Percolation description of granular superconductors

G. Deutscher, O. Entin-Wohlman, S. Fishman, and Y. Shapira
Department of Physics and Astronomy, Tel Aviv University, Tel Aviv, Israel
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We suggest a percolation model for the onset of superconductivity in granular samples. The specific heat and electrical resistance are calculated, and found to be in agreement with experimental data.

I. INTRODUCTION

Granular superconductors have been given considerable attention in the last few years, and a great deal of experimental data was collected. These materials consist of metallic grains, embedded in an insulating matrix. It is therefore plausible to divide the free energy into two parts, one is associated with the isolated grain and the other is related to the interactions among the grains. The behavior of an isolated superconducting grain which results from the first part of the free energy, has been extensively studied,[1-3] mainly with regard to the grain's size. The collective behavior of the grains arises from the second part of the free energy, which is expected to account for the critical properties of the system.[4-7] The coupling between the grains is usually assumed to be through the Josephson interaction. Then, it can be shown[5] that the second contribution to the free energy is equivalent to the Landau-Ginzburg XY model for continuous spins.

When it is assumed[4-7] that the grains are ordered on a certain lattice, and, moreover, that the interaction between them is everywhere the same, one ends up with a "pure" XY model, which predicts a sharp second-order phase transition.[8-10] This does not explain the experimental results[11-15]; in particular, the difference between the electrical transition temperature and the temperature at which there is a peak in the specific heat.[15] A possible explanation for this failure is the neglect of the randomness in the coupling between the grains. This coupling is random since the grain's sizes and the distances among them vary randomly across the sample. If this randomness were weak (i.e., a small variance of the coupling), it would have been averaged out by thermal fluctuations, leading again to the critical behavior of the pure XY model. This follows from the Harris criterion,[16] which states that when the specific-heat critical exponent α of the pure (nonrandom) system is negative (in the pure XY model $\alpha = -0.02$), a weak randomness is averaged out by fluctuations. Unfortunately, there is not yet a definite answer to the question: How weak should the randomness be for the Harris criterion to be valid? Renormalization-group studies[10] show that the pure XY model fixed point is stable with respect to randomness, with a small stability exponent (α/ν, where ν is the coherence-length critical exponent). But examination of the Hamiltonian flow lines reveals that although the pure fixed point is stable, one may not flow to it (or to any other fixed point), but instead "run away".[10,17] If a "runaway" flow line is traced, the transition is not the usual second-order one, and its nature is still an open question.

In this article we propose a percolation model for the onset of a superconducting order in granular samples. The model is described in Sec. II. We use our model to compute the specific heat and to obtain a qualitative description of the electrical transition, in conjunction with the normal-state resistivity (this is one of the parameters which characterizes a granular system). The computational details are contained in Sec. III. The results we find fit quite well the experimental data. In essence, our model transforms the problem from that of randomly interacting grains into noninteracting clusters,[18] as discussed in Sec. IV. The limitations of the model are criticized in the discussion.

II. THE MODEL

A granular superconductor is usually characterized by two parameters. The first is the grain's size, on which the single-grain properties depend[1,19,20] and the second is the barrier between the grains. The grains-size distribution is measured by electron microscopy[19] and is rather reliable. The properties of the barrier are deduced from measurements of normal-state resistivity, in conjunction with the relative concentration of the constituents and the grain's size. These give only an estimation for the average resistance of a single junction. Both parameters, the grain's size and the barrier, determine the Josephson coupling E_j.

In our model we assume, following Soymar,[21] that the grains become coupled when E_j exceeds the thermal energy (of the order $k_B T$). Since the coupling energy depends on the temperature, more and more

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grains are coupled together as the temperature is lowered. The coupling is accomplished randomly, with a temperature-dependent probability. Such mechanism is a percolation process; at a certain temperature, at which the coupling probability is equal to the percolation threshold, an infinite cluster of coupled superconducting grains is formed. Then, there exists a superconducting path throughout the sample. Hence, this temperature marks the electrical transition. At the percolation threshold, the superconducting volume included in the infinite cluster is vanishingly small. It is assumed that the specific heat of the grains connected to the infinite cluster is of the BCS form, with T_c^{BCS} being the temperature at which the grain becomes connected to the infinite cluster. The contribution of the remaining grains is that of a small isolated grain.[1] At the percolation threshold, (at which the infinite cluster is formed) the BCS contribution to the specific heat is thus negligible and the main contribution is that of a single grain. The latter, for small enough grains,[1] has almost no anomaly. It is only when the temperature is further lowered and the percentage of grains participating in the infinite cluster is increased, that an anomaly with a bulklike behavior starts to appear in the specific heat.

The randomness in the coupling energy arises from the grains-size distribution and the junctions resistance distribution. Although both distributions affect the coupling energy, it turns out that granular systems can be divided into two categories, in each, one distribution dominates the other. In the first category the normal-state resistivity is very small (less than 100 $\mu\Omega$ cm for Al-Al_2O_3), the coupling between grains is strong and from electron microscopy we know that the size distribution is quite wide.[19] In this case the randomness of the grains size predominates, as the grains become coupled immediately after the appearance of superconductivity in the grains. The second category is characterized by a very large normal-state resistivity (>500 $\mu\Omega$ cm for Al-Al_2O_3), the coupling is weak and the distribution in grains size is quite narrow.[19] Hence in this case one may ignore the differences in the sizes and consider only the distribution of junctions resistance.

When the grains are strongly coupled, the randomness in the coupling energy is brought about through the dependence on the grain size of the temperature at which the grain becomes superconducting. Unfortunately, there is no theory which gives a quantitative relationship for this dependence. We therefore consider in this article the weak-coupling case, in which one can assume that the grains are identical and make certain plausible postulations about the junctions resistance distribution. The Al-Al_2O_3 samples in Ref. 15, on which heat-capacity measurements were carried out, fall within the weak-coupling category. The problem at hand is therefore a bond percolation (as compared to the case of strongly coupled grains which is a site-percolation problem). As such, it offers also the possibility of calculating the electrical resistance as a function of temperature. The details of the bond percolation problem pertaining to weakly-coupled Al-Al_2O_3 samples are described in Sec. III.

III. COMPUTATIONAL PROCEDURE

As stated above, we assume that the grains interact with each other via the Josephson interaction, and become coupled once the Josephson energy exceeds the thermal energy; i.e.,[21]

$$\frac{1}{4}\pi\frac{\hbar}{e^2}\frac{1}{R_n}\Delta(T)\tanh\frac{\Delta(T)}{2k_BT}\gtrsim k_BT \ , \tag{1}$$

in which R_n is the normal-state resistance of the junction between two grains, and $\Delta(T)$ is the order parameter in each grain. When condition (1) is fulfilled, the bond between the grains is "connected." The order parameter of a small grain is calculated in Ref. 1. However, since fluctuations are neglected in our model (this point is commented upon in the discussion), we chose to use the BCS form for $\Delta(T)$, with $2\Delta(0)=3.45k_BT_c$. This assumption is supported by experimental results[22,23] obtained on granular materials. Note that T_c is about the same for all the grains, since their size distribution is very narrow. Using a certain distribution for the resistance R_n (to be discussed in the following), one can find, at each temperature, the percentage of connected bonds. Then, from percolation calculations, the percentage of grains participating in the infinite cluster can be obtained.

In order to use results of percolation models, one has to specify the structure of the system. As can be judged from electron microscopy, the Al-Al_2O_3 samples have a structure of random closed packing (RCP). This type of structure is best described[24] by models dealing with dense random packing of hard spheres (DRPHS).[25,26] There are no percolation calculations for these structures; however, it was shown that[27,28] in many "more-ordered" structures (e.g., sc, bcc, hcp), the bond percolation yields $zp_c\simeq 1.5$. Here z is the number of nearest neighbors and p_c denotes the percolation threshold. For DRPHS, the number of nearest neighbors is about[25] 12; so, assuming that $zp_c\simeq 1.5$ holds for this structure as well, we find $p_c=0.125$. Apart from the value of the percolation threshold, one also needs the probability $P(p)$ that a connected bond belongs to the infinite cluster when a certain percentage p of the bonds are already connected. This function, for a RCP structure, was not computed so far. We therefore resort to the universality argument,[18] which states that $P(p)$, close to the per-

colation threshold, is a universal function of $(p-p_c)$, and the details of the specific lattice structure are not relevant to it. Thus we used the numerical form of $P(p)$ derived for other structures.[29]

The Josephson-coupling energy was calculated using the assumption that the normal-state resistances of the junctions, R_n, obey a normal distribution. It was further assumed that the variance of the distribution is proportional to the mean value; the proportionality constant was the only adjustable parameter of the calculation and it was fixed by fitting the specific-heat data, to be 0.6. The mean value of the distribution was determined from the measured value of the normal-state resistivity ρ_n. We write ρ_n as a product, $R \cdot S$, where S is a certain characteristic length of the system, which we take as the grain's diameter.[30] The value of R thus obtained is identified as the percolation threshold resistance. In doing this, we follow Ambegaokar *et al.*,[31] who stated that the resistance is mainly determined by the percolating cluster of the smallest resistances. Namely, R is the minimum resistance for which all the bonds with $R_i < R$ form a percolating cluster. Thus, the values of R and p_c suffice to determine the normal distribution of R_n.

Once the function $P(p)$ at a certain temperature is found, the specific heat can be calculated as described in Sec. II. The experimental results for the specific heat obtained on specimens of 30-Å grains are shown in Fig. 1. Our results, for the same values of ρ_n and grains size are depicted in Fig. 2; it should be noted that the specific heat of the isolated grain was extracted from Ref. 1. There, the grain's size is specified by the parameter $\bar{\delta}$, $\bar{\delta}=1/N(0)k_B T_c \Omega$, where $N(0)$ is the density of state and Ω is the grain's volume. For 30-Å grains $\bar{\delta}$ is greater than 1 (assuming that the density of states at the Fermi level in a granular system is the same as in bulk, assumption supported by experimental evidence[11]). The fifth graph in Fig. 2, in which the specific-heat anomaly is washed out, is in agreement with the data of Ref. 15 where it was mentioned that for $\rho_n = 10^{-2}$ Ω cm no heat-capacity transition is observed. Figure 3 pertains for larger grains, for which $\bar{\delta}=0.1$ (about 150-Å diameter). The difference between the two cases is in the single-grain contribution to the specific heat (as opposed to the BCS contribution of the infinite cluster). As the grain becomes larger, the anomaly in the (isolated grain) specific heat is more marked.[1]

It should be noted that all the plots presented in Fig. 2 were computed with only one adjustable parameter, namely the standard deviation of the resistance distribution. This was fitted to be 60% of the mean value of the distribution. (The same stand-

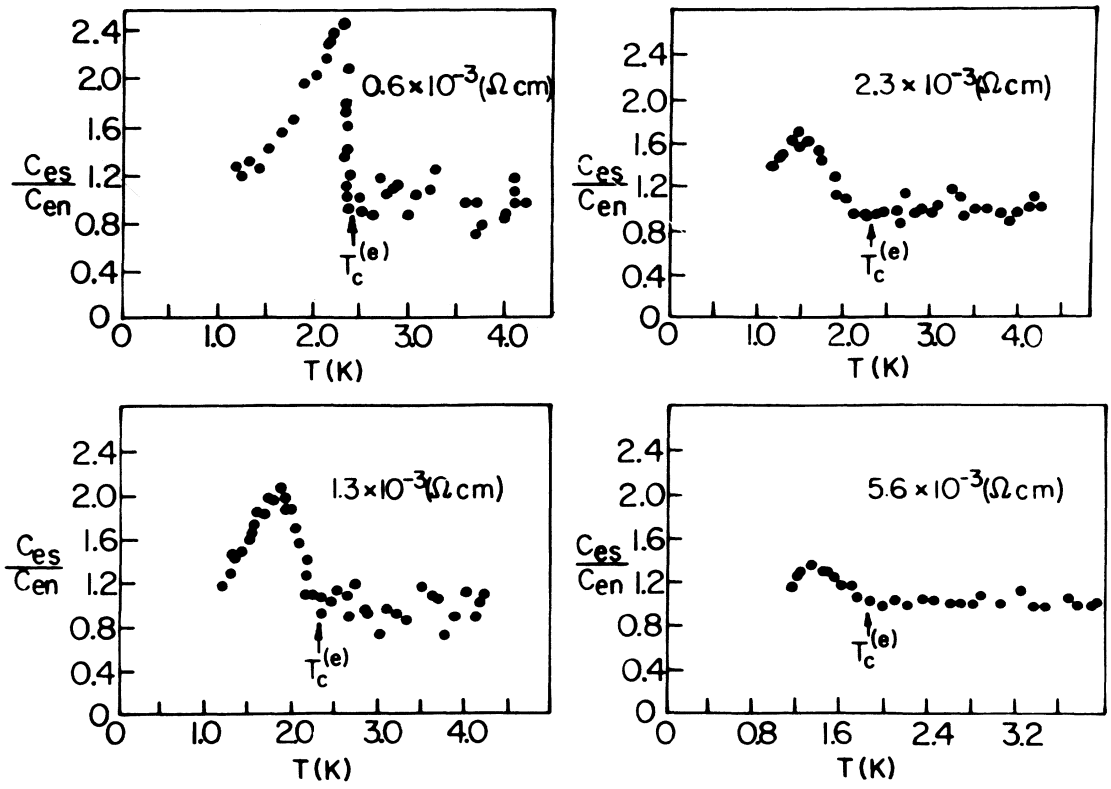

FIG. 1. Experimental heat-capacity data of Al-Al_2O_3 as a function of temperature, for various values of ρ_n (after Ref. 15).

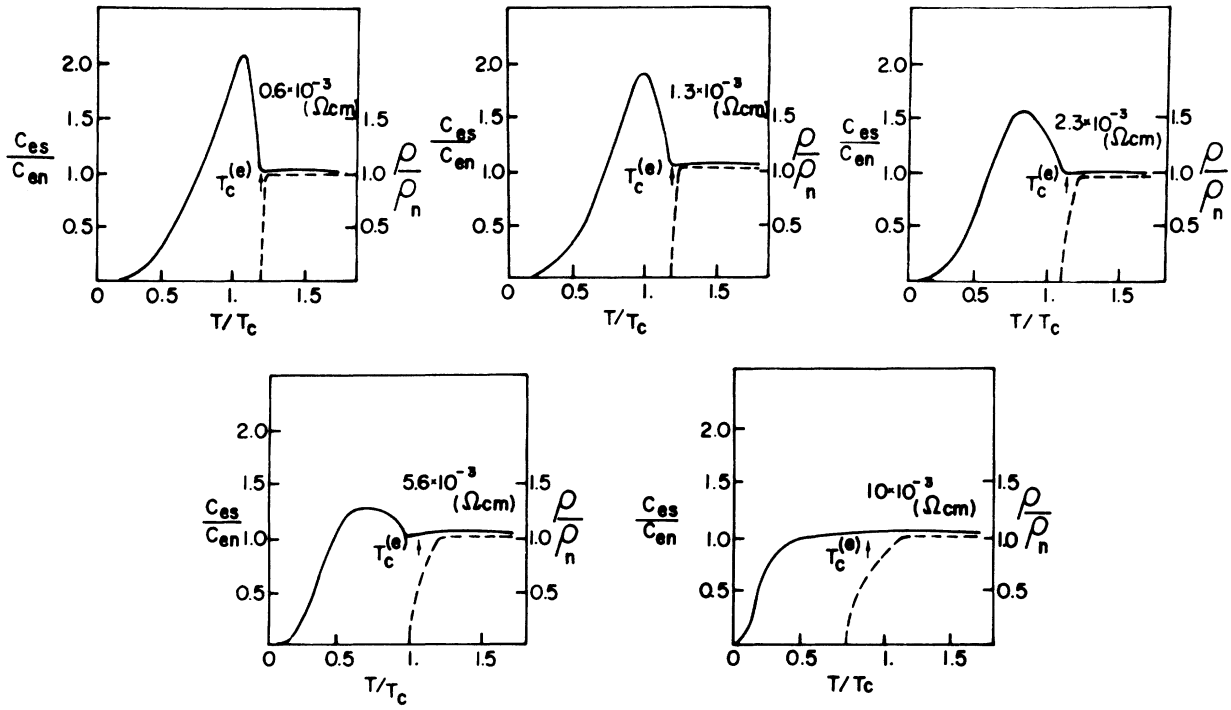

FIG. 2. Calculated curves of heat capacity (full line) and electrical conductivity (dashed line) as a function of reduced temperature, for $\bar{\delta} > 1$ (about 30-Å grains). Each of the curves is compatible with one of the curves of Fig. 1. The arrow $T_c(e)$ denotes the midpoint of the electrical transition.

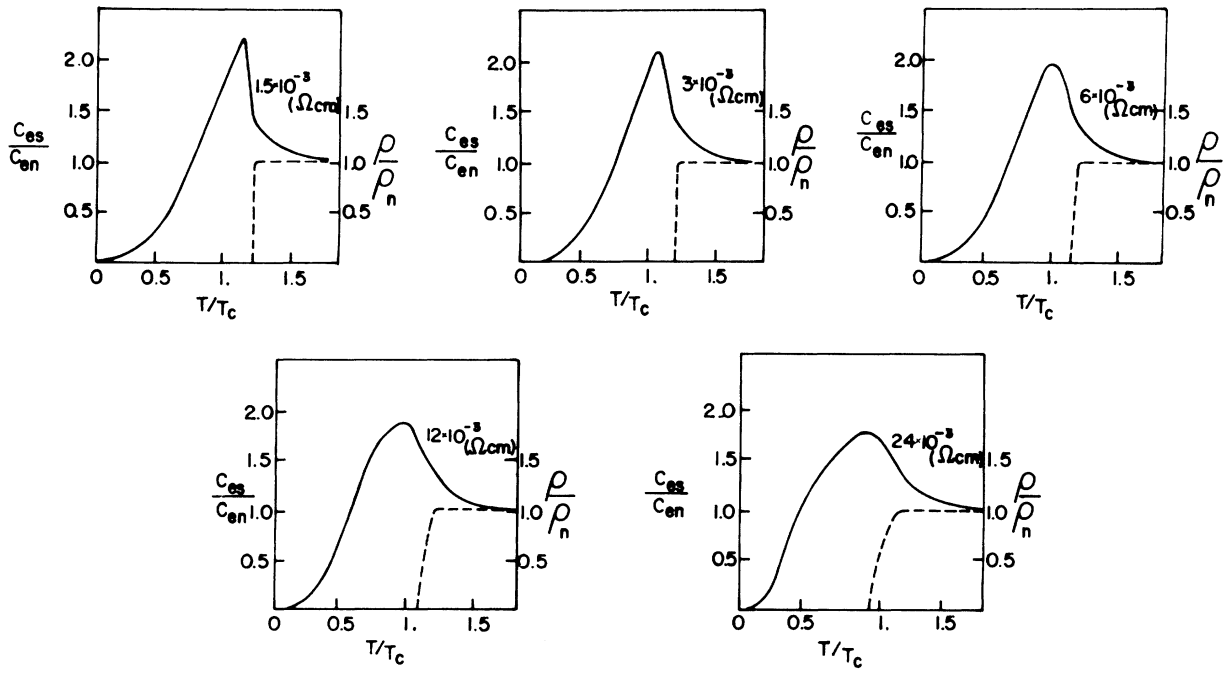

FIG. 3. Calculated curves of heat capacity and electrical conductivity as a function of reduced temperature for $\bar{\delta} = 0.1$ (about 150-Å grains).

ard deviation was used for the curves in Fig. 3.) In every case, we have found that the computed results are not sensitive to the details of the parameters chosen. That is, taking p_c as twice as large caused the fitted standard deviation to be about 40% of the mean value, to give the same characteristic as presented here. The same conclusion holds true for the cutoff criterion (1). Changing $k_B T$ to $2k_B T$ results in a relatively small change of the standard deviation, sufficient to yield the same results.

In Figs. 2 and 3, we also present the behavior of the electrical resistance as a function of temperature. In our model we have a bond percolation in which the bonds resistance has a normal distribution and part of the bonds are shorted (i.e., their conductivity is infinite). Percolation calculations of this type of problem were accomplished only in the case of simple cubic lattice with all the connected bonds possessing the same resistance.[32] We have used this data, again relying on the universality argument,[18] to construct the conductivity σ of a RCP structure as a function of p. This was done by shifting the $\sigma(p)$ curve to $p_c = 0.125$. Of course, this is just a crude estimation, but it may give a qualitative description of the electrical transition; e.g., the width of the electrical transition (defined as the temperature interval over which the resistance rises from 10% to 90% of its final value) increases as ρ_n becomes larger. For $\rho_n = 5.6 \times 10^{-3}\,\Omega$cm the width is $0.16 T_c$ (see Fig. 2). This fits quite well the experimental data of Ref. 19.

IV. DISCUSSION

The model presented here transforms the system of interacting grains into a system which consists of two parts: an infinite cluster and isolated grains. The interactions among the isolated grains are neglected and therefore the problem can be handled in a relatively simple way.

The basic postulate is that randomness of the coupling in granular superconductors is essential for the description of the onset of superconductivity. That is, we claim that superconducting order is achieved by a percolation process rather than due to a coherent phenomenon. The use of existing percolation theory results, enabled us to compute the specific heat of granular samples, and as was shown above, the agreement with the experimental data is rather good. In addition, we were able to calculate qualitatively the behavior of the electrical resistance close to the electrical transition. It was found (see Fig. 4), that the width of the electrical transition increases with ρ_n. Moreover, our results explain the observed difference between the electrical transition temperature (defined as the point where the resistance is reduced to half its value) and the temperature at which the specific heat is maximal. This difference is attributed

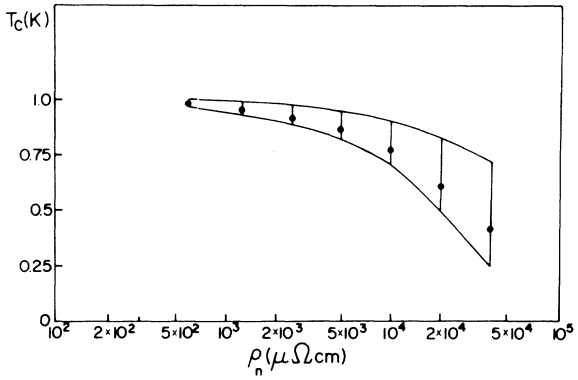

FIG. 4. Calculated curve of T_c normalized to one as a function of ρ_n (the normal-state resistivity). The upper and lower lines represent the points where the conductivity falls to 90% and 10% of its normal-state value, respectively. The dots are the points where the resistivity falls to half its normal-state value.

to the fact that the resistance disappears when the percolation threshold p_c is reached, while the peak in the specific heat just starts there to buildup. The difference increases with ρ_n, as was observed experimentally (see Fig. 1), and at the same time the specific-heat anomaly is decreased. For $\rho_n \gtrsim 10^4 \times \mu\Omega$ cm the anomaly in the specific heat is washed out, but there is still an electrical transition, of width $0.2 T_c$.

In our model it is assumed that the interplay between the Josephson-coupling energy and the thermal energy determines whether the bond between two grains is connected. Making this assumption, we have ignored effects of grain charging.[33,34] Abeles *et al.*[34] have calculated the charging energy and found that for $\rho_n = 10^3\,\mu\Omega$ cm it is three orders of magnitude higher than the Josephson energy. In order to explain the fact that in such samples there is an electrical transition, they suggested that only junctions with extremely small R_n [see Eq. (1)] do participate in the formation of the infinite cluster. However, a quantitative inspection of this idea reveals that ρ_n must be at least three orders of magnitude higher than the resistivity of 12.5% of the junctions. There is no way to accomplish this unless we choose a very unsmooth resistance distribution. Moreover, calculation of the electrostatic energy at the vicinity of the transition,[15] based on conductivity data above T_c, leads to a result which is four orders of magnitude smaller than the one computed from Abeles *et al.*[33,34] It was thus concluded[15] that electrostatic effects cannot be important in specimens with $\rho_n \lesssim 5 \times 10^3\,\mu\Omega$ cm. This may be attributed to the fact that such samples possess a high tunneling rate and therefore the grains cannot be considered as isolated capacitors.

The situation is changed for higher values of ρ_n. It was experimentally observed that in every granular

system, superconductivity is absent for high enough values of ρ_n.[19,35–37] In Fig. 4, we have presented the results of our model for the width of the electrical transition as a function of ρ_n (grain's size ~ 30 Å). These are in qualitative agreement with experimental data, up to $\rho_n \sim 40\,000\ \mu\Omega$ cm, without invoking charging mechanism. (See Fig. 8 in Ref. 19.) According to our model, a junction becomes connected once E_j exceeds $k_B T$. This means that for any value of ρ_n there would always be a temperature below which superconductivity appears. But when the metal concentration is low (near and below the percolation threshold for a metallic behavior), the charging energy cannot be ignored.[38] In this region E_j decreases as the concentration is lowered, while the charging energy increases. Once the latter exceeds about $10E_j$, superconductivity disappears.[39] Indeed, the disappearance of superconductivity is always associated with a negative slope[19,35] of R vs T, and always coincides with an increase in the negative value of the slope.[40] This is further supported by measurements performed[41] on Al-Ge.

In calculating the order parameter in a single grain [see Eq. (1)], we have used the (bulk) BCS form. That is, we have neglected altogether critical fluctuations. These are important in small grains.[1] The inclusion of fluctuations in the present model must be carried out self-consistently. The reason is that the fluctuations depend on the grain's size. As the grains are coupled together and form clusters, the effective grain's size changes and this, in turn, affects the fluctuations. This limitation of the model is related to another point overlooked in the calculations. Namely, the neglect of the contributions arising from finite clusters, which do not belong to the infinite cluster. (But note that the specific heat of such clusters was not calculated so far, because of their uneven structure.[18]) A more complete theory should take into account the finite clusters, and deal self-consistently with the effect of the fluctuations [using, e.g., $\Delta(T)$ of an isolated grain[1] with a suitable effective size]. It is expected that these corrections will cause the computed curves to be more rounded and smeared near T_c. In addition, it should be stressed that our results are based on bond percolation. In the case of strongly coupled granular specimens, for which there exist specific-heat measurements[11,13] one should use site percolation. The main obstacle preventing such calculation is the lack of quantitative information concerning the relation between the transition temperature and the grain's size.

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