PHYSICAL REVIEW B VOLUME 38, NUMBER 1 1 JULY 1988

Electrical transport and superconductivity in a Au-$YBa_2Cu_3O_7$ percolation system

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(Received 30 March 1988)

Percolation behaviors of normal-state conductivity and superconductivity have been studied in a Au-$YBa_2Cu_3O_7$ granular system. The normal-state conductivity shows a percolation threshold at a Au volume fraction (p_{Au}) of 23%, whereas the superconducting network shows a threshold at $p_{Au} \sim 60\%$. The presence of Au has negligible effect on the superconducting $YBa_2Cu_3O_7$ phase. In the dilute limit, the ratio of the Meissner signal to the diamagnetic-shielding signal approaches unity.

The discovery of the new ceramic high-temperature superconductors (HTS's) is a revolutionary breakthrough in condensed-matter physics. In only a few months, materials in many different forms such as sintered powders, single crystals,[1] and polycrystalline and grain-oriented thin films[2,3] have been successfully fabricated. Intensive research has revealed many unexpected properties in this class of superconductors, for which new superconducting mechanisms have been proposed. However, to date, there has been very little work on small particles of HTS's.[4] The study of superconducting small aggregates, clusters, or particles is very important from both fundamental and technological standpoints. Small particles are excellent media for the studies of percolation and fractal properties, quantum size effects, thermal fluctuations, size effects on superconductivity, etc. These effects are particularly interesting because of the unusually short coherence length[5] and large penetration depth[5,6] in these new HTS's ($\xi \sim 10$ Å and $\lambda \sim 1000$ Å). Granular superconductors may also exhibit different, and in some cases enhanced T_c, as in the case of granular Al solids.[7] Technologically, metal-HTS composites offer the attractive features of a current shunt and improved environmental resistance.

Experimentally, composites of the HTS $YBa_2Cu_3O_7$ (1:2:3 compound) and a second medium, metallic or insulating, have proven to be very difficult to achieve without severely compromising the superconducting properties.[8,9] The 1:2:3 phase requires high-temperature (~950 °C) annealing in an oxygen atmosphere in order to retain its superconducting properties. Under such adverse conditions, most metals and insulators will react with the 1:2:3 compound and degrade the superconductivity.[8,9] Furthermore, the 1:2:3 compound is essentially a line compound in the phase diagram;[10] off-stoichiometric mixtures inevitably lead to multiphase samples with poor superconducting properties or without superconductivity at all.

In this paper, we present the study of electrical transport and superconducting properties in a Au-$YBa_2Cu_3O_7$ percolation system. We have investigated effects of numerous materials on the HTS's, including all the 3*d* transition metal oxides,[8] noble metals, and other oxides such as $LiNbO_3$, Al_2O_3, SiO_2, etc. This is the first realized system in which particles of the 1:2:3 compound and a metallic material could coexist with well-defined separated phases left intact by the stringent annealing conditions. Percolation behaviors in both the normal state and the superconducting state have been observed. Superconducting properties such as transition temperature (T_c) and Meissner effect remain unaffected in this metal-HTS composite system. The success of the Au-$YBa_2Cu_3O_7$ composite opens the door for many other important studies. We shall discuss some of the implications and consequences.

We have fabricated Au-$YBa_2Cu_3O_7$ granular solids with the Au volume fraction (p_{Au}) ranging from 0 to 100%. Fine powders of 1:2:3 compound were obtained by grinding presintered 1:2:3 bulk materials.[8] The 1:2:3 powders were then thoroughly mixed with Au powders (99.95% pure, 325 mesh) of appropriate proportions (using densities of 19.3 g/cm^3 and 6.4 g/cm^3 for Au and 1:2:3, respectively). Scanning electron microscope measurements have revealed that the size of the 1:2:3 particles is in the range 1–3 μm. The samples were cold pressed into thin disks, and annealed in flowing oxygen at a temperature of 950 °C for 15 h. The cooling rate was 2 °C/min to assure proper oxygen content. The samples were dry cut into well-defined geometrical shapes, for example, a strip of $7 \times 1.8 \times 0.17$ mm^3 for resistivity measurements, and a rectangular sheet of $4 \times 3 \times 0.17$ mm^3 for magnetization measurements. The structure of the granular solids was studied by x-ray diffraction. A typical example ($p_{Au} = 39.2\%$) of the θ-2θ diffraction patterns is shown in Fig. 1. There are two sets of peaks, corresponding to the 1:2:3 phase and Au.

The resistivity of the samples was determined by using a standard four-wire probe with a computer-controlled data acquisition system. In Fig. 2, the temperature dependence of the normalized resistivity for samples with various p_{Au} is displayed. We first discuss the electrical transport in the normal state. The resistivity (ρ) and the temperature coefficient of resistivity [$\alpha = (1/\rho)d\rho/dT$] at $T = 297$ K are shown in Fig. 3(a) as a function of p_{Au}. In its normal state the 1:2:3 compound is a rather poor metallic solid ($\rho \sim 1$ mΩ cm, nearly three orders of magnitude higher than that of Au). The normal-state resistivity of the Au-1:2:3 samples is dominated by Au, with a significant drop of ρ occurring near $p_{Au} \sim 20\%$. The behavior of ρ correlates with that of α, which increases sharply towards that of Au starting from $p_{Au} \sim 20\%$.

The conductivity of a binary random mixture can be de-

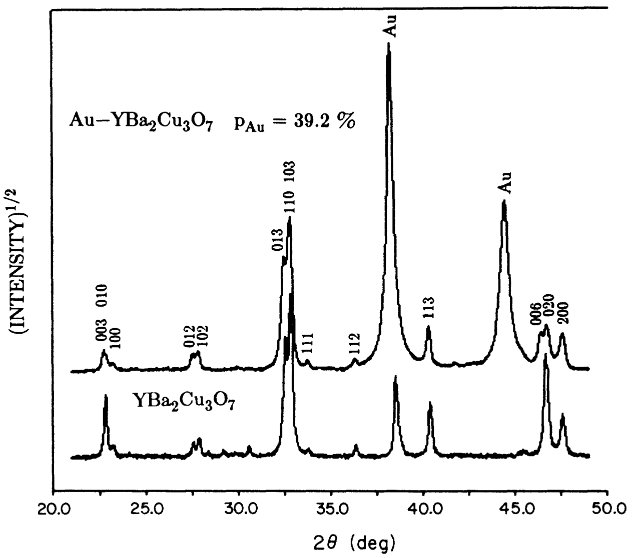

FIG. 1. θ-2θ x-ray diffraction patterns of a Au-YBa$_2$Cu$_3$O$_7$ (p_{Au}=39.2%) sample and a pure YBa$_2$Cu$_3$O$_7$ compound. Note that there are two sets of peaks in the composite samples, corresponding to the YBa$_2$Cu$_3$O$_7$ phase and Au.

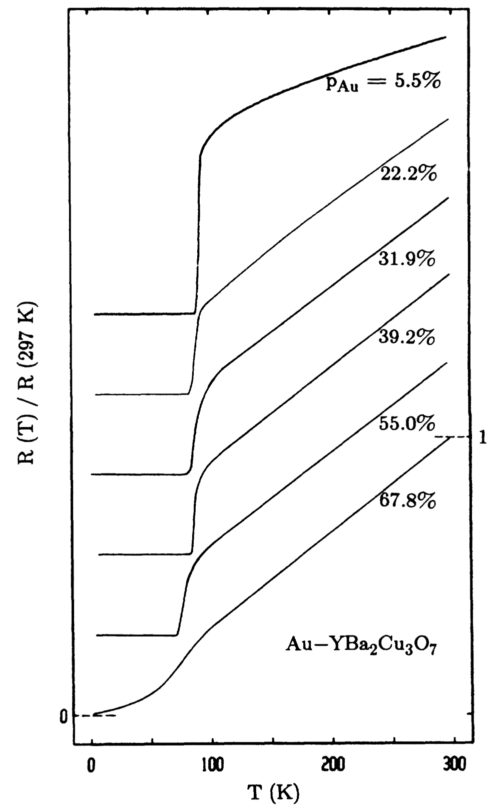

FIG. 2. Temperature dependence of the normalized resistivity of Au-YBa$_2$Cu$_3$O$_7$ samples with various p_{Au}. Note that at p_{Au}=67.8%, the zero-resistance state of the bulk sample is no longer achieved, due to the loss of the superconducting path.

scribed using a percolation model.[11,12] There are two scales of conduction pertinent to the model, ρ_0 and ρ_0', which along with the percolation threshold, p_c, determine the conduction. Percolation theory predicts that the conduction will vary as

$$\rho=\begin{cases}\rho_0(p_{\mathrm{Au}}-p_c)^{-t}, & p_{\mathrm{Au}}>p_c,\\ \rho_0'(p_c-p_{\mathrm{Au}})^{u}, & p_{\mathrm{Au}}<p_c,\end{cases} \qquad (1)$$

where $t\sim1.7$, $u\sim0.7$ in three dimensions.

p_c was chosen such that a log-log plot of ρ vs $p_{\mathrm{Au}}-p_c$ yielded a straight line. A least-squares fit was performed to determine the slope, which will be the exponent t or u mentioned above. Figure 3(b) shows the plots, with p_c=0.23, t=0.73, and u=0.71. For low volume fraction, the system is seen to behave as predicted, while for $p_{\mathrm{Au}}>p_c$ the value of t obtained is smaller than typically observed. The system is not, however, a "perfect" percolation system, with ideal conductors and insulators. The ratio of ρ_{Au} to $\rho_{1:2:3}$ is not as large as one sees in, for example, a granular metal-insulator system. The resistivity thus increases much less rapidly, as observed. Another possible explanation involves the morphology of the sample. As p_{Au} approaches 1.0, we see that the sample resistivity approaches a value higher than that of pure Au,

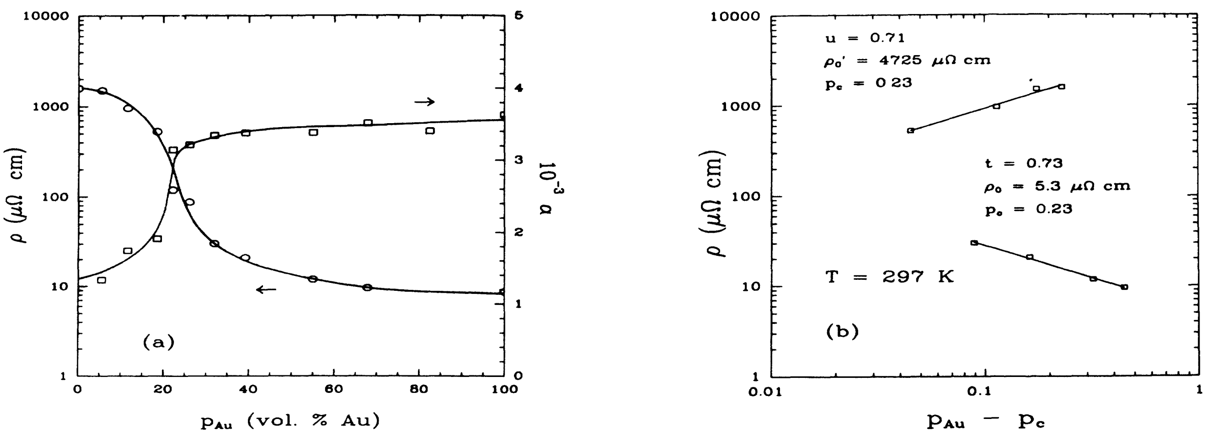

FIG. 3. (a) The variation of resistivity ρ and temperature coefficient of resistivity α with Au volume fraction. (b) Log-log plot of the resistivity against $p_{\mathrm{Au}}-p_c$. The straight lines are the best fits to relations (1).

since the sample has many defects and voids. This will have more of an effect on the exponent t than u, since for $p_{\mathrm{Au}} < p_c$, the conduction is dominated by the 1:2:3 matrix.

In addition to the percolation threshold p_c observed for Au, there exists a *different* threshold p_c' for the superconducting matrix. As shown in Fig. 2, the superconducting transition in the Au-1:2:3 system is essentially undisturbed by the addition of Au, as long as the volume fraction of the 1:2:3 phase is larger than $p_{1:2:3} = 1 - p_{\mathrm{Au}} = 45\%$. Below $p_{1:2:3} = 32.2\%$, a resistivity drop (starting at $T \sim 90$ K) is observed, but the $\rho = 0$ state can no longer be achieved in the bulk samples, indicating the loss of a superconducting path. Therefore, the superconducting percolation threshold p_c' lies between $p_{1:2:3} = 32.2$ to 45%. For a random continuous two-component medium with black and white symmetry, the percolation threshold for both components should be around 17%. In the current system, the fact that the percolation thresholds differ is indicative of a loss of black-white symmetry (i.e., the Au and 1:2:3 particles have different morphologies). The abundance of weak links at the high-p_{Au} side is also an important factor, which effectively reduces the number of superconducting paths. This would result in a higher percolation threshold.

For granular superconductors, a magnetization measurement is an effective tool in characterizing the superconducting properties because it can directly probe individual superconducting grains. We have measured the low-field magnetization of the Au-1:2:3 system with a superconducting quantum interference device (SQUID) magnetometer. Samples with their planes parallel to the external magnetic field were measured in both the zero-field-cooled (diamagnetic shielding effect) and field-cooled (Meissner effect) modes under a field of 50 Oe. Magnetizations normalized by the volume fraction of the 1:2:3 particles are shown in Fig. 4(a). In every case, including the samples below the superconducting percolation threshold p_c', there is a sharp superconducting transition at $T \sim 92$ K, corresponding to the T_c of the bulk 1:2:3 sample. The ratio (M_m/M_s) of the Meissner signal to the diamagnetic shielding signal of $T = 5$ K bears an interesting relation with p_{Au} as shown in Fig. 4(b). In sintered ceramic superconductors, the porous nature of the sample causes flux-trapping in field-cooled mode (Meissner effect). As a result, M_m/M_s is rather small for the pure 1:2:3 sample (~ 0.36). However, in the Au-1:2:3 percolation system, the 1:2:3 particles become more and more dispersed as p_{Au} is increased. At the high p_{Au} side, the measured magnetizations are effectively those from individual grains, which are expected to be dense and uniform. Indeed, as seen in Fig. 4(b), M_m/M_s gradually approaches *unity* with increasing p_{Au}. The result clearly shows that the porosity in most bulk samples is the main reason for the reduced Meissner signal in comparison with the diamagnetic signal.

The absolute Meissner values, which provide information about the penetration depth, are about 18–28% of the theoretically possible value at $T = 5$ K. Various measurements[5,6] have indicated that λ in the 1:2:3 compound at low temperatures is about 1000–1500 Å. Therefore, for particles 1–3 μm, the effective superconducting volume can be reduced by as much as 40% due to field penetration. Interface diffusion at the Au-1:2:3 boundaries may further increase the penetration depth and reduce the

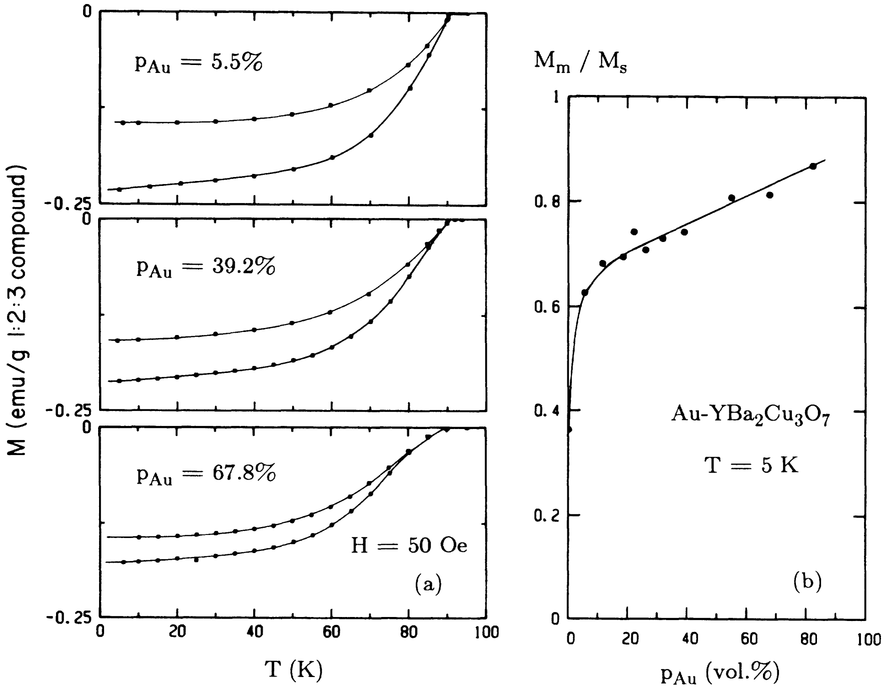

FIG. 4. (a) Magnetization of $YBa_2Cu_3O_7$ particles under a field of 50 Oe from diamagnetic shielding and a Meissner effect as a function of temperature for samples with various p_{Au}. (b) The variation of M_m/M_s (ratio of Meissner signal to diamagnetic-shielding signal) with Au volume fraction at $T = 5$ K.

Meissner signal. At temperatures close to T_c, we expect a larger decrease in the Meissner effect due to divergence of λ at T_c. This is indeed the case. As shown in Fig. 4(b), progressively less sharp transitions in the magnetizations of the Au-1:2:3 samples at the high p_{Au} side were observed.

Under the annealing conditions required for the fabrication of the 1:2:3 superconductor, almost all materials will react detrimentally with the 1:2:3 compound. After an exhaustive search, Au and 1:2:3 are found to maintain separated phases with their own characteristics. Au not only remains metallic under the severe annealing conditions, but also has negligible effects on the intrinsic superconducting properties of the 1:2:3 phase. This paves the way to make granular Au-1:2:3 solids with ultrafine 1:2:3 particles (20–1000 Å) using thin-film deposition techniques (research is currently underway). These ultrafine particles would be very useful for various fundamental studies, particularly the size effect and thermal fluctuations. Au-1:2:3 superlattice structures are another interesting possibility. Such structures are advantageous for the study of proximity effects in this new class of HTS's. Technologically, Au-1:2:3 superlattices and Au buffer layers for HTS thin films provide the benefits of a markedly reduced normal state resistivity, current shunts, and environmental resistance.

This work was supported by National Science Foundation Grant No. MEM-87-18496.

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