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# Destruction of superconductivity in granular and highly disordered metals

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The destruction of superconductivity in granular and highly disordered metals is discussed in the light of the modern picture of the metal-insulator transition induced by Anderson localization. For small grains superconductivity is lost when localization sets in. Systems composed of large grains may phase lock at a temperature, $T_C$, much smaller than the $T_C^0$ of the clean metal. $T_C$ is estimated as a function of the appropriate parameters and the results are shown to be consistent with existing experiments.

## I. INTRODUCTION

The question of how superconductivity is weakened and eventually destroyed in highly resistive granular metals has recently attracted considerable attention.[1–14] In the limit where the grain size becomes as small as the typical interatomic distance, the granular metal can be regarded as amorphous or glassy—a situation which is itself of interest. Looking at granular metals in this limit might be a useful new way of considering the latter problem. The qualitative understanding of the normal metal-to-insulator transition has recently undergone significant advances. The scaling theory of the Anderson localization transition,[15–18] augmented by electron-electron Coulomb interaction effects[19–21] is capable of explaining qualitatively how the normal granular metal becomes an insulator (at $T=0$, and a poor conductor at finite low temperatures) when, say, the insulating intergrain barriers are made thicker. For the superconducting transition, the Josephson intergrain coupling and its competition with both the thermal fluctuations and the Coulomb energies,[22–27] in the appropriate regimes, become important. In this paper we shall consider the superconducting transition in the context of the modern metal-nonmetal transition picture. Our main finding is that for a conductor composed of small grains,[6,28] superconductivity is lost along with normal metallic conduction. However, for large grains, a superconducting transition in a semiconducting system which would otherwise become an insulator as $T\to 0$, is possible

The disorderer which exists in these systems is taken into account in our picture on the same level as in the scaling theory of localization. Percolation-type effects[29,30] for systems which may be viewed as macroscopic mixtures of conductors and nonconductors are not considered. Very close to the metal-insulator transition, percolating systems are believed[31,32] to cross over to quantum localization-dominated behavior, which should be covered by our treatment.

## II. NORMAL METAL-INSULATOR TRANSITION IN GRANULAR SYSTEMS

In this section we discuss the application of the scaling theory of localization to the granular metal-nonmetal transition. In addition to the grain size, $L$, the granular normal metal is characterized by its temperature, $T$, and by at least three possibly important energy scales, all of which are randomly varying throughout the system. These are the following:

(1) The typical separation between energy levels of a single grain[33] at the Fermi energy, $w_L$,

$$w_L \cong \left(L^3 \frac{dn}{dE}\right)^{-1} = \left(\frac{dN}{dE}\right)^{-1} , \tag{1}$$

where $dn/dE$ is the density of states per unit volume at the Fermi energy of the grain meterial. $w_L$ is also the typical mismatch in energy levels of two grains around the Fermi energy.

(2) The typical coupling matrix element, $t_L$, between states in neighboring grains. It is convenient to characterize this by a characteristic energy (Refs. 33, 18, 25) $V_L$, for electron transfer between neighboring grains

$$\frac{\hbar}{\tau_L} = V_L = 2\pi \frac{\langle |t_L|^2 \rangle_{\rm av}}{w_L} , \tag{2}$$

where $\langle |t_L|^2 \rangle_{\rm av}$ is an appropriate average of $|t_L|^2$, and $\tau_L$ is the lifetime of an electron in a given grain against tunneling to a neighboring one. The second equality is obtained from the Fermi golden rule and its validity is determined by that of the latter.

(3) The charging energy, (Refs. 22-25, 34, and 35) $E_{CL}$, that is involved with the transfer of an electron

between neighboring grains

$$E_{CL} = e^2/2C \ , \tag{3}$$

where $C$ is the effective intergrain capacitance determined both by geometry and the *appropriate dielectric constant.*

It is useful to note that the intergrain resistance is given by[18,25] the tunnel junction formula.

$$\frac{1}{R_L} = \frac{e^2}{\tau_L}\frac{dN}{dE} \cong \frac{e^2}{\tau_L w_L} = \frac{e^2}{\hbar}\frac{V_L}{w_L} \ . \tag{4}$$

This constitutes the well-known relation[33] between the dimensionless conductance, $g_L = \hbar/2e^2R_L$, and the Thouless number, $V_L/w_L$. A further energy scale, which is not independent of the previous ones, is related to the integrain resistance-capacitance ($RC$) time constant[34]

$$\frac{\hbar}{RC} = 4E_{CL}g_L \ . \tag{5}$$

The key quantity which determines whether the granular system is metallic or semiconducting is the dimensionless conductance $g_L$. According to the scaling theory of the Anderson localization transition,[15] there exists a critical value of the microscopic $g_L$, $g_C$, such that the system is metallic or insulating (at $T=0$) depending on whether $g_L > g_C$ or $g_L < g_C$, respectively. This, in fact, means that the corresponding critical value of the normal resistivity $\rho_C$ is up to a numerical constant of order unity[18]

$$\rho_C = \frac{\hbar}{e^2}L \ , \tag{6}$$

which agrees with a result of theoretical arguments by Abeles and Sheng[34] and Adkins.[35] This value of $\rho_C$, unlike the one obtained from usual maximum metallic resistivity arguments, agrees with experiment in both order of magnitude and dependence on $L$. The latter was checked for a few orders-of-magnitude variations of $L$ in several materials.[35] For the limit of an amorphous metal ($L \to a$), $\rho_C$ becomes of the same order of magnitude as the Mott maximum metallic resistivity.[36] For a thin film which constitutes a two-dimensional array of grains, the above condition implies that the critical value, $R_{\square,C}$, of the resistance per square, $R_\square$, is a numerical constant, $A$, times $\hbar/e^2 (\cong 4.1\ \mathrm{k}\Omega)$

$$R_{\square,C} = A\hbar/e^2 \ . \tag{7}$$

Values of $\sim 10$–$30\ \mathrm{k}\Omega$ for $R_{\square,C}$ are thus mentioned in the literature.[13,14] For an amorphous film of atomic thickness, $a$, such a value for $R_\square$ would imply a mean free path, $l \sim a$. We emphasize that the same condition that assured delocalization also makes the Coulomb interaction unimportant.[25,34]

For $g_L < g_C$, the system is macroscopically an insulator at $T=0$, and its finite conductivity at finite low temperatures is determined by inelastic effects.[33] It appears that the latter are often dominated by electron-electron interactions,[19,20] which yield an inelastic mean free path, $l_{\mathrm{inel}}$ which is in many cases of the order of $l_{\mathrm{inel}} \sim \sqrt{\hbar D/kT}$, with $D$ the electronic diffusion coefficient. The temperature coefficient of the resistivity is obviously negative in the insulating phase and it also turns out[16,17] to be negative in the metallic phase near the transition, for $g_L > g_C$. When $g_L$ tends to $g_C$ from the metallic side, the zero-temperature conductivity, in three dimensions (3D), goes to zero as

$$\sigma(0) \sim \frac{e^2}{\hbar\xi} \ , \tag{8}$$

where $\xi$, the characteristic scale length of the transition, diverges as

$$\xi \sim L\left(\frac{g_C}{g_L - g_C}\right)^{\nu} \tag{9}$$

with $\nu$ a characteristic exponent[15] which is smaller but on the order of unity. Equation (8) is also approximately valid once the temperature is low enough so that $\xi \ll l_{\mathrm{inel}}$. When $l_{\mathrm{inel}} \ll \xi$ (but for temperatures still so low that, e.g., the "Fermi smearing" can be neglected) $\sigma$ is given by[17]

$$\sigma(T) \sim \frac{e^2}{\hbar l_{\mathrm{inel}}} \ , \tag{10}$$

yielding a negative temperature coefficient of resistance (TCR) although still in the metallic phase.

The $T=0$ system behaves strictly like a metal only for lengths larger than $\xi$, while on microscopic scales ($L \ll \xi$) the dependence of the conductivity on the length scale $L$ does not follow the macroscopic (Ohm's) law. Moreover, on the latter scales, the insulator and the conductor behave similarly, the difference between them is mainly manifested for $L \gg \xi$.[16] Similar remarks also hold for the dielectric constant.[21,37] The strong metallic screening, $\epsilon_q \propto 1/q^2$, for wave numbers $q \ll 1/\xi$ holds only in the conducting phase, while $\epsilon_q \to \epsilon_{q=0} = \mathrm{const}$ in the insulating phase. For $q \gg 1/\xi$ both phases behave similarly. From this it follows that the macroscopic dielectic constant $\epsilon_{q=0}$ diverges as one tends to the metal-insulator transition, $g_L \to g_C$, from the insulating side. The latter divergence[38] must occur due to continuity considerations. It has been shown to exist in other metal-insulator models and has been argued to be a general phenomenon in such systems.[39] On the other hand, the dielectric screening on the scale $L$ (the grain size) is strong only in the metallic phase and the insulating phase near the transition, as long as $\xi \gg L$. Once the insulating phase is far enough from the transition, so that $\xi$ is no longer much larger than $L$, the appropriate dielectric constant on the scale $L$ will approach the finite macroscopic

dielectric constant of the insulator. We shall see that this circumstance will turn out to be of decisive importance for granular superconductivity. $\epsilon_{q\sim 1/L}$ determines the intergrain charging energy, which under the appropriate conditions is crucial for determining whether the system can be superconducting.

For the case of effectively two-dimensional (2D) films—which certainly includes a 2D array of grains and also thicker films, provided their thickness $d$ is much less than both $\xi$ and $l_{\text{inel}}$—the situation is somewhat different. The localization theory for noninteracting electrons for any finite amount of disorder appears to predict[15] that all the states are always localized, and the system is thus always an insulator at $T=0$. Practically speaking, however, there is a rather sharp crossover between strong localization behavior, for $\rho_L \gg \rho_C$, to weak localization, for $\rho_L \ll \rho_C$. In the latter case the localization length becomes quickly astronomically large[40] and the localization is obviously almost irrelevant. One is then always in the $l_{\text{inel}} \ll \xi$ range and $\rho(T)$ displays a weak (negative TCR) logarithmic dependence on temperature.[15,40] This should be contrasted with the $\rho_L \gtrsim \rho_C$ case, where the localization length can become short, including the possibility of $\xi < l_{\text{inel}}$, where strong localization effects may become observable. Thus the 2D case, while very different in principle, may behave in practice as if it had effectively a "metal"-insulator crossover around $\rho_L \sim \rho_C$. Thus we shall assume that our subsequent discussion for the 3D case has a qualitative validity also for 2D. This clearly needs further justification.

## III. SUPERCONDUCTING TRANSITION IN THE GRANULAR SYSTEM

When considering the superconducting metal, a further coupling energy which may be relevant for weakly coupled grains is the Josephson coupling energy, $E_J$, which is temperature dependent and given by

$$E_J(T) = E_J(0)\frac{\Delta(T)}{\Delta(0)}\tanh\frac{\Delta(T)}{2k_BT} \quad , \tag{11a}$$

where $\Delta(T)$ is the temperature-dependent energy gap of each of the superconductors constituting the junction (they are assumed, for simplicity, to be the same) and[41]

$$E_J(0) = \frac{\pi}{4}\frac{\hbar}{e^2}\frac{\Delta(0)}{R_n} \quad , \tag{11b}$$

$R_n$ being the normal resistance of the junction, in our case $R_n = R_L$.

In order that the single grain will behave roughly like a bulk superconductor, and will exhibit an effective gap, $\Delta$, its size, $L$, must be large enough[6,28] so that

$$w_L \ll \Delta, \text{ i.e., } L \gg L_0 \quad , \tag{12}$$

where

$$L_0 = \left(\frac{\Delta}{dn/dE}\right)^{1/3} \tag{13}$$

defines the characteristic size scale for the grains, which are referred to as "large" or "small" depending on whether $L \gg L_0$ or $L \ll L_0$; $L_0 \sim 30$ Å for typical metals.

The large number of relevant parameters, together with the disorder, make the granular superconductor problem rather complex. Previous treatments of the problem have invariably neglected one or two of the above parameters and were thus valid only over limited ranges of the latter. Here, we should like to draw on the recently accumulating understanding of the dirty normal metal-to-insulator transition, to try to construct a fuller, albeit qualitative, picture of granular and amorphous superconductivity and its destruction by a strong enough disorder.

We first note that Eq. (7) also implies that, from Eq. (11b), $E_J(0)$ is on the order of $\Delta(0)$. Since the relevant coupling that determines the superconducting $T_C$ in the Josephson-coupled grain model is $ZE_J$, it is clear that as long as the material is a conductor ($g > g_C$) its Josephson coupling is enough to support superconductivity at temperatures not too low compared to the material $T_C$. So that one already has at this stage the important result that on the metallic side ($g > g_C$) $T_C$ is not depressed substantially.

However, the above discussion neglects the Coulomb charging energy that has been pointed out[22,23] to be detrimental to the Josephson coupling, provided that

$$ZE_J \lesssim E_{CL} \quad . \tag{14}$$

The transition temperature is of the order of $ZE_J$ only in the "classical" limit $E_{CL} \equiv E_C \ll ZE_J$. When $E_C$ increases it will depress $T_C$ once the above inequality is not satisfied, and, in fact, $T_C$ should vanish once $E_C/(ZE_J)$ is large enough.[22–25] Simanek[26] has recently treated this problem in the mean-field theory, which should give $T_C$ correctly to within a numerical factor in 2D and certainly in 3D. We have repeated his calculation, keeping only wave functions that are $2\pi$ periodic in the phases of the grains superconducting order parameter. We find that the latter restriction changes Eq. (6) of Ref. 26 for $x \equiv E_C/2kT_C$ in terms of the parameter $\alpha \equiv ZE_J/E_C$ to the following equation:

$$\alpha\frac{1-2\sum_n e^{-xn^2}/(4n^2-1)}{1+2\sum_n e^{-xn^2}} = 1 \quad . \tag{15}$$

$T_C/ZE_J$ as a function of $\alpha$, obtained numerically from Eq. (15) is shown in Fig. 1.[27] We note that the classical limit, $kT_C = ZE_J$ is correctly obtained when

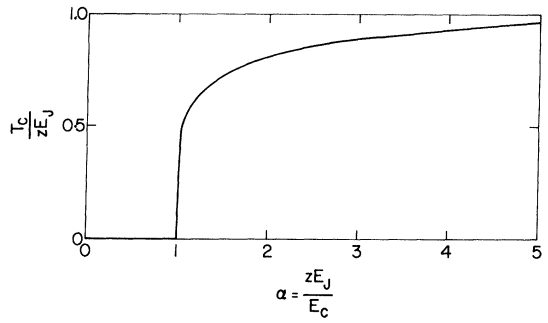


FIG. 1. $T_C/ZE_J$ plotted as a function of $\alpha = ZE_J/E_C$ from Eq. (15). Note that $T_C/ZE_J \to 1$ as $\alpha \to \infty$ and $T_C/ZE_J \to 0$ as $\alpha \to 1$ [see Eq. (16)].

$\alpha \to \infty$. $T_C$ is depressed for finite $\alpha$ and vanishes when $\alpha \to 1$. It should be noted that there is no reentrant normal phase in this model. An interesting feature of Fig. 1, which may have to do with the sharp dependence of $T_C$ on $\rho$ that is observed experimentally,[2,3] is the extremely fast drop of $T_C$ to zero around $\alpha = 1$. In fact, for $\alpha \to 1$ [$(\alpha - 1) << 1$], $T_C$ vanishes as

$$\frac{kT_C}{ZE_J} = \frac{2}{\alpha \left| \ln \frac{3}{8}(\alpha - 1) \right|} \ . \tag{16}$$

We are now in a position to estimate the superconducting transition temperature of a granular system if $E_J$ and $E_C$ are known. Typical values of $E_J$ are easy to estimate from the normal-state-barrier conductances; it is more difficult, however, to estimate $E_C$, due to the effective values of the dielectric constant being poorly known. It has turned out that $E_C$ was typically less[24] than what naive estimates would have given. Instead of endeavoring to estimate $E_C$ better, we now point out that, as mentioned before, for a metal as well as for an insulator which is close enough to the limit,[6,7] the effective screening is strong enough on the scale $L$. Thus the Coulomb energy on the scale of the grain size is *screened out* and one need not worry about the charging energy. This is also consistent with the macroscopic argument[34] of comparing $\hbar/(R_L C_L)$ with $E_{CL}$. Using Eq. (5), the former is larger for $g_L \gtrsim O(1)$. To discuss what happens when $g_L \lesssim g_C$, we note that deep enough in the insulating phase, the dielectric constant does *not* provide screening on a scale $L$, so that $E_{CL}$ has to be taken into account. The behavior now depends on the grain size $L$. Notice that the condition that Coulomb effects which should not be crucial in the normal metal is[25]

$$E_{CL} \lesssim ZV_L \ , \tag{17}$$

while the same condition for the superconductor is the inverse of[10]

$$E_{CL} \lesssim ZE_J \sim Zg_L \Delta(0) \sim ZV_L \frac{\Delta(0)}{w_L} = ZV_L \left( \frac{L}{L_0} \right)^3 \ , \tag{18}$$

where we used Eqs. (11b), (1), (13), and (4). Thus it should be emphasized that Eq. (18) may be less restrictive than the appropriate condition for the normal metal[25] for large grains. We now discuss separately the cases of small and large grains.

### A. Large grains

Here one may have $ZV_L \lesssim E_{CL} << E_J$ if $g_L \lesssim O(1)$. This means that the normal metal is insulating at $T \to 0$, but that the Josephson coupling is strong enough to restore superconductivity. The $T_C$ of the latter is determined by $E_C$ and $E_J$. It is roughly given by

$$kT_C \cong ZE_J(T_C) \quad \text{for } E_C << E_J \ , \tag{19}$$

and, more generally, by Eqs. (15) and (16) and Fig. 1. $T_C$ can be much lower than the $T_C$ of the bulk material, if the grains are well enough separated. This "insulator"-superconductor transition is between superconducting units and should thus still be similar to the phase-locking transition discussed in Refs. 4–6 and it is similar to the phase transition in the $xy$ model. When the intergrain resistance $R_L$ is increased, $E_J$, and hence $T_C$, decreases. $T_C$ finally vanishes when $ZE_J$ becomes comparable to $E_{CL}$. Note, however, that the limit of 30 000 $\Omega/\square$, often mentioned as a limit for whether a 2D system can be superconducting, does not have any basis on these arguments, and in fact data show[1] that superconductivity can exist when $R_\square > 30\,000\ \Omega$. This order of magnitude for $R_\square$ (or $R_L$ in 3D) just marks the beginning of a substantial decrease of $T_C$ of the granular system below the "$T_C^0$" of the grain material, with increasing $R_\square$.[42] Note that the grains display a smeared transition around the latter $T_C^0$. For $R$ sufficiently larger than the critical value, one expects the transiton to occur as follows. Around $T_C^0$ the grains go superconducting (with a small "paraconductivity" above $T_C^0$).[42] Below $T_C^0$ the resistance is dominated by the intergrain resistances. In an ordered grain array the resistance should decrease with temperature, due to fluctuations in the Josephson coupled 2D or 3D $xy$-like system, and vanish at the "real" phase-locking $T_C$. Of course, since real granular systems are disordered and may show percolation-type effects, much of the decrease in the resistance between $T_C^0$ and the final locking transition $T_C$ may be due to these effects.[43] Thus, e.g., clusters that are more strongly coupled may go superconducting before the rest of the system. With a small disorder, such as

may exist in ordered arrays,[44] these effects should become irrelevant near the $xy$ transition.[45] In experiments[1,43] with $R_\square > 30$ k$\Omega$ careful low-temperature and current-dependence[1,9,43] studies are required to establish the phase locking $T_C$. The fact that drops in the resistivity of more than two orders of magnitude do occur in such systems strongly suggests that $T_C$ has at least been approached.

### B. Small grains

Here superconductivity is destroyed when $g_L$ is decreased below $g_C$ due to two effects, the increase of $E_C$ due to the weakening screening, as discussed above, and the onset of localization. The latter restores the single-grain-level discreteness which destroys superconductivity even in the single grain. In addition, the total density of states at the Fermi energy is reduced,[12,19–21] which also decreases $T_C$. From Eqs. (17) and (18) it follows that the condition for superconductivity, Eq. (18), is strongly violated when the normal conductivity is just destroyed due to Eq. (17) becoming invalid. Thus $T_C$ should reduce very sharply and *there will be no superconductivity for small grains once $R_L$ is greater than a few $\hbar/e^2$*, probably $\sim 10$ k$\Omega$. The reason for the sharp decrease of $T_C$ with increasing $R_L$ is not only the localization and density-of-states effect but mainly the effect of the charging energy $E_{CL}$ which increases sharply when $g_L$ is decreased, as discussed below. This sharp increase, coupled with the fast drop of $T_C$ to zero near $E_C/(Z E_J) = 1$ [Eq. (16) and Fig. 1] is responsible for the vanishing of $T_C$ near $\rho_C$ in 3D,[2,3] or $R_{\square,C}$ (Ref. 1) in 2D. The same physical effects should also yield the $T_C$ decrease using a microscopic theory which takes into account the density of states[46,47] and the Coulomb interactions.[48] Notice that in contrast to the large-grain case, there is *no two-stage transition here.* The superconducting $T_C$ simply should decrease sharply to zero.

## IV. COMPARISON WITH SOME EXPERIMENTAL RESULTS

As an illustration of the principles developed in Sec. III we consider some old experimental results on lead films that are discussed in Ref. 1. In this work the transition was studied for both very small grains where $L < L_0$ and large grains where the particle size $L$ is $> L_0$. Hence in the small-grain case isolated grains would lose their superconductivity and would have no transition, whereas in the large-grain case the particles can be individually superconducting. This leads to different kinds of transition curves which are discussed below. Essentially in the small-grain case there is one universal transition curve that scales with $R_\square$, whereas in the large-grain case there is a transition for the grains and then a phase-locking transition at a lower temperature.[42]

### A. Small grains

The case of the $T_C$ of strongly coupled small grains in the 2D limit was studied extensively in Ref. 1. By depositing Pb and Bi on either previously deposited SiO or Ge it was possible to achieve continuity in films whose thickness was on the order of 10 Å. It was also found in this work that $T_C$ correlated with the resistance per square, and that at an $R_\square$ of about 8000 $\Omega$ a transition temperature was no longer evident. The development of the transition from the localized state as $R$ decreases is shown in Fig. 2. Notice that at $R_\square \sim 10\,000$ $\Omega$ activated conduction is still evident with a possible trace of superconductivity at the lowest temperature, and finally at $R_\square \sim 6000$ $\Omega$ a complete transition is evident. Hence at a few times $\hbar/e^2$ superconductivity vanishes in the 2D limit as already mentioned. The film thickness when the transition is observed was estimated to be about 10- to 20 Å thick. In the above discussion we have concentrated on the high $R_\square$ regime and have mentioned the effect of localization on $T_C$. However we em-

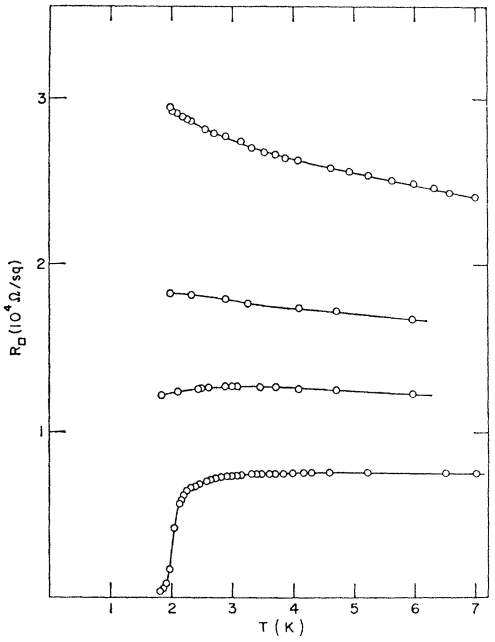


FIG. 2. Resistive behavior as Pb film is built up. First stages show nonmetallic conduction where film resistance increases as temperature is decreased. As more metal is deposited, the resistance decreases and metallic behavior and superconductivity appear. In the middle two curves, there is nonmetallic conduction in the normal state and the beginning of a superconducting transition. When the full transition appears, the film thickness, as determined by the Sloane thickness monitor, is usually from 10 to 20 Å.

phasize that $T_C$ is also found to decrease in thin films even where $R_\square$ is low and this has been the subject of much work where the depression of $T_C$ was thought to be a surface effect[1,49] which would mainly depend on thickness and microstructure. We emphasize that in the regime where continuity is first achieved the dependence of $T_C$ on $R_\square$ is the dominant factor. In the early experiments[1] two films which were evaporated simultaneously onto different substrates, under the same conditions, had different $T_C$ in the regime where continuity was first attained, and the $T_C$ correlated with $R_\square$. Since the thickness was the same, the dependence on $R_\square$ is convincingly shown.

Besides the development of superconductivity, as the conductivity changes from activated to metallic conduction shown in Fig. 2, the data in Fig. 3 show in addition the ideal nature of the transition. The solid lines are fits of the Aslamazov-Larkin (AL) theory to the transitions and it can be seen that they are extremely ideal and that $T_C$ and the transition width correlate with $R_\square$. The deviation from the mean-field AL result and the phase locking to zero resistance in the low-temperature regime has already been discussed. The main point we wish to emphasize here is the similar nature of the curves where the tail region is a given fraction of the AL width,

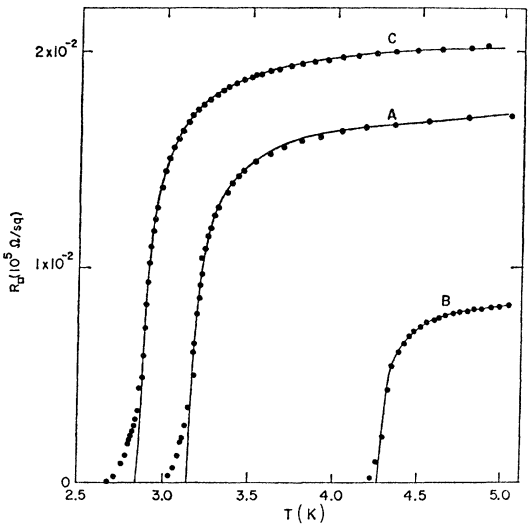


FIG. 3. Transition curves for thin Pb films on SiO. Curve A is film as initially deposited on ~20 Å of previously deposited SiO. Thickness of film $A \sim 10$ Å. Curve B is film after an additional 3 Å of Pb was deposited. Curve C is film after annealing overnight to $N_2$ temperature at pressure of about $5 \times 10^{-6}$ Torr. Curve C was also taken at a factor of 10 less current than the usual measuring current of $3.5 \times 10^{-6}$ A, and there was no change in behavior. Hence, at our measuring currents, the transitions are essentially current independent. At $35 \times 10^{-6}$ A, the $T_C$ is shifted by ~0.03 K.

which is given by $\sigma_P/\sigma_N = \tau_0/\tau$, where $\tau_0 = 1.5 \times 10^{-5} R_\square$ and $\tau = (T - T_C^{AL})/T_C^{AL}$. $T_C^{AL}$ is the transition temperature estimated from the fit of the high-temperature data to the AL theory, and is given by the extrapolation of the solid-line fits to the data. The tail region defining the temperature interval from $T_C^{AL}$ to the zero-resistance point, $T_C$, is given previously[1,50] as $\tau_0 T_C^{AL}$; recently[51] this has been interpreted in terms of the Kosterlitz-Thouless theory.[52] Thus the width of the tail and the width of the high-temperature part both scale as $R_\square$ and as mentioned in Sec. III, there is no two-stage transition and the curves have a similar shape as $R_\square$ and $T_C$ change, as is shown in Fig. 3. The dependence of $T_C$ on $R_\square$ was established in these early experiments and from the previous discussion we now understand the drop of $T_C$ for high $R_\square$ to be due to the increased Coulomb energy $E_C$ compared to $ZE_J$ as localization occurs. Furthermore, it has already been mentioned that the absence of states near $E_F$ should also be included in an estimate of $T_C$. In the original work, the decrease of $T_C$ was estimated for states being excluded near $E_F$ and was estimated to be relatively small. However, it now appears that the combined effects of the Coulomb interaction and density-of-states change due to localization do approximately describe the observed behavior. The data in Fig. 2 show that superconductivity is destroyed and localization appears at the predicted value for $R_\square \sim 10\,000\ \Omega/\square$. In the 3D case, agreement with the theory here is also attained. The experimental results[2,3] show $T_C$ rapidly decreases at $\rho \sim 10^{-3} - 10^{-2}\ \Omega$ cm for samples with 30-Å grains. This compares reasonably with the value of $\rho_c \sim (\hbar/e^2)L \sim 10^{-3}\ \Omega$ cm. Furthermore, the sharp drop in $T_C$ in this regime is consistent with the behavior of Fig. 1.

### B. Large grains

In the previous case, the transitions scaled with $R_\square$ and had similar shapes with both high- and low-temperature regimes scaling with $R_\square$. In the case of large grains, this is no longer the case and the phase-locking $T_C$, where zero resistance occurs, can be significantly below the $T_C^0$ of the grains.[1,42,43,49] In Fig. 4, a typical transition for larger Pb grains, ~75 Å, is shown. If the coupling is weak, then $l_{\rm eff}$, the effective mean free path, related to the particle size and the transmission coefficient between grains, becomes small. Now $\xi_{\rm eff}^2 \sim \xi_0 l_{\rm eff}/\tau$. In the particle itself, the coherence length is defined in the usual way as $\xi_P^2 \sim \xi_0 l/\tau$, where here $l$ is the mean free path (mfp) of the grain material. If, now, $\xi_{\rm eff}$ is much less than $L$, and $\xi_P(0) > L$ then short-wavelength fluctuations may be ignored and the expression for the pair conductivity worked out previously[42] becomes $\sigma_P/\sigma_N = \tau_0 \xi_0 l_{\rm eff}/d^2\tau^3$. In Fig. 4 we show that the observed transition width of ~0.5 K is narrower than the AL

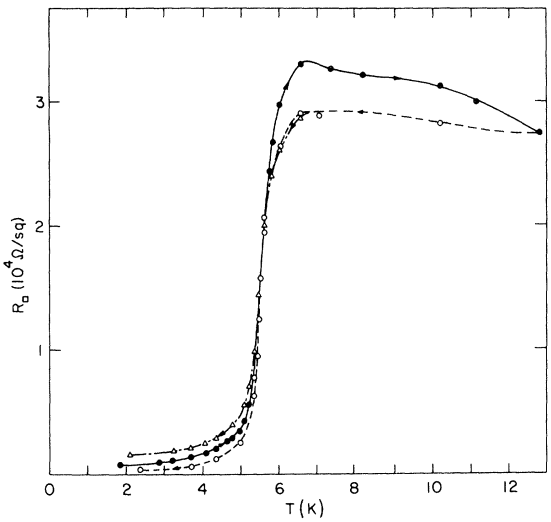


FIG. 4. Film resistance vs temperature for Pb deposited onto 20 Å of previously deposited LiF. Thickness of film is about 75 Å, width is about 0.45 mm. Δ— initial decrease of temperature; measuring current is 4 μA. ●— warming up; measuring current reduced to 0.1 μA. Change shown is due to the decrease of current and then annealing starting near 7 K. ○— cooling down again; measuring current 0.1 μA. The AL theory predicts $\tau_0 = \frac{1}{2}$, which gives a much broader transition than the curve shown here.

result; predicted as $\tau_0 \sim 1.5 \times 10^{-5} R_\square$, or about 0.5, and yielding a width of the transition at $\frac{1}{2}R_N$ of about 3 K. Note that the above expression for $\sigma_P/\sigma_N$ apparently overcorrects the AL result and makes the width too small. It may be that this result should be replaced by the result of the phenomenological theory[6] where $\sigma_P/\sigma_N \propto 1/\tau^2$. In any case, one can, in principle, derive a result for the high-temperature regime in a system composed of large grains. Note that even at $R_\square \sim 30\,000$ the high-temperature part of the transition is still sharp. However, now the phase-locking transition can be significantly less than $T_C$ and as long as $\tau_0 < 1$ it is still approximately given by a simple relationship like $\tau_0 T_C^0$, which in this case means that the phase-locking transition given by Eq. (19) is now about 3 K below $T_C^0$. When $\tau_0 \sim 1$ the phase-locking $T_C$ must be estimated for $E_J$ given in Eq. (11b) and $E_c$ using Eq. 15, 16, and Fig. 1. Note that even for $R_\square \sim 50$ kΩ a sharp high-temperature transition is observed down to a few percent of $R_N$. Whether there is complete phase locking in these samples at some lower temperature remains unclear. However, at least in principle, there appears to be no reason why this cannot happen. This high-resistance regime in granular Pb has been studied recently by Hebard[43] who finds that above $R_\square \sim 15\,000$ Ω, $T_C$ decreases faster than predicted by the Kosterlitz-Thouless[52] theory and he attributes this to the effects of localization.

## V. CONCLUSIONS

To summarize our qualitative predictions, both large- and small-grain systems will become semiconducting for $g_L < g_C < 1$ (and should exhibit a negative TCR even for a small range above $g_C$). For small grains, superconductivity is concomitantly lost, while large grains can exhibit a "semiconductor-superconductor" transition, governed by the interplay of $kT$, $E_J$ and $E_C$. For large grains, superconductivity can exist for very large $R_L$ and there should be no "30-kΩ" limit.

These simple predictions appear to qualitatively explain known experiments on granular systems. The only further effect which sometimes may be relevant can occur in cases where the structure is such that classical percolation may play an important role.[29,30,44] Even then, quantum effects are expected[31,32] to be dominant near the transition.

In this note we have discussed the 3D (or thick-film) and effectively 2D (thin-film) cases. Similar considerations apply in both cases and $R_{\square,C}$ is of the same order of magnitude as $R_{L,C}$. For extremely thin layers (and even more so for quasi-1D threads) stronger effects should occur due to the decreased screening,[20] due to the restricted dimension even in the ordered metal as well as from the tendency to form localized states.

We mention that we have recently become aware of the work by Efetov[53] who arrived at similar models from a microscopic approach and has discussed the temperature dependence of the charging energy which is neglected here.

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