# Anomalous Field Effect in Ultrathin Films of Metals near the Superconductor-Insulator Transition

G. Martinez-Arizala, D. E. Grupp, C. Christiansen, A. M. Mack, N. Markovic, Y. Seguchi,* and A. M. Goldman
*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455*
(Received 28 October 1996)

A field effect conductance modulation experiment has been performed on a series of nominally homogeneous ultrathin films of metals. The thicknesses of the films were varied over a range such that their properties traversed the insulator-to-superconductor transition. At low gate voltages $V_G$ the conductance $G(V_G)$ increased with either polarity for films on the insulating side of the transition and decreased at temperatures in the transition region for films which were just thick enough to be superconducting. A qualitative interpretation of these results suggests the consideration of Cooper pairing even for insulating films. [S0031-9007(97)02374-0]

PACS numbers: 74.40.+k, 73.40.Rw, 73.50.–h

The superconductor-insulator (S-I) transition in ultrathin films of metals, either as a consequence of disorder [1] or applied magnetic field [2], has been described by the boson Hubbard model and its variants which highlight the role of order parameter phase fluctuations [3]. In this approach, the superconducting state is considered to be a Cooper pair condensate with localized vortices, and the insulating state is a vortex condensate with localized Cooper pairs. The issue of the relevance of this theory to experiment has been challenged by tunneling investigations which have been interpreted as evidence that S-I transitions are dominated by order parameter amplitude fluctuations. Because the boson Hubbard model implies that there are Cooper pairs even on the insulating side of the transition, it is of interest to study the insulating state and the S-I transition in other ways, going beyond conductance and tunneling measurements, to determine whether there is evidence of behavior different from the usual picture of a strongly localized disordered system. This has been done through investigations of the thickness and temperature dependence of the field effect modulation of the conductance [5] of incrementally quench-deposited films of metal above and below the S-I transition. In this Letter we describe our findings which suggest the existence of a symmetry between the insulating and superconducting states implying that insulating films may be other than Coulomb glasses [6] of interacting localized electrons.

Investigations were carried out on ultrathin films of Bi or Pb ranging in thickness from 3 to 20 Å, formed on a 10 Å thick predeposited layer of $a$-Ge, with all films being grown *in situ* under UHV conditions ($\sim 10^{-10}$ to $10^{-9}$ Torr) onto single-crystal $SrTiO_3$ (100) substrates which were 0.75 mm thick. Substrate temperatures during all depositions were held at 9 K, and UHV conditions were sustained over an extended period so that sequential depositions to increase the film thickness could be carried out without contamination. It has been found that films prepared in such a manner become continuous at an average metal thickness on the order of one monolayer and, because of this, are generally considered to be homogeneous [7]. The quartz crystal monitor used to determine nominal film thickness was calibrated using Rutherford backscattering spectroscopy. Resistance was measured using standard four-probe techniques with films current biased at values less than 50 nA. Current-voltage characteristics were linear up to currents at least 3 times this value. Modulation of the conductance using the field effect was accomplished by biasing the film relative to a 150 Å thick platinum metal gate on the back side of the substrate. Single crystals of $SrTiO_3$ were chosen as substrates because of their high dielectric constant at low temperatures ($\varepsilon \sim 20\,000$) below 10 K [8]. This allowed us to induce a substantial charge at relatively low gate voltages even with a relatively thick substrate serving as the dielectric. These substrates, studied in detail for other reasons [9], were not ferroelectric, and their electrostrictive response was on the order of parts per million over the range of temperatures and electric fields used here. Their impurity concentrations, as determined by the supplier, Princeton Scientific, were in ppm: Na $< 2$, K $= 2$, Si $< 2$, Ca $= 14$, Fe $< 22$, and Ba $= 19$.

We first consider the electrical conductance, its temperature dependence, and its modulation by a gate voltage for insulating films. Although we have not presented a graph, the temperature dependence of the conductance of insulating films could be fit by

$$G = G_0 \exp(-[T_0/T]^a)\,, \tag{1}$$

with $a = 0.75 \pm 0.05$. Zabrodskii plots of the data for various films confirmed that the exponents determined by fitting were not artifacts [10]. It was *not* possible to obtain satisfactory fits with $a = \frac{1}{2}$ or $\frac{1}{3}$ appropriate to variable range hopping in two dimensions with [11] and without [12] Coulomb effects, even including a pre-exponential factor which was a power law in $T$. For films which were close to being metallic, the data crossed over to a $\ln T$ form.

Higher resistance films exhibited glasslike behavior at low temperatures. There appeared to be no sharp boundary in either temperature or sheet resistance separating films which were glasslike from those which were not.

 0031-9007/97/78(6)/1130(4)$10.00 

Because of memory effects in films exhibiting glasslike behavior, care was need to obtain reproducible data for $G(V_G)$. Detailed results depended on the manner in which data were obtained. For example, the increase in conductance at a given gate voltage was slightly smaller if $V_G$ was varied continuously at fixed temperature than if stepped changes were made in $V_G$, such as from zero to a particular value, with the film warmed to 25 K, and cooled back to the original temperature between each step. Figure 1 shows sets of curves of $\Delta G/G(0) = [G(V_G) - G(0)]/G(0)$ obtained by scanning $V_G$ at fixed temperatures $T$ for a Pb film with a sheet resistance of 40 k$\Omega$ at $T = 24$ K. An increase of the conductance as a function of gate voltage of either polarity was always observed in nonsuperconducting films.

There were additional manifestations of glasslike behavior. The conductance change after the application of a voltage step to the gate was time dependent. After an initial rapid increase and decay, $G(V_G)$ relaxed with a logarithmic dependence on time over periods which persisted for at least one day, the maximum measurement interval. The coefficient of the logarithm became larger as the temperature decreased. Another effect was the fact that the minimum in $G(V_G)$ found at $V_G = 0$ could be pinned at a finite voltage. If a film were cooled down from 25 K with $V_G \neq 0$, and $G(V_G)$ measured, then the minimum would shift to the value of $V_G$ in which the film was cooled. This shift could be annealed away by subsequent warming to high temperatures, or by repeated tracing of $G(V_G)$ at fixed temperature over an extended period of time. Also, once a scan of $G(V_G)$ was carried out at a particular temperature, it could only be reproduced by warming to 25 K and, after a short wait, cooling back down with zero gate voltage. All of these effects involved time scales which were large in comparison with any RC time constant of the system, and there were no similar phenomena in the behavior of the substrates [9].

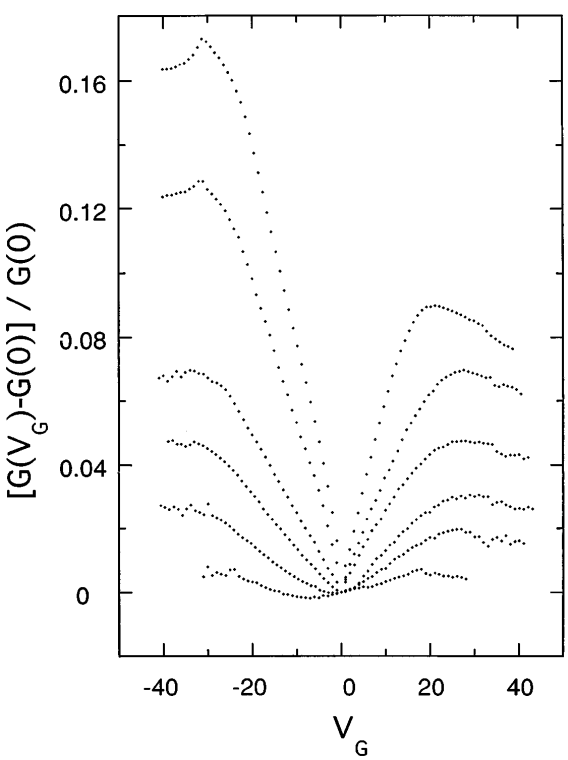


FIG. 1. Variation of $\Delta G/G(0) = [G(V_G) - G(0)]/G(0)$ with gate voltage $V_G$ and temperature $T$ for a Pb film with a sheet resistance of 40 k$\Omega$ at 24 K. The temperatures from top to bottom are 2.3, 3, 5, 8, 12, and 24 K.

The increase of the conductance in response to gate voltage of either sign observed here has been found in studies of discontinuous Au [13] and In-$In_2O_3$ films [14], with glasslike behavior also reported for the latter. The films in those investigations were about 200 Å thick and had very high sheet resistances on the order of G$\Omega$, whereas in the present work films had thicknesses of less than 10 Å, with sheet resistances ranging from hundreds of k$\Omega$ down to the order of 3 k$\Omega$. In our measurements $\Delta G/G(0)$ the fractional change in conductance at fixed charge transfer varied as $1/T$ for films in the insulating regime [15], whereas the measurements on Au films of Ref. [13] exhibited an exponentially activated form. The work on $In_2O_3$ films [14] did not contain data on the temperature dependence of $\Delta G/G(0)$. Our investigations were limited to temperatures below 25 K, since warming further would cause irreversible crystallization of the amorphous film.

We would further remark that the evidence of glasslike behavior in our work and that of Ref. [14] are similar to studies of the low temperature ac dielectric response of structural glasses to large dc electric fields [16] and of the response of the magnetic susceptibility in CuMn spin glasses to magnetic fields [17]. In these investigations memory and relaxation effects were found and there were local minima in the ac dielectric and magnetic susceptibilities at zero electric or magnetic field which could be shifted to nonzero field by either cooling in that field or waiting for an extended period.

The changes in the magnitude and sign of the conductance modulation as films became thick enough to achieve superconductivity can be seen in Fig. 2, which shows $\Delta G/G(0)$ as a function of $V_G$ for a series of Pb films ranging in thickness from 40 to 3.25 k$\Omega$. As thickness is increased and the S-I transition approached, the size of the effect and the voltage at which the response saturated both decreased, increasing once again as $\Delta G/G(0)$ changed sign going through the transition. The next film in the sequence was fully superconducting with a sharp transition. It exhibited a very tiny antisymmetric field effect in its normal state.

The temperature dependence of $\Delta G/G(0)$ for a Pb film with $R_\square = 3.25$ k$\Omega$, which is just on the superconducting side of the S-I transition, is shown in Fig. 3. Well above the transition temperature, where the temperature coefficient of resistance is slightly negative, there is a very small "symmetric" field effect in which the conductance increases with gate voltage. Very close to $T_c$, where the resistance is essentially temperature independent, $G(V_G)$

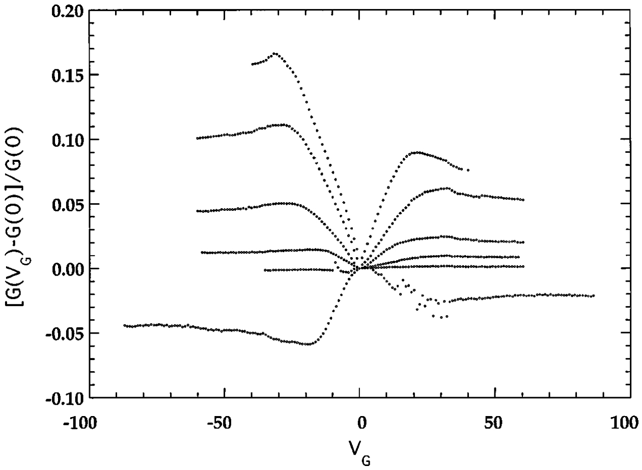


FIG. 2. Dependence of $\Delta G/G(0)$ on $V_G$ for a series of Pb films, with sheet resistances of 40, 25.34, 17.9, 11.31, 7.5, and 3.25 k$\Omega$, where $R_\square$ was measured at 24 K. The top curve shows the most resistive film, with $R_\square$ decreasing for each subsequent curve.

starts to become antisymmetric as would be expected for the metal field effect [5]. As the resistance falls to zero in the transition region, $G(V_G)$ decreases for either sign of $V_G$, in contrast with its increase for insulating films and for this particular film at higher temperatures.

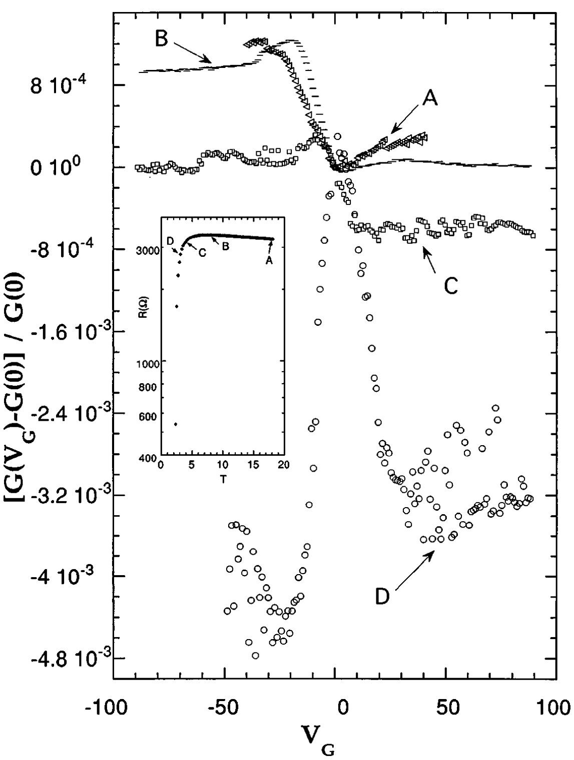


FIG. 3. Variation of $\Delta G/G(0)$ with temperature for a Pb film with $R_\square = 3.25$ k$\Omega$ at 24 K. The temperature decreases from top to bottom. Curves A through D correspond to data obtained at 18, 8, 4, and 3.0 K, respectively. Data obtained at other (lower) temperatures have been omitted for clarity. Shown in the inset is a plot of $R_\square$ vs $T$ on which the approximate position of curves A through D are indicated.

We suggest three possible qualitative explanations for the behavior of the insulating films, all of which rely on the assertion that the addition of charge of either sign will drive a film out of equilibrium [14]. We will not address effects such as the imperfect nature of the symmetry with respect to the sign of the gate voltage, the saturation of the response at high gate voltages, and the glasslike behavior. The first explanation is that of Ben-Chorin and co-workers [14], who addressed the behavior of insulating In-$In_2O_3$ films. They argued that exciting an insulating system away from equilibrium by charging with either electrons or holes always increases its conductance, because it allows sites which were either occupied or unoccupied in equilibrium, and thus not participating in the transport, to contribute to the conductance which proceeds by variable-range hopping. In this approach the behavior of insulating films would have nothing to do with superconductivity.

In the second explanation we assume localized Cooper pairs produced by fluctuations are present on the insulating side of the S-I transition of a homogeneous film [18]. Superconducting regions would be the size of the coherence length in a manner similar to actual droplets or grains in a granular material [19]. Electrical transport in such a system could involve thermal excitation and tunneling of quasiparticles between these regions. Driving a film out of equilibrium by charging would lead to suppression of the order parameter and the local value of the energy gap and an increase in the conductance. With disorder on length scales on the order of one atomic spacing, one might expect fluctuations to smear out the onset of superconducting correlations, and effects attributable to such correlations could persist to temperatures such as 25 K, well in excess of the bulk transition temperature, as is observed.

The third explanation of the data might involve a variant of the boson Hubbard model [3,20] used to explain the S-I transition. A generalization of this approach to $T > 0$ is not yet available. The insulator is described in this picture as a condensate of vortices with localized Cooper pairs. For $T > 0$ one might expect that driving the system out of equilibrium by charging, as it diminishes the vortex condensate and reduces the vortex response, would be resistance reducing.

The fact that the injection of energetic quasiparticles into a system weakens superconductivity is quite well known [21] and plays an important role in explanations two and three of the insulating films. The response of films undergoing a superconducting transition would be essentially independent of the model of the insulating state. The injection of energetic quasiparticles would be conductance decreasing as it would reduce the energy gap and lower the transition temperature. In the case of the boson Hubbard model, for the superconducting side of the transition, the weakening of the electron pair condensate through the addition of energetic quasiparticles might be thought of as increasing the vortex response, which would be conductance decreasing. A symmetric response to charging would follow as a consequence of electron-hole symmetry whenever there were superconducting correlations.

The In-$In_2O_3$ films of Ref. [14] were thicker and exhibited resistances much higher than those of our films. In our data, the symmetric response, but not the glasslike behavior, persists even for films which are nearly metallic and which do not conduct by hopping, raising the question of whether the picture developed in Ref. [14] is relevant. The difficulty with the second and third pictures is that tunneling spectra obtained for films on the insulating side of the S-I transition, driven by either thickness or magnetic field, do not exhibit an energy gap which one might expect if there were local superconducting order [4]. However, we note that the absence of a gap in the tunneling density of states does not necessarily imply a zero value for the order parameter. Ferrell and Lobb [22] have shown that phase fluctuations can bring about gap reduction, and it is known that phase fluctuations are pair breaking [23]. The latter can lead to gapless superconductivity. In support of this view are the indications of superconducting effects in films of $In_2O_3$ driven into the insulating state by magnetic fields, in the work of Hebard and Paalanen [2], and in insulating films of $In_2O_3$ in the work of Gantmakher and co-workers [24].

We are currently carrying out measurements in magnetic fields and at low temperatures to test the extent to which any of the above conjectures might be valid. We are also attempting to see whether we can develop a scaling analysis of the conductance charging effect going through the S-I transition which would establish directly the connection between the behavior in the insulating and superconducting phases in the context of these measurements.

In summary, a field effect conductance modulation experiment performed on ultrathin films above and below the S-I transition has shown that $\Delta G(V_G)$ has a different sign in the transition regions of insulating and superconducting films. We have speculated that because of this, finite temperature generalizations of the boson Hubbard model of the superconductor-insulator transition should be scrutinized further. High resistance insulating films also exhibit many phenomena characteristic of glasslike behavior.

The authors would like to acknowledge very useful conversations with Boris Shklovskii, Anatoly Larkin, Yuri Ovchinnikov, Boris Spivak, Alexei Efros, Steve Kivelson, Leonid Glazman, Myriam Sarachek, and Alexander Gerber. This work was supported in part by the National Science Foundation under Grant No. NSF/DMR 9623477.

*Permanent address: Faculty of Science and Technology, Kinki University, Osaka, Japan.

[1] D.B. Haviland, Y. Liu, and A.M. Goldman, Phys. Rev. Lett. **62**, 2180 (1989); Y. Liu, K.A. McGreer, B. Nease, D.B. Haviland, G. Martinez, J.W. Halley, and A.M. Goldman, Phys. Rev. Lett. **67**, 2068 (1991).

[2] A.F. Hebard and M.A. Paalanen, Phys. Rev. Lett. **65**, 927 (1990).

[3] Matthew P.A. Fisher, Phys. Rev. Lett. **65**, 923 (1990); Min-Chul Cha, Matthew P.A. Fisher, S.M. Girvin, Mats Wallin, and Peter Young, Phys. Rev. B **44**, 6883 (1991).

[4] J.M. Valles, Jr., R.C. Dynes, and J.P. Garno, Phys. Rev. Lett. **69**, 3567 (1992); S-Y. Hsu, J.A. Chervenak, and J.M. Valles, Jr., Phys. Rev. Lett. **75**, 132 (1995).

[5] A.F. Hebard and A.T. Fiory, in *Novel Superconductivity*, edited by S.A. Wolf and V.Z. Kresin (Plenum, New York, 1987), p. 9.

[6] Don Monroe, A.C. Gossard, J.H. English, B. Golding, W.H. Haemmerle, and M.A. Kastner, Phys. Rev. Lett. **59**, 1148 (1987); J.H. Davies, P.A. Lee, and T.M. Rice, Phys. Rev. Lett. **49**, 758 (1982); J.H. Davies, P.A. Lee, and T.M. Rice, Phys. Rev. B **29**, 4260 (1984); R.N. Bhatt and T.V. Ramakrishnan, J. Phys. C **17**, L639 (1984).

[7] M. Strongin, R.S. Thompson, O.F. Kammerer, and J.E. Crow, Phys. Rev. B **1**, 1078 (1970).

[8] H.M. Christen, J. Mannhart, E.J. Williams, and Ch. Gerber, Phys. Rev. B **49**, 12 095 (1994).

[9] Daniel E. Grupp and Allen M. Goldman (unpublished).

[10] A.G. Zabrodskii and K.N. Ninov'eva, Zh. Eksp. Teor. Fiz. **86**, 727 (1984) [Sov. Phys. JETP **59**, 425 (1984)].

[11] A.L. Efros and B.I. Shklovskii, J. Phys. C **8**, L49 (1975); B.I. Shklovskii and A.L. Efros, Fiz. Tekh. Poluprovodn. **14**, 825 (1980) [Sov. Phys. Semicond. **14**, 487 (1980)].

[12] N.F. Mott, Philos. Mag. **19**, 835 (1969).

[13] C.J. Adkins, J.D. Benjamin, J.M.D. Thomas, J.W. Gardner, and A.J. McGeown, J. Phys. C **17**, 4633 (1984).

[14] M. Ben-Chorin, D. Kowal, and Z. Ovadyahu, Phys. Rev. B **44**, 3420 (1991); M. Ben-Chorin, Z. Ovadyahu, and M. Pollak, Phys. Rev. B **48**, 15 025 (1993).

[15] To obtain the temperature dependence of $\Delta G/G(0)$ at fixed charge transfer, values of $V_G$ were adjusted in accordance with the measured value of the temperature dependence of the dielectric constant for the particular substrate.

[16] D.J. Salvino, S. Rogge, B. Tigner, and D.D. Osheroff, Phys. Rev. Lett. **73**, 268 (1994); Sven Rogge, Douglas Natelson, and D.D. Osheroff, Phys. Rev. Lett. **76**, 3136 (1996).

[17] P.W. Fenimore and M.B. Weissman, J. Appl. Phys. **76**, 6192 (1994).

[18] M. Ma and P.A. Lee, Phys. Rev. Lett. **32**, 5658 (1985).

[19] In the actual system there may be real physical droplets. Reflection high energy electron diffraction studies which we have carried out on these films indicate that they contain small clusters even before they are warmed to 25 K.

[20] M. Makivic, N. Trivedi, and S. Ullah, Phys. Rev. Lett. **71**, 2307 (1993).

[21] For a review of nonequilibrium superconductivity, see *Nonequilibrium Superconductivity*, edited by D.N. Langenberg and A.I. Larkin (North-Holland, Amsterdam, 1986).

[22] R.A. Ferrell and C.J. Lobb (private communication).

[23] Soon-Gul Lee and Thomas R. Lemberger, Phys. Rev. B **37**, 7911 (1988).

[24] V.F. Gantmakher *et al.*, Zh. Eksp. Teor. Fiz. **109**, 1765 (1996) [Sov. Phys. JETP **82**, 951 (1996)].