Fe-Induced Magnetization of Pd: The Role of Modified Pd Surface States

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The magnetic properties of Fe-Pd multilayers are strongly affected by the high magnetic polarization of Pd. The origin of the magnetization of Pd in contact with Fe is examined. We found that a surface Pd(100) photoemission structure persists upon preparation of 1 and 2 monolayers Fe. Comparison with an *ab initio* calculation identifies this structure as a state distributed equally between the Fe and the adjacent Pd layer. Spin analysis of the photoelectrons shows that this state is magnetic, and the calculation reveals that it contributes to the large Pd moment at the interface of $0.32\mu_B$.

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Long period oscillatory exchange coupling and giant magnetoresistance are two exciting new discoveries. Both are displayed by ferromagnetic layers separated by nonmagnetic spacer layers. Increasing the thickness of the spacer layer can alternate the exchange coupling of successive magnetic layers from ferromagnetic to antiferromagnetic and vice versa [1]. In an RKKY picture [2] as well as in a quantum well picture [3] the oscillation period is related in a simple way to the Fermi surface of the spacer material as experimentally verified by photoemission experiments of quantum well states [3–5]. While theory [2,6] and experiments [3–5,7–9] are in good agreement for noble metal spacer layers, RKKY theory cannot be applied to Pd or Pt spacers. The RKKY theory describes basically the asymptotic behavior of the interlayer coupling of ferromagnetic layers with unperturbed spacers. For Pt and even more so for Pd the combination of the electrostatic Coulomb interaction and the Pauli principle leads to a large magnetic polarizability of these materials, and in contact with a magnetic layer a large proximity magnetization of the Pd spacer is expected. This has been extensively studied for $3d$ impurities in Pd. Large scale calculations [10] for $3d$ impurities surrounded by more than 1000 Pd atoms show an exponential decay of the polarization of Pd as a function of the distance from the impurity and no RKKY oscillations. In line with these arguments, one observes experimentally for Fe/Pd/Fe multilayers [11] a damped ferromagnetic coupling on which, however, oscillations of the coupling strength are superimposed resulting in a net ferromagnetic coupling for Pd spacers up to 12 monolayers (ML) thickness. This complicated behavior cannot be understood without knowledge of the modifications the Fe causes in the Pd electronic structure.

In this Letter we demonstrate for the system Fe/Pd(100) that a nonmagnetic surface state of Pd is modified due to hybridization with a ferromagnetic Fe overlayer such that a magnetic state, localized at both the Fe and the Pd layer, is created. This mutual Fe-Pd state leads to the magnetization of the interface Pd atom of $0.32\mu_B$ and conveys the proximity magnetization of Pd through which the ferromagnetic coupling is induced. As this mutual Fe-Pd state is mainly located away from the Brillouin zone center, it was not observed in previous experimental [12] and theoretical [13] photoemission studies, which were performed in normal emission geometry only.

Surface cleanliness of the sputtered and annealed Pd(100) crystal has been checked by Auger spectroscopy and the surface order by low-energy electron diffraction (LEED). Fe was evaporated at rates of 0.3 ML/min, measured with an oscillating quartz thickness monitor, onto the Pd held at room temperature (RT). Thereby the base pressure rose from below 2×10^{-10} mbar to 7×10^{-10} mbar. Synchrotron light from TGM 1 and TGM 5 monochromators at BESSY has been used to excite photoelectrons from the remanently in-plane magnetized sample held at RT. Spin analysis was performed using a Mott detector.

While there is general agreement on the pseudomorphic growth at RT of *thick* Fe on Pd(100) [12,14,15], there are some unresolved questions about the morphology of the monolayer and of submonolayers of Fe/Pd(100) [12,16,17]. The Fe atoms were found to occupy sites in registry with the substrate [12]. Auger kinks at 1 and 2 ML were observed [16], but no LEED oscillations [12]. Intermixing might occur, however, of a much smaller extent than for Fe deposited on Au(100) and Cu(100) [17].

In Fig. 1(a) angle-resolved photoemission spectra of the clean Pd(100) at 40 eV photon energy are displayed. The emission angle varies between 0° ($\bar{\Gamma}$,$\mathbf{k}_\parallel$=0) and 22.5° ($\bar{X}$,$\mathbf{k}_\parallel$=1.14 Å^{-1}) in the $\bar{\Delta}$ direction of the surface Brillouin zone (SBZ). The electronic states probed are of even symmetry ($\bar{\Delta}_1$). The feature highlighted by hatching in Fig. 1(a) has been identified as a surface localized state by Elliott, Smith, and Kevan [18]. It is sensitive to hydrogen [18] and to oxygen (this work) adsorption. It disperses with $\mathbf{k}_\parallel$ from 0 to 1.45 eV binding energy and does not disperse with photon energy. It crosses the Fermi level in the vicinity of the $\bar{X}$ point. Turning to the spectra displayed in Figs. 1(b)–1(d), which were measured under the same conditions as (a) but after deposi-

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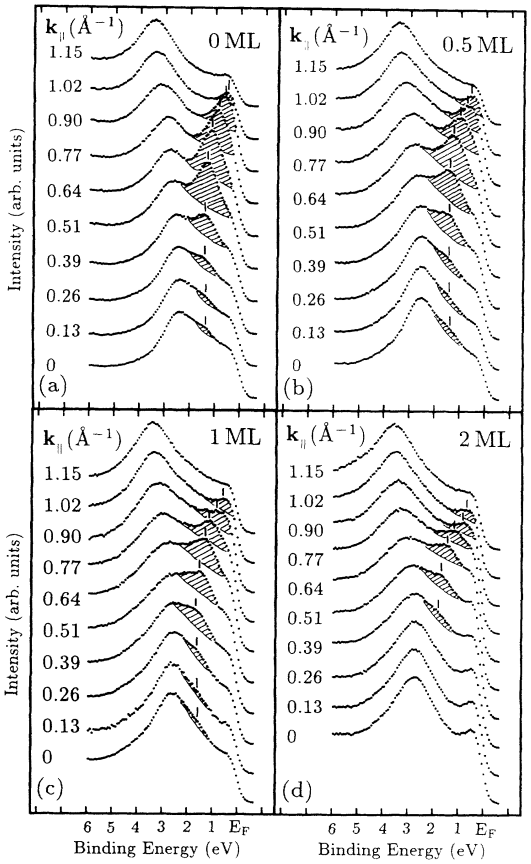

FIG. 1. Angle-dependent photoemission spectra at 40 eV photon energy for clean Pd(100) (a), 0.5 ML (b), 1 ML (c), and 2 ML (d) Fe coverage. The values of $k_{\parallel}$ refer to 1 eV binding energy. The hatched regions highlight the pure surface state and the mutual Fe-Pd state.

tion of 0.5-, 1-, and 2-ML Fe, we notice that the former surface signal only changes slightly during the growth of the first and second layers. This indicates that the former surface state still exists, even though in a modified form, in the overlayer system.

To gain more insight into the experimental results we have performed first-principles band structure calculations for Pd(100), 1-ML Fe/Pd(100), and 2-ML Fe/Pd(100) using the full-potential linear augmented-plane-wave (FLAPW) method [19]. Self-consistent calculations have been carried out for nine-layer-thick Pd(100) films, nine-layer-thick 1-ML Fe/Pd(100) films consisting of seven-layer Pd(100) films covered with one layer of Fe on each side of the Pd surface and eleven-layer-thick 2-ML Fe/Pd(100) films. The Fe-Pd interlayer spacing was chosen to be the average of the bulk lattice spacings, and for the Fe-Fe interlayer spacing the bulk Fe lattice spacing was used. Although the film thickness is sufficient to determine the work function and electronic structure reliably, the distinction of surface states, interface states, and double-layer states from bulk-projected bands and the observation of partial gaps in the band structure remain difficult. Therefore, we use thick films of 23 to 27 layers of both Fe and Pd to analyze the band structure.

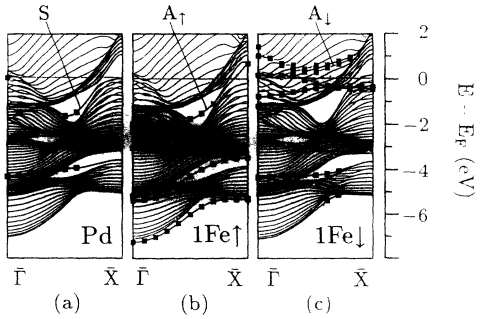

FIG. 2. First-principles calculations of $E(\mathbf{k}_{\parallel})$ dispersion relations for a 25-layer slab Pd(100) (a), majority (b), and minority (c) spin of a 25-layer slab of 1-ML Fe/Pd(100) for states of $\bar{\Delta}_1$ symmetry. The squares mark in (a) surface states of Pd(100) whose localization in the top surface layer, measured in terms of the normalized charge density of this state in the muffin-tin spheres, is larger than 50% and in (b) and (c) interface localized states whose localization at the Fe and Pd interface atoms is larger than 50%.

Figure 2 shows the calculated band structure in the $\bar{\Delta}$ direction of the SBZ for states characterized by even symmetry ($\bar{\Delta}_1$) for Pd(100) (a) and of 1-ML Fe/Pd(100) for majority spin (b) and minority spin (c). The regions that are "cross hatched" by bands represent essentially the projection of the Pd bulk band structure onto the (100) surface. Three partial gaps below E_F are readily observed. Here we want to concentrate on the stomach-shaped gap resulting from *s-d* hybridization which is found between E_F and about 2 eV binding energy. Its position and shape are in perfect agreement with the projected bulk band structure of Ref. [18] as well as with the experimentally determined bulk band structure in the Λ direction (which is contained in the projection along $\bar{\Delta}$) in Ref. [20]. *In agreement with the experimental observation a split-off surface state is found inside the gap* [*S* in Fig. 2(a)]. Its surface character is revealed by the squares which mark states whose wave functions exhibit more than 50% charge density in muffin-tin spheres of the surface layer. However, its energy position is somewhat shifted towards the center of the gap with respect to the one measured here and in Ref. [18]. This might be caused by modifications of the Pd surface potential due to a surface relaxation of Pd(100) recently reported [21].

For 1-ML Fe on Pd(100) the calculation predicts ferromagnetic order of the Fe film. Figure 2(b), displaying the *majority-spin* band structure, shows a band ($A_\uparrow$) penetrating the stomach gap whereas this gap is rather void of *minority-spin* states (c). The squares in (b) and (c) mark states fulfilling the criterion "more than 50% in the two outer layers." Among these, exchange-split bands can be assigned readily due to their characteristic

dispersions: Of special relevance here is the observation that *the majority-spin band inside the gap ($A_\uparrow$) is exchange split with respect to the minority-spin band above E_F ($A_\downarrow$)* that disperses upwards on the way to $\bar{X}$. We have analyzed more closely the wave functions of this pair of states, $A_\uparrow$ displayed in Fig. 3(a) and $A_\downarrow$ in Fig. 3(b), throughout the gap. Strikingly, *$A_\uparrow$ turns out to be shared almost equally between the Fe monolayer and the Pd layer underneath.* Further, it is extremely localized at this interface because the presence of the gap makes a deep penetration into the Pd bulk band structure impossible. Indeed, a small coupling of $A_\uparrow$ to the bulk occurs only outside the gap ($\mathbf{k}_\parallel \leq 0.34$ and $\mathbf{k}_\parallel \geq 0.80$ Å^{-1}). This means that a new mutual Fe-Pd state has developed out of the Pd surface state. On the other side, $A_\downarrow$ proves to be a pure state of the Fe monolayer with only very little coupling to the Pd. We conclude from this that coupling of the Fe overlayer electronic structure to the Pd substrate is facilitated by the presence of surface states on the Pd substrate.

It can be shown now that this subtle interaction of Pd surface and Fe states indeed affects magnetism at the interface. In Figs. 3(c) and 3(d) the spin-resolved local density of states (DOS) *at the Pd site* underneath the Fe is displayed for 1-ML Fe/Pd(100). Remarkable of the otherwise quite symmetric majority- and minority-spin band structures is a broad majority structure between 1 and 2 eV binding energy (hatched) which does not exist for minority spin. The fact that the energy position of this majority-spin structure coincides with that of the state $A_\uparrow$ in the gap means that the mutual Fe-Pd state contributes to this DOS and thus to the magnetic moment of the Pd at the interface ($0.32\mu_B$/atom [22]). In this way the magnetization of Pd atoms at the interface is traced to a particular state, which originates from the Pd surface electronic structure and is spin polarized due to the hybridization with the Fe $3d$ majority orbitals.

It remains to be shown that the conclusions drawn from the comparison between the experimental and the calculational results hold if we extend our measurements to include the electron spin. In a magneto-optical Kerr effect study, Liu and Bader [23] found that 1-ML Fe/Pd(100) deposited at RT is ferromagnetic at RT with an in-plane easy axis. Our thinnest sample showing nonvanishing spin polarization was about 1.3 ML thick. We leave this discrepancy to possible differences in thickness calibration. However, the small spin polarization leads to spectra of almost equal intensity for both spin channels. Therefore, we present in Fig. 4 the spin-averaged spectrum and the spin-polarization spectrum for 1.5 ML and the spin-resolved spectrum for 2-ML Fe coverage. The spectra were measured at 45° off-normal emission which corresponds to $\mathbf{k}_\parallel = 1.53$ Å^{-1} for a state with 1 eV binding energy in the second SBZ corresponding to 0.75 Å^{-1}

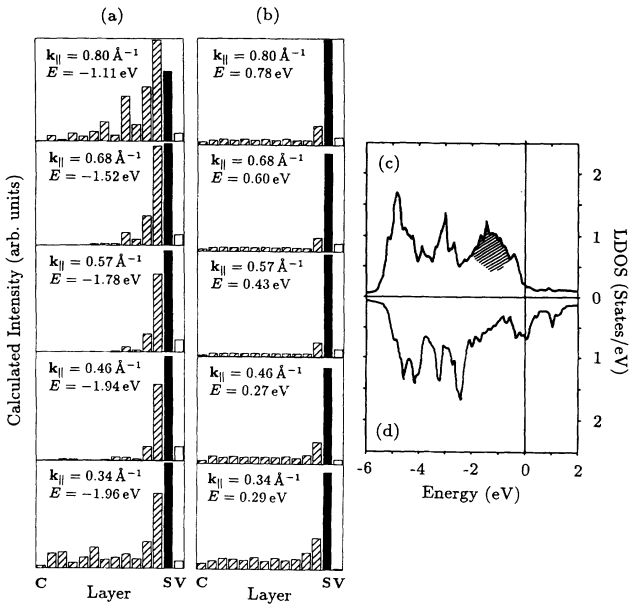

FIG. 3. Results of the calculation for 1-ML Fe/Pd(100). Left: Distribution of the interface state in the direction perpendicular to the surface. Majority-spin mutual Fe-Pd state (a) and its exchange split minority-spin counterpart (b) for different $\mathbf{k}_\parallel$ points in the $\bar{\Delta}$ direction. The column heights represent the strength in muffin tin spheres for Pd layers (hatched) and the Fe overlayer (black). Also the contribution outside of the muffin tins (vacuum) is shown (white). C and S denote central and surface layer; V denotes vacuum. Right: Layer resolved density of states (DOS) *at the site of the Pd layer underneath the Fe* for majority (c) and minority (d) spin electrons.

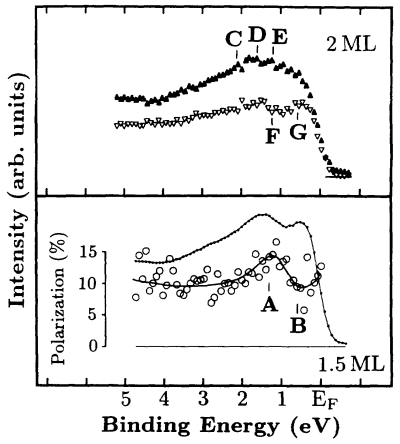

FIG. 4. Photoemission spectra of Fe/Pd(100) at $h\nu = 24$ eV and 45° off-normal emission ($\mathbf{k}_\parallel = 1.53$ Å^{-1}). For 1.5-ML Fe a spin-averaged spectrum (●) and the polarization spectrum (○) are shown. The spin polarization is calculated by $P = (n^\uparrow - n^\downarrow)/(n^\uparrow + n^\downarrow)$ from the numbers of majority- ($n^\uparrow$) and minority-spin ($n^\downarrow$) electrons. For 2-ML spin-resolved spectra for majority (▲) and minority (▽) spin are displayed. Vertical bars indicate calculated energies at which emission should occur.

of the first SBZ. The photon energy was chosen to be 24 eV, such that the atomic photoionization cross section of Pd $4d$ is 5 times larger than that of Fe $3d$. Further, for binding energies of 0.5 to 1.6 eV (the range of the gap at $\mathbf{k}_{\parallel}=0.75$ Å^{-1}) Pd bulk bands should not contribute to the spectrum. Thus emission from the Fe overlayer and from Pd bulk is small, which enhances relatively the signal from the interface. The 1-ML calculation predicts the majority-spin mutual Fe-Pd state $A_{\uparrow}$ at 1.3 eV (A in Fig. 4) and a minority-spin state localized at the Fe overlayer at 0.6 eV (B). We notice that both A and B coincide with extremal values of the polarization spectrum.

Increasing the Fe thickness, the stomach-shaped Pd gap will be filled with Fe states, and indeed the calculated majority DOS of Pd keeps changing exactly in the energy region of the stomach gap, thus new mutual Fe-Pd states are appearing. On the other side our calculations show also that the Pd moment at the interface as well as the minority DOS of Pd remain unchanged. The latter means that the weight of the minority Fe states at the Pd site is small. As an example, for 2 Fe layers on Pd the calculation predicts three majority states with energies in the gap region: two spin polarized mutual Fe-Pd states (C,E) and one pure Fe double layer state (D), as well as two minority states (F,G), which have predominantly Fe character with some small weight at the interface. These states are marked in Fig. 4 and correspond to structures observed in the spectrum.

In summary, we have observed how a nonmagnetic surface state of Pd develops into a spin polarized mutual Fe-Pd state localized at the interface between the two materials. This was possible by comparing photoemission spectra for Fe films on Pd with results of first-principles calculations for 1- and 2-ML Fe/Pd(100) as well as clean Pd(100). This state, which is due to the hybridization of Fe $3d$ with Pd $4d$ wave functions, determines the magnetism of Pd at the interface and contributes to a magnetic moment of $0.32\mu_B$ at the Pd site. However, the importance of this state goes beyond this magnetic moment. It conveys the proximity magnetization to Pd atoms off the interface causing the damped ferromagnetic coupling, and, as it approaches the Fermi level, the state penetrates deep into the Pd spacer and might directly contribute to the oscillatory coupling superimposed on the damped one found for Fe/Pd/Fe multilayers. Increasing the Fe thickness will lead to additional spin polarized Fe-Pd states acting analogously. The physics discussed in this Letter will be applicable for a large variety of (100) multilayers with late $4d$ or $5d$ transition metal spacers, although the interlayer coupling exhibited will be quite different and depends on the details of the electronic structure.

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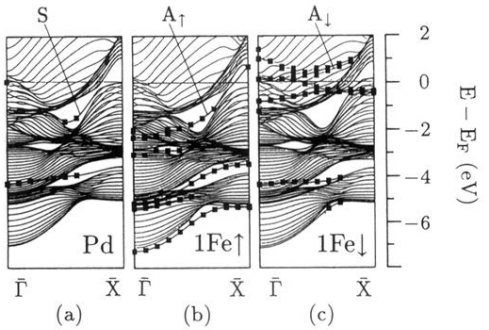

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