Experimental Observation of the Spin Screening Effect in Superconductor/Ferromagnet Thin Film Heterostructures

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We have studied the nuclear magnetic resonance (NMR) of ^{51}V nuclei in the superconductor/ferromagnet thin film heterostructures $Pd_{1-x}Fe_x/V/Pd_{1-x}Fe_x$ and Ni/V/Ni in the normal and superconducting state. Whereas the position and shape of the NMR line in the normal state for the trilayers is identical to that observed in a single V layer, in the superconducting state the line shape definitely changes, developing a systematic distortion of the high-field wing of the resonance line. We consider this as the first experimental evidence for the penetration of ferromagnetism into the superconducting layer, a phenomenon which has been theoretically predicted recently and dubbed the spin screening effect.

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The interplay of the electronic states at the interfaces of thin film heterostructures has been a fascinating topic in solid state physics ever since the availability of modern thin film preparation techniques. In recent years heterostructures composed of complex oxides such as the high temperature superconductor $YBa_2Cu_3O_7$ with the ferromagnetic perovskite $La_{0.67}Ca_{0.33}MnO_3$ [1] or $LaAlO_3$ with $SrTiO_3$ [2] moved into the center of interest and opened an intriguing field of new physical phenomena and devices with new functionalities. A well-known phenomenon at the interfaces of thin film heterostructures is the penetration of the superconducting pair wave function from a superconductor S into a normal metal N; this is known as the classical proximity effect. More exotic and still a subject of actual research interest is the penetration the pair wave function into a ferromagnetic metal F at an S/F interface (see, e.g., [3,4] for recent reviews). The penetration depth of the Cooper pairs into the F layer is actually very small, only of the order of 0.7 nm for the elemental ferromagnets Co, Fe, and Ni [4], but nevertheless it is remarkable that very thin F layers at an S/F interface can simultaneously be ferromagnetic and superconducting.

One might ask intuitively, whether the reverse effect, namely, an S-layer attaining a spontaneous magnetic moment at the S/F interface, is also possible. Actually this really should happen as has been proven theoretically only very recently [5,6]. Originally, in Ref. [5], this phenomenon was called the inverse proximity effect. Qualitatively the physical origin of the ferromagnetism in the S layer can be explained by a spatial asymmetry of the Cooper pair density for the spin-up and spin-down electrons with the spin-up electrons (the majority spins in the F-layer) residing with a higher probability in the F layer and the spin-down electrons due to superconducting correlations with a higher probability in the S layer. Thus, the magnetic moment in the S layer should be oriented antiparallel to the magnetization of conduction electrons in the F layer. Theoretically, for a very thin F-layer the induced magnetic moment of conduction electrons in the S layer at distances of the order of the Cooper pair size ξ_s from the S/F interface should exactly compensate the moment of conduction electrons in the F layer [6]. This is the reason why we use the term "spin-screening effect" instead of inverse proximity effect, because it characterizes the physical situation more precisely.

The theoretical prediction of the spin screening immediately triggered experimental efforts to confirm the effect. In a multilayer $[YBa_2Cu_3O_7/La_{0.67}Ca_{0.33}MnO_3]$ a change of the magnetization profile as determined by neutron reflectivity was tentatively interpreted as spin screening in the superconducting layers [7]. Later it turned out, however, that the physical mechanism is quite different, namely, a charge transfer across the interface leading to an orbital reconstruction [1]. In a paper on F/S mesoscopic thin film structures it was detected that the quasiparticle density of states in the superconductor is modified up to distances of the superconducting correlation length ξ_s from the S/F interface [8]. The authors in Ref. [8] called this observation, too, inverse proximity effect, but actually it is fundamentally different from the spin screening effect we are discussing here. Thus, until now there is no unequivocal experimental evidence for the spin screening effect in the literature.

The amplitude of the magnetization induced by the spin screening effect in the S layer can be very small, especially when taking into account the limited transparency of the S/F interface in a real thin film system [4]. Thus, one needs an experimental technique with very high sensitivity for small changes of the spin polarization in the S layer. The induced spin polarization in the superconductor shifts the local resonance fields for the nuclei of the S layer located at the distance of the order of ξ_s from the S/F interface. The nonuniform distribution of local fields thus produced nearby the S/F interface distorts the NMR line shape in a characteristic fashion. We show that actually it is possible to observe the effect in $F/S/F$ trilayers using the ^{51}V NMR as a distortion of the high-field wing of the resonance line.

We prepared $F/S/F$ trilayers with V as the S layer and either an alloy $Pd_{1-x}Fe_x$ or Ni as the F layers (see Table I). All layers were grown on single-crystalline MgO(001) substrates by molecular beam epitaxy in a growth chamber with a base pressure below 5×10^{-10} mbar at a growth temperature of 300 °C. For V, Ni, and Pd we used electron beam evaporation and a growth rate of 0.15, 0.03, and 0.05 nm/s, respectively. The $Pd_{1-x}Fe_x$ alloy layers were produced by coevaporation of Pd and Fe. To prevent oxidation, all samples were capped by Pd layers. The thickness and the quality of the films were checked by conventional small-angle x-ray reflectivity. Well-resolved Kiessig fringes from the total layer thickness were observed. Fits using the modified Parratt formalism [9,10] gave the thickness of the V layer d_V and the interface roughness parameter (Rough) included in Table I.

In order to detect a noticeable magnetic polarization due to the spin screening effect, the S-layer thickness in the S/F heterostructures should match the superconducting coherence length. In our case it is restricted to about 40 nm (see Table I), implying that the number of V nuclei involved in the resonance signal will be extremely small, and conventional NMR technique then encounters serious sensitivity problems. In order to improve the sensitivity we built a supersensitive NMR spectrometer based on a Robinson-scheme generator (see, e.g., [11]) operating in a continuous mode at the frequency of about 6 MHz [12]. MESFET transistors operating at 4 K enable the immersion of the HF generator into liquid helium in close vicinity to the sample pick-up coil. This strongly reduces thermal noise and excludes losses in the connecting line. Since the gyromagnetic ratio for the Cu and V nuclei are close to each other, the resonator coil as well as the magnetic field modulation coils were wound from high-purity Ag wire. At liquid-helium temperatures, the resonance circuit has a high Q value that also considerably enhances the NMR spectrometer sensitivity.

The upper critical field $H_{c2}^{\perp}(T)$ for the magnetic field direction perpendicular to the film plane has been measured resistively by standard four point dc technique. As expected theoretically, the critical field depends linearly on temperature, i.e., $H_{c2}^{\perp}(T) = H_{c2}^{\perp}(0)(1 - T/T_c)$. The values of $H_{c2}^{\perp}(0)$ and T_c are given in Table I. The superconducting transition temperature T_c of the samples lies between 3.6 and 5 K (Table I). From the residual resistivity ratio $RRR = R(300\text{ K})/R(5\text{ K})$ (Table I) we determine the residual resistivity ρ_0 [13] and using the Pippard relations [14] we calculate the mean free path l of the conduction electrons given in Table I. With the BCS coherence length of V $\xi_0 = 44$ nm we then derive the superconducting coherence length $\xi_s = \sqrt{\xi_0 l/3.4}$ given in the last column of Table I.

The NMR measurements were performed on the ^{51}V nuclei in the temperature range 1.4–4.2 K. Since the operating frequencies are slightly different for different samples, all data were rescaled to the same frequency ν, in our case to $\nu = 5542.3$ kHz. The signal-to-noise ratio does not exceed 3 and therefore we accumulated signals from at least 20–30 sweeps of the magnetic field during two minutes each.

In Fig. 1(a) we show the NMR signal in the normal state for the single V layer. The resonance line shape is described by the derivative of a Gaussian absorption curve. Fitting this theoretical curve we can determine the resonance line position with an absolute accuracy below 0.5 Oe. For the resonance line width (the peak-to-peak distance of the absorption line derivative) we get a value of 12.2 Oe. The resonance field at $H_0 = 4923.1$ Oe is found to be shifted by $\delta H = 29.1$ Oe relative to the position in an insulator (4952.2 Oe for ^{51}V), thus, for the Knight shift in the normal state, which is defined as the ratio of the NMR line shift relative to its position in an insulator, we get $0.59 \pm 0.01\%$, in good agreement with the value measured previously [15,16].

When decreasing the temperature below T_c, the resonance line shifts to higher magnetic fields together with some broadening. The resonance line shape in the S state is still described by a Gaussian absorption curve [Fig. 1(b)].

TABLE I. Experimental parameters of the studied samples: S1 is the single V layer, S2 is the $Pd_{0.98}Fe_{0.02}/V/Pd_{0.98}Fe_{0.02}$ trilayer, S3 is the $Pd_{0.97}Fe_{0.03}/V/Pd_{0.97}Fe_{0.03}$ trilayer, and S4 is the Ni/V/Ni trilayer. Given are the thickness of the V layer d_V, the roughness parameter Rough, the superconducting transition temperature T_c, the upper critical field $H_{c2}^{\perp}(0)$ at zero temperature, the residual resistivity ratio RRR, the electron mean free path in the V layer l, and the superconducting coherence length ξ_s. The thickness of the magnetic layers is about 3 nm for all trilayer samples.

Sample	d_V (nm)	Rough (nm)	T_c (K)	$H_{c2}^{\perp}(0)$ (kOe)	RRR	l (nm)	ξ_s (nm)
S1	30	0.3	4.65	7.4	11	15	14
S2	36	1.3	3.02	10.2	4.6	5	8
S3	42	1.3	3.55	9.5	6	7	10
S4	44	1.6	4.05	12.0	4.4	5	8

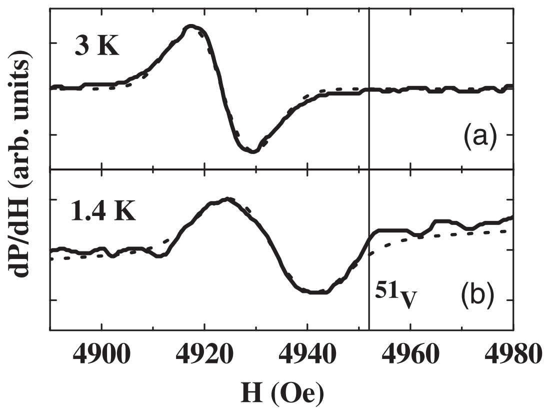

FIG. 1. NMR spectra for the single V layer (sample S1) in the normal ($T = 3$ K) (a) and the superconducting ($T = 1.4$ K) (b) state. All data are given for the external magnetic field perpendicular to the sample plane. The NMR spectra are simulated with a Gaussian line shape (dashed curves).

In our NMR experiments, with the external magnetic filed perpendicular to the film plane, the V film is in the vortex state. For a detailed theory of the local field distribution in the triangular vortex state see [17,18]. Inhomogeneity of the magnetic filed in the mixed state of the type II superconductor leads to a broadening and shifting of the NMR line to higher fields. In real samples pinning of the vortex lattice should take place. Brandt [19,20] argued that to observe the particular distribution of the local fields in the vortex state one needs a pin-free ellipsoidal sample made of high-purity single-crystalline material with the Ginzburg-Landau parameter $\kappa \sim 1$ (for example, ultrapure Nb). For our thin film samples with $\kappa \simeq 3$–4 the pinning forces lead to a transformation of the singular field distribution to a Gaussian one with a width estimated as $\delta H_v \sim (H_{c2} - H_0)/2\kappa^2$. With $H_{c2} \simeq 5000$ Oe and $H_0 = 4920$ Oe this gives $\delta H_v \sim 3.5$ Oe. If the NMR line shape in the normal state is Gaussian then in the S state it should keep the Gaussian shape with the additional broadening estimated above. This is just what we observe in our experiment [Fig. 1(b)].

The NMR line for the $F/S/F$ trilayer samples in Fig. 2(a)–2(c), however, reveals notably different behavior in comparison with the single V layer samples. After the transition to the S state the NMR line shape is markedly changed with the high-field wing appearing strongly distorted. As we have shown above the transition to the S state should not change the Gaussian shape of the NMR line. For our $F/S/F$ trilayers we have $\kappa \simeq 4$–5 and expect stronger pinning forces because of the sandwiching of the S layer by the F layers [20]. Therefore, there are no physical reasons for deviation of the line shape from Gaussian. Thus, we regard the strong distortion of the high-field wing of the NMR line as a clear manifestation of the spin screening effect.

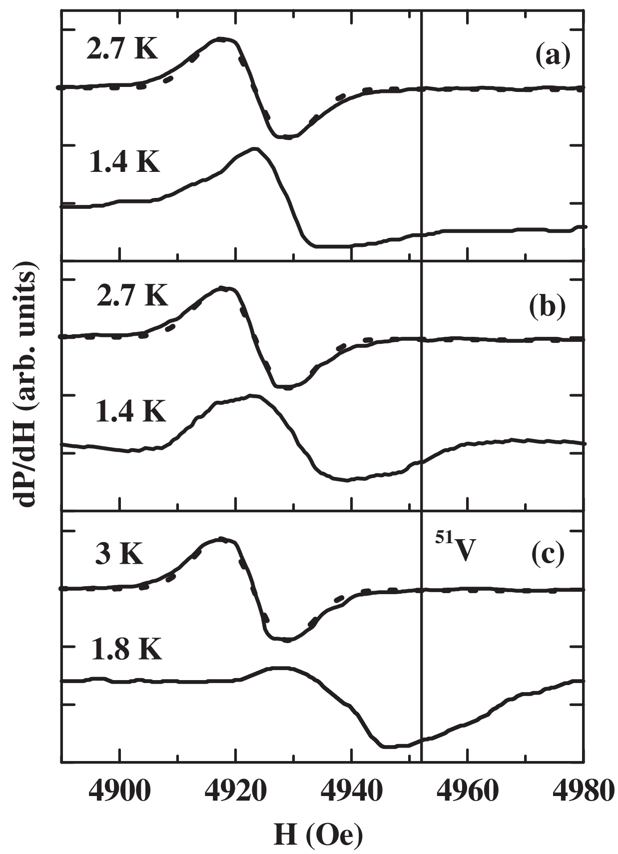

FIG. 2. NMR spectra for $Pd_{0.98}Fe_{0.02}/V/Pd_{0.98}Fe_{0.02}$ trilayer (sample S2) in the normal ($T = 2.7$ K) and the superconducting ($T = 1.4$ K) state (a), $Pd_{0.97}Fe_{0.03}/V/Pd_{0.97}Fe_{0.03}$ trilayer (sample S3) in the normal ($T = 2.7$ K) and the superconducting ($T = 1.4$ K) state (b) and Ni/V/Ni trilayer (sample S4) in the normal ($T = 3$ K) and the superconducting ($T = 1.8$ K) state (c). The NMR spectra for the normal state are simulated with the Gaussian line shape (dashed curves).

According to the model of the spin screening [5], the spin polarization of the electrons from the interfacial region penetrates into the S layer. By means of the hyperfine interactions this spin-polarization induces a local field $H_{\rm loc}$ on the V nuclei with a direction opposite to the external magnetic field, and the NMR resonance line shifts to higher fields accordingly. In quantitative terms, in order to calculate the NMR line shape, one must take the spatial distribution of the spin polarization in the S layer into consideration. The induced spin-polarization $\sigma(x)$ in the superconductor is expected to decay exponentially with the distance x from the interface [5] with a decay length given by the coherence length ξ_s. The additional local magnetic field on a nucleus thus is

$$H_{\rm loc} = H_m \exp(-x/\xi_s) \propto \sigma(x), \tag{1}$$

where $x = 0$ defines the position of the F/S interface [5]. The local field distribution,

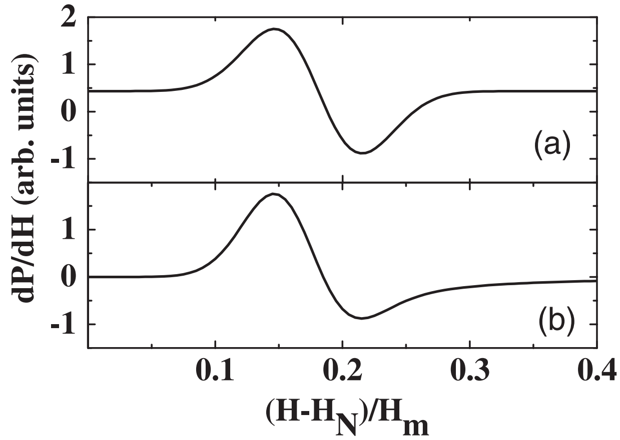

FIG. 3. (a) The pure Gaussian line shape derivative with peak-to-peak width and position equivalent to the model spectrum below. (b) Model calculations of the NMR line shape in an $F/S/F$ trilayer with $\xi_s/d = 0.2$ and the Gaussian broadening parameter $\sigma/H_m = 0.06$. H_N is the resonance field in the normal state. Only the line shape distortion and the line shift due to the inverse proximity effect were considered in calculation of the spectrum (b).

$$F(H) = \frac{1}{d}\int_0^d dx\delta(H - H_{\rm loc}(x)), \qquad (2)$$

has to be convoluted with the unperturbed NMR Gaussian line shape derived by fitting of the normal-state NMR line.

The result of a numerical simulation of the NMR line shape in an S film with a finite spin polarization penetrating through the S/F interface is shown in Fig. 3(b). The NMR line clearly exhibits a broadened high-field wing, strikingly similar to the experimental spectra observed for PdFe/V/PdFe and Ni/V/Ni trilayers in Figs. 2(a)–2(c). The low-field side of the resonance line is mainly determined by the V nuclei in the core of the V layer essentially unaffected by inhomogeneity of the spin polarization. The high-field side, however, is modified, since here the V nuclei from the region close to the S/F interfaces contribute to the NMR signal.

In summary, the character of the NMR line distortion and the systematic increase of the distortion with the strength of the ferromagnet below the superconducting transition temperature in the $F/S/F$ trilayers leads us to the conclusion that we have observed a manifestation of ferromagnetism penetrating into the superconductor; i.e., the novel mechanism coined the spin screening effect in Refs. [5,6].

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