Magnetization of Pd(111) Films by Contact with Ferromagnetic Ni(111) Films

U. Gradmann and R. Bergholz
Physikalisches Institut, Technische Universität Clausthal, D-3392 Clausthal-Zellerfeld, Germany
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The magnetic moment of oligatomic Ni(111) films on Re(0001) was measured in ultrahigh vacuum at 320 K, where they became ferromagnetic above 2.5 atomic layers. The magnetic moment increased when Ni(111) was coated by Pd(111) or prepared on a Pd(111) interlayer. Apparently, the Pd film is magnetized, by contact with Ni(111), with roughly $0.1\mu_B$ per atom in the first five monolayers of the Pd coating or $0.2\mu_B$ per atom in the last seven monolayers of the Pd interlayer. The measurements give some indication of ferromagnetic live layers, which might appear for $T < 180$ K on top of pure Pd(111) films prepared on Re(0001).

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An important contribution to recent progress in surface magnetism comes from the study of ferromagnetic single-crystal films consisting of few atomic layers. Theoretically, powerful methods have been developed for self-consistent spin-dependent band calculations of such films, the surface of which can be taken as a good approximation of bulk crystal surfaces.[1] In addition the properties of layered structures, composed of magnetic and nonmagnetic components, have been calculated,[2] making the ferromagnetic-nonferromagnetic interface accessible to theoretical analysis.

In a closely related experimental approach, flat epitaxial ferromagnetic films of a few atomic layers ("oligatomic ferromagnetic films"[3]) are prepared on nonmagnetic single-crystal surfaces. Magnetic surface and interface properties are obtained from magnetometry of these films and analysis of their magnetic moments and anisotropies as a function of film thickness. This experimental approach was used previously for $3d$-ferromagnetic films, coated with various materials, with magnetometry of the coated structures carried out in air.[3] The full strength of this magnetometric approach, however, becomes apparent when magnetometry can be done in ultrahigh vacuum, both on films with clean surfaces and during any type of physicochemical processes on them; it then provides a powerful approach to surface magnetochemistry and magnetic interface interactions. It is applicable to interfaces and to surface processes both at low and at high pressures, and it results directly in surface magnetization and magnetic surface anisotropy. Therefore, this magnetometric approach provides an important complement to the analysis of magnetic surfaces by diffraction of spin-polarized electrons,[4] which is limited to surfaces, and requires involved analysis using dynamical scattering theories.

We therefore constructed a high-sensitivity torsion magnetometer, capable of detecting 10^{11} Bohr magnetons [$\approx 10^{-3}$ atomic layers of Ni(111) on our samples], working in ultrahigh vacuum. Magnetometry can be done during epitaxial growth of the magnetic film on various nonmagnetic substrates, and during adsorption of metals and gases on them. Facilities are provided for testing the films by low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES). Details of the instrument and the mode of magnetic analysis are to be published elsewhere.[5]

In this paper, we present, for the first time, measurements of magnetic moments of oligatomic ferromagnetic films, performed in ultrahigh vacuum during film growth, for the example of Ni(111) on Re(0001). In addition the magnetic interaction of Ni(111) with Pd(111) is studied, with Pd(111) used both as substrate and as coating material of the Ni(111) films. All magnetic measurements given in this paper were done at room temperatures near 320 K. Magnetic anisotropies, which come out from the magnetometric analysis at the same time, are discussed elsewhere.[5]

Ni(111) films were prepared near 320 K on a Re(0001) platelet cleaned immediately before preparation by flashing at 2500 K, by sublimation from 99.995% Ni rods, with a growth rate of 0.06 Å/s. During evaporation, the pressure was below 2×10^{-8} Pa; the base pressure of the system was in the 10^{-9}-Pa range. Film thickness was controlled with a quartz crystal monitor. With these growth conditions, flat Ni(111) films were formed layer by layer (Frank–van der Merwe mode). This was established by measuring the Auger amplitudes of substrate and films as a function of film thickness, which showed the usual polygonized shape with edges indicating the completion of one monolayer.[6]

In the first monolayers, the lattice of the growing Ni(111) films is modulated by periodic distortions, caused by mechanical interaction with the misfitting Re substrate (with nearest-neighbor distance $d_{Ni}=2.492$ Å or $d_{Re}=2.760$ Å, the misfit is given by $f_{NiRe}=(d_{Ni}-d_{Re})/d_{Re}=-9.7\%$). They were detected by superstructure multiplets in the LEED pattern, fading out between five and ten atomic layers.[7] However, the mean lattice parameter took the bulk value, starting from the monolayer on.

The evolution of the ferromagnetic saturation moment (achieved at ≈0.1 T) during film growth of Ni(111) on Re(0001) at 320 K is shown in the lowest curve of Fig. 1. The abscissa gives the number of atomic layers, D_{Ni}, as taken from the quartz-crystal monitor, using the bulk density of Ni. The ordinate gives the magnetic moment $m(D_{Ni})$ of the growing film, normalized to the moment of one monolayer of bulk Ni(111) with the area of our sample, m(bulk monolayer) = 0.634 $\times 10^{-14}$ Wb m. For comparison, $m_0(D_{Ni}) = (0.634 \times 10^{-14}$ Wb m$) \times D_{Ni}$ is inserted (broken line), which should be expected if the film were magnetized homogeneously with the bulk magnetization. Note that $m(D_{Ni})$ and $m_0(D_{Ni})$ are parallel, which means that the reduction of magnetic moment of the film, in comparison with bulk Ni, is independent of D_{Ni}. This behavior is expected for large D_{Ni} from a model with two noninteracting surfaces; the same behavior results, for small D_{Ni}, from the spin-wave theory of magnetic size effects in thin films (for a review compare Ref. 3). As a consequence of this reduction of m, ferromagnetic order starts only at a critical number of atomic layers, $D_c(T)$,[8] characterizing the onset of magnetic order at temperature T. Note that the Curie temperature as a function of film thickness, $T_C(D)$, is given by the inverse function of $D_c(T)$. For Ni(111) on Re(0001), we observed $D_c(320\ \mathrm{K}) = 2.5$, which may be interpreted alternatively as $T_C(2.5) = 320$ K. With $T_C(\infty) = 627$ K, this means $T_C(2.5) = 0.51\,T_C(\infty)$. It is quantitatively this reduction of T_C and m which was measured previously[3] for NiFe films in a Cu matrix and was shown there to agree with standard theories of the bare magnetic size effect, i.e., of a model where homogeneous magnetization of the film is proposed for $T=0$, and all reductions of T_C and of m are treated as a result of finite-temperature spin dynamics. This implies the expectation that at low temperatures Ni(111) films on Re(0001) should become ferromagnetic, starting from the ferromagnetic monolayer on [$D_c(0) < 1$]; the magnetic interaction of Ni(111) with Re(0001) can be neglected.

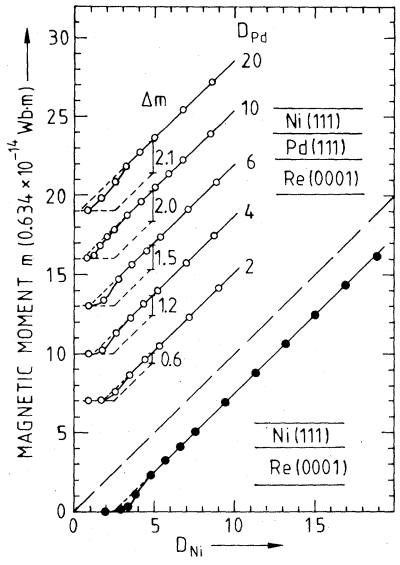

FIG. 1. Magnetic moment m of Ni(111) films growing on Re(0001) (closed circles) and on Pd(111) on Re(0001) (open circles, shifted along the m axis), at 320 K, as a function of the number of atomic layers in the Ni film, D_{Ni}. The Pd layer consists of D_{Pd} atomic layers. The unit of magnetic moment, 0.634×10^{-14} Wb m, belongs to one monolayer of bulk Ni(111) with the area of our sample. For Ni/Re, the magnetic moment resulting from the bulk magnetization, $m_0 = D_{Ni} \times 0.634 \times 10^{-14}$ Wb m, is given for comparison (dashed line). For Ni/Pd/Re, the results of Ni/Re are inserted for comparison (dashed line). The Pd interlayer results in an additional magnetic moment Δm, which is indicated (in units of 0.634×10^{-14} Wb m).

As an interesting candidate for strong magnetic surface interactions we chose Pd in contact with Ni, because of its high, exchange-enhanced susceptibility. As a result of this enhanced susceptibility, Ni impurities in bulk Pd form giant moments of ≈ 5 Bohr magnetons,[9] caused by the magnetic Ni impurity which has a moment of ≈ 1 μ_B, via magnetic polarization of the Pd matrix, with a total additional moment of $\approx 4\mu_B$, distributed on roughly 100 Pd atoms. The starting question of the present experiment was whether an analogous polarization takes place also in a Ni-Pd interface. (A theoretical discussion of ferromagnetic order in a three-layer Pd-Ni-Pd film has been given recently by Coutinho, Edwards, Mathon[10]).

We therefore prepared a series of Ni(111) films on Pd(111) interlayers, which in turn were prepared by epitaxial growth on Re(0001). Diffusion-

free layer growth was established in advance both for Pd(111) on Re(0001) and for Ni(111) on Pd(111), using LEED and AES. The same type of lattice distortions in Ni(111) were observed as on Re ($d_{Pd}=2.751$ Å $=0.997 d_{Re}$). Magnetic moments were measured for a series of Ni(111) films, prepared on Pd interlayers of varying number of atomic layers D_{Pd}, with stepwise increase of D_{Ni}. Results are included in Fig. 1, which gives the magnetic moment of the whole samples as a function of D_{Ni}, with D_{Pd} as a parameter. For clarity, the curves are shifted along the m axis. The data for $D_{Pd}=0$ are inserted for each shifted curve, for comparison. Evidently, the Pd layer results in an additional magnetic moment, as expected. The saturation value of this additional moment, reached at $D_{Pd}=20$, equals the moment of 2.1 monolayers Ni(111).

In a complementary second experiment, we coated a series of Ni(111) films, prepared on Re(0001), by Pd(111) and followed the change of the magnetic moment caused by stepwise increase of D_{Pd}. Diffusion-free layer growth was established again by means of LEED and AES. The additional magnetic moment, Δm, is shown in Fig. 2, as a function of D_{Pd}, with D_{Ni} as parameter. Anticipating the interpretation of the additional moment as a result of magnetization in Pd, we took in Fig. 2 as unit of magnetic moment of a hypothetical ferromagnetic Pd(111) monolayer on our sample, magnetized with 1 μ_B per atom, $m(1\ \mu_B/\mathrm{Pd})=0.924\times10^{-14}$ Wb m. As expected, the magnetic moment again is increased by the Pd coating. The saturation value of the additional moment for high D_{Pd}, when projected to one single Pd layer, amounts to $0.2\mu_B$ per Pd atom for $D_{Ni}=6$. It increases to $\sim 0.5\mu_B$ for $D_{Ni}\geq 18$ (the differences for $D_{Ni}=18$, 24, 30 amount to less than 0.5% of the total moment of the sample and therefore cannot be taken as significant).

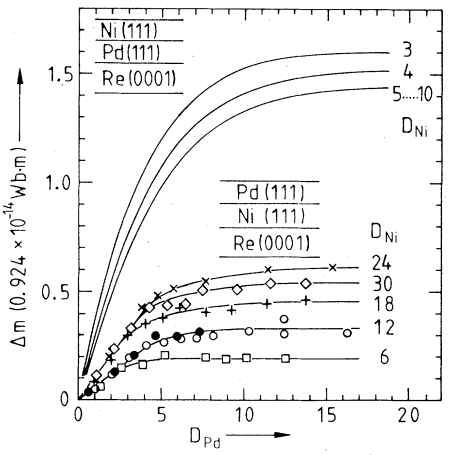

FIG. 2. Additional moment Δm, caused by a Pd(111) film of D_{Pd} atomic layers in contact with a Ni(111) film of D_{Ni} layers. For the case of a Pd coating (Pd/Ni/Re) the points of measurement result directly from magnetometry on Ni films with given D_{Ni}, with successive increase of D_{Pd}. For the case of a Pd interlayer (Ni/Pd/Re), the curves are transformed data of Fig. 1.

For comparison, the results of the experiment with the Pd interlayer are included in Fig. 2 (transformed data of Fig. 1). Both experiments agree qualitatively in an increase of magnetic moment caused by Pd in contact with the Ni film. From the bare experimental results, we cannot decide whether the additional moment is situated in Ni or in Pd. However, in view of what is known of giant moments near Ni impurities in Pd, by far the most probable interpretation of the additional moment is the expected magnetization of Pd in contact with Ni.

The main difference between the two experiments is the magnitude of the additional moment: For the case of the Pd interlayer, it amounts to a saturation value of $1.5\mu_B$ when projected to one single Pd layer, or, in a more probable interpretation, considering the initial slope of $\Delta m(D_{Pd})$ in Fig. 2, a magnetization with roughly $0.2\mu_B$/Pd in the first 7.5 monolayers. For the case of Pd coating, the saturation ($D_{Ni}\geq 18$) amounts to $0.5\mu_B$ in a single layer or $0.1\mu_B$/Pd in the first five monolayers.

Probably, the increased polarizability of the Pd substrate comes from its preparation on Re(0001). With atomic distances $d_{Re}=2.760$ Å or $d_{Pd}=2.751$ Å, the misfit is given by $f_{PdRe}=-0.3\%$. Perfect pseudomorphism is expected for this small misfit up to roughly twenty monolayers, resulting in a homogeneous strain of 0.3% in the Pd-film plane. Apparently, this increase of atomic distances results in a narrowing of the energy band, increase of density of states at the Fermi level, and finally an increase of the Stoner enhancement, i.e., the increased polarizability observed. Similarly, increased magnetic susceptibility, caused by pseudomorphic strain, has been reported previously for Pd films on Au by Brodsky and Freeman.[11]

The order of magnitude of induced moment per Pd atom agrees with the case of giant moments on Ni in Pd, where $4.0\mu_B$ of additional moment are distributed in a Pd cluster of roughly 100

atoms.[9] The results of our experiments with Pd interlayer or Pd coating differ by the fact that Δm decreases with increasing D_{Ni} for the Pd interlayer, but increases for the Pd coating. To some extent, this is caused by different ranges of D_{Ni} prepared: For the Pd interlayer, measurements were restricted to $D_{Ni} \leq 10$, because of strict requirements on the relative reproducibility of D_{Ni} measurements, which are proportional to $1/D_{Ni}$ in this case. Δm is enhanced for $D_{Ni} = 3$, 4 because ferromagnetism of the uncoated Ni film starts just below at $D_{Ni} = 2.5$ (compare Fig. 1). On the other hand, the increase Δm with D_{Ni} for the Pd coating can be explained to some extent from the reasonable assumption that Δm is proportional to the surface magnetization of the uncoated Ni film. Roughly estimated, the latter increases by a factor of 2 from $D_{Ni} = 6$ to $D_{Ni} \geq 18$. Details of the dependence of Δm on D_{Ni} remain to be explained.

One note should be added to Fig. 1 with respect to the critical number of layers for inset of magnetic order, D_c(320 K), and its dependence on D_{Pd}. For the case of preparation on pure Re(0001), i.e., for $D_{Pd} = 0$, we observe D_c(320 K) = 2.5, which can be interpreted as magnetic size effect as discussed above. This implies the expectation that $D_c(T)$ should decrease in the usual way[3] with decreasing T, resulting finally in $D_c(0) < 1$. On the other hand, as a result of the Pd interlayer, D_c(320 K) decreases with increasing D_{Pd}, reaching D_c(320 K) < 1 for $D_{Pd} \geq 10$. In a rough approximation, one might suppose a linear superposition of both types of decrease of D_c, induced by decreasing T and increasing D_{Pd}. With this assumption, one should expect, for thick Pd interlayers ($D_{Pd} \geq 10$), a disappearance of $D_c(T)$ below $T \approx 180$ K; that means ferromagnetic order in Pd without coating by Ni(111). The weak dependence of Δm on $D_{Pd} \geq 10$ indicates ferromagnetic order confined to a surface layer. Therefore, the present experiments provide an experimental indication for ferromagnetic "live layers", supposed to exist at low temperatures in the surface of Pd; these have been discussed previously by Muscat *et al.*[12] for bulk Pd. Note that the indicated live layers are features of Pd films on Re and might be connected with their pseudomorphic strain and enhanced polarizability. However, alternative interpretations must be considered, for which magnetic order near the Pd surface appears only as a result of a Ni coating. Test measurements at low temperatures to decide between the two interpretations are in preparation.

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[1]For a review compare A. J. Freeman, J. Magn. Magn. Mater. 35, 31 (1983).

[2]J. Tersoff and L. M. Falicov, Phys. Rev. B 26, 6186 (1982).

[3]U. Gradmann, Appl. Phys. 3, 161 (1974), and J. Magn. Magn. Mater. 6, 173 (1977).

[4]R. J. Celotta, D. T. Pierce, G. C. Wang, S. D. Bader, and G. P. Felcher, Phys. Rev. Lett. 43, 728 (1979); R. Feder, S. F. Alvarado, E. Tamura, and E. Kisker, Surf. Sci. 127, 83 (1983); G. Waller and U. Gradmann, Phys. Rev. B 26, 6330 (1982); U. Gradmann, G. Waller, R. Feder, and E. Tamura, J. Magn. Magn. Mater. 31–34, 883 (1983).

[5]U. Gradmann and R. Bergholz, to be published; R. Bergholz, doctoral thesis, Universität Clausthal, 1983 (unpublished).

[6]E. Bauer, H. Poppa, G. Todd, and F. Bonczek, J. Appl. Phys. 45, 5164 (1975).

[7]The same type of distortions was observed previously for Ag(111) on Cu(111) [$f_{AgCu} = +13\%$; U. Gradmann, Phys. Condens. Matter 3, 91 (1964)] and for Fe(110) on W(110) [$f_{FeW} = -9.5\%$; U. Gradmann and G. Waller, Surf. Sci. 116, 539 (1982)].

[8]It was just this feature of a critical number of layers, below which no ferromagnetic order takes place, which was observed by L. Liebermann *et al.* [Phys. Rev. Lett. 25, 232 (1970)] and called "dead layers". This impressive word turned out to be misleading in that it suggested the idea of nonmagnetic layers at the surface of a ferromagnetic crystal. We therefore avoid this term.

[9]A. T. Aldred, B. D. Rainford, and M. W. Stringfellow, Phys. Rev. Lett. 24, 897 (1970).

[10]S. Coutinho, D. M. Edwards, and J. Mathon, J. Phys. F 13, L143 (1983).

[11]M. B. Brodsky and A. J. Freeman, Phys. Rev. Lett. 45, 133 (1980).

[12]J. P. Muscat, M. T. Béal-Monod, D. M. Newns, and D. Spanjaard, Phys. Rev. B 11, 1437 (1975).