Evidence of classical percolation theory in the transport properties of ceramic $YBa_2Cu_3O_{7-\delta}$

V. F. Gantmakher, A. M. Neminskiĭ, and D. V. Shovkun
Institute of Solid State Physics, Academy of Sciences of the USSR

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Percolation theory is used for a comparative analysis of curves of the superconducting transition in ceramic $YBa_2Cu_3O_{7-\delta}$ in a zero magnetic field found through measurements of the resistance, $R(T)$, and the dynamic susceptibility, $\chi(T)$. When there is an oxygen deficiency ($\delta > 0$), the grains have a wide distribution with respect to the superconducting transition temperature T_c.

Ceramic high-T_c superconductors are usually inhomogeneous at the macroscopic level. The inhomogeneity which is discussed most frequently stems from the presence of Josephson junctions at intergrain boundaries. If the resistance of the Josephson junctions, R_J, is not very high in the normal state, however, the junctions between superconducting grains are also superconducting in a zero magnetic field if the applied electromagnetic field is sufficiently weak (the opposite case of large values of R_J was studied experimentally in Ref. 1). The presence of superconducting junctions makes it possible to study an inhomogeneity of another sort, which stems from differences in the superconducting properties of the grains themselves, e.g., a scatter of their superconducting transition temperatures T_c. Here in turn, two cases are possible.

The grains size d may be shorter than the coherence length ξ. The establishment of a common, phased superconducting state of the entire sample is then described by the Ginzburg–Landau equation, for which the geometric structure of the medium determines the boundary conditions.[2,3] In ceramic $YBa_2Cu_3O_{7-\delta}$ the opposite inequality holds because of the small value of ξ:

$$d \gg \xi. \qquad (1)$$

Under these conditions each individual grain goes superconducting in a manner which does not depend on the states of the surrounding grains. Classical percolation theory can thus be used to describe the state of the sample, and the details of the superconductivity need not be considered.

Our purpose in the present letter is to show that that approach can be taken in a description of the superconducting transition in ceramic $YBa_2Cu_3O_{7-\delta}$ with an oxygen deficiency, i.e., with $\delta > 0$.

Experimental procedure. Two identical ceramic samples $3 \times 3 \times 10$ mm in size were studied. One sample had brazed silver contacts for measurements of the resistance R by the four-terminal method. The density of the ceramic was 5 g/cm^3; the average size of the crystals in the (a,b) plane was about 5 μm. The sample with contacts was used for the measurements of $R(T)$, and the sample without contacts was used for measurements of the dynamic susceptibility $\chi(T)$ at a frequency of 10^5 Hz. After curves of the superconducting transition were measured by these two methods, the samples were placed in a vacuum chamber and annealed at a fixed temperature. The change in resistance, ΔR, served as a measure of the extent of the annealing. After this annealing, the low-temperature measurements were repeated. In each cycle, the $R(T)$ and $\chi(T)$ curves were thus compared for samples with identical values of δ—values which decreased from cycle to cycle. The state of the sample is characterized not by δ, as it usually would be, but by $\kappa = R_{300}/R_{300}^{(0)}$, i.e., the resistance at room temperature divided by the resistance of the sample in its original state.

The annealing procedure and conditions are described in detail in Ref. 4. Measurements of R were carried out by the standard dc method. It is important to note that the mounting of the sample was not disturbed at any point in the entire series of measurements. In the susceptibility measurements the sample was placed within one of two identical pairs of mutual-inductance coils, and the unbalance signal was measured. To keep the background thermal drift at a negligible level, the coils were wound around the outside of a small inverted Dewar. Its temperature was varied by supplying "cold" to it from a helium bath or heat from a heater.

In this letter we will discuss only the real part of the dynamic susceptibility $\chi(T)$. This quantity is proportional to the magnetic flux which is expelled from the volume of the sample, V. In the accompanying figures, a complete exclusion of flux from volume V corresponds to a value of one on the ordinate scale.

Experimental results. Figure 1 shows the evolution of the $R(T)$ and $\chi(T)$ curves in the region of the superconducting transition as the state of the sample is varied by the escape of oxygen. The correspondence among the curves is determined from the value of κ beside the curves. The most important and most interesting feature of this family of curves is the change in slope on the $\chi(T)$ curves at the fixed value $\chi = \chi_k \approx 0.11$. A similar change in slope can be seen on corresponding curves in many published papers (e.g., Ref. 5). The discussion that follows is an effort to explain why the change in slope occurs at a fixed value along the χ scale.

Let us assume that at temperatures $T \leqslant T_{c0}$ there exists a distribution $g(T)$ of transition temperatures of the individual grains. The volume of the superconducting phase, V_s, divided by the total volume of the sample, is

$$v = \frac{V_s}{V} = \int_T^{T_{c0}} g(T)dT. \tag{2}$$

We assume that the grain size d is large enough that the following inequality holds:

$$(\lambda_0/d)^2 \ll \delta T_c/T. \tag{3}$$

This inequality means that the width of the distribution function, δT_c, is much greater than the temperature interval ΔT in which the depth to which the magnetic field penetrates into the given grain, $\lambda_0(1 - T/T_c)^{-1/2}$, is comparable to the typical grain size d. In this case one can ignore both the penetration depth itself and its divergence near T_c, under the assumption that the varying magnetic flux lies entirely outside the

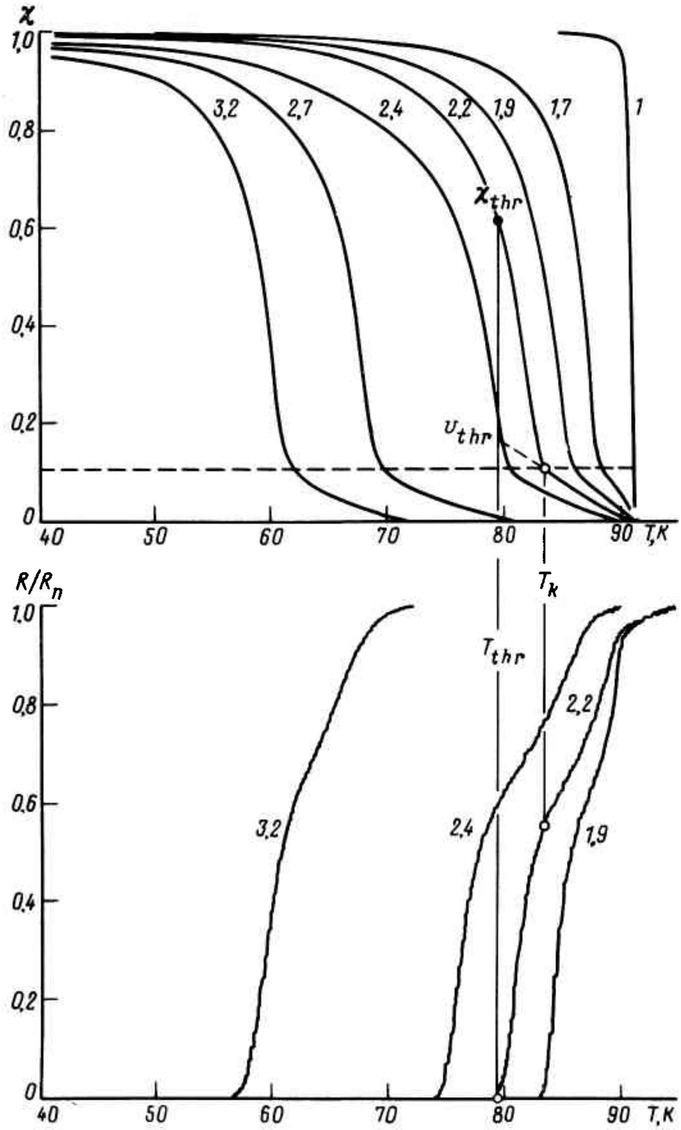

FIG. 1. Families of $R(T)$ and $\chi(T)$ curves ($H_{ac} = 0.07$ Oe) measured for one sample, as the oxygen content decreases. The curves are labeled with the values of κ. The procedure for determining $\chi_{\rm th}$ and $v_{\rm th}$ is demonstrated for the pairs of curves with $\kappa = 2.2$.

superconducting grain. In our case, an estimate yields $\Delta T \approx 0.1$ K, so inequality (3) would hold.

Only a small number of grains are in a superconducting state near T_{c0}, so the average number of grains in superconducting clusters is on the order of unity. It follows from (2) and the normalization of χ specified above that the equality $\chi(T) = v(T)$ holds within the ratio of the demagnetizing factors of the sample and of an individual grain, if inequality (3) holds. The derivative of $v(T)$ is the distribution function $g(T)$. The slope change is observed at the time at which the fraction of superconducting phase in the sample reaches $v_k = 0.11$. From this time on, progressively more clusters appear. In these clusters the number of grains is large enough that there are rings inside the clusters which encircle nonsuperconducting regions. The diamagnetic response χ then becomes greater than v. At the temperature T_{th}, at which the resistance R vanishes, an infinite cluster forms in the sample. For all curve pairs $\{R(T), \chi(T)\}$ found in the present experiments we have

$$\chi_{th} = \chi(T_{th}) \approx 0.65 - 0.7. \tag{4}$$

Furthermore, for all the $\chi(T)$ curves an extrapolation of the curve from the region $0 < \chi(T) \leqslant 0.11$ to T_{th} [this temperature is determined from the $R(T)$ curve] yields

$$\chi^{(extr)}(T_{th}) = v(T_{th}) \approx 0.17 \tag{5}$$

in complete agreement with percolation theory. Figure 1 illustrates the graphical procedure for determining χ_{th} and $v(T_{th})$ for one particular pair of curves.

All calculations of the susceptibility of a percolation superconducting cluster of which we are aware have been carried out in the "small-element limit," in which the inequalities opposite (1) and (3) hold:[2,3] $d < \xi, \lambda$. To find a qualitative estimate of the ring contribution to the susceptibility, we consider a regular three-dimensional lattice of grains with the symmetry of closely packed spheres. In such a lattice, each pair of neighboring grains has a common face. Each element has $s_1 = 12$ nearest neighbors; a cluster of $i = 2$ elements has a shell of $s_2 = 18$ neighbors; etc. We assume that the flux is completely expelled from a configuration of "i normal grains plus s_i shell grains" if the shell contains at least $s_i/2$ superconducting grains. We than have

$$\chi = v + \sum_i a_i (1-v)^i v^{s_i/2}, \quad a_i = (i + s_i) k_i C_{s_i}^{s_i/2}, \tag{6}$$

where v is the fraction of superconducting grains, and the coefficient k_i incorporates the number of configurations of i normal grains. The first two terms of this series gives us

$$\chi \approx v + 10^4 (1-v) v^6 + 10^7 (1-v)^2 v^9. \tag{7}$$

The coefficients in (6) and (7) are clearly too high. On the other hand, if we were to construct series (6) in a different way, counting the number of rings of j elements ($j = 6,7,8,...$), then terms with v^7 and v^8 would appear in series (7). We have written series (6) and (7) out to demonstrate that the coefficients a_i in series of this sort are quite large. Figure 2 compares a curve of (7) in the interval $0 < v < 0.16$ with one of the experimental curves (Fig. 1).

The picture which we are proposing here is supported by measurements at various amplitudes of the alternating field H_{ac} (Fig. 3; see also Ref. 5). In the region

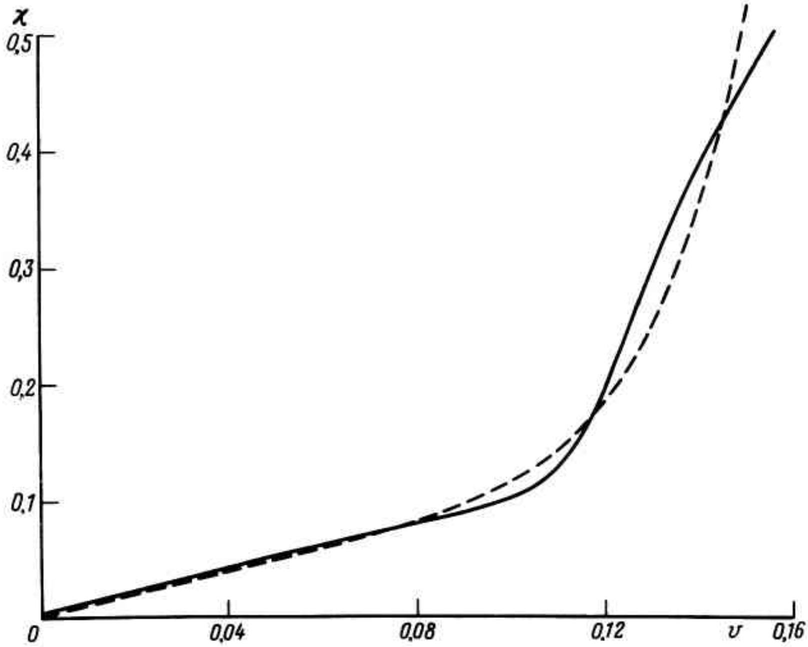

FIG. 2. Comparison of function (7) (the dashed line) with the $\chi(T)$ curve for the value $\kappa = 2.2$.

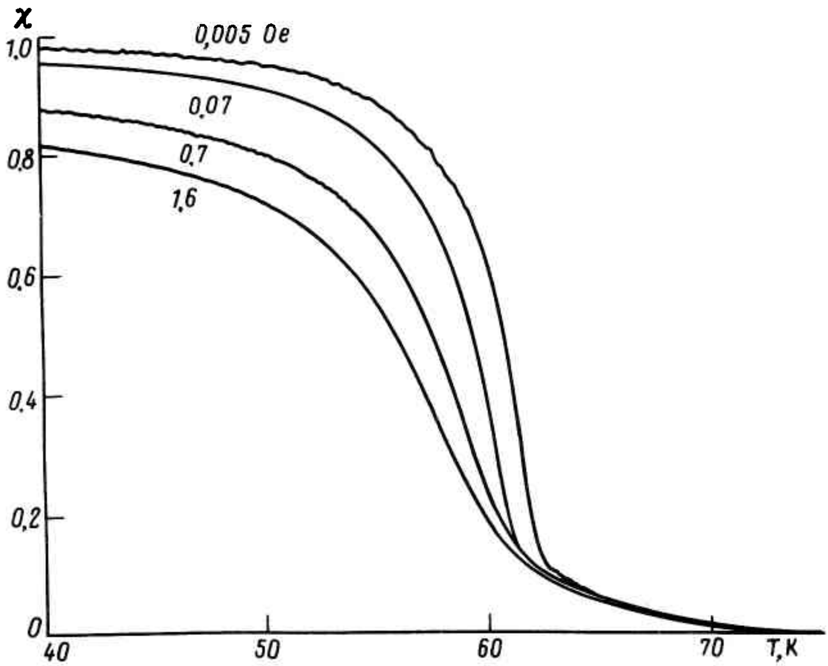

FIG. 3. $\chi(T)$ curves for various values of H_{ac}. The curves are labeled with the value of H_{ac}, in oersteds. The state of the sample is characterized by the value $\kappa = 3.2$.

$\chi < \chi_k$ there is no dependence of χ on H_{ac}: This is the region in which the screening currents flow along the surface of isolated grains. A dependence $\chi(H_{ac})$ arises at $\chi < \chi_k$, at which the screening is performed by the currents in the rings.

Equating the magnetic moment of a diamagnetic sphere of radius r ($M_s \propto r^3$) to that of a ring of the same radius, carrying a current I ($M_r \propto Ir^2$), we find that the screening current in a ring is proportional to r: $I \propto r$. Since r is on the order of the product of the number of grains in a ring, n, and the grain size d, while the width of the ring is on the order of d, the density of the superconducting current per unit surface area of the ring is $J \approx I/d \propto n$. Accordingly, even if the critical current in an individual grain is the same as that in a ring, the rings will be the first to react to an increase in H_{ac}. The presence of Josephson junctions in the rings increases the difference between isolated grains and rings. Analysis of how χ depends on H_{ac}, T, and the frequency would probably reveal the importance of the junctions.

Conclusion. Measurements of the dynamic susceptibility $\chi(T)$ in a zero magnetic field make it possible to determine the initial part of the distribution of grains of ceramic $YBa_2Cu_3O_{7-\delta}$ with respect to the superconducting transition temperature. When the superconducting phase fills a fraction $v \approx 0.10$–0.11 of the sample, a slope change occurs on the $\chi(T)$ curve, as a result of the appearance of hollow superconducting clusters which screen the normal regions that they enclose. When an infinite cluster appears, at $v \approx 0.17$, the resistance $R(T)$ drops to zero, and the susceptibility of the ceramic amounts to 0.6–0.7 of the maximum value of $1/(4\pi)$.

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