Dependence of T_c on the normal-state resistivity in granular superconductors

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The transition temperature of a granular superconductor is derived from a percolation description for the onset of superconductivity in these systems. The variation of T_c with the normal-state resistivity is calculated and found to be in agreement with experimental data.

I. INTRODUCTION

In a recent article[1] we have suggested a percolation model for the description of superconducting properties of granular systems. We have assumed that the coupling between the superconducting grains is established through the Josephson interaction, and that the grains become coupled when the coupling energy E_J exceeds the thermal energy (of the order of $k_B T$). Since E_J increases when the temperature decreases, more and more grains are coupled as the temperature is lowered. On the other hand, E_J is inversely proportional to the normal-state resistance of the junction between two grains, and depends on the grain size.[1] When it is assumed that the normal-state resistance and the grain size are randomly distributed, the coupling between the grains is accomplished at random, with a temperature-dependent probability. Then, at the temperature at which the coupling probability equals the percolation threshold p_c, an infinite cluster of superconducting grains is formed. This temperature marks the electrical transition end point of the granular sample.

The main feature of our model is the randomness in the coupling between the grains, which arises from the distribution of the junction resistances and the grain sizes. In this sense our model differs from other models invoked to treat granular superconductors (see Ref. 1 and references listed there). In these treatments it is assumed that the grains are ordered on a certain lattice, and that the interaction between them is the same everywhere. Namely, the granular system is considered as a "pure" XY model, in which the randomness in the coupling is neglected.[2] We have shown[1] that the percolation model gives good agreement with specific-heat data and describes well the electrical transition in a certain class of granular materials.

In this article we investigate in detail the electrical transition temperature of a granular system. This is carried out using the percolation description, which is modified to include the effect of the charging energy.

Electrostatic effects are not important in metallic samples[3] (e.g., Al-Al_2O_3 with $\rho_n \lesssim 10^{-3}$ Ω cm, where ρ_n denotes the normal-state resistivity). However, in high-resistance specimens the charging energy cannot be neglected.[3–6] Indeed, the inclusion of the charging energy in our percolation model is essential. The reason is that when the charging energy is neglected, the percolation model yields a transition temperature (although very low) for high resistance samples.[1] This feature is unphysical and does not agree with experimental data.[7–9]

We therefore assume that in high resistance samples the grains become coupled when the Josephson energy exceeds the thermal energy and the charging energy. We relate the charging energy to the normal-state resistance of the junction, and in this way obtain a criterion for the coupling which depends on grain size and the temperature. Then, invoking an argument by Ambegaokar *et al.*[10] which relates the normal-state resistivity to the percolation probability p_c we find an expression for the transition temperature.

The details of the calculation are given in Sec. II. In Sec. III we discuss our results and compare them with experimental data.

II. DETERMINATION OF THE ELECTRICAL TRANSITION TEMPERATURE

Granular superconductors may be roughly divided into two classes.[1] In the first, the grains are strongly coupled and the grain-size distribution is rather wide.[7] The grains become coupled immediately after the appearance of superconductivity in the grains. In the second class, the grains are weakly coupled, either by a thin bridge of metal, i.e., a weak link, or by the Josephson coupling which connects two superconducting grains separated by a thin insulating layer.[7,11,12] In this class the grain-size distribution is narrow.[7,9] We may assume that the grains are equal in size and consider only the distribution in the separating layers between them.

In this article we focus on the second class for the following reason. The transition temperature of a single grain depends on its size.[7,8] However, there

is no quantitative theory for this dependence. We therefore cannot treat a system consisting of grains of various sizes. On the other hand, when all the grains are of the same size, it can be assumed that they have the same transition temperature. In this case the randomness in the coupling arises from the distribution in the link sizes.

The weakly coupled granular systems can be further divided into two categories, according to the percentage of the metal in the samples. (i) When the metal percentage is such that the normal-state resistivity decreases with the temperature, the samples are metallic. In this range the grains are connected mainly by weak links. For weak links the charging energy is negligibly small[8,13] whereas the opposite is true for Josephson junctions. Therefore, even though there is a certain fraction of Josephson junctions in the metallic samples, the infinite superconducting cluster consists mainly of weak links, which become connected more easily than the Josephson junctions. (ii) When the normal-state resistivity increases as the temperature decreases[3,7–9] the samples are nonmetallic. In this range the coupling between the grains is through Josephson junctions, and the charging energy cannot be neglected. In particular, in the nonmetallic samples the charging energy leads to the disappearance of superconductivity at a certain value of the normal-state resistivity.

We now turn to the determination of the transition temperature in metallic and nonmetallic systems.

A. Metallic samples

In this regime the coupling between the grains is established by the interplay between the superconducting coupling energy and the thermal energy, and the charging energy can be neglected. That is, two grains become connected when[1,14]

$$E_J \geq \tfrac{1}{2} k_B T \ , \tag{1}$$

where

$$E_J = \frac{\pi\hbar}{4e^2 R_n} \Delta(T) \tanh \frac{\Delta(T)}{2k_B T} \ . \tag{2}$$

Here R_n is the normal-state resistance of the link and $\Delta(T)$ is the order parameter in each grain. The normal-state resistances R_n are randomly distributed across the sample since the link size is randomly distributed. Let us denote the distribution function by $f(y_n)$, where y_n is the normal-state resistance in dimensionless units

$$y_n = R_n/\alpha, \quad \alpha = \pi\hbar/4e^2 = 3152\,\Omega \ . \tag{3}$$

Then, from (1), the fraction p of "connected" grains at each temperature (i.e., those links which are superconducting) is

$$p = \int_0^{4X(T)} dy_n f(y_n), \tag{4}$$

$$X(T) = \frac{\Delta(T)}{2k_B T} \tanh \frac{\Delta(T)}{2k_B T} \ .$$

The electrical transition temperature occurs when $p = p_c$, where p_c is the percolation probability at which an infinite cluster of superconducting grains is formed. Hence

$$p_c = \int_0^{4X(T_c)} dy_n f(y_n) \ . \tag{5}$$

On the other hand, the normal-state resistivity ρ_n is proportional to the percolation threshold resistance R introduced by Ambegaokar *et al.*[10] They stated that the sample resistance (in the normal state) is mainly determined by the percolating cluster of smallest resistances. That is

$$p_c = \int_0^{R/\alpha} dy_n f(y_n) \ , \tag{6}$$

where

$$R = \rho_n / L \tag{7}$$

and L is a certain characteristic length (this length is discussed below). From Eqs. (5)–(7) we obtain

$$4L\alpha X(T_c) = \rho_n \ . \tag{8}$$

To compute Eq. (8) we need to know the order parameter in the grains, $\Delta(T)$ [see Eq. (4)]. the order parameter of a small grain is calculated in Ref. 15, where it is found that it is much affected by critical fluctuations. In our model we neglect fluctuations, and use the BCS form for $\Delta(T)$. (This point is discussed in Ref. 1.) We have solved Eq. (8) on the computer and found T_c/T_{c0} as a function of $\rho_n/\alpha L$. Here T_{c0} is the transition temperature of the single grain with $2\Delta(0) = 3.52 k_B T_{c0}$. The results are depicted in Fig. 1 (the circles). In two limiting cases it is easy to analyze Eq. (8) analytically.

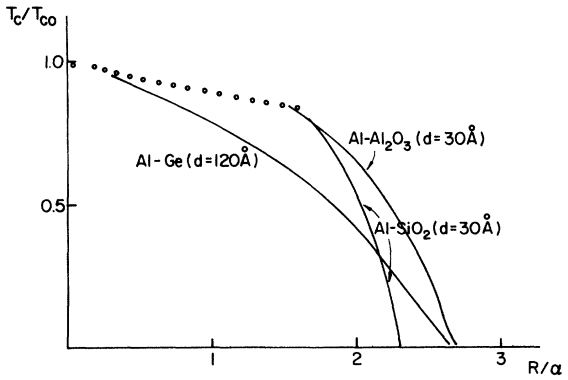

FIG. 1. T_c/T_{c0} as a function of R/α computed from Eqs. (8) (circles) and (19) (solid lines). The circles are computed without the charging energy and therefore are independent of the grain size. ($\alpha = \pi\hbar/4e^2$.)

1. $T_{c0}-T_c \ll T_{c0}$

When the transition temperature of the sample is close to the transition temperature of the single grain,

$$X(T_c)\sim\left[\frac{\Delta(T_c)}{2k_BT_c}\right]^2\sim 2.34\left[1-\frac{T_c}{T_{c0}}\right] . \tag{9}$$

Thus, from (8),

$$T_c/T_{c0}=1-0.1\rho_n/L\alpha \tag{10}$$

and T_c/T_{c0} decreases linearly with ρ_n.

2. $T_c \ll T_{c0}$

When the transition temperature is well below T_{c0},

$$X(T_c)\sim\frac{\Delta(T_c)}{2k_BT_c}\sim\frac{\Delta(0)}{2k_BT_c}\sim 0.88\frac{T_{c0}}{T_c} ,$$

and, from (8),

$$T_c/T_{c0}\sim 3.52L\alpha/\rho_n . \tag{12}$$

It should be stressed that the range $T_c \ll T_{c0}$ is probably not accessible experimentally. For ρ_n high enough so that Eq. (12) is valid, the sample will not be metallic and therefore the charging energy cannot be neglected. The percolation model relates T_c/T_{c0} to the normal-state resistivity ρ_n. Recently Laibowitz *et al.*[2] have presented a calculation of T_c/T_{c0} based on the assumption that the granular system can be described by an ordered XY model. Their calculation relates T_c/T_{c0} to the average junction resistance. However, it should be noted that the average junction resistance differes from ρ_n/L.[10]

B. Nonmetallic samples

In this case the infinite superconducting cluster consists mainly of Josephson junctions. The charging energy E_c cannot be neglected, and the criterion (1) for a junction to become coupled should be modified as follows:

$$E_J \geq \tfrac{1}{2}k_BT+E_c . \tag{13}$$

The charging energy E_c has been given considerable attention in the literature.[8] It can be easily evaluated in the limit $s \ll d$, where d is the grain diameter and s is the spacing between grains. In this case we may approximate the junction by a plate capacitor, and obtain

$$E_c=\beta\frac{2q^2}{\epsilon_I d}\frac{s}{d} . \tag{14}$$

Here ϵ_I is the dielectric constant, and q is the charge transferred. The appropriate value for the dielectric constant was discussed in the literature.[8,16] It is argued that ϵ_I for tunneling mechanism between grains, is probably smaller than the dielectric constant of the insulating matrix. The argument is based on the fact that the characteristic tunneling time is much shorter than the relaxation time of the accompanying polarization wave. The numerical factor β (of the order 0.1) is invoked in order to account for the influence of the surrounding grains. That is, each grain participates in several junctions and the charge transferred from one of them is spread over the rest. Such an argument suggests that[17] $\beta\sim 1/Z$, where Z is the coordination number ($Z=12$ in random close package structures[1]). The conclusion that the coupling energy should exceed about 0.1 of the charging energy of a single junction for a superconducting link to be established is also reached in the XY model[4,5] for different reasons.

Our approximate derivation for E_c differs from other treatments given in the literature.[8,18,19] We calculate directly the insulating barrier capacitance, and we assume that the charge transfer is q. The result [Eq. (14)], differs by a numerical factor from the former results. However, the difference is not significant for the results we derive, as discussed below.

The spacing s between the grains is related to the normal-state resistance R_n of the junction. To show this we note that R_n enters the expression for E_J [see Eq. (2)] from a calculation of the transition probability through a tunneling barrier.[20] In the WKB approximation[21] the normal-state resistance of a junction is given by

$$R_n=e^{2\chi s}16\pi\alpha/Ak_F^2 , \tag{15}$$

where $\alpha=\pi\hbar/4e^2\Omega$, s and A are the junction's thickness and area, respectively, k_F is the Fermi wave vector, and

$$\chi=[2m(V_0-E_F)/\hbar^2]^{1/2} . \tag{16}$$

Here V_0 is the height of the potential barrier. [It should be noted that (15) is valid for $\chi s>1$.] The WKB calculation leading to (15) is carried out for a rectangular barrier; in order to take into account the fact that tunneling between grains is not strictly one dimensional, Abeles *et al.*[8,18] have introduced a correction factor, $\gamma=[(d+s)\chi]^{-2}$, where d is the grain diameter. This factor seems to be too small. We have recalculated the factor γ (see the Appendix) and found

$$\gamma\sim(\chi d)^{-1} . \tag{17}$$

It should be noted that the factor in front of the exponent in Eq. (15) is different from the one given in Ref. 8. We treat the junction as a link between metallic grains whereas in Ref. 8 the grains are assumed to be small enough so that quantization effects become important. In our opinion, in the

granular specimens discussed in Sec. III the grains are metallic, as is verified by electron microscopy.[7–9] From Eqs. (15)–(17) we find

$$s=\frac{1}{2\chi}\ln\left[\frac{R_n}{\alpha}\gamma\frac{Ak_F^2}{16\pi}\right] . \tag{18}$$

Inserting (2), (14), and (18) into (13), we obtain the following criterion for a Josephson junction to be connected:

$$4X(T)\geq y_n+K(T)y_n\ln\left[y_n\gamma\frac{Ak_F^2}{16\pi}\right] , \tag{19}$$

where y_n is the normal-state resistance of the junction in dimensionless units ($R_n=\alpha y_n$), $X(T)$ is given by Eq. (4), and

$$K(T)=\frac{\beta}{\chi}\frac{q^2}{\epsilon_I d^2}\frac{1}{k_B T} . \tag{20}$$

Equation (19) provides us with an upper bound on y_n. Once this upper bound is found, we can determine T_c as has been done in Sec. II A above. Namely, the temperature at which the upper bound is equal to $\rho_n/L\alpha$ is T_c. [See Eqs. (4)–(7).] Thus we have to solve Eq. (19) when the inequality sign is replaced by an equality sign (and then $T=T_c$). This was carried out on the computer. The results are the solid lines in Fig. 1. The parameters used in the computation are discussed in Sec. III.

III. COMPARISON WITH EXPERIMENTAL DATA

As is explained above, the transition temperature in the percolation model is determined from Eq. (19) with the inequality sign replaced by an equality sign. When trying to compare the calculated T_c/T_{c0} with the experimental results, we encounter two main sources of possible errors. The first is connected with the granular structure of the system. In Eqs. (14) (the charging energy) and (15) (the normal-state resistance) we have had to introduce correction factors (β and γ, respectively) which are associated with the granular character. The second source of errors is parameters which cannot be measured. These are the potential barrrier height V_0 which enters the expression for χ [Eq. (16)] and the dielectric constant ϵ_I which is lower from that of the (bulk) insulating matrix.[8,16]

In the computation we have used the following values for the parameters in Eq. (19). The correction factor β [Eq. (14)] is $1/Z$, where Z is the coordination number, with[1] $Z=12$. For γ we have used Eq. (17) in which χ enters. In the calculation of χ [Eq. (16)] we have put $V_0-E_F=\frac{1}{2}E_g$, where E_g is the energy gap of the insulating matrix. (In doing this we have assumed that the Fermi energy of the insulator is at the middle of the energy gap and neglected surface effects.) The junction area [see Eq. (15)] is evaluated according to the calculation in the Appendix. For $Z=12$ we find $A=0.11\pi d^2$. For k_F [Eq. (15)] we have chosen the value of bulk Al, $k_F=1.75\times10^8$ cm^{-1}, and ϵ_I is taken as one-half the value of the static dielectric constant of the corresponding insulating matrix.[22] We have used the value $q=e$ for the charge transfer. However, we note that, taking into account that β and γ can change from the values chosen for them, the choice for q is not crucial. The parameters used in the computation are given in Table I.

TABLE I. Parameters used in the computation of Eq. (19). The values for T_{c0} are from Refs. 9 (Al-Ge); 7 (Al_2O_3), and 23 (Al-SiO_2).

	d (Å)	E_g (eV)	ϵ_I	T_{c0}
Al-Ge	120	0.74	16	1.8
Al-Al_2O_3	30	7.3	12.2	2.2
Al-SiO_2	30	8	4.5	3.1

Figure 2 portrays experimental data accumulated from Refs. 7, 9, and 23. Comparing the experimental data with the computed curves, we see that the characteristic length L introduced in Eq. (7) is 2–3 times the grain size. In view of the large experimental errors (mostly due to sample inhomogeneities at high resistivities) the overall agreement between theory and experiment is rather good.

As was mentioned above, the WKB calculation leading to Eq. (15) is valid for $\chi s>1$, i.e., at sufficiently low values of R_n the calculation is not valid

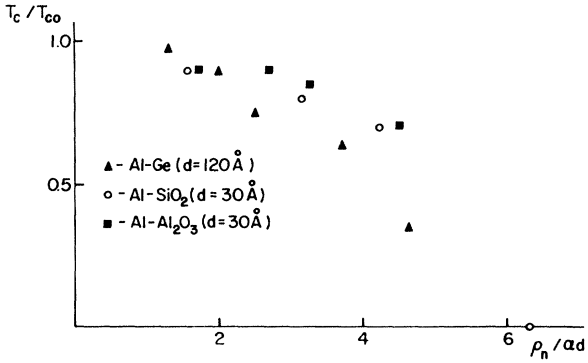

FIG. 2. Experimental data for T_c/T_{c0} as a function of $\rho_n/\alpha d$, accumulated from Refs. 9 (Al-Ge); 7 (Al-Al_2O_3), and 23 (Al-SiO_2). ($\alpha=\pi\hbar/4e^2$.)

any more. At this region the charging energy becomes less and less important, and the solid curves in Fig. 1 go into the circles (calculated without the charging energy). The regions where the two curves join each other depend on the grain size.

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APPENDIX: CALCULATION OF γ

Here we calculate γ, which is the correction factor to Eq. (15) arising from the fact that the tunneling between two grains is not one dimensional.

According to the WKB approximation[21] we have to consider the quantity Q

$$Q=\exp\left[-2\int_{x_l}^{x_r} k_\perp dx\right] , \tag{A1}$$

where x is the coordinate along the junction between x_l and x_r, $k_\perp$ is the wave vector normal to the junction, $k_\perp=\chi$, and χ is given by Eq. (16). For a rectangular junction, $Q=\exp(-2\chi s)$. For a junction between two grains we perform the following:

$$Q=\frac{1}{\pi h_m^2}\int_0^{h_m} dh\, 2\pi h \times\exp(-2\chi\{s+2[r-(r^2-h^2)^{1/2}]\}) . \tag{A2}$$

Here r is the radius of the grain, and h_m is given by

$$h_m=r\tan\theta_m , \tag{A3}$$

where $\cos\theta_m=1-2/Z$ (Z is the coordination number, i.e., the number of nearest neighbors). That is, h_m is defined in such a way that the tunneling takes place over a space angle $4\pi/Z$, corresponding to one neighbor. Carrying out the integration in (A2), we obtain

$$Q=\frac{1}{2\chi r}\frac{1}{\tan^2\theta_m}e^{-2\chi s} \times\left[1-\frac{1}{4\chi r}+\left(\frac{1}{4\chi r}-(1-\tan^2\theta_m)^{1/2}\right) \times\exp\{-4\chi r[1-(1-\tan^2\theta_m)^{1/2}]\}\right] . \tag{A4}$$

For $\chi r\gtrsim 5$ and $Z=12$, this gives for the correction factor $\gamma\sim 1/2\chi r$. The condition $\chi r\gtrsim 5$ is usually satisfied. This justifies our approximation.

[1]G. Deutscher, O. Entin-Wohlman, S. Fishman, and Y. Shapira, Phys. Rev. B 21, 5041 (1980).
[2]R. Laibowitz, A. Broers, D. Stroud, and B. R. Patton, in *Inhomogeneous Superconductors,* edited by D. U. Gubser, T. L. Francavilla, J. R. Leibowitz, and S. A. Wolf, AIP Conf. Proc. No. 58 (AIP, New York, 1980).
[3]T. Worthington, P. Lindenfeld, and G. Deutscher, Phys. Rev. Lett. 41, 316 (1978).
[4]W. L. McLean and M. J. Stephen, Phys. Rev. B 19, 5925 (1979).
[5]E. Simanek, Solid State Commun. 31, 419 (1979).
[6]B. Abeles, Phys. Rev. B 15, 2828 (1977).
[7]G. Deutscher, H. Fenichel, M. Gershenzon, E. Grunbaum, and Z. Ovadyahu, J. Low Temp. Phys. 10, 231 (1973).
[8]B. Abeles, *Applied Solid State Science* (Academic, New York, 1976), Vol 6, p. 1.
[9]Y. Shapira and G. Deutscher (unpublished).
[10]V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B 4, 2612 (1971).
[11]A. Fontaine and F. Meunier, Phys. Konden. Mater. 14, 119 (1972).
[12]G. Deutscher, M. Rappaport, and Z. Ovadyahu, Solid State Commun. 28, 593 (1978).
[13]K. K. Likharev, Rev. Mod. Phys. 51, 101 (1979).
[14]L. Solymar, *Superconducting Tunneling and Application* (Chapman and Hall, London, 1972).
[15]B. Muhlschlegel, D. J. Scalapino, and R. Denton, Phys. Rev. B 6, 1767 (1972).
[16]J. Pryer, D. Gore, and R. Speiser, J. Vac. Sci. Technol. 10, 316 (1973).
[17]S. Alexander (private communication).
[18]B. Abeles, P. Sheng, M. D. Coutts, and Y. Arie, Adv. Phys. 24, 407 (1975).
[19]W. L. McLean, T. Chui, B. Bandyopadhay, and P. Lindenfeld, in Ref. 2.
[20]B. D. Josephson, in *Superconductivity,* edited by R. D. Parks (Marcel-Dekker, New York, 1969).
[21]W. A. Harrison, Phys. Rev. 123, 85 (1961); C. B. Duke, in *Tunneling Phenomena in Solids,* edited by E. Burstein and S. Lundquist (Plenum, New York, 1969).
[22]O. V. Krylov, *Catalysis by Nonmetals* (Academic, New York, 1970).
[23]B. Abeles and J. J. Hanak, Phys. Lett. 34A, 165 (1971).