Spin Proximity Effect in Ultrathin Superconducting Be-Au Bilayers

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We present a detailed study of the effects of interface spin-orbit coupling on the critical field behavior of ultrathin superconducting Be/Au bilayers. Parallel field measurements were made in bilayers with Be thicknesses in the range of $d = 2$–30 nm and Au coverages of 0.5 nm. Though the Au had little effect on the superconducting gap, it produced profound changes in the spin states of the system. In particular, the parallel critical field exceeded the Clogston limit by an order of magnitude in the thinnest films studied. In addition, the parallel critical field unexpectedly scaled as $H_{c\parallel}/\Delta_0 \propto 1/d$, suggesting that the spin-orbit coupling energy was proportional to Δ_0/d^2. Tilted field measurements showed that, contrary to recent theory, the interface spin-orbit coupling induces a large in-plane superconducting susceptibility but only a very small transverse susceptibility.

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In conventional BCS superconductivity, the condensate is time reversal invariant and is formed from Cooper pairs consisting of electrons of opposite momentum and opposite spin [1]. In nonconventional superconductors, however, this simple symmetry can be modified by the underlying crystal structure and/or the symmetry of the pairing interaction. A compelling example of the latter is the recently discovered heavy fermion superconductor $CePt_3Si$, whose crystal structure lacks inversion symmetry [2]. $CePt_3Si$ exhibits a line node gap structure [3–5] which is believed to be, in part, a consequence of strong spin-orbit coupling in a noncentrosymmetric crystal symmetry [2,6,7]. This has stimulated renewed interest in the possibility of realizing nonconventional pairing states from the convolution of broken inversion symmetry and spin-orbit coupling, neither of which violates time reversal invariance. In the present Letter, we present a magnetotransport study of the effects of interface spin-orbit coupling (ISOC) on the superconducting behavior of Be films coated with 0.5 nm of Au. This bilayer configuration not only represents a model realization of broken inversion symmetry, but it also affords a controllable ISOC strength. Historically, a similar superconducting/normal-metal geometry was used in the original investigations of the proximity effect [8]. We have employed bilayers in which the nonsuperconducting Au layer is too thin to have an appreciable effect on the magnitude of the superconducting Be order parameter. Nevertheless, the Au layer produces an interfacial spin-mixing interaction that profoundly alters the otherwise spin-singlet character of the Be layer condensate via a "proximity effect" in the spin degrees of freedom.

In the experiments described below, we use critical field measurements to determine the SO coupling strength in Be/Au films of varying Be thickness. The Maki equation [9,10] is a useful tool for extracting the spin response of the superconductor from the orbital response, particularly when the film is not in the thin-film limit and/or the field is not parallel to the film surface. In general, the critical field of a thin film is a function of the superconducting gap Δ_0, the film thickness d, the electron diffusivity D, and the spin-orbit coupling parameter b. Traditionally, b is interpreted as an intrinsic spin-orbit scattering rate $b = \hbar/3\tau_{so}$. By mixing spin states, it induces a finite spin susceptibility χ^s in the superconducting phase and in the limit $b \gg \Delta_0$, $\chi^s(0)/\chi^n \approx 1$–$2\Delta_0/3b$ [11], where Δ_0 is the superconducting gap and χ^n is the normal state spin susceptibility. The effect on the critical field H_c is determined by the implicit function [12]:

$$\ln\left(\frac{T}{T_c}\right) = \psi\left(\frac{1}{2}\right) - \frac{\alpha_+}{2\gamma}\psi\left(\frac{1}{2} + \frac{\epsilon + 2\alpha_-}{4\pi k_B T}\right) + \frac{\alpha_-}{2\gamma}\psi\left(\frac{1}{2} + \frac{\epsilon + 2\alpha_+}{4\pi k_B T}\right), \tag{1}$$

where

$$\alpha_\pm = b \pm \gamma, \qquad \gamma = (b^2 - \mu_B^2 H_c^2)^{1/2},$$

T_c is the critical temperature, and ψ is the digamma function. ϵ is a function of the angle between the plane of the film and the magnetic field,

$$\epsilon(\theta) = D[2eH_c \sin(\theta) + \tfrac{1}{3}(deH_c \cos(\theta))^2/\hbar],$$

where $\theta = 0$ corresponds to a field parallel to the film plane. The parallel field solutions of Eq. (1) in the $d \to 0$ limit, where orbital effects are negligible, are of particular relevance [1],

$$\frac{2\mu_B H_{c\parallel}}{\Delta_0} \approx \sqrt{2}, \qquad b/\Delta_0 \ll 1, \tag{2}$$

$$= \sqrt{3b/\Delta_0}, \qquad b/\Delta_0 \geq 1, \tag{3}$$

where Eq. (2) is the familiar Clogston critical field [13–15]. Note that the parallel field can become arbitrarily high in the limit $b \gg \Delta_0$. In contrast, if the Zeeman coupling is neglected then, at any finite thickness $d < \xi$, the parallel critical field is limited by the orbital term,

$$\frac{2\mu_B H_{c\|}}{\Delta_0} = \sqrt{\frac{3\hbar^3}{m^2 D \Delta_0}}\frac{1}{d}. \tag{4}$$

Numerous studies of the spin-paramagnetic transition in ultrathin Al and Be films have shown that these two light elements have a very low intrinsic spin-orbit scattering rate [16–18] and are true spin-singlet superconductors. Consequently, they make ideal candidates for systematic studies of the effects of ISOC induced by heavy element coatings [19,20]. Recent analysis of the spin states of two-dimensional superconductors lacking inversion symmetry, and, in particular, superconducting-normal-metal bilayers, predicts that ISOC will introduce an anisotropic spin triplet component into the superconducting ground state [21,22]: $\chi_\|^s \sim \chi^n/2$, $\chi_\perp^s \sim \chi^n$, where $\chi_\|^s$ is the in-plane superconducting susceptibility and $\chi_\perp^n$ is the transverse susceptibility. This would imply that the parallel critical field of a bilayer, such as Al/Pt of Ref. [16], would never be larger than $\sqrt{2}H_c^{\mathrm{Clogston}}$ [23]. However, the critical field enhancements observed in those early experiments were significantly greater than this upper limit.

Be/Au bilayers of varying Be thickness were prepared by e-beam evaporation in an initial vacuum of $\sim$0.2 μTorr. All of the depositions were made on fire-polished glass substrates held at 84 K. First, a Be film with thickness in the range 2.–30.0 nm was deposited at a rate of 0.14 nm/s; then a 0.5 nm Au film was deposited at 0.01 nm/s without breaking the vacuum. The morphology of the Be and Be/Au films was probed via atomic force microscopy and found to be very smooth and homogenous, with no evidence of islanding or granularity [18]. The films were trimmed in order to eliminate edge effects, and resistive measurements were made in a dilution refrigerator with a base temperature 50 mK using a standard four-probe lock-in method. The films were aligned with the magnetic field via an *in situ* mechanical rotator. In the data presented below, the transition temperatures were defined by the temperature at which the resistance fell to 10% of its normal state value and the critical field was determined by the midpoint of the resistive transition [24].

In Fig. 1, we plot the resistance of a number of Be/Au bilayers of varying Be thickness as a function of temperature and parallel magnetic field. Note that the transition temperature of the bilayers decreases monotonically with decreasing thickness, but the critical field is not a monotonic function of thickness. Be films with $d < 2$ nm are known to display a nonperturbative zero bias anomaly in their tunneling density of states, which is associated with the emergence of the Coulomb gap [25]. As can be seen in Fig. 2, this is also the critical thickness below which the zero temperature superconducting phase is lost and the

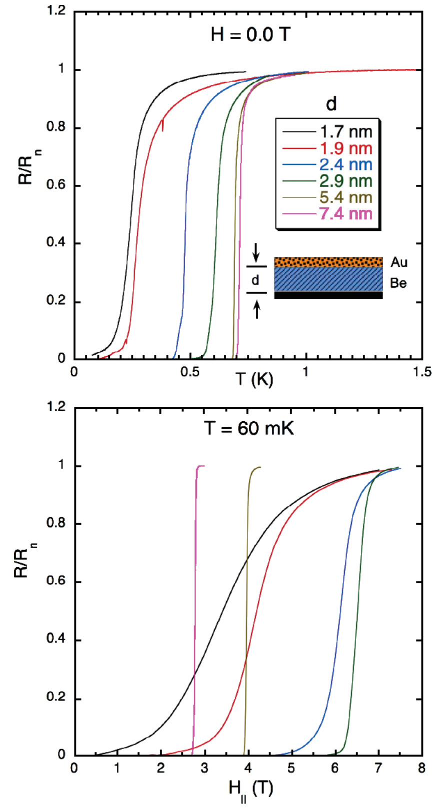

FIG. 1 (color). Upper panel: Temperature dependence of the normalized resistivity of Be/Au bilayers of varying Be thickness d and constant Au thickness of 0.5 nm. R_n is the normal state resistance. Lower panel: Corresponding low temperature parallel critical field transitions.

electron diffusivity goes to zero. In order to make use of Eq. (1), it was necessary to fit the thickness dependence of T_c and D with an empirical functional form. In particular, the solid lines in the main panel and the inset in Fig. 2 are the functions

$$T_c(d) = T_{co}\tanh[(d - 1.35)/1.29)], \tag{5}$$

$$D(d) = D_o \tanh[d^2/23.3], \tag{6}$$

where $T_{co} = 0.68$ K and $D_o \sim 3\hbar/m$. D_o was determined from films with $d > 10$ nm using the relation $1/R = 2e^2\nu_0 D_o d$, where R is the sheet resistance and ν_0 is the density of states per spin of Be. The BCS coherence length for a Be film with $T_c \sim 0.7$ K is $\xi_o \sim 4$ μm. For the range of diffusivities plotted in the inset in Fig. 2, the mean free path is always $l_o < 1$ nm and the corresponding Pippard coherence lengths are in the range $\xi = 0.85\sqrt{\xi_o l_o} \approx$ 20–40 nm. Consequently, all of the data discussed below are in the "dirty" limit where $l_o \ll d < \xi$.

We have measured the parallel critical field $H_{c\|}$ of Be films of varying thickness ($d \approx$ 2–30 nm) with and without 0.5 nm Au overlayers; see Fig. 1. The Au coatings *increased* the normal state resistances by 10%–50%. In Fig. 3, we plot $2\mu_B H_{c\|}/\Delta_0$ as a function of the inverse Be thickness at 60 mK, where we used the relation $\Delta_0 = 2.1k_B T_c$ [17]. The triangular symbols correspond to

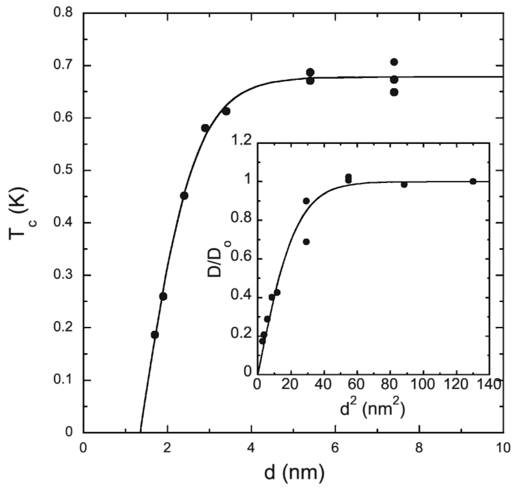

FIG. 2. Transition temperature of Be/Au bilayers as a function of Be thickness as extracted from data such as those in Fig. 1. The Au thickness was 0.5 nm in each sample. The solid line is a best fit to the data using the empirical form of Eq. (5). Inset: Relative diffusivity of Be/Au bilayers as a function of Be thickness. The solid line is a fit to Eq. (6).

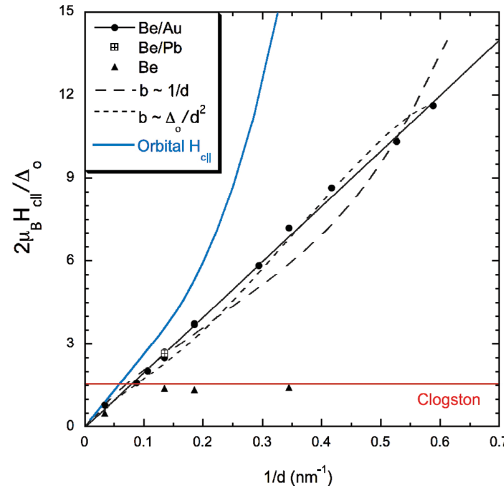

FIG. 3 (color). Reduced parallel critical fields as a function of Be thickness for Be/Au bilayers (circles), Be/Pb (crossed box), and pure Be films (triangles). The blue line represents the orbitally limited critical field given by Eq. (4). The solid black line is a linear least-squares fit to the Be/Au data and is provided as a guide to the eye. The horizontal red line represents the Clogston critical field. The dashed lines represent solutions to Eq. (1) using the indicated functional forms for the SO coupling parameter.

pure Be films. Note that, except for the thickest Be sample, the critical field is independent of d and precisely that of Eq. (2). In contrast, the reduced critical field of the Be/Au bilayers (circular symbols) is not only a strong function of thickness, but it exceeds the Clogston limit by more than a factor of 8 in the thinnest bilayer.

The blue line in Fig. 3 represents the thickness dependence of the orbital critical field of Eq. (4) using Eqs. (5) and (6). Though the reduced critical fields of the thinnest bilayers (i.e., $d < 5$ nm) greatly exceed the Clogston limit, they fall well below the finite-thickness orbital limit represented by this line, suggesting that the transitions remain Zeeman mediated up to the highest reduced critical fields. If one can indeed neglect orbital contributions, then the critical field is simply determined by Eq. (3) and the linearity of the data in Fig. 3 can be accounted for by a SO coupling parameter that scales as $b \sim \Delta_0/d^2$. Of course, orbital effects cannot be neglected over the entire thickness range of the data set in Fig. 3. As a consistency check, we have numerically solved Eq. (1) and performed least-squares fits to the data using specific forms for $b(d, \Delta_0)$. The long-dashed line represents a best fit using $b = b_o/d$ in which only the prefactor b_o was varied. Though this form was suggested by Bergmann [26,27] from magnetoresistance studies of nonsuperconducting Mg/Au bilayers, it does not give good agreement with the data. In contrast, the short-dashed line in Fig. 3 represents a best fit using the form suggested by Eq. (3), $b = b_o\Delta_0/d^2$, where only the prefactor b_o was varied. As expected, this form reproduces the scaling behavior of the critical field data quite well. The gap dependence of b may be related to fact that the critical field measures the coupling parameter as averaged over the thickness of the Be layer. If this is the case, then the critical field is sensitive to the spin penetration depth, i.e., the length scale over which the mixed-spin states penetrate the interior. This would suggest that the correspondence between the normal state SO scattering rate and the superconducting SO coupling parameter is nontrivial.

By comparing the angular dependence the critical field Be/Au bilayers with that of pure Be films, we can extract the spin anisotropy of the bilayers. Upon tilting the sample out of parallel orientation, orbital contributions to the critical field quickly dominate. Consequently, it is difficult to infer any anisotropy in the Zeeman response from the raw rotational data (see insets in Fig. 4). To circumvent this, we have measured the ratio of the Be/Au critical fields to that of pure Be films of equal thickness at a variety of tilt angles θ. Typical behavior is shown in Fig. 4, where we plot the critical field ratio of a 5.4 nm Be/Au bilayer and a 5.4 nm Be film. We believe that the dip structure near 20° is a consequence of an anisotropic susceptibility in the Be/Au bilayers. This behavior was observed over a wide range of thicknesses $d = 3$–7 nm. Because the perpendicular critical field H_{c2} of the bilayer was a factor of 3 higher than that of the Be film in Fig. 4, the ratio is not unity at $\theta = 90°$. The solid line is the expected angular dependence of Eq. (1), with $b = 0.013$ mV for the Be film and $b = 1.85$ mV for the bilayer, as determined from fits to the inset data. For both samples $\Delta_0 \sim 0.1$ mV, and the bilayer was in the strong ISOC limit with $b/\Delta_0 \sim 15$. As can be seen by the solid line, if b is angle independent, then one obtains a solution that is a monotonic interpolation between the parallel and perpendicular field ratios, independent of the relative thickness, T_c, resistance,

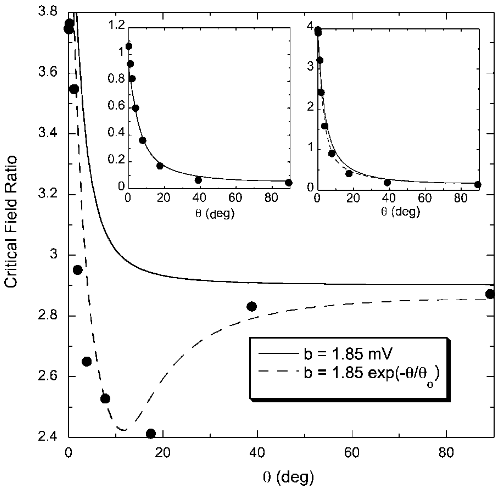

FIG. 4. Ratio of the critical field of a 5.4 nm Be/Au bilayer ($T_c = 0.68$ K, $H_{c2} = 0.137$ T, $R = 240\ \Omega$) and 5.4 nm Be film ($T_c = 0.505$ K, $H_{c2} = 0.048$ T, $R = 162\ \Omega$) as a function of tilt angle. The solid line is the solution of Eq. (1) assuming an isotropic SO coupling parameter of $b = 1.85$ mV for the Be/Au bilayer and $b = 0.0132$ mV for the Be film. The dashed line is the solution of Eq. (1) assuming that the Be/Au SO parameter is exponentially attenuated with increasing tilt angle. Left inset: Fit of Eq. (1) to the Be film data. Right inset: The solid line is a fit of Eq. (1) to the Be/Au data with a constant b. The dashed line is a somewhat better fit using an exponentially form $b = b_o \exp(-\theta/\theta_o)$.

and/or perpendicular critical fields of the two films. In contrast, the dashed line depicts the solution to Eq. (1) assuming an exponentially attenuated parameter $b = 1.85 \exp(-\theta/\theta_o)$ mV, with a characteristic angle $\theta_o = 2.5°$. This angular dependence must also be reflected in the spin susceptibility of the bilayer. We contend that the behavior in Fig. 4 is, in fact, a manifestation of an anisotropic superconducting spin susceptibility that has an *in-plane* component that is of the order of the normal state susceptibility but a transverse component that is small.

In summary, we have used critical field measurements to show that a $\sim$1 monolayer coating of Au on a thin Be film produces a large, anisotropic enhancement to the Zeeman component of the critical field, the magnitude of which scales as the inverse of the Be thickness. We believe that the scaling represents the superconductor's attempt to reconcile a mixed-spin boundary condition at the Au interface with the intrinsic spin-singlet ground state of Be. Naively, one would expect that the ISOC penetration depth would be of the order of ξ, but it may be significantly shorter in the presence of disorder. Nevertheless, the anisotropic spin susceptibility is clearly evident in the tilted field data.

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