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Electronic density of states at the surface of a superconductor in contact with a magnetic insulator

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A threefold splitting of the main conductance peak has been observed in symmetric tunneling junctions with Pb electrodes and barriers of $Ho(OH)_3$, a material which is a ferromagnet in bulk. The results are consistent with the existence of an electronic bound state in each of the electrodes near the barrier at an energy below that of the gap.

The study of the interplay of magnetism and superconductivity is a subject which has been pursued vigorously since the pioneering theoretical work of Abrikosov and Gor'kov.[1] The recent fabrication of multilayer structures consisting of alternate magnetic and superconducting layers in contact[2] has provided the newest direction for research on this subject, one in which interfacial effects may be important. Such effects can be investigated in geometries containing only one interface using electron tunneling. In this Brief Report, we report the observation of a threefold splitting of the conductance peak in Pb/Pb superconducting junctions with barriers of $Ho(OH)_3$, a material which is a ferromagnet in bulk.[3] It is argued that this splitting is evidence of a bound state in each of the electrodes near the barrier at an energy below that of the gap. Such a state could result from the weakening of the pair potential by the exchange coupling of the conduction electrons and the localized spins in the barrier.

Lead films about 4000-Å thick were prepared by vacuum evaporation from a crucible, and polycrystalline rare-earth trihydroxide insulating layers were prepared by triode sputtering of a nominally 10-Å-thick layer of the rare-earth metal, followed by oxidation in an oxygen plasma. Sufficient water vapor was present in the system to assure the formation of the trihydroxide rather than the sesquioxide as verified by x-ray photoemission spectroscopy (XPS) and Auger analysis.[4] The edges of the base electrode were masked by SiO films so that junctions 6.25×10^{-4} cm^2 in area were defined. Measurements were made using a conductance bridge in a cryostat which was electrically and magnetically shielded.

In Fig. 1. we show the low-temperature conductance-voltage characteristics $G(V)$ of typical $Pb/Ho(OH)_3/Pb$, $Pb/Er(OH)_3/Pb$, and $Pb/Lu(OH)_3/Pb$ junctions. In bulk at

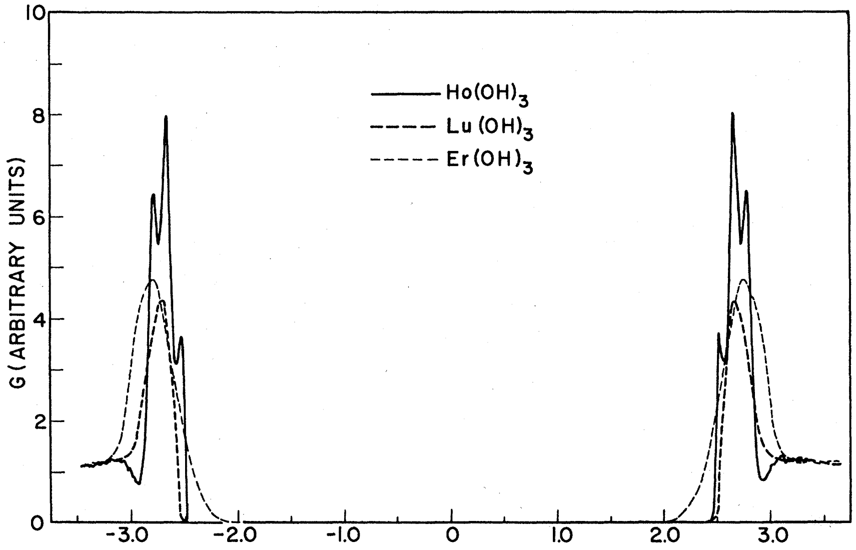

FIG. 1. Conductances vs voltage of representative Pb/Pb junctions with $Ho(OH)_3$, $Lu(OH)_3$, and $Er(OH)_s$ barriers at $T=1.1$ K. The curves are arbitrarily normalized to the same value at $V=3.5$ mV. The general broadening and weakening of all of the various peaks relative to those of Pb/PbO/Pb junctions is believed to result from damage to the base electrode as a consequence of the fabrication process.

$T > 1$ K, Er(OH)$_3$ and Lu(OH)$_3$ are paramagnetic and nonmagnetic, respectively.[5] The three-peak structure has been observed in six Ho(OH)$_3$ barrier junctions with normal tunneling resistances ranging from 649 Ω to values in excess of 40 000 Ω. At low temperature ($T \sim 1.1$ K) the voltages at which the various maxima and minima have been observed appear to be junction independent. The extra structure smears out with increasing temperature, disappearing at about 4.5 K. The broadened characteristic exhibited by Er(OH)$_3$ barrier junctions has been seen in five samples, with normal tunneling resistances in the same range. The characteristic of nonmagnetic Lu(OH)$_3$ barrier junctions has been observed in two samples with normal tunneling resistances of about 5000 Ω.

There are three obvious explanations of a threefold splitting similar to that of the Ho(OH)$_3$ barrier junctions: (1) a multigap structure such as that reported for Pb and a number of other superconductors resulting from an intrinsic gap anisotropy and tunneling into either a single crystal or a partially oriented film,[6] (2) magnon- or paramagnon-assisted inelastic tunneling, and (3) a modification of the density of states of each electrode resulting from interaction of the electrons with the barrier.

Gap anisotropy can be ruled out for a number of reasons. The conduction-electron mean free path l of the Pb electrodes, estimated from measurements of the resistivity at 10 K, is ~ 1000 Å and thus does not satisfy the required condition $l \gg \xi_0$, where ξ_0 is the coherence length.[7] Furthermore, splitting is only observed in junctions with Ho(OH)$_3$ and Er(OH)$_3$ barriers and not in junctions with identically prepared Pb electrodes but with Lu(OH)$_3$ and Er(OH)$_3$ barriers. The latter junctions should also have exhibited splittings if they were due to gap anisotropy. The essentially identical nature of the electrodes in junctions with Lu(OH)$_3$ and Ho(OH)$_3$ barriers is further supported by studies of the dependence of the tunneling conductances on a magnetic field applied parallel to the plane of the junctions. At temperatures above $T \approx 5$ K an abrupt (first-order) transition to the normal state is observed in both types of junctions at a field which can be identified as $H_c(T)$. Above this field $G(V)$ is independent of voltage. Below 5 K, with increasing field, there is first a transition at H_c to a tunneling characteristic of a symmetric junction with both electrodes in a gapless state, followed by a transition from this surface superconducting state to the normal state at a field which can be identified as the surface critical field H_{c3}.[8] Data are presented in Fig. 2 for both a Lu(OH)$_3$ and a Ho(OH)$_3$ barrier junction. The temperature at which $H_{c3} \approx H_c$ and the magnitude of this field are seen to be independent of the barrier material. These results imply that the electrodes of the two types of junctions are really the same. At a temperature as low as 5 K, the generalized Ginzburg-Landau parameters $\kappa_1(T)$ of the electrodes, which determine the ratios H_{c2}/H_c and H_{c3}/H_c, and which depend on material parameters ξ_0 and l,[9] seem to be independent of the barrier material. On the other hand, at low temperatures where the splitting of the peaks is observed, although $H_c(T)$ is the same for both types of junctions as it is at high temperatures, $H_{c3}(T)$ of nonmagnetic Lu(OH)$_3$ barrier junctions is about 5 to 10% greater than that of junctions with Ho(OH)$_3$ barriers. This result is qualitatively consistent with the weakening by magnetic scattering of surface superconductivity in the latter.

The magnetic field dependences of the various peaks of the Ho(OH)$_3$ barrier junctions have also been found to be different. The low-voltage peak does not shift with field and retains its shape up to H_c, whereas the middle- and high-voltage peaks shift and smear out. These results, which are shown in Fig. 3, would probably not be found if the splitting were due to gap anisotropy.

Magnon-assisted inelastic tunneling can also be ruled out as an explanation of the splitting because of the absence of a strong temperature dependence of the relative amplitudes of the high- and low-voltage peaks, which would correspond to tunneling with magnon absorption and emission, respectively. The relative probabilities of the two peaks would be given by the ratio $\exp(-\hbar\omega/k_B T)$, leading to a variation by a factor of 4 over the temperature range from 1 to 4 K for a splitting of 0.16 meV. The latter is not observed.

The structure in the junctions with Ho(OH)$_3$ barriers probably results from a modification of the electronic density of states in each electrode. A two-peak density of states in each electrode of a symmetrical junction will result in a conductance $G(V)$ with three peaks. The low-voltage peak in the conductance would then follow from the convolution of the bound-state density-of-states peak with itself, whereas the middle- and high-voltage peaks, respectively, would follow from the cross-convolutions of the continuum and bound-state peaks and the convolution of the continuum peak with itself.

The two-peak density of states of the present work is similar to that found in normal-superconductor (NS) proximity sandwiches.[10] In the latter, the bound state results from Andreev reflection[11] of tunneling-injected quasiparticles at the NS boundary, where there is a relatively abrupt change in the magnitude of the pair potential. Here, An-

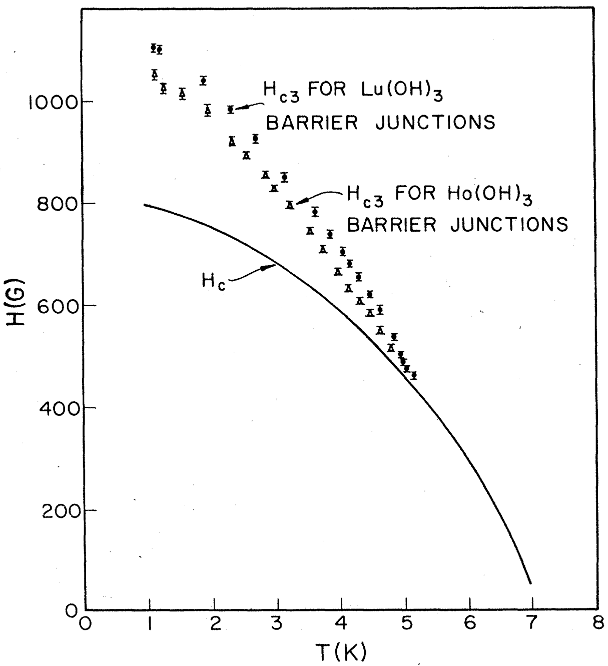

FIG. 2. Parallel critical fields H_c and H_{c3} of junctions with Ho(OH)$_3$ and Lu(OH)$_3$ barriers. $H_c(T)$ as a function of temperature was the same for the two types of junctions and is thus shown as a solid line, whereas actual data points are shown for $H_{c3}(T)$.

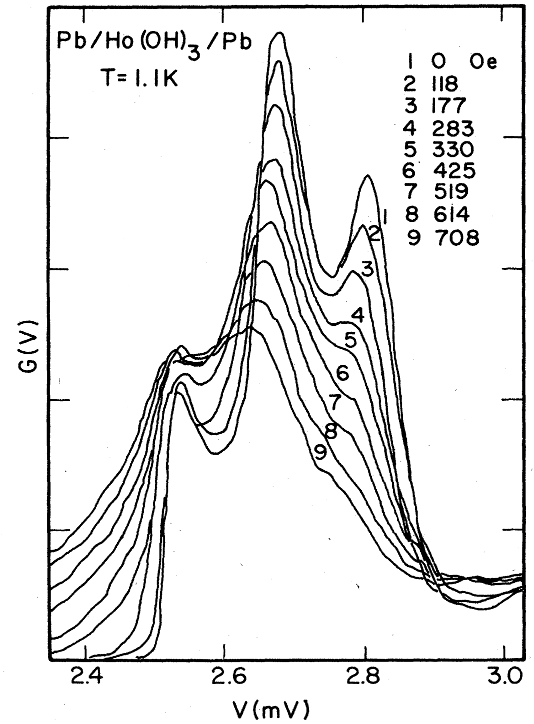

FIG. 3. Magnetic field dependence of the conductance peaks of a Pb/Ho$(OH)_3$/Pb junction. This data was obtained with the field parallel to the plane of the junction.

dreev reflection could also be relevant. The fact that splitting is observed only in junctions with magnetic barriers suggests that the effects are magnetic in origin. The scattering of electron pairs from a magnetic boundary can bring about a weakening of the pair potential near the surface more gradual in its spatial dependence than at an NS boundary. Scattering would result from the exchange interaction produced by the overlap of electronic wave functions in the superconducting metal and localized electronic wave functions on the magnetic atoms in the insulator. Spin polarization occurring at the boundary would also contribute to the weakening of the superconductivity near the interface. The interface in effect introduces a *sheet* of impurity spins into the superconductor. While a single impurity spin would depress the pair potential only within a few lattice constants of the spin,[12] such a *macroscopic* wall of spins could produce an effect on a scale given by the coherence length. The above magnetic effect is different from spin-flip scattering. The latter would just broaden the conductance peak at the gap, as is observed in the case of junctions with Er$(OH)_3$ barriers which are paramagnetic over the range from 1 to 7 K.

Although there is no first-principles theory of the above effect, the theory of quasiparticle states in the presence of a spatially varying pair potential has been addressed by a number of authors.[13] To estimate the depression of the pair potential, we adopt the results of Bar-Sagi and Kuper,[14] who find a single bound state at approximately {assuming $[\Delta_\infty - \Delta(0)]/2\Delta_\infty << 1$}

$$E_0 = \Delta_\infty \left\{ 1 - \tfrac{1}{2} \left| \frac{\Delta_\infty - \Delta(0)}{\Delta_\infty} \right|^2 \right\} . \tag{1}$$

The observed relative splitting $(\Delta_\infty - E_0)/\Delta_\infty$ is ~ 0.06, so we estimate the pair potential at the interface to be $\sim 65\%$ of its value deep in the superconductor. Within the same approximations, the tunneling density of states is found to contain a sharp bound-state peak at E_0, to vanish between E_0 and Δ_∞, and then to exhibit a sharp rise at Δ_∞ to a peak just above Δ_∞, followed by a decrease approaching the usual asymptotic limit for $E >> \Delta_\infty$. Currently, there exists no theory which accounts for *both* the effects of a spatially varying pair potential and elastic scattering, but it is reasonable that the net effect of the latter would be to smooth out sharp structures. Such a theory would have to explain why a magnetic field has a smaller effect on the peaks identified with the bound state than on the peaks associated with the feature at the gap.

We cannot actually demonstrate that a nominally 30-Å-thick Ho$(OH)_3$ polycrystalline layer of the tunneling barrier actually orders at the bulk Curie temperature of 2.54 K. Because this material is an Ising system,[3] there may be order even though the barrier is nearly two dimensional. Then the question is why splitting is observed above the bulk Curie temperature. We suggest two possible explanations for this. First, the interaction times for electron scattering from the barrier are orders of magnitude shorter than typical spin-fluctuation lifetimes. Thus, conduction electrons cannot distinguish between a ferromagnetically ordered barrier and a paramagnetic one exhibiting long-lived magnetic fluctuations. The second possibility is that there is a real broadening of the magnetic transition by fluctuations resulting from the geometrical constraint of having tiny crystallites of the trihydroxide in an ultrathin barrier.

In conclusion, we have observed a splitting of the tunneling characteristic of superconducting junctions containing barriers of Ho$(OH)_3$. The results are consistent with the existence of a bound state below the Pb gap in each of the electrodes near its interface with the magnetic layer. This finding may have implications for the study of artificial structures containing magnetic and superconducting layers. This bound state has a physical origin different from that of the magnetic-field-induced bound state at the surface of a Type-I superconductor, predicted by Pincus[15] and discussed most recently by Doezema *et al.*[16] Such a state cannot be observed by tunneling because it involves electrons traveling accurately antiparallel to the Meissner screening currents which are parallel to the surface, whereas tunneling experiments are sensitive to quasiparticles traveling perpendicular to the surface.

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[1] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 243 (1961)].

[2] C. Uher, Roy Clarke, and I. K. Schuller, Phys. Rev. B **30**, 453 (1984).

[3] C. A. Catanese and H. E. Meissner, Phys. Rev. B **8**, 2060 (1973), and references therein.

[4] G. T. K. Swami, F. E. Stageberg, and A. M. Goldman, J. Vac. Sci. Technol. A **2**, 767 (1984).

[5] W. P. Wolf (private communication).

[6] For a critical review of gap anisotropy studies, see J. L. Bostock and M. L. A. Macvicar, in *Anisotropy Effects in Superconductors*, edited by Harald W. Weber (Plenum, New York, 1977), p. 213, and references therein.

[7] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1956); D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

[8] Surface superconductivity in Pb tunneling junctions has been studied by Y. Goldstein, Phys. Lett. **12**, 169 (1964).

[9] Bernard Serin, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 2, Chap. 15.

[10] E. L. Wolf and G. B. Arnold, Phys. Rep. **91**, 31 (1982), and references therein.

[11] A. F. Andreev, Zh. Eksp. Teor. Fiz. **46**, 1823 (1964) [Sov. Phys. JETP **19**, 1228 (1964)].

[12] R. Kummel, Phys. Rev. B **6**, 2617 (1972).

[13] J. Bardeen, R. Kummel, A. E. Jacobs, and L. Tewordt, Phys. Rev. **187**, 556 (1969); R. Kummel, Phys. Rev. B **3**, 784 (1971); C.-R. Hu, *ibid.* **12**, 3635 (1975); G. Eilenberger and A. E. Jacobs, J. Low Temp. Phys. **20**, 479 (1975).

[14] B. Bar-Sagi and C. G. Kuper, Phys. Rev. Lett. **28**, 1556 (1972); J. Low Temp. Phys. **16**, 73 (1974).

[15] P. Pincus, Phys. Rev. **158**, 346 (1967).

[16] R. E. Doezema, J. N. Huffaker, S. Whitmore, J. Slinkman, and W. E. Lawrence, Phys. Rev. Lett. **53**, 714 (1984).