Spin-Polarized Tunneling Study of s-f Exchange in Superconductors

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Spin-polarized tunneling into the side of an Al film covered with a submonolayer of Gd reveals the presence of the localized Ruderman-Kittel-Kasuya-Yosida spin polarization in the normal state and its absence in the superconducting state. This result is attributed to the fact that the long-range part of the spin susceptibility in the superconductor vanishes at low temperature. The exchange constant is derived from the Zeeman splitting of the superconductor density of states, and its value agrees with that obtained from the Abrikosov-Gor'kov theory.

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The existence of superconducting compounds having a sublattice of rare-earth elements weakly coupled to the conduction electrons gives a dramatic realization of the variety of effects involving superconductivity and magnetism,[1] for example, the magnetic-field–induced superconductivity[2] in $Eu_xSn_{1-x}Mo_6S_8$ arising from the Jaccarino-Peter effect,[3] or the oscillatory superconducting-magnetic (coexistence) state in $HoMo_6Se_8$,[4] $HoMo_6S_8$,[5] and $ErRh_4B_4$,[6] involving the modification[7,8] of the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling[9] between local moments in a superconductor. Long-range magnetic ordering is found in the high-T_c superconductors.[10] Other unusual effects are found in $CePb_3$ (Ref. 11) and the heavy-fermion superconductors.[12] It appears that a full understanding of exchange effects from a lattice of local moments has yet to be formulated.[13] Superconductivity provides a sensitive probe of the details of local moment formation in metals. Maple has reviewed the use of measurements of the superconducting transition temperature T_c and specific heat in this context.[14] However, tunneling techniques have been little used in a quantitative fashion[15] in spite of the energy resolution that tunneling provides. Furthermore, tunneling measurements are not restricted to the superconducting-normal-state phase boundary. The spin-polarized tunneling technique[16,17] offers, in addition, spin resolution, which lends itself to a quantitative analysis of exchange and spin-orbit effects. We have used this technique to study quantitatively the effects of the exchange interaction between rare-earth (RE) moments and the conduction electrons in superconducting Al thin films. The RKKY polarization also was observed.

Though bulk polycrystalline materials have traditionally been used to study the interaction of superconductivity and magnetism, the use of thin films provides a level of control not otherwise possible. Spin-dependent perturbations of the electron states can be introduced by the deposition of the appropriate surface layer. For example,[18] the deposition of one-half monolayer of platinum onto a thin film of Al increases its spin-orbit scattering rate by a factor of 30. A similar approach using magnetic surface layers to introduce exchange scattering is presented here.

In all cases samples were formed by vacuum deposition onto liquid-nitrogen–cooled glass substrates. Two types of samples were prepared. For the first type, RE/Al-Al_2O_2-Ag, the rare earth was deposited first followed by 4 nm of Al and a glow discharge in oxygen to form the base electrode and tunnel barrier. Silver cross strips 100 nm thick completed the junction. The second type of junction Al-Al_2O_3-Gd/Al required the deposition and oxidation of a 4-nm Al layer followed by the rare earth and the top electrode of 4-nm Al. Junctions with and without the rare-earth metal, and with different thicknesses of the rare-earth metal, were simultaneously prepared. The deposition of the submonolayer RE was monitored with the standard quartz-oscillator technique giving a thickness error of $\simeq 3\%$. Depositions using a rotating chopper gave a relative error between differing thicknesses of less than 1%. For example, a thickness reading of 0.1-nm Gd is equivalent to an areal number density of 3 nm^{-2} or 0.31 atomic layer with use of a metallic radius of 0.18 nm. Critical-field measurements imply that the thickness of the unoxidized part of the Al film is about 3.0 ± 0.2 nm. Thus a thickness reading of 0.1-nm Gd in contact with a oxidized Al film corresponds to an effective impurity concentration of $c = 1.7\% \pm 0.1\%$.

Woolf and Reif measured[19] the tunneling conductance of junctions formed on Pb films with up to 2% Gd impurity concentrations and fitted the Abrikosov-Gor'kov (AG) theory[20] to their results. This and other experiments[14] have verified that the heavy rare-earth impurities act on superconductivity in accord with the AG theory. That is, the trivalent ions have long-lived local moments with weak itinerant-local electron mixing; the exchange constant is positive and $\simeq 100$ meV in size, arising from the "direct" exchange integral. As a result, the scattering can be treated in the Born approximation, and the scattering rate is temperature independent (i.e., no Kondo effects). The decrease in T_c from its value T_{c0} in the absence of impurities is given by the AG expres-

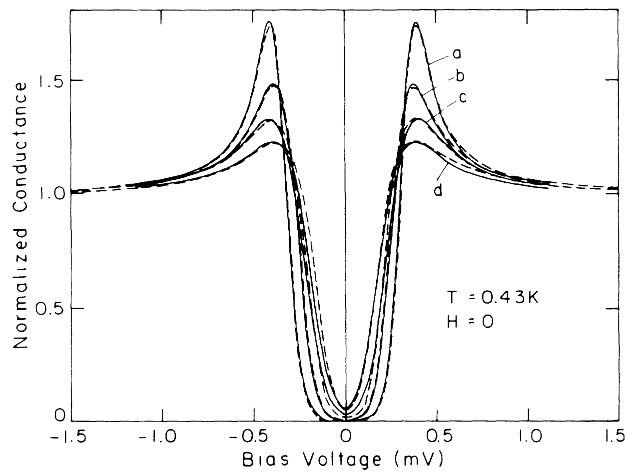

FIG. 1. The measured tunneling conductance (solid curve), and fits by the AG theory (dashed curves *a*-*d*) of Gd/Al-Al_2O_3-Ag junctions corresponding to Gd coverages of 0, 1, 2, and 3 nm^{-2}, respectively.

sion for "temperature-independent pair breaking,"

$$\ln(T_{c0}/T_c) = \psi(\tfrac{1}{2} - \rho/2) - \psi(\tfrac{1}{2}). \quad (1)$$

The pair-breaking parameter ρ is proportional to the scattering rate,

$$\hbar/\tau_{ex} = \pi k_B T_c \rho = (\pi/2) c N_0 J^2(0) S(S+1). \quad (2)$$

Here $J(q=0)$ is the spatial average of the exchange interaction multiplied by the number of lattice sites in the crystal, and $N_0 = 7.20\times10^{11}$ erg^{-1} is the density of states per unit cell for a single spin direction taken from the specific heat γ of bulk Al.[21] Pair breaking arises from both spin-flip and spin-nonflip parts of the exchange interaction,[8]

$$H_{ex} = -J(\mathbf{r})\mathbf{S}\cdot\mathbf{s} = -J(\mathbf{r})\{S_z s_z + (S_+ s_- + S_- s_+)/2\}. \quad (3)$$

The fits of the theory to the conductance (Fig. 1) yield values of the two input parameters T_{c0} and ρ (Table I). As expected, T_{c0} is essentially constant, the scattering rate increases linearly with Gd coverage, and there is excellent agreement between the resistively measured T_c and that calculated from Eq. (1). The exchange constant was determined by our inverting Eq. (2).

Independent of the AG theory, one can determine $J(0)$ in the following manner. With the application of a magnetic field of 1 T at a temperature of 0.45 K, the impurity spins are nearly aligned. The first-order perturbative effect of the exchange interaction due to *aligned* rare-earth moments acting on the spins of the electrons is that of a uniform field $B_{ex} = cJ(0)\langle S_z\rangle/g\mu_B$. As shown by Sarma,[22] such a field commutes with the BCS Hamiltonian and does not induce pair breaking but causes a Zeeman splitting of the density of states which leads to a first-order transition to the normal state.[17] For a superconductor-insulator-normal (*S*-*I*-*N*) junction, the zero-field peak in the conductance at the gap energy Δ is split by the applied magnetic field B and the uniform exchange field B_{ex} into two peaks at $\Delta \pm \mu_B(B+B_{ex})$. The conductance to the sample with the smallest Gd coverage in an applied field of 1 T is shown in the inset of Fig. 2, with an apparent splitting of 3.5 T corresponding to $B_{ex} \simeq 2.5$ T. An additional consequence of the alignment of the spins in a magnetic field is that the part of the exchange scattering from the inelastic spin-flip terms in Eq. (3) no longer contributes. A reasonable fit by the theory of Alexander *et al.*[23] is obtained with no spin-flip scattering. However, as expected,[24] the pair-breaking effect is not diminished.

The saturation value of the exchange field (Fig. 2) was used to determine $J(0)$, and comparison is made in Table I to the value obtained in zero field from the AG theory. The agreement is excellent considering the simplifying assumptions made by the AG theory. We have verified these results in the cases of Sm, Tb, Dy, and Ho with exchange constants obtained of the order of 10 meV. The exchange effects for the other rare earths (excepting Ce) are small. The exchange constant for Ce is of the order of 100 meV and the pair breaking appears anomalous in accord with other measurements.[25] When the Gd layer is sandwiched between two 2-nm Al films, the exchange constant is found to be a factor of 2–3 larger and in accord with the results of Woolf and Reif.

The discussion so far has been restricted to the case

TABLE I. Comparison of the exchange constant determined from the AG theory and the Zeeman splitting of the density of states.

Gd areal density (nm^{-2})	ρ	T_{c0} (K)	$1/\tau_{ex}$ (10^{10} sec^{-1})	T_c (calc) (K)	T_c (measured) (K)	$J(0)$[b] (meV)	B_{sat} (T)	$J(0)$[a] (meV)
No Gd	0.017(3)	2.35(5)	1.54(34)	2.26(6)	2.27(2)	...	...	...
1.01(3)	0.067(4)	2.35(5)	5.54(42)	2.01(6)	2.00(2)	12.9(9)	3.5(5)	20.7(33)
2.02(5)	0.127(6)	2.50(5)	9.82(52)	1.88(6)	1.90(2)	13.0(8)	5.1(7)	15.1(23)
3.03(7)	0.199(7)	2.40(5)	12.88(59)	1.58(5)	1.52(5)	12.5(6)	8.1(12)	15.9(12)

[a]From AG theory.

[b]From Zeeman splitting.

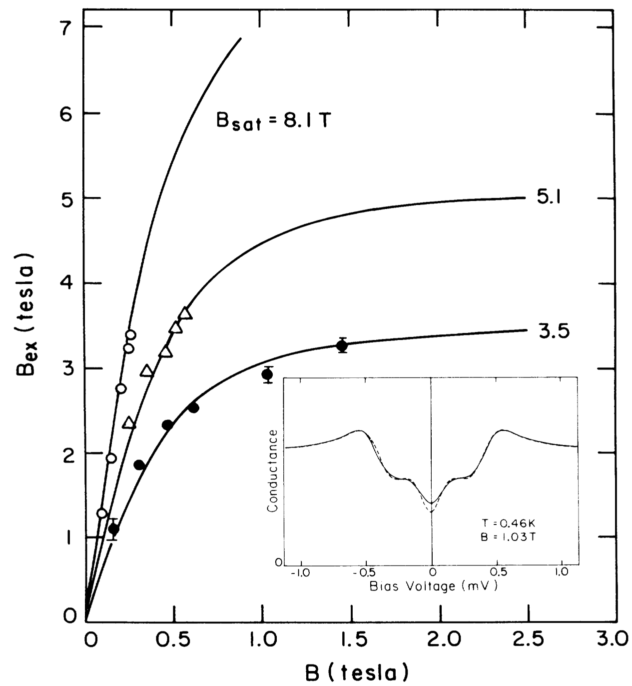

FIG. 2. The uniform exchange field as a function of the applied magnetic field obtained from the Zeeman splitting of the conductance for the junctions corresponding to curves *b*, *c*, and *d* in Fig. 1. The curve drawn through the points corresponding to the lowest Gd coverage saturates at $B_{ex} \simeq 3.5$ T. This curve was scaled by a constant factor to obtain the saturation curves for the greater coverages. Inset: The Zeeman splitting of the conductance for the lowest Gd coverage and a fit (dashed) by the theory with no spin-flip scattering.

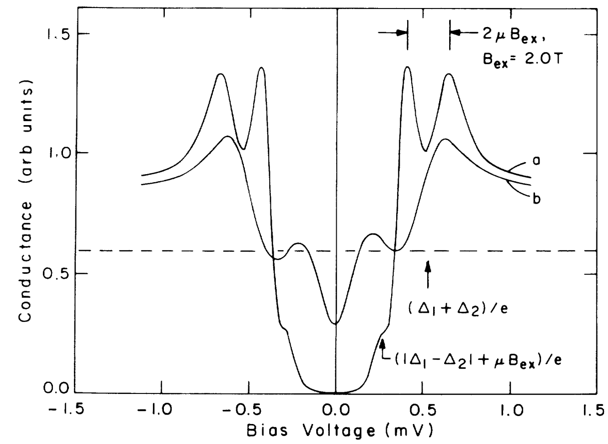

FIG. 3. The conductance of a Al-Al_2O_3-Gd(3 nm^{-2})/Al junction measured in an applied magnetic field for which the top electrode (Gd/Al) is (curve *a*) superconducting, $B=0.17$ T, and (curve *b*) normal, $B=3.72$ T.

where the tunneling was directed into the surface of the Al film opposite the side covered with Gd. Since the thickness of the film is much smaller than the (bulk) mean free path and the coherence length, the Zeeman splitting and energy gap, respectively, are uniform throughout the film. However, in the normal state one expects a RKKY spin polarization within a few Fermi wavelengths of the RE ions. Tunneling directed into the Gd/Al surface serves as a probe of this localized feature in the density of states.

Consider tunneling in a junction in the case that one electrode has spin-polarized itinerant electrons. The tunneling probability then differs for the two spin directions. As a result the conductance measured in an applied field is asymmetric with respect to zero bias voltage. This asymmetry has been measured for a number of $4f$ (Ref. 26) and $3d$ (Ref. 27) metals from which it has been concluded that the degree of asymmetry is proportional to the magnetic moment of the itinerant electrons at the surface of the film.

In Fig. 3 the conductance of an Al-Al_2O_3-Gd/Al junction is shown for two values of the applied field. In curve *a*, the applied field is below the critical field of both electrodes. No asymmetry is observed. In the case of S_1-I-S_2 tunneling, the conductance is split by the *difference* $2\mu B_{ex}$ in the Zeeman splitting of electrons in the top and bottom electrodes. The curve *b* was taken above the critical field of the top electrode. The bottom electrode remains superconducting but the spin states are Zeeman split by the applied magnetic field $2\mu_B B = 0.43$ meV. The conductance is asymmetric indicating a 2.9% polarization of the itinerant electrons in the (normal state) top electrode. This is the expected order of magnitude considering that the polarization observed[26] in Gd metal is $\simeq 13\%$ and the sample has $\simeq \frac{1}{3}$ atomic layer coverage of Gd. The asymmetry is a large effect in comparison to other features routinely measured by tunneling, for instance, those due to phonons. The fact that the conductance is symmetric in the case where the top electrode is superconducting can be attributed to the fact that the long-range part of the spin susceptibility is reduced in the superconducting state, resulting in a suppression of the RKKY response.

In summary, spin-polarized tunneling was used to obtain the density of states of thin Al films covered with submonolayer thicknesses of rare-earth metals. Three consequences of the exchange interaction are observed in this thin-film system. Depairing due to exchange scattering provides a value for the exchange constant in agreement with the value derived from the Zeeman splitting of the conduction electron energy. Tunneling into the side of the Al film covered with isolated Gd ions reveals RKKY spin polarization of the itinerant electrons in the normal state only. Similar studies of the Al(Ce) and Be(U) systems and their relationship to the heavy-fermion compounds $CeAl_3$ and UBe_{13} are in progress.

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