Onset of Superconductivity in the Two-Dimensional Limit

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The onset of superconductivity in homogeneous ultrathin films is found to occur when their normal-state sheet resistance falls below a value close to $h/4e^2$, the quantum resistance for pairs. The data further suggest that in the $T \rightarrow 0$ limit such films are either superconducting or insulating. The existence of a threshold in systems which are not granular implies that its explanation involves more general arguments than those which follow from the modeling of films by Josephson-coupled arrays.

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Since the appearance of the theory of localization[1] and its predictions for the behavior of the conductivity of disordered metallic systems, the interplay between superconductivity and localization has been the subject of intensive study.[2] Although there is a wealth of data, and considerable theoretical work, few quantitative conclusions have been reached regarding the nature, or even existence, of a macroscopic quantum phase-coherent state in systems where the electrons are localized. Of particular interest are two-dimensional systems, as theory predicts that they are localized for any amount of disorder.

Thin films, prepared by deposition onto cold substrates, are particularly advantageous for the study of localization phenomena because the crucial parameter, the sheet resistance R, can be continuously varied by incrementing the thickness only slightly. In studying such films deposited onto glass substrates, quasireentrant superconductivity, or a local minimum in $R(T)$ near the bulk transition temperature, was found to be the precursor to a zero-resistance state as the sheet resistance was decreased.[3] Careful examination of the onset of zero resistance in films of a number of different metals showed that it always occurred when the normal-state resistance was close to a threshold value $h/4e^2 = 6.45$ kΩ.[4] The films, which are believed to consist of metallic grains coupled by tunneling, exhibited no substantial depression of their superconducting transition temperatures from bulk values.

Theories explaining the resistance threshold model the films as arrays of tunneling junctions of very small capacitance. Because of the large charging energies of the junctions, quantum fluctuations of the phase of the superconducting order parameter on the various sites in the array result in finite resistance below T_c. The quenching of these fluctuations gives rise to superconducting behavior. There are two competing theoretical approaches to the description of the suppression of these zero-point fluctuations. In one approach, damping of the fluctuations is realized by coupling the macroscopic phase variable to dissipative degrees of freedom.[5] In the other, the virtual tunneling of quasiparticles acts to substantially reduce the charging energy and therewith the quantum phase fluctuations.[6] Within the context of these two approaches, the normal-state sheet resistance can be regarded as the control parameter for the appearance of superconductivity at low temperatures. A threshold value of R of the order of $h/4e^2$ is found in the limit of very small capacitance. These ideas relating to films have received substantial confirmation in recent experiments on both random and artificially constructed regular arrays.[7]

Other thin-film systems prepared in a similar fashion, but deposited onto Ge substrates, do not exhibit the quasireentrance phenomenon.[8] In these films, which are believed to be homogeneous and microscopically disordered, there is a significant suppression of T_c from its bulk value which has been attributed to the enhancement of the Coulomb interaction.[9]

In this Letter we present the results of very detailed measurements of the onset of superconductivity determined from the thickness dependence of the resistance versus temperature, $R(T)$, of thin films of Bi and Pb deposited onto Ge substrates. A suppression of T_c is found, and no quasireentrance is seen down to a temperature of 0.45 K. However, a resistance threshold occurring at a value close to $h/4e^2$ is observed.[4] The threshold, rather than being associated with the onset of zero resistance as was observed in granular films, appears as a separatrix between sets of $R(T)$ curves which exhibit insulating or superconducting behavior in the $T \rightarrow 0$ limit. These new observations imply that arguments somewhat more general than those previously applied to granular thin-film systems may be required to explain the onset of superconductivity in ultrathin films.

Films were grown by the vapor deposition of metals onto liquid-He–cooled substrates, a technique which was pioneered by Shal'nikov,[10] and later employed extensively by Buckel and co-workers.[11] The substrates were first coated with a 6-Å-thick layer of Ge, which was also deposited at low temperatures, as it was found a number of year ago that extremely thin (submonolayer thick) conductive films could be grown this way.[12] These films, in contrast with those grown on glass, or glazed ceramic substrates, which almost certainly consist of clusters or grains in the early stages of growth, are believed to be continuous and homogeneous. The reason for this is that an onset of measurable conductance is found when they are extremely thin. However, it is important to note that detailed morphological studies have never been carried out on such systems for obvious technical reasons, and it is not certain what role the Ge underlayer plays in the conduction process. The Ge underlayer may not be inert in regard to the superconductivity of the thin films deposited on it as Dwir and Deutscher[13] have recently shown that a sandwich of Au between two Ge layers can be a superconductor. The films are deposited *in situ* using commercial Knudsen cell sources, which permit precise control of deposition rate and thickness. The film thicknesses are nominal. They are computed from the frequency shift resulting from a mass of metal deposited onto a quartz-crystal oscillator, together with the effective exposed area of the crystal, and the density of the deposit, assumed to be that of the bulk metal.

The onset of superconductivity was studied in both Pb and Bi films grown in the above manner. In the Pb films measurable conductance was first observed at a nominal thickness of only 1.86 Å. Evidence of superconductivity, in the form of a downturn in $R(T)$, with T_c suppressed below the measuring limit, was observed in a 3.28-Å-thick film. For Bi, the first evidence of superconductivity was found in a 6.73-Å-thick film. For thicker films of both Pb and Bi, the transition temperatures moved to higher values with increasing thickness. Conduction at thicknesses which correspond to a deposit of less than one monolayer means that either the Ge underlayer is playing a substantial role in the conduction process, or that the films are forming such that conduction is occurring via a percolated path of metal atoms. Indeed, a fit of two-dimensional percolation theory to the measured resistance versus thickness could be carried out. Assuming that the nominal thickness d is proportional to the areal occupation probability in the percolation problem, it was found that $R(d)=R_0(d-d_c)^{-t}$, where the conductivity exponent $t=1.3$, as predicted by theory.[14] The resistances used in the fit were determined at $T=14$ K where their temperature dependence could for the most part be neglected. The critical thicknesses, d_c, were 4.08 and 1.86 Å for Bi and Pb, respectively.

Figure 1 shows the evolution of $R(T)$ curves with thickness for a Bi film. The separatrix between curves which appear to be insulating (R increasing as $T\rightarrow 0$) and those which appear to be superconducting (R decreasing as $T\rightarrow 0$) occurs very close to the resistance value $h/4e^2$. Whether or not the $R(T)$ curves fall to zero immediately after this separation is not possible to resolve by the present measurements which were limited to a range of temperatures above 0.45 K. If they do fall to zero, then the separation condition would correspond to a resistance threshold like that found in granular systems. The similarity of these curves to a renormalization flow diagram suggests the existence of an unstable fixed

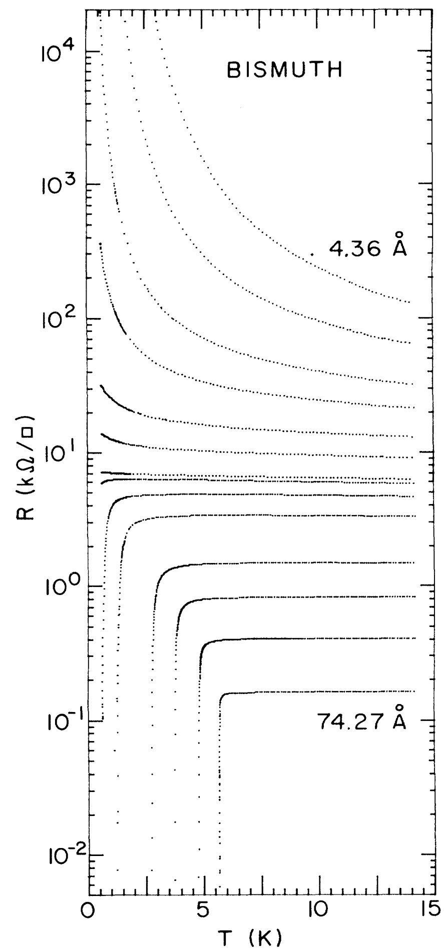

FIG. 1. Evolution of the temperature dependence of the sheet resistance $R(T)$ with thickness for a Bi film deposited onto Ge. Fewer than half of the traces actually acquired are shown. Film thicknesses shown range from 4.36 to 74.27 Å.

point at $T=0$ separating insulating and superconducting behavior. In the case of Bi the separatrix occurred very close to $R=h/4e^2$ or 6.5 kΩ/□. In the case of Pb films it occurred at somewhat greater resistance, $R=9.5$ kΩ/□, but in addition, a tail in $R(T)$ could be observed. The connection between these observations and those tails seen in the resistive transitions of granular films, where the downturn in $R(T)$ occurred at resistances always greater than $h/4e^2$, will require further investigation to lower temperatures.[4]

A second interesting feature of the data is the thickness dependence of the mean-field transition temperature. The latter could be obtained by noting the temperature at which the resistance falls to $R_N/2$, or by fitting the Aslamazov-Larkin theory[15] to the 2D fluctuation conductivity, which yields essentially the same value of temperature. Figure 2 shows the variation of T_c with $1/d$ for both Pb and Bi films. The data almost fall on

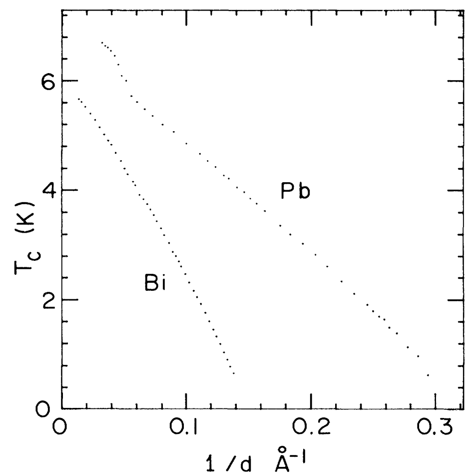

FIG. 2. Dependence of the mean-field transition temperature of Bi and Pb films on the inverse of thickness.

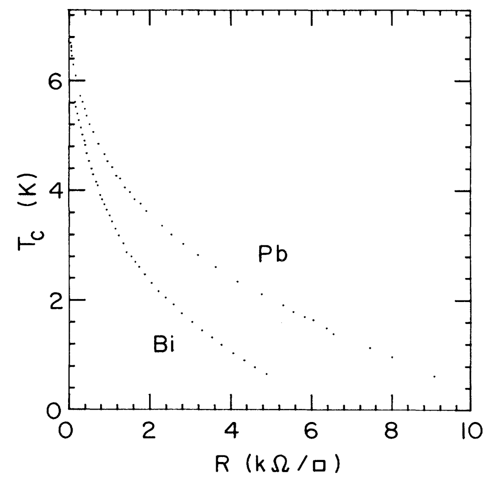

FIG. 3. Dependence of the mean-field transition temperature of Bi and Pb films on sheet resistance.

straight lines when plotted in this manner, consistent with other observations on similar systems.[12,16,17] A fit by a straight line would be consistent with a simple Landau-Ginzburg model of the transition in thin films with a modified boundary condition on the order parameter.[18] Such a condition may be physically realized as the leaking of the pair wave function outside of the region of finite pairing interaction. A substantial contribution to the reduction of T_c in ultrathin films may be the effect of the surface, or the quantum size effect, and not simply the action of Coulomb or localization effects.

A third feature of the data is the dependence of the mean-field transition temperature on the sheet resistance R. Its shift from the bulk value T_{c0} is shown in Fig. 3 for both Pb and Bi. Only in the case of $T_{c0}-T_c \rightarrow 0$ does T_c reduction depend linearly on sheet resistance as was reported for Mo-Ge films.[16] It is interesting to note the behavior of the Bi film for which the mean-field T_c extrapolates to zero near $R=h/4e^2$. For all other metals that we have prepared by quench evaporation the initial downturn in $R(T)$ is found at a larger value of the sheet resistance.[4] The results on Bi films suggest that the thresholds for zero electrical resistance and for pairing may be manifestations of the same phenomenon.

All of the above considerations suggest that the resistance threshold for superconductivity in ultrathin films which are nominally homogeneous may be somewhat different from that in granular films. In the latter the superconducting transition may be considered to be a two-step process, first involving the establishment of an equilibrium order parameter on the grains which is followed by phase coupling of the grains through the suppression of quantum fluctuations with the normal resistance serving as a control parameter. In the case of nominally homogeneous films, when the high-temperature, or normal, resistance falls to a value close to that of the quantum resistance for pairs, superconducting behavior is found at low temperatures without any obvious evidence of the local superconductivity of granular systems. The quantum resistance divides films into two categories: those which become superconducting and those which become insulating at low temperatures, with no intermediate, metallic configuration as was observed in the granular systems. Furthermore the curves of $R(T)$ resemble renormalization flows to an unstable fixed point at $T=0$. This implies that the initial transition to zero resistance at threshold may not actually occur until $T=0$.

The existence of a fixed point at $T=0$ with $R=h/4e^2$ separating superconducting and insulating behavior has been suggested by Pang[19] using reasoning combining ideas from the theory of electronic localization and quantum transport. Pang's argument is independent of the material and its structure. The present results may support this point of view. The generality of Pang's argument would also suggest that all films in the $T\rightarrow 0$ limit have the same properties independent of their being amorphous or granular. This can only be tested by investigating the properties of systems to temperatures substantially lower than those achieved thus far. Thus, the detailed nature of the relationship between the phenomena reported here for nominally homogeneous films and the near universal resistance threshold for superconductivity reported earlier for granular films remains an open question.

The difference in the resistances of the separatrix curves, $R(T)$, for Bi and Pb suggests the possibility of a material-dependent correction to the threshold. Alternatively there may be morphological differences between the Bi and Pb films which make the latter behave more like the granular films reported earlier. It should be noted that crystalline impurities in Pb would be superconducting whereas they would be semimetallic in the case of Bi. In any event, measurement of $R(T)$ to temperatures far lower than the presently available 0.45 K would be required to definitively rule out the eventual occurrence of quasireentrant behavior in any of these nominally homogeneous films.

In summary, studies of the onset of superconductivity in extremely thin, nominally homogeneous, metal films have revealed a threshold condition which suggests a transition between superconducting and insulating behavior in the $T \rightarrow 0$ limit which depends on the normal-state sheet resistance falling below a value very near $h/4e^2 = 6.45\ \mathrm{k}\Omega$. The existence of this phenomenon in films which are not granular implies that its explanation involves more general arguments than those which follow from the modeling of films by Josephson-coupled arrays.

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