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Thermoelectric power of inhomogeneous superconductors: A new kind of percolation

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A theoretical analysis of a recent observation of vanishing thermopower at the superconducting transition temperature on some samples containing a minute fraction of superconductor is presented. An argument due to Jha, Reddy, and Sharma which demonstrates that the percolation threshold for thermoelectric power can be much smaller than the usual percolation threshold for conductance is analyzed. It is argued that a nonzero percolation threshold for thermoelectric power is essentially a finite-size effect, in which the size exponent is so small that for macroscopic samples of interest the threshold is more or less size independent.

In a recent paper[1] one of the present authors has reported data on thermoelectric power, x-ray diffraction, and resistivity of some oxygen-deficient and highly inhomogeneous specimens of $YBa_2Cu_3O_{7-x}$. The x-ray diffraction data revealed the presence of trace amounts of orthorhombic phase present in a predominently tetragonal phase. The resistance of these samples remained nonzero to temperatures below 77 K, but the thermoelectric power dropped to zero at 82 K and stayed zero at lower temperatures. Since the thermoelectric-power behavior is similar to other specimens with oxygen more than 6.5, one imagines that the superconducting transition occurs, but the superconducting fraction is so small that no connected percolation paths exist and the resistance does not vanish. Grant *et al.*[2] and Cooper *et al.*[3] have drawn similar conclusions about the possible existence of a superconducting phase in La_2CuO_4 from thermopower measurements. At first sight, one expects that the thermoelectric power should vanish only when the macroscopic resistance vanishes, as only that condition seems to ensure a zero drop in voltage. However, it is well known that the discontinuities that can have a drastic influence on resistance may have little influence on thermoelectric power. So in view of the above observation, Jha, Reddy, and Sharma[4] have put forward an interesting argument that suggests that the critical concentration of the superconducting fraction to make thermoelectric power zero is considerably smaller than the usual percolation threshold p_c. Similar arguments were suggested earlier, though less explicitly by Kaiser[5] and Grant *et al.*[2]

The argument of Jha *et al.*[4] can be understood by referring to Fig. 1(a), which shows paths which are not completely in superconducting fraction, but along which the voltage drop is zero. These paths are such that they go along the direction of the temperature gradient in the superconducting fraction, while they go perpendicularly to the direction of temperature gradient in the normal fraction as shown in Fig. 1(a). If there is no voltage discontinuity at the interface between superconducting and normal components, clearly such paths will have zero voltage drop. Such paths can clearly occur at a concentration lower than p_c, as they only require that the various isolated clusters overlap in one direction only, that of the temperature gradient. The purpose of this Brief Report is to examine this idea further and provide estimates for the percolation threshold for this new sort of process.

We begin by first examining the basic point of the above argument regarding how a superconducting grain in parallel with a normal grain gives rise to zero thermoelectric power. Since a microscopic analysis for this problem is too difficult, one resorts to an equivalent circuit analysis in which we replace the two grains by two cells with emf's E_1 and E_2 and internal resistances r_1 and

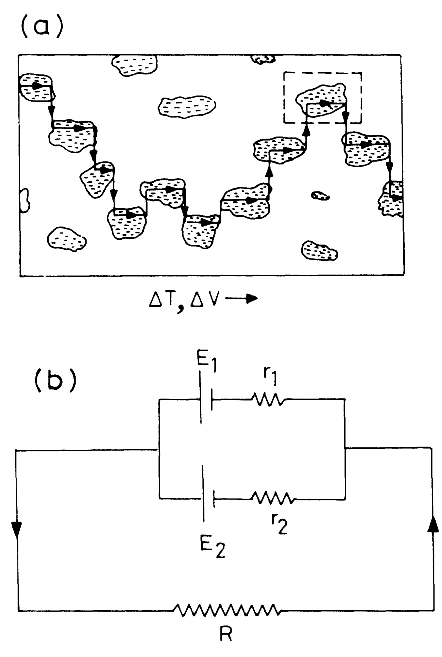

FIG. 1. (a) Paths that go along the temperature gradient through the superconducting portion (shaded) and transverse to the temperature gradient through the normal portion. Such paths can occur below the percolation threshold p_c. (b) The equivalent circuit for a portion contained within the box of dotted lines in (a).

r_2, respectively, as shown in Fig. 1(b). The total emf of the combination is given by

$$E_{\text{eff}}=\frac{r_1E_2+r_2E_1}{r_1+r_2} . \quad (1)$$

From this formula one sees that if E_1 and r_1 go to zero, as would happen if grain 1 becomes superconducting, the total emf will become zero. One can apply this argument for each portion of the specimen spanned by a superconducting grain to show that the potential drop is zero, whenever the situation shown in Fig. 1(a) prevails.

Before going into various physical aspects of the percolation process, let us consider the following ideal problem. Consider a two-dimensional square lattice of linear size L, whose sides are occupied with probability p and empty with probability $1-p$. We draw a linear lattice A of size L parallel to one of sides. Along each column of the lattice perpendicular to A, we look for a pair of occupied sites on a bond. If there exists one, we occupy the corresponding bond on A and ask for a connected cluster on A. This is the ideal analog of the connectivity that we need for considering the thermoelectric power. On A, the bond probability ought to be unity for percolation to happen. The probability p_1 of occupying a bond on A is clearly equal to the probability of finding at least one occupied bond along the entire length of the column. Hence it is given by

$$p_1=1-(1-p^2)^L . \quad (2)$$

Now, as $L\rightarrow\infty$, $p_1\rightarrow 1$ for any nonzero p. Thus the percolation probability for the projected percolation process is zero.[6]

For reasons that will become clear in the following, it is crucial to consider finite-size effects for the above problem. The probability P_L of finding a cluster of size L on A (i.e., the percolation cluster) is clearly

$$P_L=[1-(1-p^2)^L]^L,\quad d=2 , \quad (3)$$

$$P_L=[1-(1-p^2)^{L^{d-1}}]^L,\quad d>2 , \quad (4)$$

where in Eq. (4) we write the straightforward generalization of the two-dimensional result to arbitrary dimension d. A typical plot of P_L as function of p for some values of L is shown in Fig. 2. From this curve, one can see that for a finite L also, one has a well-defined threshold of p, where P_L changes from a nearly zero value to a value of nearly unity. This L-dependent threshold $p_T(L)$ can be defined to be the point of inflection of $P_L(p)$. Setting the second derivative of $P_L(p)$ to zero, for large L one obtains the following equation for p_T:

$$2p_T^2L^{d-1}-1=(2L^dp_T^2-1)(1-p_T^2)^{L^{d-1}} . \quad (5)$$

For large L, the leading term in the solution is

$$p_T(L)=[\ln L/L^{d-1}]^{1/2} . \quad (6)$$

To verify this analysis, we have also carried out numerical simulation for a two-dimensional lattice. In these simulations we do observe a well-defined threshold for large L and numerical estimates compare well with the formula in Eq. (6), as may be seen from Table I. Equation (6) shows an interesting departure from the power-law scaling one normally expects.

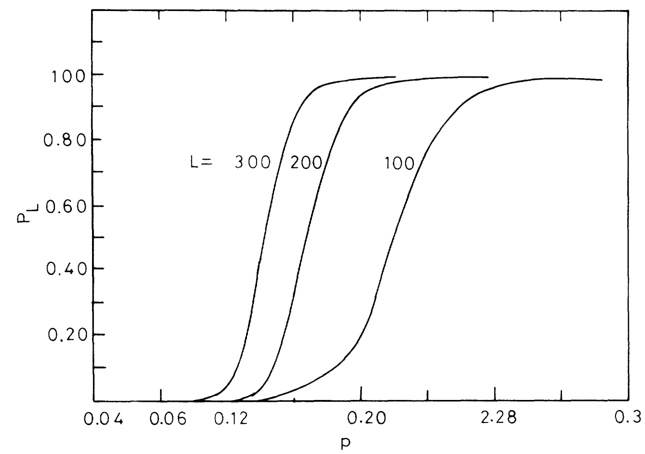

FIG. 2. Variation of P_L as function of p is shown for a few values of L. The sharp change in P_L as a function of p helps us define an L-dependent threshold p_T.

Let us now turn to some more physical aspects of the above problem. The first point is that the superconducting regions cannot occur at the length scale of an atomic cell, since it must have a minimum size related to the superconducting coherence length. Let this minimum size be denoted by ξ_m (in units of cell dimension). This feature can be incorporated into earlier considerations by dividing the volume of the system into blocks of linear size ξ_m. Now we can regard a block occupied if more than half of it is filled with a superconducting fraction, and take it unoccupied otherwise. This prescription reduces this problem exactly to the lattice problem discussed above, with L getting replaced by L/ξ_m. Thus

$$p_T^2(L)=\frac{\ln(L/\xi_m)}{(L/\xi_m)^{d-1}} . \quad (7)$$

For a macroscopic sample, L is of order 10^8, but L/ξ_m could be up to 2 orders of magnitude smaller, where the finite-size scaling effect may have a quantitative significance.

Actually, Eq. (7) is not quite the answer we need for some purposes. Experimentally, it is easier to estimate the fraction of orthorhombic cells by the x-ray method. But this fraction is not the same as the superconducting fraction, because there is the possibility of having clusters of orthorhombic cells that are not large enough to undergo superconducting transition. This leads us to consider the following more difficult percolation problem. Let the lattice sites be occupied by probability p as before, but we omit all the clusters which have a linear size smaller than ξ_m while projecting them on the linear lattice A. This problem can at least be approximately tackled along the lines given above. We do the block problem with block occupation probability given by $f(p)=\xi_m^d n_{\xi_m}(p)$, where

TABLE I. Comparison between values of p_T obtained by numerical simulation (denoted by $p_T^{(1)}$) and those obtained from Eq. (6) (denoted by $p_T^{(2)}$).

L	100	200	300	400	500	800	1000
$p_T^{(1)}$	0.200	0.181	0.144	0.123	0.105	0.085	0.08
$p_T^{(2)}$	0.215	0.163	0.138	0.122	0.122	0.091	0.083

$n_{\xi_m}(p)$ is the number per site of the clusters of linear size greater than ξ_m at concentration p. Then our formula for p_T takes the form

$$f(p_T)=\left[\frac{\ln(L/\xi_m)}{(L/\xi_m)^{d-1}}\right]^{1/2} . \tag{8}$$

Since p_T is expected to be quite small, we can use an asymptotic form for $n_{\xi_m}(p)$. If s denotes the total number of sites in a cluster, then[7] for small p,

$$n_s(p)=\frac{A}{s^{\theta}}(\lambda p)^s , \tag{9}$$

where A and λ are lattice-dependent constants, and θ is a dimension-dependent exponent. Next, we have to relate the total number of sites s and the linear size ξ_m. This cannot be done unambiguously for an arbitrary value of ξ_m. But if we make the assumption that ξ_m is of the same order as ξ_p, the percolation correlation length, we can use the relation[8] which expresses average size $\langle s\rangle$ in terms of ξ_p, i.e., write $\langle s\rangle=\xi_m^{d_f}$. Here $d_f=2D-d$, where D stands for the fractal dimension of the percolation cluster at the threshold p_c. In three dimensions D is numerically determined[8] to be 2.5, which gives $d_f=2$. Use of Eq. (9) into Eq. (8) then yields

$$p_T=\frac{1}{\lambda}\left[\frac{\xi_m^{2(d_f\theta-d)}}{A^2}\frac{\ln(L/\xi_m)}{(L/\xi_m)^{d-1}}\right]^{\xi_m^{d_f}/2} . \tag{10}$$

It remains to incorporate one last point in Eq. (10). The above analysis assumes that the orthorhombic regions can occur at the scale of the unit atomic cell. However, the transition from tetragonal to orthorhombic phase should also not occur at a length scale smaller than ξ_0, where ξ_0 is related to a coherence length associated with this transition. This can be taken into account by taking the size of the basic lattice to be ξ_0. Measuring both L and ξ_m in terms of ξ_0 then modifies the above formula to

$$p_T=\frac{1}{\lambda}\left[\left[\frac{\xi_m}{\xi_0}\right]^{2(d_f\theta-d)}\frac{1}{A^2}\frac{\ln(L/\xi_m)}{(L/\xi_m)^{d-1}}\right]^{(\xi_m/\xi_0)^{d_f}/2} . \tag{11}$$

It is worth noting an interesting point about this formula. p_T is essentially nonzero due to the finite-size effect, which is normally negligible for macroscopic-sized samples. But here the situation is quite different due to the fact that p_T goes to zero with a power of L given by $-[(d-1)/2](\xi_m/\xi_0)^{d_f}$, which may be so small as to make the dependence on L even at macroscopic length scales negligible. In fact, for $\xi_m/\xi_0>4$, the value of p_T is largely determined by λ, which is a bulk parameter of the lattice percolation. This is the only instance we know of where a finite-size effect leads to a result that is more or less bulk like.

We now make a typical numerical estimate of p_T. In three dimensions the numerical estimates based on series analysis yield[9] $\theta=1.5$ and for simple cubic lattice $\lambda=8.35$. To determine the value of A, we use the Bethe approximation,[9] which gives $A=0.096$. If we take the sample size to be 1 cm and the lattice size to be 4 Å, then $L=2.5\times10^7$. Since the parameters ξ_m and ξ_0 are not available experimentally or theoretically, we just have to make a plausible estimate. We take $\xi_m=50$ and calculate p_T for different values of the ratio ξ_m/ξ_0. These values are shown in Table II. One observes that for $\xi_m/\xi_0>4$, p_T is almost independent of L and is of order 0.1. In this range our assumption regarding the relation between s and ξ_m is also consistent. However, as p_T gets lowered, the percolation correlation length gets smaller than ξ_m and in principle we do not have a simple relationship between s and ξ_m. To improve upon the situation in this range, one may have to resort to large-scale simulation. However, before resorting to this exercise, the model should be improved in other respects as well, as discussed in the next paragraph.

Now we would like to discuss a few other physical factors that need to be considered in the analysis of this problem. First, crucial to our argument is the equivalent circuit analysis of a segment containing superconducting and normal components in parallel. The circuit equivalence is clearly rather crude for this complicated transport situation. On its basis one cannot rule out the possibility of a voltage drop across the interface between superconducting and normal components. Second, if p_T is much smaller than p_c, the transverse distances between the successive superconducting fractions can be very large. Given the fact that the thermal conductivities of the two components are different, the equipotentials for

TABLE II. Variation of p_T with the parameter (ξ_m/ξ_0).

ξ_m/ξ_0	10	9	8	7	6	5	4	3	2	1
p_t	0.107	0.105	0.101	0.097	0.09	0.08	0.065	0.041	0.011	8.87×10^{-6}

temperature may not be the transverse planes, and the voltage drop along the transverse paths need not be zero. The inclusion of these factors and a full-fledged study of transport would require an elaborate analysis and is deferred to a future study.

In conclusion, we have presented a simplified analysis of a novel type of percolation problem that arises in the study of thermoelectric power of inhomogeneous superconductors. The percolation threshold for thermoelectric power is found to be much lower than the usual threshold, and our analysis provides a way to understand this. The curious point of the analysis is that this threshold is nonzero due to a finite-size effect that is appreciable even at macroscopic sizes. This analysis shows that thermoelectric power measurements can prove to be a very sensitive probe to detect minute superconducting phases in the materials. Such a point of view has also been advocated by other authors.[2,4,10]

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