Interface Spin-Orbit Coupling in a Non-centrosymmetric Thin-Film Superconductor

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We present a detailed study of the effects of interface spin-orbit coupling (ISOC) on the critical field behavior of non-centrosymmetric (NCS), ultra-thin 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 no significant 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 $H_{c||}/\Delta_o \propto 1/d$ suggesting that the spin-orbit coupling energy was proportional to Δ_o/d^2. Tilted field measurements showed that contrary to recent theory, the ISOC induces a large in-plane superconducting susceptibility but only a very small transverse susceptibility.

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One of the most fundamental characteristics of a superconductor is the symmetry of its condensate wavefunction. Indeed, this has proven to be a central issue in the description of a number of non-conventional superconductors such as high-T$_c$ systems [1] and the ruthenates [2, 3]. 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 [4]. In non-conventional 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 former is the recently discovered heavy fermion superconductor $CePt_3Si$, whose crystal structure lacks inversion symmetry [5]. $CePt_3Si$ exhibits a line node gap structure [6–8] which is believed to be, in part, a consequence of strong spin-orbit coupling in a non-centrosymmetric (NCS) crystal symmetry [5, 9, 10]. This has stimulated renewed interest in the possibility of realizing non-conventional pairing states from the convolution of broken inversion symmetry and spin orbit coupling, neither of which violate time reversal invariance. In the present Letter, we present a study of interface spin-orbit coupling (ISOC) in thin Be films coated with 0.5 nm of Au via critical magnetic field measurements. Contrary to recent theoretical predictions [11–13], we find that the ISOC induced in-plane superconducting spin susceptibility is significantly larger than the corresponding perpendicular susceptibility. Furthermore, the ISOC cannot be described in terms of Abrikosov-Gorkov impurity formalism [4] in that the coupling appears to be a function of the superconducting gap.

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 [14, 15] 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_o, the film thickness d, the electron diffusivity D, and the spin-orbit coupling parameter b. The critical field H_c is determined by the implicit function [15]:

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

where

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

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,

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

where $\theta = 0$ corresponds to 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 [4],

$$\frac{2\mu_B H_{c||}}{\Delta_o} \approx \sqrt{2} \qquad b/\Delta_o \ll 1 \tag{2}$$

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

where Eq. (2) is the familiar Clogston critical field [16–18]. Note that from Eq. (3) the critical field can be arbitrarily high with increasing b. 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,

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

Numerous studies of the spin-paramagnetic transition in ultra-thin Al and Be films have shown that these two light elements have a very low intrinsic spin-orbit scattering rate [19–21] and are true spin-singlet superconductors. Consequently, they make ideal candidates for systematic studies of the effects of ISOC induced by impurity coatings [11, 22].

Recent analysis of the spin states of two-dimensional NCS superconductors, and, in particular, superconducting-normal metal bilayers, predicts that ISOC will introduce an anisotropic spin triplet component into superconducting ground state [12, 13]: $\chi^s_{||} \sim \chi^n/2$, $\chi^s_{\perp} \sim \chi^n$, where $\chi^s_{||}$ is the in-plane superconducting susceptibility and χ^n is the normal state susceptibility. If $\chi^s \neq 0$ then Eq. (2) can be generalized,

$$2\mu_B H_c = \sqrt{2}\Delta_o/\sqrt{1 - \chi^s/\chi^n}. \tag{5}$$

This would imply that the parallel critical field of a bilayer, such as the Al/Pt samples of Ref. 19, would never be larger than $H_{c||} = \Delta_o/\mu_B$. 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 a initial vacuum of ~ 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. Both the Be and Be/Au films were found to be very smooth and homogenous, with no evidence of islanding or granularity, see Fig. 1. The films were subsequently trimmed in order to eliminate edge effects. Resistive measurements were made in a dilution refrigerator with a base temperature 50 mK by 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.

The transition temperature of the homogeneously disordered Be/Au films used in this study are plotted as a function of Be thickness in Fig. 2. Films with $d < 2$ nm are known to display a non-perturbative zero bias anomaly in their tunneling density of states, which is associated with the emergence of the Coulomb gap [23]. As can be seen in Fig. 2, this is also the critical thickness below which the zero temperature superconducting phase is lost and the 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 of Fig. 2 are the functions:

$$T_c(d) = T_{co}\tanh[(d - 1.35)/1.29)] \tag{6}$$

$$D(d) = D_o\tanh[d^2/23.3], \tag{7}$$

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 of 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 is 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. The Au coatings did not significantly affect T_c but did *increase* the normal state resistances by $10 - 50\%$. In Fig. 3 we plot $2\mu_B H_{c||}/\Delta_o$ as a function of the inverse Be thickness at 60 mK, where we used the relation $\Delta_o = 2.1k_BT_c$ [20]. The triangular symbols correspond to 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 normalized 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 dashed line in Fig. 3 represents the thickness dependence of the orbital critical field of Eq. (4) using Eqs. (6) and (7). Clearly, the critical field of bilayers with $d < 5$ nm is Zeeman mediated giving us a direct probe of the ISOC.

In the context of Eq. (1) one would attribute the linear critical field behavior in Fig. 3 to the thickness dependence coupling parameter b. In a related study Bergmann [24, 25] used magnetoresistance measurements to determine the spin-orbit scattering rate in non-superconducting Mg/Au bilayers. The strength of the Au-induced spin-orbit scattering was found to scale as $b \sim 1/d_{Mg}$. This scaling behavior, however, is incompatible with the linear behavior in Fig. 3. If one assumes that Eq. (3) is applicable for the thinnest bilayers, $d \leq 5$ nm, then the SO coupling parameter must scale as $b \sim \Delta_o/d^2$ in order for the normalized critical field to be proportional to $1/d$. This suggests that the ISOC is not simply a scattering process. In fact, ISOC does not break time reversal symmetry, and is therefore not a pair-breaking interaction. Alternatively, it seems more appropriate to characterize ISOC as a boundary condition on the spin states of the superconductor.

In order to address spin anisotropy we have made a comparative study of the angular dependence of the critical field of Be films and Be/Au 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 of Fig. 5). 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. In order to better display the overall structure of the curves we have normalized the parallel field ratios to unity in this plot. Note the dip structure near 20° in each curve, which we believe is consequence of an anisotropic susceptibility in the Be/Au bilayers. In Fig. 5 we plot the angular dependence of the critical field ratio of a 5.4 nm Be/Au bilayer and a 5.4 nm Be film. The perpendicular critical field H_{c2} of the bilayer was a factor of 3 higher than that of the Be film, hence the ratio is not unity at $\theta = 90°$. The solid line in Fig. 5 is the expected angular dependence of Eq. (1), using an isotropic coupling parameter of $b = 0.013$ mV for the Be film and $b = 1.85$ mV for the bilayer, as determined from fits to the inset data. For both samples $\Delta_o \sim 0.1mV$. An isotropic b leads to a monotonic interpolation between the parallel and perpendicular field ratios, independent of the relative thickness, T_c, resistance, 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 analysis suggests that the superconducting susceptibility of the Be/Au system has a large in-plane component (of the order of the normal state susceptibility) and a small transverse component. The sense of this anisotropy is of the opposite sign of that calculated for non-disordered 2D NCS superconductors, where the in-plane component is expected to be half that of the transverse component.

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 is, in fact, a manifestation of 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 healing length 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. A high field study of the local tunneling density of states at the Be/Au and the Be/substrate interfaces, respectively, should provide an important local probe of the extent of spin-mixing at the two boundaries.

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Figures

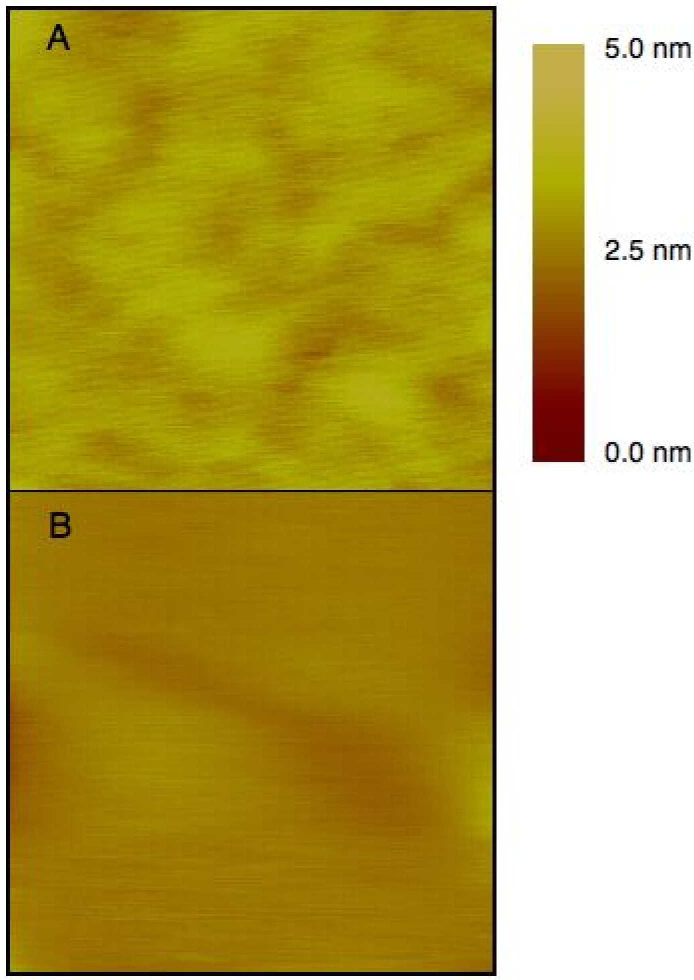

FIG. 1: A) 0.1 x 0.1 μm atomic force micrograph of a 6 nm thick Be film evaporated onto glass at 84 K. B) Micrograph of a Be film coated with 0.5 nm of Au.

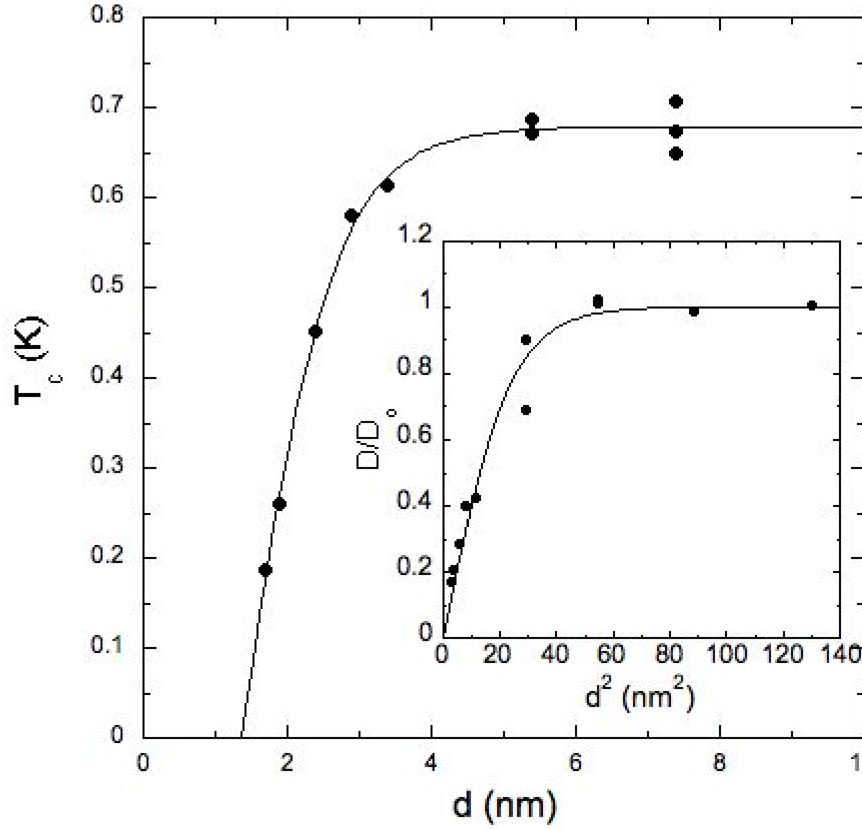

FIG. 2: Transition temperature of Be/Au bilayers as a function of Be thickness. The Au thickness was 0.5 nm in each sample. The solid line is a best fit to the data using the empirical form of Eq. (6). Inset: relative diffusivity of Be/Au bilayers as a function of Be thickness. The solid line is a fit to Eq. (7).

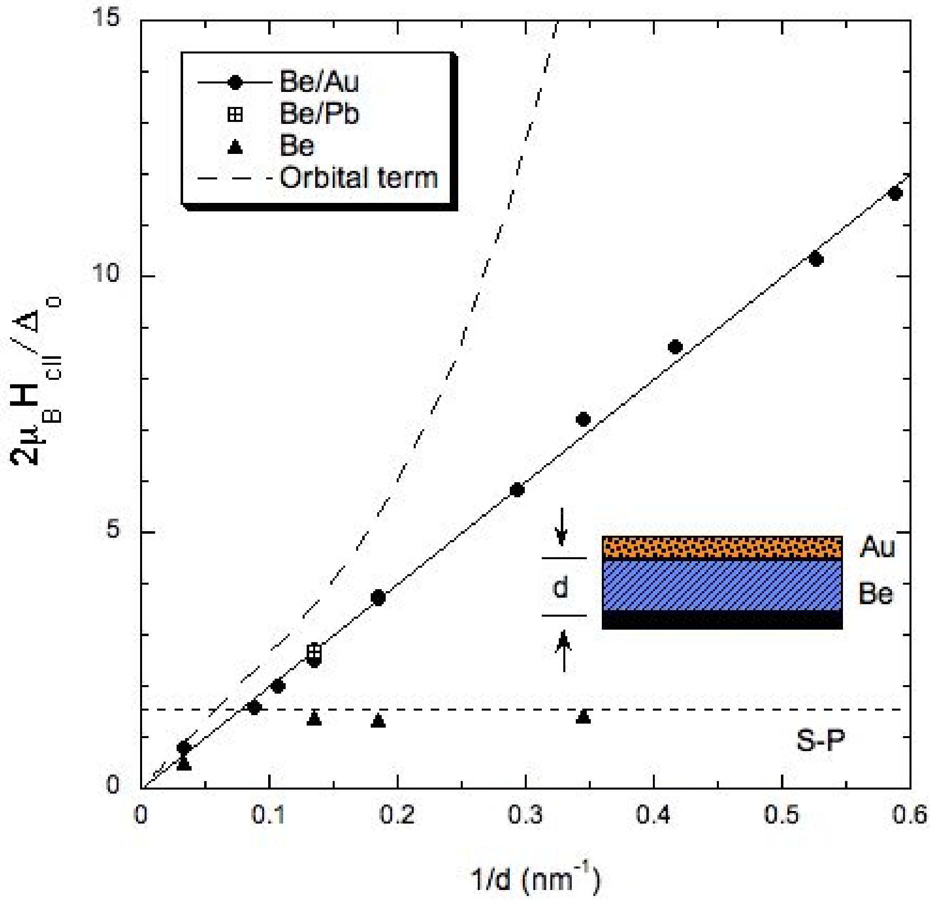

FIG. 3: Normalized parallel critical fields as a function of Be thickness for Be/Au bilayers (circles), Be/Pb (crossed box), pure Be films (triangles). The long dashed line represents the theoretical orbitally limited critical field given by Eq. (4). The solid line is a guide to the eye. The horizontal dashed line represents the Clogston critical field.

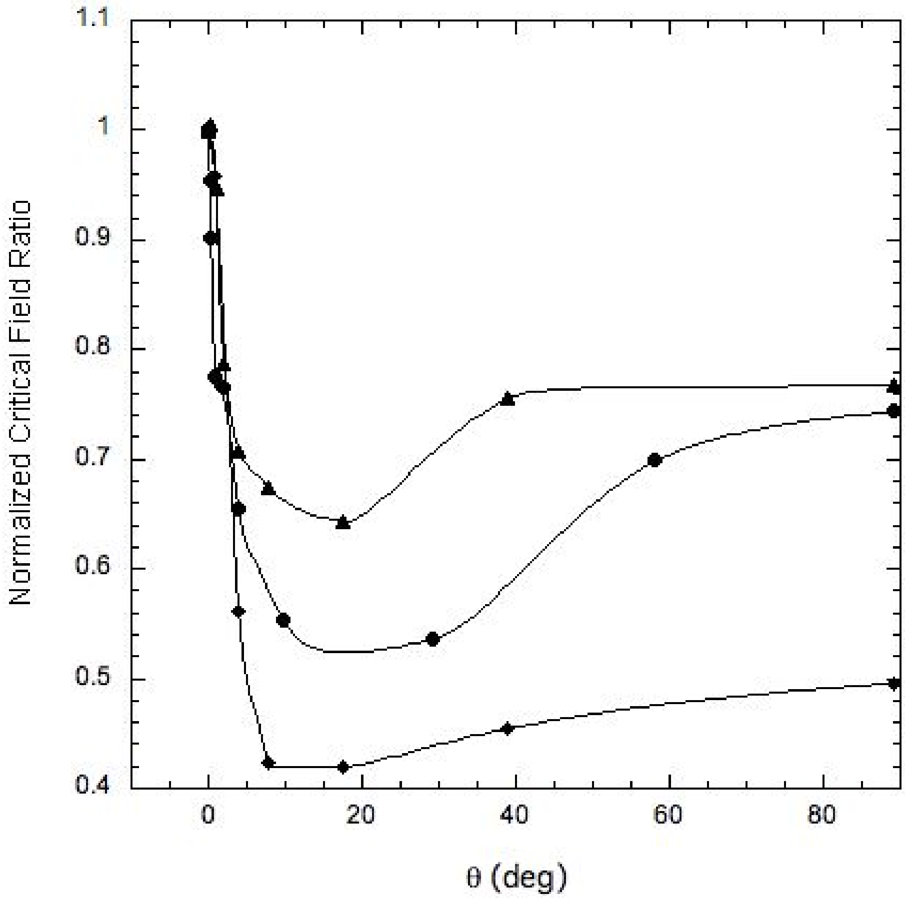

FIG. 4: Ratio of the critical field of Be/Au bilayers and Be films of equal Be thickness as a function of tilt angle, $\theta = 0$ corresponds to parallel field. triangles: $d = 7.4$ nm, circles: $d = 5.4$ nm, diamonds: $d = 2.9$ nm. The solid lines are a guide to the eye.

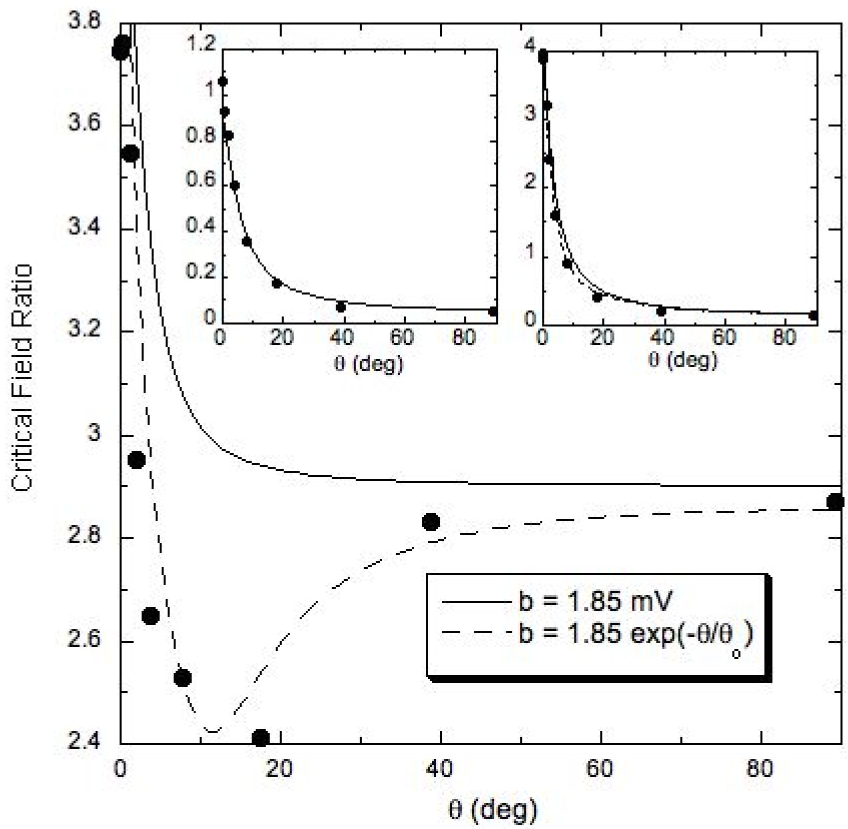

FIG. 5: Ratio of the critical field of a 5.4 nm Be/Au bilayer ($T_c = 0.68$ K, $H_{c2} = 0.137$ T, $R = 240\ \Omega$) and 5.4 nm Be film ($T_c = 0.505$ K, $H_{c2} = 0.048$ T, $R = 162\ \Omega$) as a function of tilt angle. Solid line is the solution of Eq. (1) assuming an isotropic SO coupling parameter 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: 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 $b = b_o \exp(-\theta/\theta_o)$.