State Memory and Reentrance in a Paramagnetically Limited Superconductor

V. Yu. Butko* and P. W. Adams
Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803

E. I. Meletis
*Department of Mechanical Engineering, Materials Science and Engineering Program, Louisiana State University,
Baton Rouge, Louisiana 70803*

(Received 30 April 1999)

We report observations of a new quasistatic nonequilibrium phenomenon in the density of electronic states (DOS) of a superconductor. Tunneling measurements of the DOS of ultrathin Al films, at the spin paramagnetically limited parallel magnetic field transition, reveal a strongly hysteretic DOS spectrum. We show that the hysteresis can be characterized as a quasistatic *state memory effect* in which the state of a film (normal or superconducting) is determined by its state prior to entering the hysteretic region. We also show that state memory can lead to the onset of superconductivity with *increasing* temperature, i.e., reentrance.

PACS numbers: 74.76.Db, 74.25.Dw, 74.40.+k, 74.50.+r

Recently it has been recognized that the superconductor to insulator (S-I) transition in disordered two-dimensional (2D) metal films is an important realization of a 2D quantum phase transition [1]. This has motivated a number of experimental investigations in which a perpendicular magnetic field is used to tune the transition in the zero temperature critical regime [2]. Curiously, however, there have been very few experimental studies of the S-I transition in which the magnetic field is applied along the plane of the film. Nevertheless, the parallel field interacts with superconductivity via a completely different mechanism than that of the perpendicular field [3]. Furthermore, the parallel field preserves time-reversal symmetry in a thin film [4]. Thus it can be a powerful probe of the underlying physics of the disordered, low-dimensional superconducting state.

For thin metal films in a parallel magnetic field, the orbital motion of the electrons is suppressed by the film thickness. If the film thickness is much less that of the penetration depth, then the parallel critical field transition will, in fact, be mediated by the Zeeman splitting of the Cooper pairs. In metals with a small spin-orbit scattering rate, such as Al and Be, for instance [5], the transition occurs when the Zeeman splitting, $g\mu_B H_\parallel$, is of the order of the superconducting gap, Δ (μ_B is the Bohr magneton and g is the Landé g factor). This is the spin-paramagnetic transition. It has long been expected that in the case of no spin-orbit scattering, the spin-paramagnetic transition should be first order at low temperatures [4]. Early transport studies down to $T \sim 0.5$ K have suggested that the spin-paramagnetic transition in Al films becomes first order at about 0.6 K, but no significant hysteresis was ever reported to substantiate this claim [6,7]. More recently these experiments were extended to mK temperatures and it was found that the resistive critical field transition becomes hysteretic below $T = 270$ mK in granular Al films [8,9] and $T = 190$ mK in nongranular Be films [10]. In the experiments described in Refs. [8] and [9] the critical field transition widths were about the same as the widths of the hysteresis loops. As a consequence, though the films could be brought out of thermodynamic equilibrium in the hysteretic regime, the nonequilibrium states were unstable and always exhibited a measurable time dependence. Some of the more exotic and unexpected manifestations of the time dependencies included stretched-exponential relaxations, avalanches, and self-organized criticality [11,12]. Obviously, a deeper understanding of the spin-paramagnetic transition and its associated dynamics is predicated on gaining some insight into the effects of disorder, film morphology, and transition width on the nonequilibrium behavior. In particular, it is still not known what dynamical properties of the hysteresis are intrinsic to the spin-paramagnetic transition and which ones are mediated by the details of the film morphology. Furthermore, hysteresis has been observed only in transport measurements of the spin-paramagnetic transition in highly disordered films. So it is still unclear as to whether or not the hysteresis is simply a disorder induced effect or is a more fundamental property of the superconducting condensate.

Obviously, to get at the above issues it would be best to probe the behavior of the superconducting condensate directly in substantially more homogeneous films than was used in the previous studies. Transport can give only an indirect measure of local superconducting characteristics [13]. In contrast, electron tunneling gives a direct areal probe of the microscopic superconducting properties of the film. In fact, at low temperatures the tunneling conductance is proportional to the density of electronic states (DOS) of the film [14]. With this in mind, we have made a detailed electron tunneling study of the spin-paramagnetic transition in Al films that were engineered to have extremely sharp parallel critical field transitions. By ensuring that the widths of the transitions are much

0031-9007/99/83(18)/3725(4)$15.00

less than that of the hysteresis loops, we are afforded the opportunity to investigate the essential nonequilibrium quantum features of the spin-paramagnetic transition.

The Al films used in this study were made by thermal evaporation of Al onto fire polished glass microscope slides that were cooled to 84 K. The film area was 1.5 mm × 4.5 mm and the typical film thickness was 2–2.5 nm. The films were deposited in a system with a base pressure of 2×10^{-7} Torr at a rate of 0.03 nm/sec. Transmission electron microscopy was used for microstructural analysis of 5 nm thick Al films deposited onto cleaved NaCl crystals under the same conditions. High magnification micrographs revealed a dense polycrystalline structure with broadly distributed grain sizes, ranging from 10 to 40 nm. Electron diffraction studies showed a well-defined metallic diffraction pattern with a preferred 1-1-1 texture. The oxide layer appeared to be amorphous. The Al films used in this study had a transition temperature $T_c \sim 2.7$ K, parallel critical field $H_{c\|} \sim 6$ T, and a tricritical point $T_{\rm tri} \sim 600$ mK that were significantly higher than the previous values of $T_c \sim 1.8$ K, $H_{c\|} \sim 5$ T, and $T_{\rm tri} \sim 300$ mK obtained from anodized films [8]. Furthermore, the parallel critical field transitions were 5 times sharper than before. The tunnel junctions were formed by exposing the films to the atmosphere for 0.1–3 h in order to form a native oxide, then a 9 nm thick Al counterelectrode was deposited directly on top of the film with the oxide serving as the tunnel barrier. The junction area was 0.7 mm × 0.7 mm. This technique produced tunnel junction resistances $R_J \sim 1$ to 1000 kΩ depending upon the exposure time and other factors. We were always careful to ensure that $R_J \gg R_{\rm film}$. The integrity of the junctions was tested by measuring the dc I-V characteristics in zero magnetic field at $T = 30$ mK. The subgap impedance of a "good" junction was always greater than 10^8 Ω. Because the counterelectrode was relatively thick, it's parallel critical field was ~2.7 T whereas the film's critical field was ~5.8 T. All of the tunneling data presented in this Letter are either *normal-insulator-superconducting* or *normal-insulator-normal* tunneling. The films were aligned to within 0.1° of parallel by an *in situ* mechanical rotator.

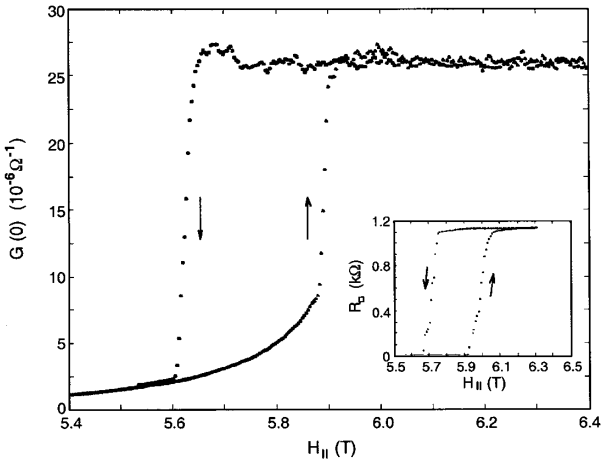

FIG. 1. Hysteresis in zero-bias tunneling conductance as a function of the parallel field for a 1 kΩ/sq Al film at 30 mK. Arrows depict the field sweep direction. Inset: corresponding hysteresis in film resistance.

We have made measurements of the tunneling conductance as a function of the parallel magnetic field at low temperatures. At the critical parallel field the tunneling spectrum changes abruptly and displays a surprisingly complete hysteresis. This effect is clearly seen in Fig. 1 where we have plotted the zero-bias tunnel junction conductance $G(0)$ as a function of the parallel field at the critical field transition of a 1 kΩ/sq Al film. The precipitous attenuation in $G(0)$ as the field is lowered through the transition is due to the sudden opening of the superconducting gap in the single particle density of states. As a consequence there is an exponential suppression of the zero-bias tunneling conductance [14]. The finite conductance tail on the superconducting side of the transitions in Fig. 1 is probably a consequence of orbital depairing due to the field [14,15]. The hysteresis in the DOS indicates that the nonequilibrium aspects of the transition are intrinsic to the superconducting condensate itself. Earlier tunneling studies of more inhomogeneous Al films fabricated via electrochemical anodization showed no such hysteresis in the DOS though their transport was hysteric [8]. Evidently the DOS hysteresis is much more sensitive to disorder and/or inhomogeneities than the transport hysteresis.

In Fig. 2 we have produced a phase diagram by plotting the up-sweep and down-sweep critical fields as a function of temperature, where we define the critical field by the

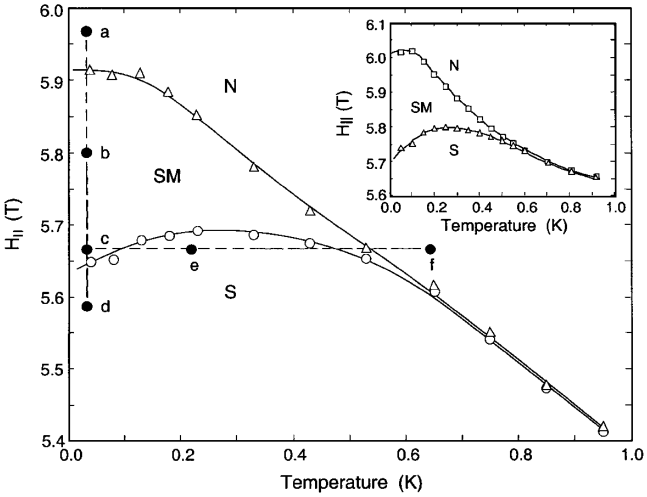

FIG. 2. Parallel critical fields as a function of temperature as measured by the zero-bias tunnel junction conductance. Triangles refer to up-sweep transitions and circles to down-sweep transitions. The letters and dotted lines are provided as a guide to the field, and temperature cycles are discussed in the text. S: Superconducting phase. N: Normal phase. SM: State memory region. Inset: Parallel critical fields as measured by resistive transitions.

onset of a gap in $G(0)$. Using this diagram as a guide, we can further investigate nonequilibrium effects in the DOS. The dashed lines in Fig. 2 are provided to help the reader visualize the field and temperature cycles used in the experiments described below.

In order to test whether the entire DOS spectrum is hysteric we have measured the tunneling ac I-V characteristics at the spin-paramagnetic transition after two different field cycles at $T = 30$ mK. Referring to the map in Fig. 2, the first was taken after going from 5.97 to 5.80 T ($a \rightarrow b$) and the second after going from 5.57 to 5.80 T ($d \rightarrow b$). The resulting tunneling spectra are shown in Fig. 3 and both were taken at the same magnetic field ($H_{\parallel} = 5.80$ T). The difference between the two spectra in Fig. 3 is striking. The curve $d \rightarrow b$ with the two large peaks on either side of $V = 0$ is, in fact, representative of a superconducting spectrum in which the usual BCS DOS has been Zeeman split by the field. As first reported by Meservey *et al.* [5] the BCS conductance peaks are positioned at $V = \Delta/e \pm \mu_B H_{\parallel}/e$, where in our case $\Delta/e \sim 0.45$ mV. The $a \rightarrow b$ curve with the three small dips is the normal state tunneling spectrum. The origin of the anomalous normal state spectral features has been discussed elsewhere [16,17]. The dual nature of the film at 5.8 T is interesting in that it implies that the system has a quasistatic *state memory* in which the state of the system (normal or superconducting) in the hysteretic region is determined solely by the system state prior to entering the region. This robust effect was observed in all samples which had a sharp, hysteretic critical field transition in transport. Furthermore the state memory effect was relatively insensitive to film resistance and tunnel junction impedance as can be seen by the spectra in the inset of Fig. 3.

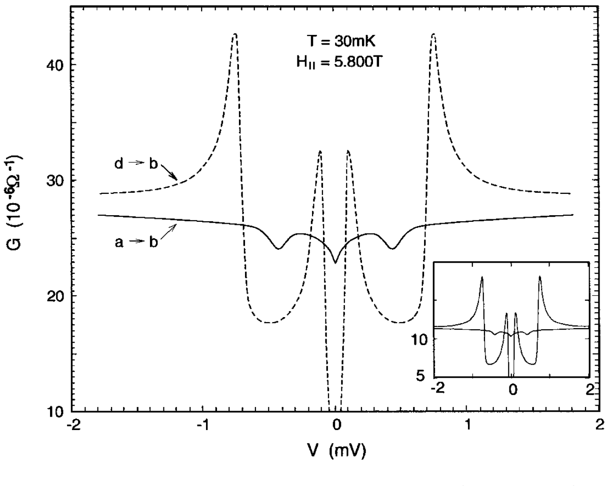

FIG. 3. Tunnel junction conductance as a function of bias voltage in the hysteretic region for two different field cycles. The letters refer to the points in the phase diagram shown in Fig. 2. The $d \rightarrow b$ curve represents a Zeeman splitting of the usual BCS superconducting DOS, and the $a \rightarrow b$ curve is the normal state spectrum. Inset: Tunneling spectra of a 0.66 kΩ/sq Al film with a $R_J = 85$ kΩ junction using the same field cycles as in the main figure.

The spectra in Fig. 3 were, in fact, very stable in time. We observed no discernible changes in the spectral features of either state over a 24 h period, indicating that the dynamical time scales are quite long in the interior of the hysteresis loop. Of course, at the very edges of the hysteresis loop we did see dynamical behavior. Interestingly, the state memory effect can be used as the basis of a novel superconducting switch by simply superimposing a magnetic pulse train on top of the static field. For instance, pulses of ± 0.2 T would switch the film between the normal and superconducting phases at 5.8 T.

The quasistatic character of the state memory suggests that there is a field dependent nucleation barrier of order T_{tri} between the superconducting and normal phases. It seems likely that this barrier is a surface energy associated with the boundary between local normal (superconducting) domains and the surrounding superconducting (normal) phase. Electron exchange interactions may also play a role. In any case, our tunneling results compel one to believe that the quasistatic *state memory* is intrinsic to the transition and is, in fact, mediated by an unusual interplay between superconductivity and the system's spin degrees of freedom.

Referring back to the phase diagram in Fig. 2, we note that the down-sweep critical field curve has a peculiar local maximum near 250 mK. A similarly strong maximum is also present in the spin-paramagnetic phase diagram of homogeneous Be films [10]. We have investigated this anomalous temperature dependence by first putting the system into a nonequilibrium normal state by ramping the field from $a \rightarrow c$. (The tunneling conductance remained unchanged over a 12 h period while at point c.) We then cut horizontally across the phase diagram by raising the temperature to point e and then point f at constant field. Shown in Fig. 4 are the tunneling spectra at points c, e, and f. Note that though the film starts out in the normal

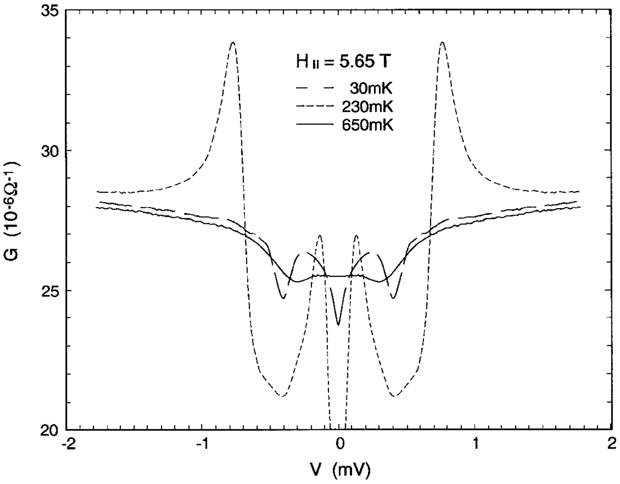

FIG. 4. Reentrant behavior in the tunneling DOS as the temperature is raised at a constant field of $H_{\parallel} = 5.65$ T. The curves were taken at points c, e, and f in Fig. 2.

state at 30 mK, it actually enters the superconducting state upon warming to 230 mK. Upon further warming to 650 mK it then reenters the normal state. When the film was alternatively cycled from $a \longrightarrow c$ then $c \longrightarrow e$ and then back to $e \longrightarrow c$ it ended up in the superconducting state, indicating that the state memory is retained in temperature cycles as well as field cycles. We point out that this reentrance effect is not in any way related to commonly observed quasireentrance in granular superconducting films. This latter effect is reversible and is never manifest in the tunneling DOS [18].

In conclusion, we have demonstrated that the two-dimensional spin-paramagnetic transition is a fundamentally hysteretic first-order quantum phase transition. The physical ramifications of this peculiar nonequilibrium aspect of the transition include state memory and reentrance, both of which are associated with the stability of the nonequilibrium phases in the interior region of the hysteresis loop. At present there is no microscopic theory for these effects.

We thank Wenhao Wu, Dana Browne, Igor Aleiner, Boris Altshuler, and John DiTusa for helpful discussions. This work was supported by the National Science Foundation under Grant No. DMR 95-01160 and No. DMR 92-04206.

---

*Also at the Ioffe Physical Technical Institute (PTI), Russian Academy of Sciences, Polytekhnicheskaya Stranitsa, 26, 194021, St.-Petersburg, Russia.

[1] M. P. A. Fisher, Phys. Rev. Lett. **65**, 923 (1990).
[2] A. F. Hebard and M. A. Paalanen, Phys. Rev. Lett. **65**, 927 (1990).
[3] A. M. Clogston, Phys. Rev. Lett. **9**, 266 (1962).
[4] P. Fulde, Adv. Phys. **22**, 667 (1973).
[5] R. Meservey, P. M. Tedrow, and P. Fulde, Phys. Rev. Lett. **25**, 1270 (1970).
[6] P. M. Tedrow and R. Meservey, Phys. Rev. B **8**, 5098 (1973).
[7] T. Suzuki, T. Tsuboi, and H. Takaki, J. Phys. Soc. Jpn. **53**, 3311 (1984).
[8] W. Wu and P. W. Adams, Phys. Rev. Lett. **73**, 1412 (1994).
[9] W. Wu, R. G. Goodrich, and P. W. Adams, Phys. Rev. B **51**, 1378 (1995).
[10] P. W. Adams, P. Herron, and E. I. Meletis, Phys. Rev. B **58**, 2952 (1998).
[11] W. Wu and P. W. Adams, Phys. Rev. Lett. **74**, 610 (1995).
[12] Hysteretic effects have also been seen in the critical current behavior of thin Al films; see Z. Ovadyahu, Phys. Rev. Lett. **45**, 375 (1980).
[13] R. P. Barber, Jr., L. M. Merchant, A. La Porta, and R. C. Dynes, Phys. Rev. B **49**, 3409 (1994).
[14] M. Tinkam, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996).
[15] P. M. Tedrow and R. Meservey, Phys. Lett. **58A**, 237 (1976).
[16] W. Wu, J. Williams, and P. W. Adams, Phys. Rev. Lett. **77**, 1139 (1996).
[17] I. L. Aleiner and B. L. Altshuler, Phys. Rev. Lett. **79**, 4242 (1997).
[18] Alice E. White, R. C. Dynes, and J. P. Garno, Phys. Rev. B **33**, 3549 (1986).