Density of states, entropy, and the superconducting Pomeranchuk effect in Pauli-limited Al films

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We present low-temperature tunneling density of states measurements of Pauli-limited Al films in which the Zeeman and orbital contributions to the critical field are comparable. We show that films in the thickness range of 6–7 nm exhibit a reentrant parallel critical field transition which is associated with a high-entropy superconducting phase, similar to the high-entropy solid phase of ^{3}He responsible for the Pomeranchuk effect. This phase is characterized by an excess of states near the Fermi energy so long as the parallel critical field transition remains second order. Theoretical fits to the zero-bias tunneling conductance are in good agreement with the data well below the transition but theory deviates significantly near the transition. The discrepancy is a consequence of the emergence of *e*-*e* interaction correlations as one enters the normal state.

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I. INTRODUCTION

Phase transitions are ubiquitous in physics and continue to be a large and important part of current condensed matter research. Perhaps the most common example of a classical phase transition is one in which a system undergoes a first-order transition from a disordered phase to a phase exhibiting long-range order, such as a liquid to solid transition. Because liquid has a higher entropy, latent heat must be removed from the system before the solid phase can form. Though examples are exceedingly rare in nature, systems that undergo a transition from a disordered phase to an ordered phase of higher entropy exhibit a number of counterintuitive and fascinating properties such as reentrance and negative latent heats. The most famous example is the liquid to solid transition in ^{3}He. Subtle correlations between its spin and coordinate degrees of freedom produce an anomalously low entropy in liquid ^{3}He. Consequently, the entropy of solid ^{3}He is higher than that of the liquid[1] near the melting curve. As was first pointed out by Pomeranchuk,[2] the resulting negative latent heat can be used to produce a cooling effect if one converts liquid to solid by increasing the pressure. This is commonly known as the Pomeranchuk effect and it was, in fact, the method used to cool liquid ^{3}He in the series of experiments that led to the discovery of superfluid ^{3}He.[1] The only other quantum system known to exhibit a high-entropy ordered phase is Pauli-limited superconductivity.[3,4] In analogy to ^{3}He, the anomalous entropy is associated with the interplay between electronic spin and orbital degrees of freedom where the superconducting phase plays the role of the solid, the normal phase the liquid, and a parallel magnetic field the role of pressure. In the present paper, we address the possibility of realizing a superconducting version of the Pomeranchuk effect.

Magnetic fields generally have a detrimental effect on superconductors via two independent channels. The first is an orbital effect associated with the fact that cyclotron motion is incompatible with the formation of Cooper pairs and hence superconductivity; for the vast majority of superconducting systems the critical field transition is completely dominated by the orbital response of the conduction electrons. If a magnetic field is applied in the plane of a superconducting film whose thickness is much less than the superconducting coherence length and whose electron diffusivity is low,[3] then the critical field transition is, in fact, mediated by the Pauli spin polarization of the electrons: the system will undergo a well-defined first-order phase transition to the normal state when the electron Zeeman splitting is of the order of the superconducting gap.[5,6] When realized in low-atomic-mass superconductors such as Al and Be, this "spin-paramagnetic" (S-P) transition, as it is commonly known, exhibits a variety of novel phases along with some very unusual dynamics.[3,7–10] Here we present tunneling measurements of the density of states (DOS) in Al films which are about 2–3 times thicker than those typically used in S-P studies.[11] In this marginally Pauli-limited regime, the critical field behavior of the films can become reentrant.[12] The reentrance occurs because the superconducting state has higher entropy than the normal state. This excess entropy is expected to be reflected in an enhancement of the Fermi energy DOS *above* that of the normal state.[9,12,13]

In a classic S-P geometry a planar magnetic field is applied to a film of thickness much less than the Pippard coherence length ξ. The relative importance of the orbital response compared with the spin polarization can be quantified by the dimensionless orbital depairing parameter[3]

$$c = \frac{D(ed)^2\Delta_0}{6\hbar\,\mu_B^2} \tag{1}$$

where D is the electron diffusivity, d is the film thickness, e is the electron charge, Δ_0 is the zero-temperature, zero-field gap energy, and μ_B is the Bohr magneton. Fulde and co-workers[3] showed that in the absence of spin-orbit coupling, the low-temperature critical field behavior would remain first order for $c \leq 1.66$, but interestingly, for (thicker) films with values in the range $1.66 < c < 2.86$, the critical field behavior was predicted to be reentrant. Reentrance has indeed been observed in Al (Ref. 14) and TiN (Ref. 15) films of comparable thickness to those used in this study. Tunneling DOS studies, however, have been quite limited and though considerable theoretical work has been done on the problem,[12,16] to the best of our knowledge a quantitative comparison between theory and experiment was never made in the regime where the DOS enhancement is present.

II. EXPERIMENTAL DETAILS

A series of Al films with thicknesses ranging from 6 to 8 nm and corresponding 100 mK normal state sheet resistances ranging from $R=10$ to $20\ \Omega$ were fabricated by *e*-beam deposition of 99.999% Al onto fire-polished glass microscope slides held at 84 K.[10] The depositions were made at a rate of ~ 0.2 nm/s in a typical vacuum $P<3\times 10^{-7}$ Torr. After deposition, the films were exposed to the atmosphere for 0.5–4 h in order to allow a thin native oxide layer to form. Then a 14-nm-thick Al counterelectrode was deposited onto the film with the oxide serving as the tunneling barrier. The counterelectrode had a parallel critical field of ~ 1.1 T due to its relatively large thickness, which is to be compared with $H_{c\parallel}\sim 3$ T for the films. The junction area was about 1×1 mm^2, while the junction resistance ranged from 10 to 20 kΩ depending on exposure time and other factors. Only junctions with resistances much greater than that of the films were used. Measurements of resistance and tunneling were carried out on an Oxford dilution refrigerator using a standard ac four-probe technique. Magnetic fields of up to 9 T were applied using a superconducting solenoid. A mechanical rotator was employed to orient the sample *in situ* with a precision of $\sim 0.1°$.

III. RESULTS AND DISCUSSION

Shown in the upper panel of Fig. 1 is the temperature dependence of the parallel critical field of a 2.5-nm-thick Al film having $T_c=2.7$ K, $\Delta_0/e=0.41$ mV, $\xi\sim 15$ nm, and sheet resistance $R\sim 1$ kΩ. Using the bulk DOS for Al $\nu_0=2\times 10^{22}(\text{eV cm}^3)^{-1}$ to estimate D in Eq. (1), the orbital depairing parameter for this film is $c=0.02$.[17] The upper panel of Fig. 1 represents the classic S-P phase diagram in which a high-temperature line of second-order phase transitions terminates into a line of first-order transitions at the tricritical point $T_{tri}\sim 0.3T_c$.[18] The low-temperature superconducting (S) and normal (N) phases are separated by a robust coexistence region in which the state of the system is solely determined by the system state prior to entering the region, i.e., the state memory (SM) region.[8] In the lower panel of Fig. 1 we show the corresponding phase diagram for a 6-nm-thick Al film having $T_c=2.1$ K, $\Delta_0/e=0.32$ mV, $\xi=56$ nm, and $R=20\ \Omega$. Note that this thicker film has a substantially lower critical field as a consequence of orbital depairing, and that the structure of its phase diagram is dramatically altered. The critical field behavior is now reversibly reentrant by virtue of the local maximum in the parallel critical field near $T/T_c=0.45$. Indeed, a naive estimate of the orbital depairing parameter $c\sim 2.2$ falls within the reentrant range. In the upper inset we show that the resistive parallel critical field at

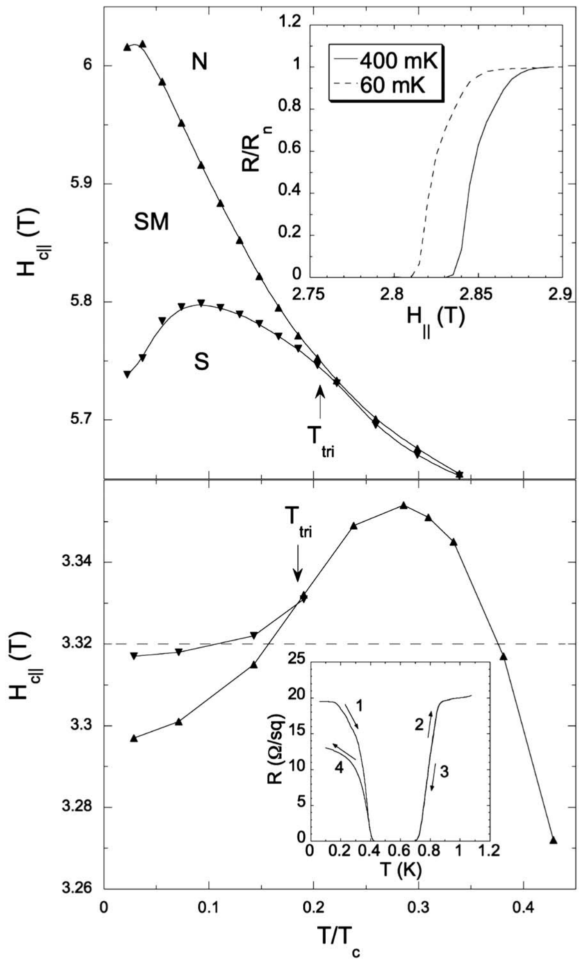

FIG. 1. Upper panel: phase diagram of a 2.5-nm-thick Al film ($T_c=2.7$ K) in parallel field, where S is the superconducting phase, N the normal state, SM the state memory coexistence region, and T_{tri} the tricritical point. Lower panel: phase diagram of a 6-nm-thick Al film ($T_c=1.9$ K). Note the local maximum in the second-order portion of the critical field curve. The horizontal dashed line represents a reentrant cut through the phase diagram. Upper inset: Two resistive critical field transitions in the 6 nm film showing a higher $H_{c\parallel}$ at higher temperature. Lower inset: Reentrant superconducting transition corresponding to the cut through the 6 nm phase diagram represented by the dashed line. The numbers represent the temperature scan sequence.

400 mK is higher than it is at 60 mK. Reentrance is easily demonstrated by cutting across the phase diagram along the dashed line in Fig. 1, as is shown in the lower inset. The numbers in this curve represent the sequence of temperature scans at a constant field. The reentrant region was entered at 60 mK by lowering the field from a supercritical value of 3.5 T to the field at which the temperature scans were performed, 3.320 T. The low-temperature hysteresis is a consequence of the fact that the transition becomes first order below ~ 0.4 K.

Shown in Fig. 2 are tunneling spectra at several values of parallel critical field. At the temperatures at which these data were taken the tunneling conductance is simply proportional to the electronic DOS.[19] The Zeeman splitting of the BCS coherence peaks can be seen in the 2.2 T curve.[20] As the

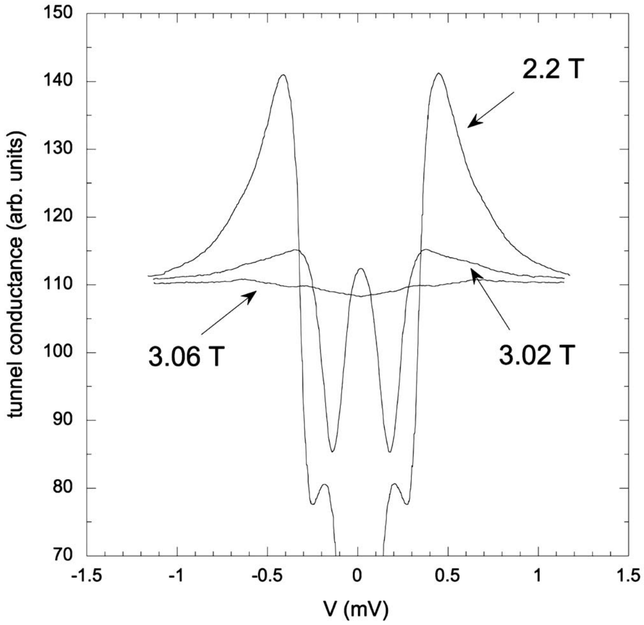

FIG. 2. Tunneling density of states spectra of a 7 nm Al film in several parallel magnetic fields. Note that the zero-bias peak in the 3.02 T curve rises above the 3.06 T normal-state curve. The modest suppression of the DOS at zero bias in the normal-state curve is an *e-e* interaction effect and is commonly known as the zero-bias anomaly.

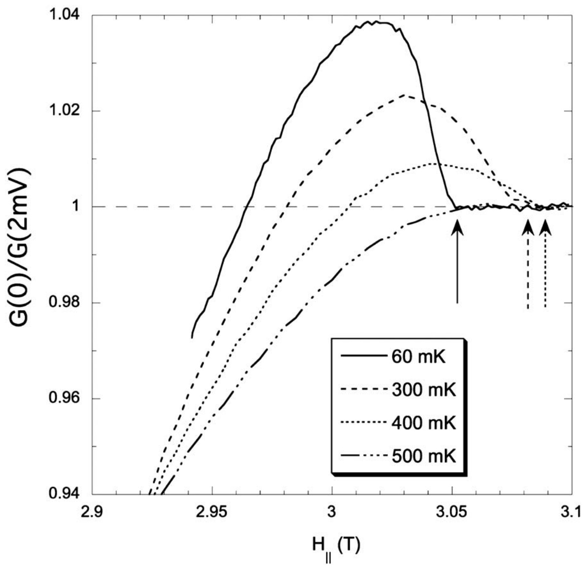

FIG. 3. Normalized density of states at zero bias for a 7-nm-thick film. The peaks correspond to excess states at the Fermi energy associated with the onset of superconductivity. Note that the onset critical fields, indicated by the arrows, are not monotonic in T.

field is increased, the gap begins to collapse due to orbital pair breaking, and near the critical field transition the subgap Zeeman features reach the Fermi energy, thereby producing a zero bias peak in the DOS curve. This superconducting DOS enhancement is evident in the 3.02 T curve of Fig. 2, where the DOS at V=0 is clearly higher than that of the 3.06 T normal state curve.

In Fig. 3 we plot the zero-bias tunneling conductance as a function of parallel field at a variety of temperatures for a 7 nm Al film of resistance $R=15.8\ \Omega$. The tunneling conductance has been normalized by the normal-state value. The arrows indicate the onset of superconductivity. Because of the reentrance effect, the onset is not monotonic in temperature. Suzuki and co-workers[14,21] reported a $\sim 1\%$ DOS enhancement over only a very narrow range of temperatures $550 < T < 650$ mK in Al films in the thickness range of 7–9 nm. In contrast to these earlier reports, the DOS enhancement peak appears below 500 mK and, in fact, grows in magnitude with decreasing temperature. This film did not exhibit a tricritical point; therefore we believe that the transition remained second order down to 60 mK. Theoretically one can compute such curves, assuming that the film's parameters are known, by numerically solving the self-consistent equations for the order parameter and the "molecular" magnetic field together with the Usadel equations for the semiclassical Green's functions; these equations are derived in Ref. 13, and we refer the reader to this work for the details (see also Ref. 15 for numerical calculations of the temperature dependence of the critical field). Here we recall that the input parameters needed to solve these mean-field equations at a given temperature T are the orbital pair-breaking parameter c [cf. Eq. (1)]; the spin-orbit scattering parameter $b=\hbar/3\Delta_0\tau_{so}$, where τ_{so} is the spin-orbit scattering time; the Fermi-liquid parameter G^0 which, in the normal state, describes the renormalization of the spin susceptibility; and the gap Δ_0. In Fig. 4 we compare our data to theoretical curves calculated using parameters values $c=0.79$, $b=0.052$, $G^0=0.155$, and the measured gap $\Delta_0=0.32$ meV, for three different temperatures. We note that the value of b is in agreement with what is found in the literature,[13] while G^0 is consistent with what was previously measured in experiments performed in the normal state on similar samples.[8] On the other hand, the value of c used to fit the data is significantly lower than that estimated by Eq. (1) and ostensibly below the reentrant threshold discussed above. However, the range of c over which reentrance can be observed is affected by both spin-orbit scattering and the Fermi-liquid effect, as discussed in detail, e.g., in Refs. 3 and 15. Furthermore, Eq. (1) is valid only in the "local" limit $\ell \ll d$, where ℓ is the mean free path for impurity scattering. A more general relation for c is found by multiplying Eq. (1) by a function $f(\ell/d)$, which describes the crossover between the "local" and "nonlocal" ($\ell/d \gg 1$) electrodynamics in thin films,[16] and whose asymptotic behavior is $f(x) \simeq 3/4x$ for $x \gg 1$; from the measured conductance of our sample, the bulk DOS ν_0, and the bulk Fermi energy $E_F=11.7$ eV, we estimate that $\ell/d \approx 3.4$ and hence $c \simeq 0.73$, in good agreement with the numerical fitting; therefore the values of all three fitting parameters c, b, and G^0 are consistent with independent measurements or estimates.

At fields well below the critical field there is excellent agreement between theory and experiment. As the field increases, however, the measured zero-bias tunneling DOS falls below the computed value by an amount we define as η in Fig. 4. The origin of η cannot be attributed to superconducting fluctuations near the critical field, as the Cooper pair-

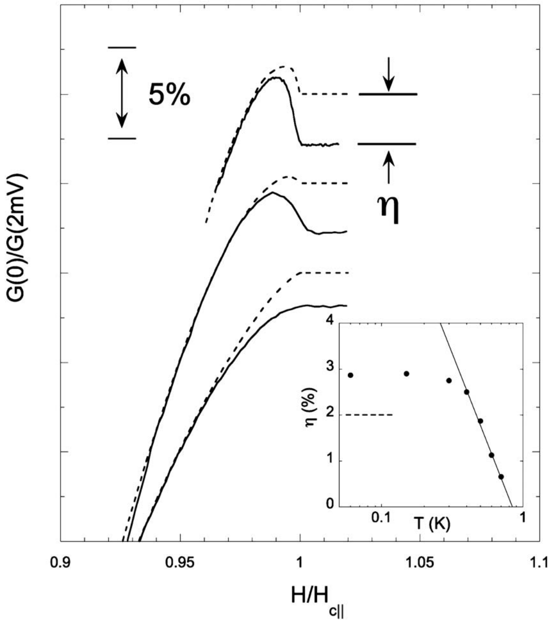

FIG. 4. The dashed lines represent theoretical fits to the zero-bias tunneling data at 60, 300, and 500 mK, top to bottom. The respective curves have been shifted for clarity. Only that portion of the data well below the critical field was used in the fits. The magnitude of the discrepancy between the theory and data near the transition is represented by the parameter η. Inset: magnitude of the offset between theory and data in the normal state as a function of temperature for the 7 nm Al film. The solid line is provided as a guide to the eye. The horizontal dashed line represents the relative magnitude of the zero-bias anomaly in the film.

ing contributions to the DOS are shifted by the parallel magnetic field to energies of the order of the Zeeman energy;[8] it can, however, be explained as follows: increasing the field depresses the order parameter, so that more electrons can contribute to interaction correlations which are not included in the mean-field analysis of Ref. 13; these correlations cause a renormalization of the DOS close to the transition. In fact, it is well known that *e*-*e* interactions lead to a logarithmic zero bias correction to the two-dimensional tunneling DOS, $\delta\nu \propto \ln(T\tau)$, where τ is the elastic scattering time.[22] In the inset of Fig. 4 we plot η as a function of $\ln T$. Note that, above 300 mK, η is well described by a $\ln T$ temperature dependence. The low-temperature saturation is partly a consequence of the $\sim 10\ \mu$V probe voltage used to measure the tunnel conductance.[23] The horizontal dashed line in the inset represents the magnitude of the ZBA as obtained by a direct measurement of the normal state DOS at 60 mK. Note that the ZBA and η are of the same magnitude and that a close inspection of the data in Fig. 4 reveals that the region over which there is disagreement between mean-field theory and experiment grows with increasing temperature, as would be expected.

In Fig. 5 we plot the magnitude of the DOS peak as a function of temperature for a 7 nm and a 6 nm film. Interestingly, the temperature dependence of the peak is quite different for the two films. The critical field behavior of the

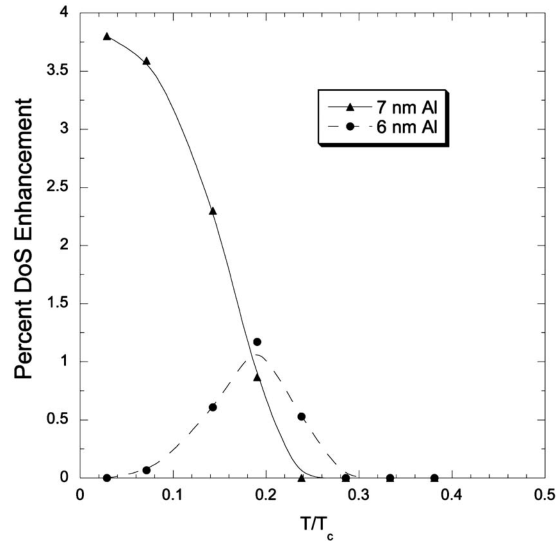

FIG. 5. Magnitude of DOS enhancement peaks such as those in Fig. 3 as a function of reduced temperature for a 6- and a 7-nm-thick Al film. The 7 nm film did not exhibit a finite tricritical point. The 6 nm film critical field transition became first order below $T/T_c \sim 0.2$.

7 nm film did not show any signs of hysteresis down to 60 mK, indicating that the transition remained second order. In contrast, the 6 nm film exhibited a tricritical point at $T/T_c \sim 0.2$, as can be seen in Fig. 1. Note that the DOS peak in this film has a local maximum at the tricritical point, and that the DOS enhancement is rapidly extinguished as the temperature is lowered below T_{tri}. This may explain why earlier reports of the DOS enhancements by Suzuki and co-workers[9] were limited to a relatively narrow range of temperatures, i.e., temperatures lying between a tricritical point and the maximum of the critical field curve.

In summary, we show not only that marginally thick Al films exhibit reentrance, but also that the associated DOS enhancement can be observed down to millikelvin temperatures so long as the critical field transition remains second order. Since the Pomeranchuk effect is based on the latent heat of a first-order transition, it seems unlikely that one can produce cooling in Al films. Nevertheless, the fact that the DOS enhancement peak occurs at the Fermi energy affords one an unparalleled opportunity to study the interplay between Coulombic *e*-*e* interaction fluctuations and pairing fluctuations in the vicinity of the transition. Indeed, it is fortuitous that the suppression of the DOS associated with the former is comparable in magnitude to the enhancement of the latter.

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