in the electron-phonon coupling across the transition(s).

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