Spin-paramagnetic transition of ultrathin granular Al films in a tilted magnetic field

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We report measurements of the critical fields of ultrathin granular Al films as a function of temperature and magnetic-field orientation. Due to the spin-paramagnetic effect, the parallel field ($\theta = 0°$) transition becomes first-order and strongly hysteretic below a tricritical point, $T_{tri} \sim 270$ mK. Well below T_{tri}, the width of the hysteresis collapses according to $\Delta H(\theta) = \Delta H(0°)\exp(-\theta/2.4°)$ with increasing θ. Our data suggest that the zero-temperature transition goes from first order to second order at $\theta \approx 6.5°$.

When electron-spin paramagnetism is neglected, it can be shown via the Ginzburg-Landau theory[1] that a thin superconducting film in a parallel magnetic field, $H_\parallel$, will undergo a second-order transition to the normal state if the film thickness is much less than the penetration depth. The upper parallel critical field due to the orbital motion of electrons in a thin film varies with film thickness t as $t^{-3/2}$.[2] As t is reduced, however, the orbital critical field can become so large that the Zeeman splitting of the Cooper pairs will be the dominant pair-breaking mechanism. If the spin-orbit scattering rate is small, a first-order transition will occur at low temperatures when the Zeeman splitting of the Cooper pairs is comparable to Δ.[3] This is the spin-paramagnetic limit[4] with a critical field $H_{c\parallel} \sim (18.6 \text{ kG/K})T_c$ where T_c is the zero-field superconducting transition temperature. Previous studies[5] of superconducting fluctuations and quasiparticle tunneling in Al films down to 0.4 K have suggested that the spin-paramagnetic transition becomes first order near 0.6 K. However, no significant hysteresis in the parallel critical field was ever found.

Very recently, low-temperature studies of the transport properties of ultrathin granular Al films in parallel magnetic fields[6] have revealed a tricritical point, $T_{tri} \sim 270$ mK, separating the first-order transition line from the usual second-order transition line. Below T_{tri}, the critical-field transition becomes sharper and strongly hysteretic. In this region, very unusual dynamics including avalanches and exceptionally slow, stretched-exponential relaxations have been observed.[7,8] The purpose of this paper is to report sample, temperature, and angular dependencies of the critical field $H_c(\theta)$ and the width of the hysteresis $\Delta H(\theta)$ in ultrathin granular Al films. Although the angular dependence of the critical field in the context of a second-order transition was studied in detail some years ago,[9] it has never been studied in the hysteretic region of the first-order spin-paramagnetic transition.[10] Our data show that the width of the hysteresis is suppressed exponentially with increasing θ as $\Delta H(\theta) = \Delta H(0°)\exp(-\theta/2.4°)$, suggesting that the superconducting-normal transition crosses over from first-order to second-order at a field orientation only a few degrees away from the parallel orientation.

Ultrathin granular Al films were made by a standard electrochemical anodization process. The typical grain size in a film with a normal-state sheet resistance, R, of a few kΩ/sq was about 30 nm in diameter. We believe that the thickness of the films was about 5 nm. Details about film preparation, scanning force microscopy images, and large-scale homogeneity have been discussed elsewhere.[11] The Al films were mounted on a rotator which was top loaded and immersed in the mixture of a dilution refrigerator inside the bore of a 20-T superconducting magnet at the National High Magnetic Field Laboratory in Tallahassee, Florida. The parallel field position was determined by adjusting the rotator mechanically, *in situ*, to maximize both the critical field H_c and the width of the hysteresis loops ΔH. (Misalignment reduced both H_c and ΔH.) Four-probe resistances were measured using a lock-in amplifier operating at 27 Hz with a probe current of 2 nA. The area between the two probe leads was 1.0×1.5 mm^2. For hysteresis studies, the field was swept at a rate $dH/dt = \pm 10$ G/s. The superconducting magnet had an intrinsic hysteresis width of ~ 0.2 kG, but the direction of this hysteresis was opposite to that of the Al films. The magnet hysteresis was subtracted from all of the data presented below.

Parallel critical field measurements on these films, $\theta = 0°$, reveal that a giant hysteresis loop opens up below $T_{tri} \sim 270$ mK, when the field is swept up and down through the transition.[6] We have taken the midpoints of the transitions as the critical field $H_c(\theta)$. The width of the hysteresis, $\Delta H(0°)$, is then defined as the difference of the field-up and field-down critical fields. We have found that $\Delta H(\theta°)$ increases with decreasing temperature very rapidly right below T_{tri} and saturates at the lowest temperatures of our experiments, which was about 30 mK. We plot in the main part of Fig. 1 the temperature dependences of the normalized width, $\Delta H(0°)/\Delta H(0°)_{max}$, for a number of films with R ranging from 0.1 to 80 kΩ/sq, where $\Delta H(0°)_{max}$ is the maximum width for a film measured at the lowest temperature. Although the width of the hysteresis decreased in films with $R < 1$ kΩ/sq, see the inset of Fig. 1, the temperature dependences of the normalized widths clearly fall on a single curve for all the films that we have studied. This is a strong indication that the tricritical point $T_{tri} \sim 270$ mK is not sample dependent. Of course, in very low-resistance films, $R < 0.1$ kΩ/sq, which are relatively thick, the hysteresis must disappear since the transition becomes second order.

We are not sure of the origin of the hysteresis. Previous studies[5] on Al films down to 0.4 K have suggested that the transition becomes first order near 0.6 K, based on measure-
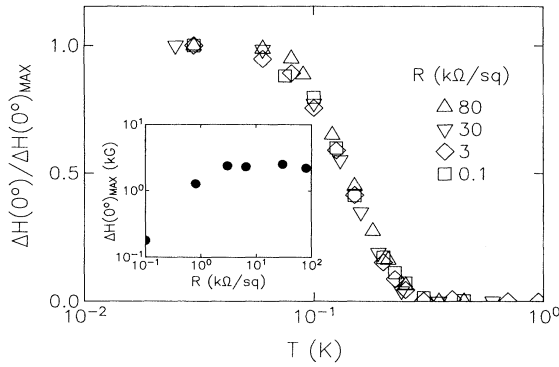
FIG. 1. Normalized hysteresis width versus temperature for samples of various sheet resistances. The collapse of data on a single curve indicates that the tricritical point $T_{tri} \sim 270$ mK is sample independent. Inset: hysteresis width as a function of normal-state sheet resistance.

ments of the superconducting fluctuations and the observation of quasireentrance in the resistance near 1 K. However, no significant hysteresis was ever found in these studies. We have found a similar quasireentrance in the same temperature range near 1 K (Ref. 12) but have only seen hysteresis below 0.27 K. Though hysteresis is not a necessary criterion for a first-order transition, it seems likely that the hysteresis in our films is directly related to the first-order spin-paramagnetic transition. It is also possible that the hysteresis is a manifestation of a more complex phase transition arising from the inherent granularity of our films. In this regard, it would be quite useful to extend previous experiments on quench-condensed samples[5] to lower temperatures to see whether or not hysteresis can be found in those systems.

We will now focus on the angular dependence of the hysteretic behavior. Figure 2(a) is a plot of sheet resistances R versus magnetic field H for a number of field orientations on a film with a normal-state sheet resistance $R = 5.2$ kΩ/sq. All of these data were taken at 26 mK. The zero-field transition temperature of this sample was $T_c \sim 1.7$ K. Note that close to the perpendicular field orientation, $\theta \sim 90°$, the resistive transition is broad and not hysteretic. With decreasing θ, however, the upper critical field increases very rapidly. For $\theta < 6.5°$, not only does the transition become sharper, but
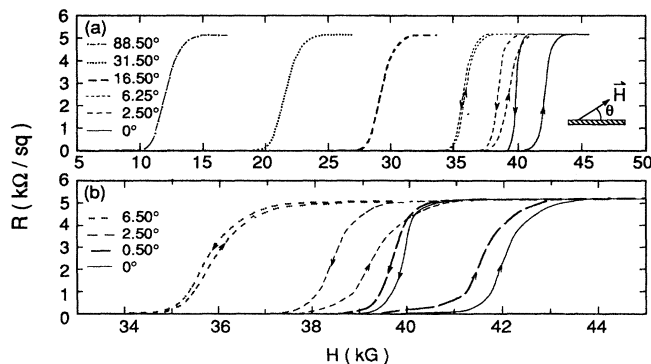

FIG. 2. (a) Sheet resistance R versus magnetic field at $T = 26$ mK for a number of field orientations. For $\theta < 6.5°$, the transitions become hysteretic. (b) Hysteretic behavior at small θ.
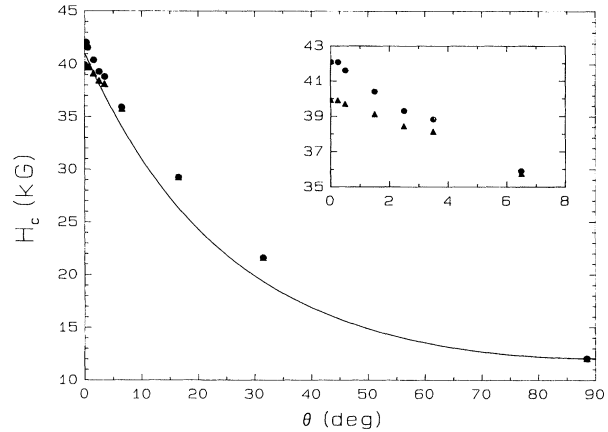

FIG. 3. Critical fields $H_c(\theta)$ versus field angle θ. $H_c(\theta)$ is defined at the midpoint of the resistive transitions in field-up (dots) and field-down (triangles) sweeps. The solid line is a plot of Eq. (1). Inset: the hysteresis at small θ.

more interestingly a giant hysteresis loop opens up. A blowup of the hysteretic behavior for small angles is shown in Fig. 2(b). We note that even at $\theta = 6.5°$ the perpendicular field component at the superconducting-normal transition, which is $H_c(6.5°)\sin(6.5°) \approx 4$ kG, is still much smaller than the perpendicular upper critical field $H_{c\perp} = H_c(90°) \approx 12$ kG. Hence, the superconducting-normal transition at $\theta = 6.5°$ is not dominated by the perpendicular component of the field.

In Fig. 3 we plot the critical field $H_c(\theta)$ versus angle θ where $H_c(\theta)$ was taken at the midpoint of the transitions in field-up and field-down sweeps. It is natural to compare the angular dependence of the critical field to Tinkham's formula,[9]

$$\frac{H_c(\theta)\sin(\theta)}{H_{c\perp}} + \left(\frac{H_c(\theta)\cos(\theta)}{H_{c\parallel}} \right)^2 = 1, \qquad (1)$$

where $H_{c\perp}$ and $H_{c\parallel}$ are the perpendicular and parallel critical fields, respectively. Although Eq. (1) does not include the spin paramagnetic effect, the agreement with data is usually fairly good even in the spin-paramagnetic limit.[10] This is because the pair-breaking parameters underlying Tinkham's formula have the same quadratic dependence as those of the spin-paramagnetic pair-breaking mechanism.[4] The solid line in Fig. 3 is a pot of Eq. (1), where $H_{c\perp}$ was determined from the measured values in Fig. 2. $H_{c\parallel}$ was obtained by averaging the $\theta = 0°$ critical field values from the field-up and the field-down sweeps. This average was taken simply because we have found that, in the hysteretic regime, neither critical field curve represents the equilibrium transition. In particular, when the field-up or field-down sweep was paused, the resistance subsequently underwent a very slow (i.e., tens of hours) stretched-exponential relaxation toward a thermodynamic equilibrium value.[7,8] This relaxation was not observed for $T > 270$ mK or $\theta > 7°$. Therefore, it seems reasonable that the critical field of the "true" equilibrium transition is somewhere in the middle of the hysteresis loop. Though Eq. (1) reproduces the gross character of the angular dependence of the critical field, there are significant deviations. This is
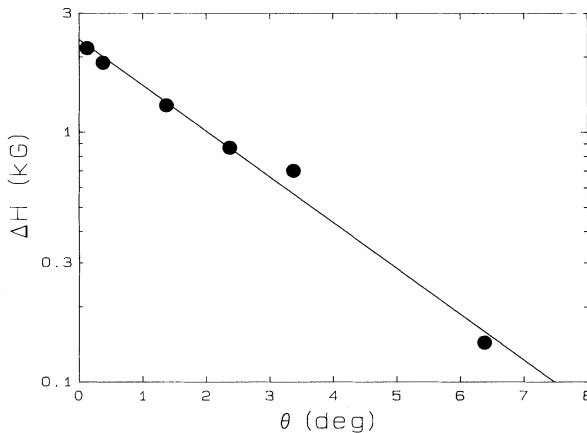
FIG. 4. Semi-log plot of the width of the hysteresis $\Delta H(\theta)$ as a function of field angle θ. The solid line is a least-squares fit showing that $\Delta H(\theta)$ decreases exponentially with increasing θ.
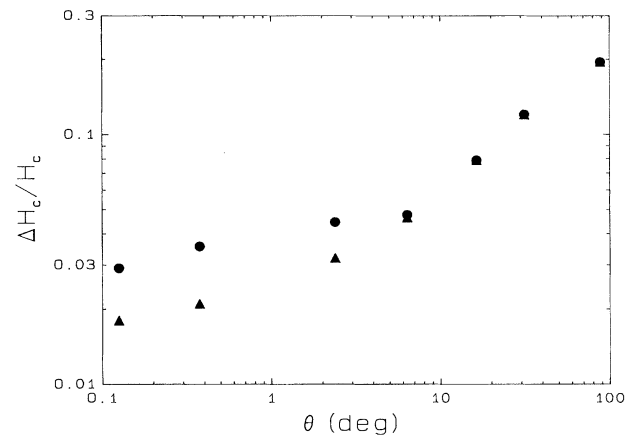

FIG. 5. The angular dependence of the normalized width of the transitions. ΔH_c is defined as the change infield necessary to bring the resistance from 10 to 90 % of R_N. Circles are from field-up sweeps. Triangles are from field-down sweeps.

not surprising since Eq. (1) is expected to be valid[10] only in the limit $H_{c\parallel}/H_{c\perp} \gg 1$. In our case $H_{c\parallel}/H_{c\perp} = 3.4$. In the inset to Fig. 3, we plot a magnified view of the critical fields from field-up (dots) and field-down (triangles) sweeps at small angles, showing the opening up of the hysteresis. The angle dependence of the width of the hysteresis $\Delta H(\theta)$ is shown in Fig. 4. The solid line in Fig. 4 is a least-squares fit to the exponential form $\Delta H(\theta) = \Delta H(0)\exp(-\theta/\theta_0)$. The data in Fig. 4 clearly show that the hysteresis collapses exponentially with increasing angle with a characteristic angle of $\theta_0 = 2.4°$. For $\theta \approx 6.5°$, the width of the hysteresis has decreased over one order of magnitude. This suggests that the superconducting-normal transition crosses over from first-order to second-order at a field orientation $\theta_c \approx 6.5°$. This evolution is also reflected in the angular dependence of the relative width of the transitions as shown in Fig. 5. Here the transition width $\Delta H_c(\theta)$ is defined as the field interval associated with a change in sheet resistance from 10 to 90 % of R_N. These data are normalized by the critical fields $H_c(\theta)$. Note that the width of the transitions decreases monotonically with decreasing θ down to $\theta \approx 10°$. Below 10° the transition becomes hysteretic with an asymmetry in

the up-sweep and down-sweep transitions. In particular, the transition in the field-down sweep is always sharper than its field-up counterpart as can be seen in the $\theta < 10°$ data in Fig. 5. Since the critical fields measured in the field-down sweeps decrease with decreasing temperature below T_{tri},[6] this asymmetry could be a supercooling effect.

In summary, studies of the angular dependence of the hysteretic critical field transition in spin-paramagnetically limited ultrathin granular Al films reveal a zero-temperature crossover from a first-order transition to a second-order transition near $\theta = 6.5°$. There is no theoretical prediction for either the hysteresis or the phase diagram of the spin-paramagnetic transition in a tilted field. Currently, tunneling experiments are in progress to probe quasiparticle energy spectrum and density of states as functions of field and angle at various temperatures.

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