Growth and Magnetic Studies of Lattice Expanded Pd in Ultrathin Fe(001)/Pd(001)/Fe(001) Structures

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A new phase of Pd with an expanded lattice (5%) was grown on Fe(001). Ultrathin Fe/Pd and Pd/Fe bilayers and Fe/Pd/Fe trilayers were studied using ferromagnetic resonance and Brillouin scattering. Pd interlayers always couple the Fe layers ferromagnetically. For thicknesses up to four monolayers the Pd is ferromagnetic, in agreement with theory. One additional atomic layer of Pd destroys the ferromagnetism, but the Pd still exhibits a fluctuating magnetic moment partly polarized by the exchange field from adjacent Fe layers. The magnetic moments in the interfaces were determined from the ferromagnetic-resonance absorption intensities.

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The magnetic properties of palladium metal have galvanized both theorists and experimentalists. The valence band of Pd metal is similar to that of Ni which has the same lattice structure and the same number of valence electrons. Since Ni is ferromagnetic, numerous attempts have been made to convert metallic Pd to the ferromagnetic state. The free Pd atom with a $4d^{10}5s^{0}$ configuration is nonmagnetic. However, in metallic Pd the $4d$ band is not entirely filled. The intra-atomic Coulomb interactions between $4d$ electrons are responsible for an anomalously large Pauli susceptibility. The repulsive intra-atomic Coulomb interaction is so strong that the d band is near the threshold of becoming ferromagnetic. The role of intra-atomic Coulomb interactions can be enhanced by increasing the atomic volume. Brodsky's group studied $A(001)/\mathrm{Pd}(001)/A(001)$ (A =Ag,Au) sandwiches and tried to trigger the ferromagnetic state in Pd by stretching the Pd lattice by about 2.4% using $A(001)$ templates.[1] They found an enhancement of several thousand times in the Pauli susceptibility, but the ferromagnetic state in the Pd layers was never achieved. Recently, interest in Pd has increased strongly. First, the Philips group used Pd interlayers in Co/Pd superlattices which showed a large perpendicular anisotropy in which the saturation magnetization was oriented perpendicular to the sample surface.[2] Second, several theoretical papers have predicted interesting magnetic properties for Pd structures which can, in principle, be grown by molecular-beam epitaxy (MBE). Nonrelativistic calculations by Moruzzi and Marcus[3] and by Chen, Brener, and Callaway[4] predicted an onset of ferromagnetism in fcc Pd for a 5% increase in the lattice constant. Recently Blugel *et al.*[5] studied a Pd(001) bulk substrate covered by $3d$-transition-metal monolayers. They showed that the Pd substrate enhances the magnetic moment in Fe by $1\mu_B$ and that the Fe overlayer induces a noticeable magnetic moment in the two nearest Pd layers ($0.32\mu_B$ and $0.17\mu_B$ in the first and second layer, respectively). Bergmann[6] and Liu and Bader[7] saw strong evidence that a submonolayer of Fe induced a magnetic moment in a bulk Pd substrate. SQUID and Brillouin-light-scattering (BLS) measurements by Hillebrands, Baumgart, and Guntherodt[8] showed an induced magnetic moment in the Pd layers of Fe(011)/Pd(111) superlattices. However, in all three cases no quantitative data were given.

We have been involved in MBE studies of $3d$ transition metals, Fe in particular, using Ag(001) substrates. Brodsky's results showed that metallic Pd layers sandwiched between Ag(001) layers remain paramagnetic. However, the growth of Pd on Fe(001) might be quite different. First, hybridization of the $3d$-$4d$ bands should enhance the magnetic moment in both Fe and Pd. Second, ultrathin layers of Pd on an Fe(001) substrate very likely grow with the lattice spacing of Fe(001) and therefore they should be laterally expanded by as much as 5.1%. Only a 2.4% expansion was observed in Brodsky's work. Therefore the growth of metallic Pd on Fe(001) represents a unique system which, according to currently held views, should have a strong tendency to become ferromagnetic.

5Fe(001)/8Pd(001) and 8Pd(001)/10Fe(001) bilayers [the numbers 5, 8, and 10 denote the number of monolayers (ML)] and 5Fe(001)/xPd(001)/10Fe(001) (x=4,5,5.5,6,8,10,11) trilayers were grown by MBE on Ag(001) singular bulk substrates ($\Theta < 0.25°$). All structures studied were covered by 20 ML of Au(001) prior to their removal from UHV. The epitaxial growths were carried out in the low 10^{-10}-Torr range with the Ag substrate held at room temperature. The details of the Fe growth can be found in our previous papers.[9,10] Pd was evaporated from a Pd wire wrapped around a W wire heater. Pd grows very well on Fe(001). Reflection high-energy electron-diffraction (RHEED) patterns show that the growth follows the Fe square mesh very closely; no reconstructions are visible for films thinner

than 12 ML. The specular spot intensity shows well-defined oscillations during deposition (see Fig. 1) proving that at most the two top atomic layers are not completely filled at any given time during the growth.[11] Good coverage of the Fe substrate layer by Pd is further attested to by the exponential decay of the Fe L_3VV Auger peak intensity with increasing Pd thickness. The electron mean free path in Pd is 20% (5.6 ML) smaller than the value calculated from the universal Seah-Dench formula (7 ML).[12] The lateral lattice spacing in the Pd overlayers is identical to that of the Fe(001) substrate. Since its lateral spacing is 5.1% larger than in regular fcc Pd, one can say that this structure is metastable and very likely fcc; possible vertical distortion cannot be determined by RHEED and must be left to future LEED or angle-resolved x-ray-photoemission studies to decide. The growth of Fe on a Pd(001) substrate developed RHEED pattern features corresponding to a surface roughening after deposting 3 ML. We had to use a smaller RHEED scattering angle (compared to the first anti-Bragg reflection angle) in order to follow the Fe oscillations throughout the whole 10-ML growth; see Fig. 1. The quoted layer thicknesses in our structures were determined from RHEED oscillations. Despite the observed surface roughness, the films of Fe grown on Pd exhibit narrow ferromagnetic-resonance (FMR) lines (210 Oe) and therefore the Fe/Pd/Fe trilayers are well suited to magnetic studies.

Our theory of exchange-coupled bilayers has been extensively reviewed in our recent papers.[10,13] In ultrathin films the magnetizations within the individual layers are uniform. In ferromagnetically coupled layers there are two resonance modes: the low-frequency acoustic mode in which all magnetizations are parallel and the higher-frequency optical mode in which the rf magnetizations oscillate out of phase; see Fig. 2. It is important to realize that two modes are observed in FMR and BLS studies (homogeneous driving) only if the Fe layers have different resonance conditions. In our case this was achieved by using Fe films having different thicknesses, which resulted in different perpendicular anisotropy fields and hence different resonant frequencies.

In our theoretical treatment the exchange interface energy E^{AB} is given by[10]

$$E^{AB} = -4(A^{AB}/a)\mathbf{M}^A \cdot \mathbf{M}^B / M^A M^B ,$$

where A^{AB} (in ferromagnetic bulk $\sim 10^{-6}$ erg cm^{-1}) is the exchange-coupling coefficient between layers, $\mathbf{M}^A$ and $\mathbf{M}^B$ are the saturation magnetizations of layers A and B, and a is the lattice constant. The positions and intensities of both modes depend in a complicated (but algebraically tractable) way on the properties of the individual layers and upon the strength of the interface exchange coupling. Since the magnetic moments in the interfaces are tightly held together by the exchange, one cannot distinguish between the Fe film properties and those of the adjacent Fe/Pd interface. One always measures the overall magnetic properties of the individual Fe layer plus its interfaces. The role of the Fe/Pd interface on the magnetic properties of the Fe film can be determined by comparing the individual Fe films with a reference sample. The Ag(001)/5Fe(001)/20Au(001) ultrathin film was used as a reference sample in all our measurements. The trilayer magnetic properties of the constituent Fe layers and their exchange coupling can be determined by using the full theory of exchange-coupled bilayers[10] starting from the magnetic properties of the individual layers (samples 5Fe/8Pd, 8Pd/10Fe). The final adjustment of the magnetic parameters is carried out by means of a χ^2 MINUIT least-squares-fitting routine. It turns out that the strength of the exchange coupling is the only variable strongly dependent on the Pd interlayer thickness. The other magnetic parameters

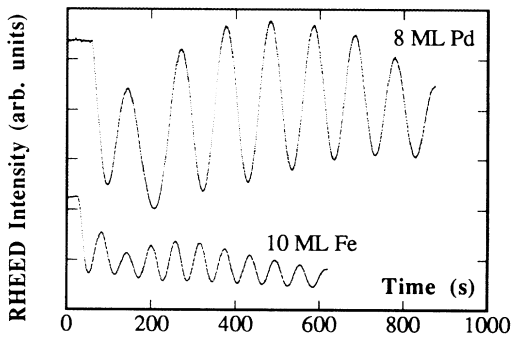

FIG. 1. RHEED intensity oscillations measured at the specular spot during the growth of the 5Fe/8Pd/10Fe trilayer on a Ag(001) single crystal. The period of the oscillations corresponds to the time required to form one atomic layer.

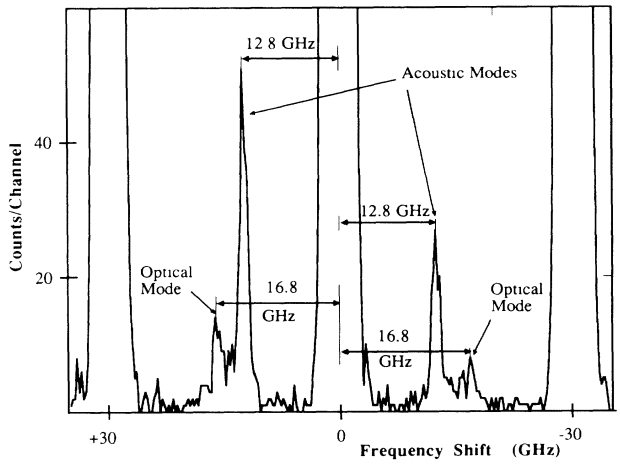

FIG. 2. Scattered light intensity vs frequency shift for a trilayer (5Fe/5.5Pd/10Fe) in an applied magnetic field of 0.82 kOe. These data were obtained for the backscattering configuration using 5145-Å light incident at 45°. The total dwell time in each of 256 channels was 1 sec.

($4\pi M_{\text{eff}}$ and $2K_1/M_S$) were very close to values measured in the individual bilayers; see Fig. 3. The FMR technique can also be employed to measure the total magnetic moment. The ability to measure the total magnetic moment in ultrathin structures is nontrivial. The contributions from the various interfaces can be disentangled by comparing the total magnetic moment in a given structure with the magnetic moment of the reference sample. The increased magnetic moment in the structures studied will be attributed to one atomic layer and the observed increase will be quoted in Bohr magneton (μ_B) per atom of the square (001) mesh.

Calculations by Blugel *et al.*[5] predict that the Fe in Fe/Pd interfaces induces a magnetic moment on two adjacent Pd atomic layers ($0.32\mu_B$ and $0.17\mu_B$ in the first and second Pd atomic layers, respectively). Therefore one would expect that the Fe/4Pd/Fe trilayer is fully ferromagnetic. Our FMR and BLS measurements in the 5Fe/4Pd/10Fe trilayer show only one resonance peak (acoustic mode), indicating a strong coupling which is in agreement with the Blugel predictions. However, the 5Fe/5Pd/10Fe trilayer, containing only one additional Pd atomic layer, exhibits two distinct peaks in the FMR and BLS data with the optical mode being at lower field and higher frequency, respectively, corresponding to a weak ferromagnetic coupling ($\sim 10^{-3}\times$ that of the bulk exchange coupling in Fe). This is a very striking result: The Pd interlayer was definitely not ferromagnetic. The strength of the exchange coupling (see Fig. 4) in samples having thin Pd interlayers (5, 5.5, and 6 ML) also exhibited a strong temperature dependence. Note that in the sample 5Fe/5Pd/10Fe this temperature dependence is almost exactly inversely proportional to the absolute temperature. The exchange coupling in this sample followed a Curie-Weiss type of dependence, $\sim 1/(T+\Theta)$. The presence of a magnetic moment in the Pd layer would definitely increase the coupling between the Fe layers since the exchange interaction scales with the moment. Therefore one can argue that the 5-ML-thick Pd still possessed a fluctuating moment which was polarized by the adjacent Fe layers. The temperature dependence of the exchange coupling in thicker Pd interlayers ($d > 8$ ML) is weak and even reverses its behavior. The 5Fe/xPd/10Fe trilayers for $x = 10,11$ ML show a decreased value of the exchange coupling at liquid-nitrogen temperature compared with that at room temperature. Thick Pd layers ($d > 8$ ML) do not possess magnetic moments throughout the whole layer. The magnetic coupling is caused by a spin transport mechanism involving unfilled $4d$ and $5s$-p Pd bands.

The magnetic moments in Fe/Pd interlayers can be investigated by comparing the Ag/5Fe/8Pd/20Au sample with a reference Ag/5Fe/20Au sample. The total magnetic moment in the sample Ag/5Fe/8Pd/20Au is larger (by approximately 8%) than the corresponding total magnetic moment in the reference sample Ag/5Fe/20Au. An 8% increase in the total magnetic moment of the 5-

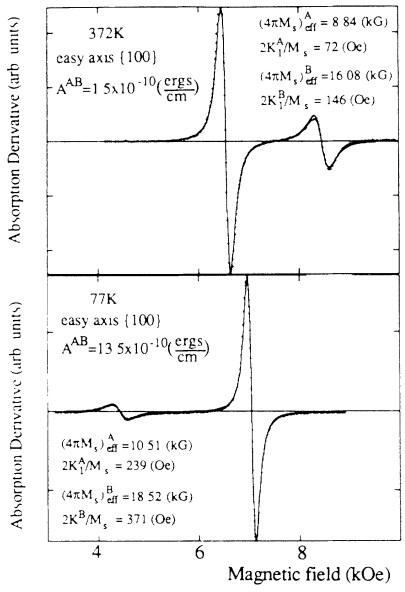

FIG. 3. The field derivative of FMR absorption at 36 GHz in the 5Fe/6Pd/10Fe trilayer (+) at 372 and 77 K. The solid line was calculated using the theory of exchange-coupled Fe layers (Ref. 10) with magnetic parameters (shown in figure) obtained from a χ^2 fit. The magnetic parameters of individual 5Fe/8Pd and 8Pd/10Fe bilayers are $(4\pi M_S)^A_{\text{eff}} = 9.05$ and 10.71 kG, $(4\pi M_S)^B_{\text{eff}} = 16.14$ and 18.56 kG, $2K^A_\uparrow/M_S = 50$ and 241 Oe, and $2K^B_\uparrow/M_S = 132$ and 308 Oe at 372 and 77 K, respectively. A denotes the 5-ML Fe layer and B denotes the 10-ML Fe layer.

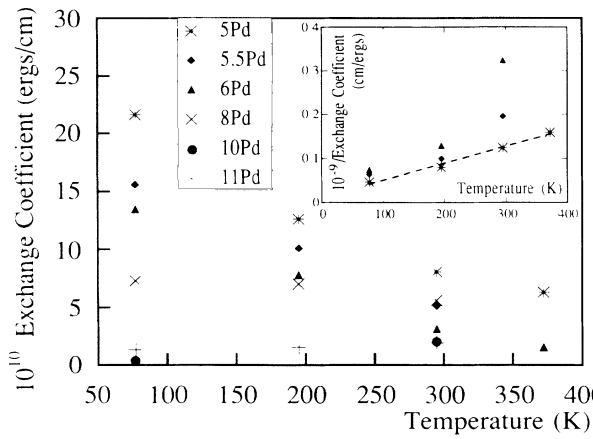

FIG. 4. FMR results of the exchange-coupling coefficient A^{AB} vs temperature in 5Fe/xPd/10Fe trilayers ($x = 5,5.5, 6,8,10,11$). FMR and BLS measurements probe an area 13 mm and 20 μm in diameter, respectively. BLS measurements at 295 K resulted in the same A^{AB} for the samples having 5, 6, 8, 10, and 11 Pd thick interlayers and gave a somewhat lower value (13%) for the sample having a 5.5 Pd interlayer. This agreement shows that the MBE-grown samples exhibit a uniform magnetic behavior.

ML-thick Fe film corresponds to $0.9\mu_B$ per interface atom (see convention above). The Ag/8Pd/10Fe/20Au sample showed a slightly decreased value of the total magnetic moment compared with the reference Ag/10Fe/20Au sample. Assuming that the Pd/Fe interface has the same magnetic moment as found in the 5Fe/8Pd sample, then a rough Fe/Au interface (see above, the growth of Fe on Pd) has a decreased magnetic moment (0.7 ML of Fe is magnetically dead). This result suggests that the surface roughening plays a significant role in the magnetic-moment formation and perhaps explains why the calculated enhancement of the magnetic moment at Fe/(noble metal) interfaces has not yet been verified experimentally.

It is desirable to compare our measured magnetic moments in 5Fe/8Pd and 5Fe/4Pd/10Fe samples with the theoretical calculations. As shown above, the Fe/Pd interface in the 5Fe/8Pd sample creates an extra magnetic moment of $0.9\mu_B$/atom. The theoretically calculated total magnetic moment in two adjacent Pd layers is $0.5\mu_B$.[5] The balance of $0.4\mu_B$ enhances the Fe magnetic moment in the interface. This is also in a reasonable agreement with the Blugel calculations which predict an increase $\sim 1\mu_B$.[5]

FMR measurements in the 5Fe/4Pd/10Fe trilayer showed that the magnetic moment was equal to the sum of the magnetic moments for the individual 5Fe/8Pd and 8Pd/10Fe films. We have shown that the Pd/Fe interface contributed $0.9\mu_B$; assuming that the interface Fe has the same increase in magnetic moment ($0.4\mu_B$) as found in the 5Fe/8Pd bilayer, then the remaining $0.5\mu_B$ ($0.9-0.4$) belongs to two Pd layers in the Pd/Fe interface. Distributing this moment evenly between Pd layers results in a magnetic moment of $0.25\mu_B$/Pd atom. Moruzzi and Marcus predict values from $0.12\mu_B$ to $0.33\mu_B$ at the onset of ferromagnetic order in Pd.

In conclusion, we have grown a 5.1% laterally expanded Pd(001) lattice. Magnetic properties of the Fe/Pd/Fe trilayers and individual Fe/Pd films were measured by means of FMR and BLS. The laterally stretched Pd interlayers were very reluctant to participate in a ferromagnetic transition even in the presence of the surrounding Fe layers. 4 ML is perhaps the maximum number of Pd atomic layers in which ferromagnetic order is maintained throughout the whole layer. One additional Pd atomic layer destroyed the ferromagnetism of the Pd; however, it still possessed a fluctuating magnetic moment which became partly polarized by the adjacent ferromagnetic layers. Therefore the popular view that metallic Pd needs just a little push to become ferromagnetic is far from being true. Pd interlayers increase the total magnetic moment in Fe/Pd films by $0.9\mu_B$/atom. A comparison of magnetic-moment measurements with recent calculations shows that our results are consistent with a magnetic-moment enhancement of $0.4\mu_B$ per Fe atom in the interface Fe/Pd, and a magnetic moment of $0.25\mu_B$ per Pd atom in ferromagnetically ordered Pd.

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