Coexistence of Ferromagnetism and Superconductivity in Ni/Bi Bilayers

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In spite of a lack of superconductivity in bulk crystalline Bi, thin film Bi deposited on thin Ni underlayers are strong-coupled superconductors below ~4 K. We unambiguously demonstrate that by tuning the Ni thickness the competition between ferromagnetism and superconductivity in the Ni/Bi can be tailored. For a narrow range of Ni thicknesses, the coexistence of both a superconducting energy gap *and* conduction electron spin polarization are visible within the Ni side of the Ni/Bi bilayers, independent of any particular theoretical model. We believe that this represents one of the clearest observations of superconductivity and ferromagnetism coexisting.

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Surprisingly, nearly 40 years ago Fulde and Ferrel [1] and Larkin and Ovchinnikov [2] (FFLO) predicted one way in which the dichotomy between ferromagnetism and superconductivity *can* be resolved, that under rather extraordinary conditions, ferromagnetism and superconductivity may curiously coexist. The essential impediment to superconductivity coexisting with ferromagnetism is the exchange (Zeeman) splitting of the carrier bands. The result is that the minority and majority Fermi surfaces are no longer identical, and time-reversed pairs with zero net momentum cannot form. Nonzero total momentum pairing *can* be accomplished when an exchange field is present. In essence, either the ferromagnetic or superconducting order parameter, or both, develops a spatial variation to accommodate the other. The competition between the exchange energy and the superconducting condensation energy is necessarily extremely delicate, and thus difficult to realize experimentally. Recently, both in the bulk [3,4] and in thin films [5–7], this curious coexistence has been observed experimentally.

In this Letter, we provide unambiguous evidence for the coexistence of superconductivity and ferromagnetism in a surprisingly simple system—Ni/Bi bilayers. Utilizing tunneling spectroscopy techniques, including spin-polarized tunneling (SPT) [8], as well as magnetometry and transport measurements, we definitively demonstrate for a narrow range of Ni thicknesses the coexistence of both a superconducting energy gap *and* conduction electron spin polarization (P) within the Ni side of Ni/Bi bilayers, independent of any particular theoretical model. We believe that this represents one of the first observations of superconductivity and ferromagnetism coexisting in a simple, well-defined system. Further, to our knowledge such coexistence has also never been shown to be unequivocally present within the ferromagnet itself, as accomplished here purely through tunneling techniques. The two states spatially coexist, and the *same* electrons are apparently responsible for both phenomena. The simplicity of the bilayer constituents, combined with the clear experimental proof of coexistence could make the novel Ni/Bi system nearly ideal for studying the interplay of magnetic and superconducting ordering.

In many respects, the Ni/Bi system is remarkably novel. Bismuth is an example of an element normally superconducting only under pressure [9] or when quench condensed onto liquid-helium cooled substrates [10]. It was shown by Moodera and Meservey [11], however, that a novel *fcc* phase of Bi can be induced by growing Bi on a thin Ni seed layer. This novel phase of Bi exhibits superconductivity with $T_C \leq 4.2$ K ($2\Delta/k_BT_C \approx 4.2$–$4.4$), and displays none of the usual band features of Bi typically observed in tunneling experiments [12], indicative that the Bi has taken a new physical and *electronic* structure. Nickel thicknesses up to $d_{\mathrm{Ni}} \sim 2.0$ nm were studied, and, in that work, no ferromagnetism was observed. In this Letter, we deal with larger Ni thicknesses, and not only does ferromagnetism in Ni set in just above $d_{\mathrm{Ni}} \sim 1.6$ nm, there is a narrow range of $d_{\mathrm{Ni}} \sim 2.0$–4.2 nm where superconductivity is present in the ferromagnetic Ni. The fact that no superconductivity of Ni was observed in Ni/Pb bilayers [13], which one would naively expect to behave similarly, further indicates how remarkably unique the Ni/Bi system is.

The spatial variation of the order parameter(s) means that Cooper pairs from the superconductor (S) are not instantaneously broken when arriving in the ferromagnet (F), but persist on a length scale $\xi_F = \hbar v_F/2\Delta E_{ex}$, ξ_F being the coherence length in the ferromagnet. Correlations thus persist in F even when the exchange energy exceeds the energy gap, $\Delta E_{ex} > \Delta$, so long as the exchange energy only weakly affects S. The real part of the order parameter within F follows a damped oscillation, as shown in the inset of Fig. 1, on a length scale dictated by ξ_F. For an F thickness of $d_F \approx 3\pi\xi_F/4$ [6], the order parameter changes sign, into the so-called π state. The oscillation is heavily damped, however, and the order

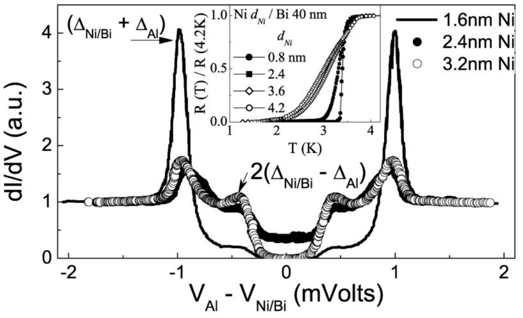

FIG. 1. Conductance (dI/dV) versus voltage for a Al 4.2 nm/Al_2O_3/Ni d_{Ni} nm/Bi 40 nm junction at $T = 1$ K for $d_{Ni} = 1.6, 2.4, 3.2$ nm. The appearance of both sum and difference gap features clearly indicates the presence of superconductivity in the Ni layer. Inset: Resistance versus temperature for several Ni thicknesses ($d_{Bi} = 40$ nm), showing a clear superconducting transition in all cases.

parameter vanishes on the scale of a several ξ_F. For bulk Ni, $E_{ex} \sim 250$ meV [14], which gives $\xi_F \sim 0.3$ nm—barely a monolayer.

Coexistence of ferromagnetism and superconductivity has recently been reported in several bulk materials, such as URhGe [3], and UGe_2 [4]. In the bulk case, the problem remains that there is often little guarantee that the superconducting and ferromagnetic states exist in the same location within the sample. In the case of F-S bilayers, some success has been had. Kontos *et al.* [5] studied quasiparticle tunneling into PdNi/Nb bilayers and found an inversion of the order parameter, resulting in an inverted BCS tunneling curve—in the FFLO model, a signature of coexistence. In their case, a dilute PdNi alloy was used to reduce the exchange energy. Further, Ryazanov *et al.* [7] and Kontos *et al.* [6], again using dilute Ni alloys, studied Josephson tunneling, which revealed a damped oscillation of the critical current as a function of the F thickness. In all of these cases, CuNi or PdNi alloys were used to reduce the exchange energy in F such that ξ_F was experimentally accessible. Still, there is no direct proof that the ferromagnetism and superconductivity are present in the ferromagnet itself, nor (also as in the bulk case) that the *same* electrons are responsible for both phenomena. The direct observation of ferromagnetism and superconductivity in a simple elemental bilayer system would greatly simplify matters and provide a model system for novel physics.

The thin film planar tunnel junctions used in this Letter were fabricated as described in our previous work [11,15]. Tunneling conductance-voltage ($dI/dV - V$) measurements were carried out with standard ac-modulation techniques at temperatures from 0.5–300 K, in fields of up to 5 T. SPT measurements were performed using the Meservey-Tedrow technique [8] at $T \approx 0.5$ K in fields up to 3.5 T in order to probe the ferromagnetism of Ni. In addition to SPT, SQUID magnetometry was utilized to characterize the magnetic properties of Ni/Bi bilayers.

Resistance versus temperature was monitored for all of the Ni/Bi bilayers, and metallic behavior was always observed (as opposed to pure Bi films which always show an increase in resistivity upon cooling). For the d_{Ni} studied, the superconductingT_C ranged from ~3.7 K to less than 0.5 K (see Fig. 1). Up to $d_{Ni} \sim 2.4$ nm, a sharp transition was observed, with an onset of ~3.5–3.8 K. For increasing d_{Ni}, the onset of the transition remains roughly constant, but the width becomes increasingly broad. For $d_{Ni} \gtrsim 5.0$ nm, the transition is generally incomplete down to $T = 0.5$ K. Thus, any ferromagnetism in the Ni is unable to quench the superconductivity of Bi until $d_{Ni} \sim$ 4–5 nm. The fact that the *onset* of the transition is roughly constant, merely becoming progressively broader as the Ni thickness is increased, seems to be indicative of the increasing magnetism in the Ni layer and its competition with the Bi superconductivity.

Tunneling spectroscopy provides more direct evidence for superconductivity in these bilayers. Figure 1 shows conductance (dI/dV) versus voltage for a Al 4.2 nm/Al_2O_3/Ni d_{Ni} nm/Bi 40 nm junction at $T = 1$ K, for $d_{Ni} = 1.6, 2.4, 3.2$ nm, well below the superconducting transition of Al ($T_C \approx 2.4$ K). Peaks at the sum and difference gap voltages are clearly observed, showing that not only are the Ni/Bi bilayers superconducting, but that superconductivity is present *at the Ni surface*. We note that our previous studies have suggested that under our growth conditions $\lesssim 1$ nm of Ni will form a closed layer when deposited on Al_2O_3.

In order to investigate the magnetic nature of the Ni, SQUID magnetometry measurements [16] were carried out on a series of Ni d_{Ni}/Bi 40 nm bilayers. Magnetization versus applied field was measured at 2 and 10 K, well below and well above the superconducting T_C, and also at 300 K. Shown in Fig. 2 is $M(H)$ for Ni 3.6 nm/Bi 40 nm and Ni 4.2 nm/Bi 40 nm bilayers at 10 and 2 K, after correction for the Bi and substrate backgrounds. For both Ni thicknesses, clear ferromagnetic behavior—both hysteresis and remanence—is observed above *and below* the superconducting transition. For the 3.6 nm Ni sample, slightly larger coercivity and saturation fields are observed compared to the 4.2 nm Ni sample. There is some indication that the magnetization may lie slightly out of the film

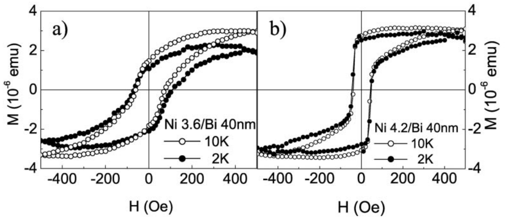

FIG. 2. Magnetization versus field for Ni d_{Ni} nm/Bi 40 nm samples at 10 (open circles) and 2 K (solid circles). Clear remanance and hysteresis are observed, indicating ferromagnetic behavior. Left: $d_{Ni} = 3.6$ nm. Right: $d_{Ni} = 4.2$ nm.

plane, which is not unusual for thin Ni films [17]. In both cases, the T_{Curie} was *estimated* to be ~400 K by comparing the magnetization drop between 2, 10, and 300 K with reference data for Ni. The observed saturation moments correspond to $\approx 0.06\mu_B/\text{Ni}$ for both films, about an order of magnitude below that of bulk Ni (viz., $0.06\mu_B/\text{Ni}$) [18]. That the moments are an order of magnitude below bulk Ni is anticipated, and we feel a clear indication of the competition between ferromagnetic and superconducting ordering.

Recently, it has been shown that the exchange-split bands in Ni can be well described by Stoner-like behavior [19], viz., $\Delta E_{\text{ex}} = \mu_B H_{\text{eff}} = 2zJ/\mu_0 g^2 \mu_B^2 N_V$, where z is the number of nearest-neighbor pairs, J the exchange constant, N_V the number of moments per unit volume, and the other symbols have their usual meanings [18]. Taking $g = 2$ and the experimentally determined moments, we deduce an exchange energy of $\Delta E_{\text{ex}} \sim 30$ meV for $d_{\text{Ni}} = 3.6$ and 4.2 nm, which implies a coherence length of $\xi_F \sim 3$ nm (with the Fermi velocity $\nu_{\text{Ni}\uparrow} = 0.28 \times 10^6$ m/s [14]). Hence, the range of thicknesses studied should put our Ni/Bi bilayers well into the regime for coexistence.

As a first attempt to show, for example, that the Ni 3.6 nm/Bi 40 nm bilayer is simultaneously ferromagnetic *and* superconducting, we have performed tunneling studies on Co 5 nm/Al 4.2 nm/Al_2O_3/Ni d_{Ni}/Bi 40 nm junctions. In this case, the Co seed layer was used to quench the superconductivity of the underlying Al electrode on half of the junctions. Thereby, no superconductivity was observed in the Co/Al bilayer down to 0.5 K, as expected. Figure 3(b) shows dI/dV versus V for junctions with $d_{\text{Ni}} = 3.6, 4.2, 5.4$ nm. A clear, though weak, energy gap is observed at $H = 0$ as well as at $H = 2.9$ T (not shown in the figure), indicating that for the bilayer with $d_{\text{Ni}} = 3.6$–5.4 nm, superconductivity is induced in the Ni layer. By 5.4 nm, the superconducting energy gap has nearly vanished, indicating that we are near the critical thickness where ferromagnetism begins to dominate in the bilayer. Combined with the SQUID results, which show clear ferromagnetism for this bilayer, this suggests the existence of superconductivity in the Ni layer.

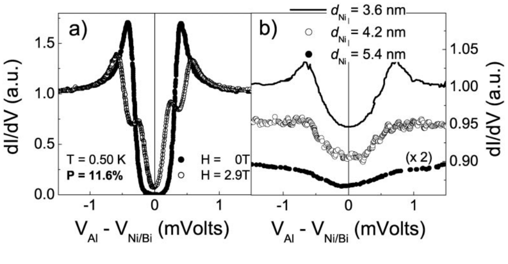

FIG. 3. Left: Spin-polarized tunneling curves in $H = 0$ (solid circles) and 2.92 T (open circles) for an Al 4.2 nm/Al_2O_3/Ni 3.6 nm/Bi 40 nm junction at $T = 0.5$ K, clearly showing spin polarization in the Ni layer (P = +11.6% in this case). Right: $dI/dV - V$ versus voltage for a Co 5 nm/Al 4.2 nm/Al_2O_3/Ni d_{Ni}/Bi 40 nm junction at $T = 1$ K for $d_{\text{Ni}} = 3.6, 4.2, 5.4$ nm. The curve for $d_{\text{Ni}} = 3.6$ nm (solid line) clearly shows the presence of an energy gap, as do the curves for $d_{\text{Ni}} = 4.2, 5.4$ nm (open, closed circles, shifted vertically).

Though the prior result establishes unambiguously that superconductivity is present at the Ni/Al_2O_3 interface, i.e., within the Ni layer, that ferromagnetism is also present *at the same Ni interface measured by tunneling* cannot be definitively determined from SQUID measurements alone. To that end, we have performed SPT measurements on otherwise identical junctions *without* the Co layer. In this case, the superconducting Al layer acts as a spin detector. In a parallel magnetic field, the quasiparticle density of states in the Al is Zeeman split, allowing a determination of the spin polarization (and hence ferromagnetism) within >1 meV of the Fermi level [8].

Figure 3(a) shows an example SPT measurement for $d_{\text{Ni}} = 3.6$ nm. For $H = 0$, the usual BCS curve is obtained, while for $H = 2.9$ T, clear Zeeman splitting is observed. The asymmetry of the peak heights conclusively shows that spin polarization is present at the Ni/Al_2O_3 interface, indicating ferromagnetism. Note that in this case the Ni/Bi gap is too weak compared to that of Al to be clearly observed. Fitting the curves to the Maki-Fulde theory [8,20], which corrects for the effects of spin-orbit scattering and orbital depairing in the superconductor, we obtain P = +11.6% in this case. (We note that pure Ni prepared identically has P ≈ 25%.) Shown in Fig. 4(a) is the P obtained for various Ni thicknesses. For $d_{\text{Ni}} \leq 1.6$ nm, no P is observed, consistent with previous studies. It is further interesting to note that the onset of P coincides with the broadening of the resistive transition. Combined with the SQUID results and the tunneling results with

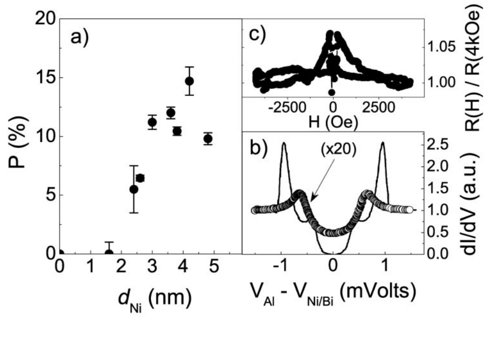

FIG. 4. (a) Measured P as a function of Ni thickness for d_{Ni}/Bi 40 nm bilayers. (b) dI/V at $H = 0$ for Co/Al/Al_2O_3/Ni 5.4 nm/Bi 40 nm and Al/Al_2O_3/Ni 5.4 nm/Bi 40 nm junctions. The former sample shows a superconducting energy gap on the Ni surface (expanded vertically), whereas the latter sample shows S-I-S tunneling (Al is superconducting), both indicating superconductivity on the Ni face. (c) Tunneling magnetoresistance in a Co/Al/Al_2O_3/Ni 3.0 nm/Bi 40 nm junction at 0.5 K.

quenched Al layers [Fig. 3(b)], which shows a clear energy gap at 2.9 T, the same field at which P is measured, this unambiguously establishes the presence of both superconductivity *and* spin-polarized carriers in the Ni/Bi bilayers. Further, not only do they coexist at the same location within the Ni, this seems to indicate that the same electrons are responsible for both phenomena. Figure 4(b) shows zero field dI/dV characteristics for Co/Al/Al_2O_3/Ni 5.4 nm/Bi 40 nm and Al/Al_2O_3/Ni 5.4 nm/Bi 40 nm junctions. The former sample shows a superconducting gap on the Ni surface (the vertical scale is expanded for clarity), as expected, whereas the latter sample shows superconductor-insulator-superconductor tunneling characteristics (Al is superconducting here), indicting superconductivity on the Ni face in both cases.

As a final check that indeed the bilayers are simultaneously ferromagnetic and superconducting, we have fabricated magnetic tunnel junctions with a Ni/Bi counter electrode, viz. Co/Al_2O_3/Ni 3 nm/Bi 40 nm. In this case, if the Ni/Bi bilayer is ferromagnetic, a tunneling magnetoresistance (TMR) effect [15] should be observed—the resistance should be lower when the Co and Ni/Bi magnetizations are parallel compared to antiparallel. Shown in Fig. 4(c) is the normalized resistance versus applied field. A clear TMR effect is observed, though the antiparallel state is not quite reached due to the broad switching of the Ni/Bi (see Fig. 2). Using the Julliere model [8,15], the observed TMR ($\sim$7%) corresponds to a P of the Ni/Bi of $\sim$8.5%, in agreement with the spin-polarized tunneling results. Additionally the Ni/Bi bilayer showed a clear superconducting transition as well as an energy gap in dI/dV—the TMR (and hence spin polarization) is observed in the *superconducting state of the Ni/Bi*. The observation of TMR at low fields where the Ni/Bi clearly remains superconducting shows unquestionably that superconductivity and ferromagnetism coexist *within the Ni layer* in this novel system.

The fact that P remains well below the value for pure Ni, even at 4.8 nm Ni, when the superconductivity is essentially quenched, suggests that the electronic structures of both Ni and Bi are strongly altered. Earlier experiments with ultrathin Ni films [21] on various substrate metals concluded that Ni on monovalent metals such as Au has no magnetically dead layers, while Ni on polyvalent substrates such as Al, Pb, or Sn has 2–3 dead layers and reduced P. Given the polyvalency of Bi, it seems reasonable that the Bi-Ni hybridization severely weakens the Ni magnetism. It was originally [11] speculated that an increased density of states of Bi may be responsible for superconductivity. Strong hybridization of Ni and Bi, leading to a larger Bi and reduced Ni density of states could plausibly explain the superconductivity of Bi, and the reduced moment and P of Ni.

Finally, we address the relation of this work to that of Kontos *et al.* [5,6] and Ryanazov *et al.* [7]. In both of those studies, ferromagnetism and superconductivity are observed in bilayers of Nb and dilute Ni alloys (NiPd and NiCu, respectively). While both of these cases are unambiguous, the presence of ferromagnetism is established by anomalous Hall effect measurements, which probes the entire bilayer stack, while superconductivity is established by tunneling measurements, which probes only the insulator/Ni-alloy interface. Thus, it is not directly indicated that both phenomena exist in the same portion of the bilayer. What we believe sets the Ni/Bi case apart is that *the presence of both ferromagnetism and superconductivity are established at the same location*, viz., the Al_2O_3/Ni interface, unambiguously and independent of any particular theoretical model.

In conclusion, we have clearly demonstrated the coexistence of superconductivity and ferromagnetism in Ni/Bi bilayers. We believe that this represents one of the first definitive observations of superconductivity and ferromagnetism involving the same electrons coexisting at the same location in a well-defined bilayer system.

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