Percolation Analyses on Transport Properties of YBa$_2$Cu$_3$O$_{7.5}$-Ag System

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The transport properties of YBa$_2$Cu$_3$O$_{7.5}$-Ag composite ceramic system have been studied from the viewpoint of the percolation theory. The percolation threshold volume fraction $f_c$ of Ag determined from the electrical resistivity and from the thermal conductivity is $f_c=0.125\pm0.005$. This markedly smaller value than the theoretical value ($f_c=0.16$) suggests the segregative distribution of Ag. The critical exponent $\ell$ depends on the component conductivity ratio $h=\sigma_{\text{YBCO}}/\sigma_{\text{Ag}}$, which can be explained on the basis of the scaling hypothesis.

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1. INTRODUCTION

One main hurdle against the application of high $T_c$ oxide superconductors in ceramic forms is the occurrence of the weak-links at the border of grains, which practically limit the effective transport critical current $I_{c\text{eff}}$ of bulk cuprate superconductors. The addition of Ag metal to cuprates is often effectual to make up for the weak-links. It is physically interesting and also useful for an applicational purpose to investigate the behavior of Ag clusters on the basis of the percolation theory. The accumulated data and analyses from the viewpoint of the percolation theory, however, are somewhat scattered and sometimes inconsistent with each other.

In this study, we try to develop synthetic analyses about the percolative behavior of Ag clusters in YBa$_2$Cu$_3$O$_{6.5}$ (YBCO) by measuring the electrical resistivity and the thermal conductivity. The conductivity ratio of Ag metal to the cuprate is widely changed by varying the amount of oxygen deficiency $\delta$ of YBCO. The experimental results are analyzed on the basis of the scaling theory for the percolation of Ag clusters.
2. OUTLINE OF THE SCALING LAW

In a two component random composite of $M$ and $I$, clusters of $M$ with an infinite scale are formed when the volume fraction $f_M$ of $M$ exceeds a certain threshold value $f_c$. Assuming $M$ to be a metal and $I$ to be an insulator, a power law holds for the bulk effective conductivity $\sigma_b$ of the composite in the critical region;

$$\sigma_b = A\sigma_M f_M^{t} f_c^s$$

for $0 < f_M f_c < 1$.  

The values of $t=1.9\pm0.1$ and $f_c=0.16$ were predicted for three-dimensional continuum media. If $I$ component is also somewhat conductive and the conductivity ratio $h=\sigma_I/\sigma_M$ is not strictly zero, the power law of eq. (1) breaks down as $\Delta f = f_M - f_c$ tends to zero. In this case, $\sigma_b$ is expected to follow the scaling hypothesis, where $z=h/\Delta f^{t+s}, s(=0.73)$ is the critical exponent governing the divergence of the conductivity in a superconductor-metal composite for $0 < f_c < f_M < 1$. The universal scaling function $\phi(z)$ can be expanded in the power series of $z$:

$$\phi(z) = A' + B'z + C'z^2 + \cdots$$

for $f_M f_c > 0$ and $z < 1$.  

The values of $h$ depend on the $t$ exponent is mainly discussed.4,7

3. EXPERIMENTAL

YBCO powder and $\mathrm{Ag}_2\mathrm{O}$ powder (Dowa Mining Co. Ltd.) were mixed with an appropriate weight ratio and pressed into pellets. The pellets were pre-sintered at 935°C for 15h in air and furnace cooled. The pre-sintered pellets were crushed, mixed and again pressed into pellets. They were sintered at 930°C for 30h in air and then furnace cooled in 15h. After the obtained pellets were cut into square pillars (~3x3x15mm$^3$), they were heated again and quenched into liquid $\mathrm{N}_2$ from various temperatures to prepare 'quenched samples'.

The density of the samples was determined by measuring the size and the mass. Figure 1 shows the filling factor of the samples, which increases with increasing nominal Ag volume fraction $f_{Ag}^N$. In this paper, the Ag volume fraction is corrected using the least square fitting curve in Fig. 1. The electrical resistivity and the thermal conductivity were automatically measured between 10K and 260K in a Gifford-McMahon refrigerator.8
4. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the electrical resistivity $\rho(T)$ of YBCO non-quenched, and quenched from 700°C, 800°C and 900°C. $\rho(T)$ of YBCO rapidly increases with increasing quenching temperature $T_q$. In the figure, $\rho(T)$ of Ag+0.22at.%Au alloy whose residual resistivity ratio (RRR) is nearly equal to the estimated RRR of Ag clusters in YBCO is also shown.

Figures 3(a)-3(c) show typical plots of $\log \sigma_b$ vs $\log (f_{Ag} f_e)$ to determine the experimental values of critical exponent $t_{ex}$ and the percolation threshold $f_e$. The conductivity values at 150K were used because RRR of Ag cluster is verified to depend on $f_{Ag}$ to some extent and the $\sigma_{YBCO} / \sigma_{Ag}$ values become dependent on RRR of Ag cluster at low temperatures. The most suitable value of $f_{ex}$ was determined to be 0.125 for the present Ag+YBCO ceramics system. This $f_e$ value is remarkably smaller than the generally accepted value of $f_e=0.16$ for 3D continuum media. The smaller value of observed $f_e$ should reflect selective distribution of Ag clusters into voids at grain boundaries of YBCO; the filling factor in Fig. 1 rapidly increases with increasing Ag composition, which also suggests that Ag metals fill up the voids of ceramic YBCO preferentially.

In order to determine $t_{ex}$, the region of $\Delta f = (f_{Ag} - f_e)$ must be carefully set up. Eqs.(2) and (3) are valid for $\Delta f > (\sigma_{YBCO} / \sigma_{Ag})^{1/16}$, which corresponds to the condition, $z<1$. On the other hand, if we go too far from $f_e$, we pass through the critical region and enter into the region where the effective medium approximation (EMA) becomes valid. In this work, we set the region to determine $t_{ex}$ as $(\sigma_{YBCO} / \sigma_{Ag})^{1/16} \leq \Delta f \leq 0.2$. The determined $t_{ex}$ values depend on the conductivity ratio $\sigma$ and are larger for smaller $\sigma$ as shown in Fig. 4. In the following, we esti-
mate the relation between observed $t_\text{ex}$ value and $h$ on the basis of the scaling law given by eqs. (2) and (3).

To calculate $\alpha_0$ based on eq. (2), the scaling function $\Phi$, of eq. (3) must be known. As a trial function, we set $\Phi(z)=A'(1+z)$ and calculated $\alpha_0$ in the range, $0.2 < \Delta f < 0.2$. Then average slope between $\Delta f = (\sigma_{YBCO}/\sigma_{Ag})^{1+z}$ and $\Delta f = 0.2$ was defined as $t^*$ and obtained $t^*$ is given by the dotted line in Fig. 4. In the present calculation, the $t$ value of 1.8 and $s$ value of 0.73 were used. The $t^*$ values

![Graph](image)

Fig. 3. The typical plots of log $\alpha_0$ vs log $(f_\text{Ag}-f_\text{c})$ to determine experimental values of critical exponent $t_\text{ex}$ and the percolation threshold $f_\text{c}$ for (a) $T_\text{q}=900^\circ\text{C}$, (b) non-quenched and (c) $T_\text{q}=800^\circ\text{C}$, respectively. Note that (c) is for the thermal conductivity. The vertical dashed line represents $\Delta f$ value for respective samples which corresponds to $z=1$.

![Graph](image)

Fig. 4. The experimentally determined $t_\text{ex}$ values and calculated $t^*$ values as a function of conductivity ratio $h=\sigma(\text{YBCO})/\sigma(\text{Ag})$ (see text).
Percolation Analyses of YBa$_2$Cu$_3$O$_7$-Ag System

Table I. The parameter values used for the calculation of $t^*$ and experimental $t_{\text{ex}}$ values. For the $\rho(T)$ analyses, $\sigma_{\text{Ag}}=1621\,\text{m}\Omega^{-1}\text{cm}^{-1}$ was used from Fig. 2.

<table>
<thead>
<tr>
<th>measurement</th>
<th>$T_q$</th>
<th>conductivity at 150K</th>
<th>$h(=\sigma_{\text{YBCO}}/\sigma_{\text{Ag}})$</th>
<th>$t_{\text{ex}}$</th>
<th>$t^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa$</td>
<td>800°C</td>
<td>$\kappa_{\text{Ag}}=4300\text{mW/cmK}$  $\kappa_{\text{YBCO}}=31.3\text{mW/cmK}$</td>
<td>$7.3\times10^{-3}$</td>
<td>0.86</td>
<td>0.78</td>
</tr>
<tr>
<td>$\rho$</td>
<td>non-Q</td>
<td>$\sigma_{\text{YBCO}}=1.36,\text{m}\Omega^{-1}\text{cm}^{-1}$</td>
<td>$8.4\times10^{-4}$</td>
<td>1.20</td>
<td>1.27</td>
</tr>
<tr>
<td>$\rho$</td>
<td>700°C</td>
<td>$\sigma_{\text{YBCO}}=0.26,\text{m}\Omega^{-1}\text{cm}^{-1}$</td>
<td>$1.6\times10^{-4}$</td>
<td>1.48</td>
<td>1.43</td>
</tr>
<tr>
<td>$\rho$</td>
<td>800°C</td>
<td>$\sigma_{\text{YBCO}}=0.114,\text{m}\Omega^{-1}\text{cm}^{-1}$</td>
<td>$7.0\times10^{-5}$</td>
<td>1.73</td>
<td>1.49</td>
</tr>
<tr>
<td>$\rho$</td>
<td>900°C</td>
<td>$\sigma_{\text{YBCO}}=0.015,\text{m}\Omega^{-1}\text{cm}^{-1}$</td>
<td>$9.3\times10^{-6}$</td>
<td>1.58</td>
<td>1.99</td>
</tr>
</tbody>
</table>

in Fig. 4 agree fairly well with the experimental $t_{\text{ex}}$ values. The parameter values used for the calculation are summarized in Table I.

5. SUMMARY

(1) The electrical resistivity $\rho$ and the thermal conductivity $\kappa$ were measured for Ag+YBa$_2$Cu$_3$O$_7$ composites and the results were analyzed. The percolation threshold volume fraction $f_c$ of Ag is determined to be 0.125, which is remarkably smaller than the generally accepted value of 0.16 for random binary mixing in three-dimensional continuum media. The observed small $f_c$ value supports the segregative distribution of Ag particles in this system.

(2) Observed critical exponent $t_{\text{ex}}$ for $f_{\text{Ag}}>f_c$ is dependent on the conductivity ratio $h=\sigma(\text{YBa}_2\text{Cu}_3\text{O}_7)/\sigma(\text{Ag})$, which was varied in this study by quenching the composites from various temperatures.

(3) On the basis of the scaling law, the trial scaling function, $\phi(z)=A(1+z)$, explains fairly well the $h$ dependence of the observed $t_{\text{ex}}$ values.

REFERENCES