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Indication of a ferromagnetic submonolayer of ruthenium on palladium

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Abstract. Thin Pd films with submonolayers of Ru are investigated by means of the anomalous Hall effect and weak localization. The anomalous Hall resistance yields the magnetization of the film as a function of the applied magnetic field B. The susceptibility is only weakly temperature dependent. This suggests that the Pd/Ru is weakly ferromagnetic showing large spin wave excitations. The maximum magnetization is found for a coverage of about 0.1 atomic layers of Ru. For larger coverages the Ru moment decreases strongly. This is confirmed by the behavior of the electron dephasing rate determined from magnetoresistance measurements.

PACS. 75.20.Hr Local moment in compounds and alloys; Kondo effect, valence fluctuations, heavy fermions – 75.70.Ak Magnetic properties of monolayers and thin films – 73.20.Fz Weak localization effects (e.g., quantized states)

Exotic magnetic systems have always fascinated solid state physicists. Several decades ago the question was investigated whether "dead layers" could be formed on the surface of ferromagnetic metals or on their interface with another material. This speculation was answered by the detection of two dead monolayers of Ni at an interface with (metallic) Bi [1]. During the last decade the reverse question has been studied intensively: Is it possible to create a (ferro- or anti-ferro) magnetic two-dimensional layer of a (normally) non-magnetic metal, either as a free-standing film or as an adlayer on a non-magnetic substrate.

There have been a number of theoretical studies for two-dimensional free standing monolayers [2,3]. These studies predicted ferromagnetism for Ru and Rh monolayers. Unfortunately the experimental realization of free standing monolayer is a challenge which has not yet been met. Therefore similar calculations have been extended to monolayers on the surface of a substrate metal. For example monolayers of Rh and Ru on the surface of Au and Ag have been studied theoretically [4–7] and predicted to be ferromagnetic. These predictions could not be verified experimentally [8–10].

As a result of these disappointing findings we decided to follow our intuition in the search of exotic ferromagnetism (in systems consisting of substrate and adlayer which are both non-magnetic in their bulk form). From our previous studies we knew that Pd enhances the magnetism of surface impurities. Single Ni atoms on a Pd surface possess a magnetic moment while they are non-magnetic on a noble metal substrate [11]. Therefore we choose Pd as our non-magnetic substrate material. For the ad-layer metal we selected Ru. Gross *et al.* [12] observed a magnetic moment for Ru impurities *in* Pd, *i.e.*, for bulk Ru impurities. This shows that the Pd matrix supports the formation of a magnetic moment at the Ru impurity (even in the bulk). There are also calculations by Stepanyuk *et al.* [13] for the moment of Ru on a Pd(100) surface. They obtained essentially the same value they found for Ru on Ag. (Our experiment yielded only a fluctuating moment for Ru on Ag and Au [10].) Our original goal in this investigation was to check whether a monolayer of Ru on Pd is ferromagnetic, based on the expectation that Pd supports the formation of Ru moments on its surface and the theoretical prediction that in a monolayer magnetic Ru atoms couple ferromagnetically with each other [4,5].

We use in our investigations two experimental tools which have been very useful in earlier research, the anomalous Hall effect and weak localization. The Pd/Ru samples are prepared by *in situ* condensation onto a quartz plate which is at helium temperature. This reduces any diffusion of the Ru into the Pd to an absolute minimum. We prepare the Pd/Ru samples in the following manner. First we evaporate about 25 atomic layers of Pd. In a typical experiment the Pd film is condensed with a resistance per square of about 130 Ω. The vacuum is better than 10^{-11} Torr. The quench condensed film is homogeneous. After the evaporation the film is annealed to 40 K. Then the Hall resistance and the magnetoresistance are measured in the temperature range between 4.5 and 20 K and the field range between −7 and +7 T.

After these measurements Ru is evaporated in several steps. The evaporation of clean Ru is a difficult task

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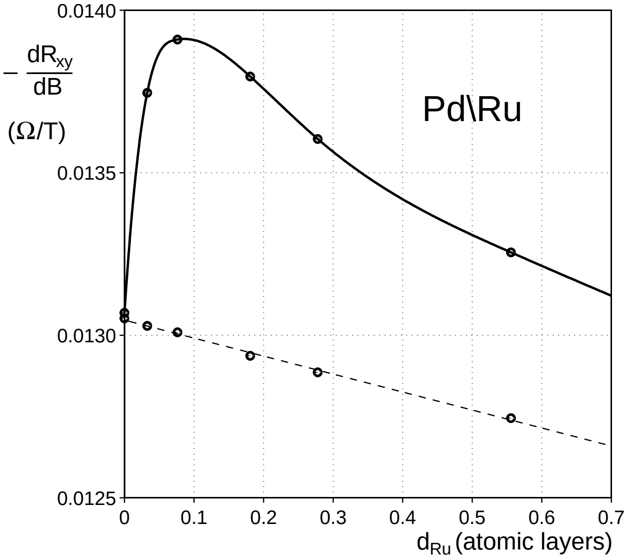

Fig. 1. The initial slope of the Hall resistance $\mathrm{d}R_{xy}/\mathrm{d}B$ as a function of the Ru coverage (measured in units of monolayers). The temperature is 9.5 K. The dashed curve gives the initial slope of the normal Hall resistance.

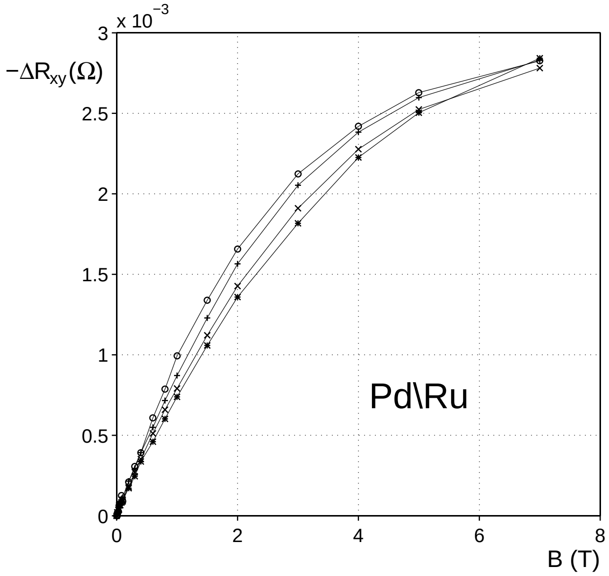

Fig. 2. The anomalous Hall resistance of the Pd/Ru sample with 0.1 atomic layers Ru coverage as a function of the magnetic field B for different temperatures. R_{xy} is essentially proportional to the magnetization.

because Ru is only available as a powder. Details of the preparation of the evaporation source and procedure have been published recently [10]. The coverage of Ru is increased in a series of evaporations from 0.033, 0.075, 0.18, 0.28, to 0.55 atomic layers. After each evaporation step the measurements of the Hall resistance and the magnetoresistance are repeated.

The Hall resistance consists of a linear normal Hall resistance and the anomalous Hall resistance (AHR). The AHR is due to the asymmetric scattering of the conduction electrons by magnetic moments [14]. The anomalous Hall resistance (as a function of applied magnetic flux B) is essentially proportional to the magnetization perpendicular to the film. The largest AHR that we observe is of the order of 3×10^{-3} Ω. This is only 3% of the total Hall resistance at 7 T. Therefore the Hall resistance has to be measured with high accuracy. This is characterized by the Hall angle Θ which is measured with an accuracy of about 10^{-7} (the Hall angle is given by $\tan\Theta = R_{xy}/R_{xx}$). To achieve this goal we need a relatively large current. As a matter of fact for the temperatures of 6.5 K and 9.5 K the heating of the sample is completely performed by the measurement current through the film. Nevertheless, film, quartz plate, and thermometer are in thermal equilibrium.

In Figure 1 the initial slope of the "total" Hall resistance is plotted *versus* the thickness of the Ru for the temperature of 9.5 K. This slope consists of the slope of the normal Hall resistance (which is linear in B) and the initial slope of the AHR. The normal Hall resistance is essentially due to the Pd film. The small Ru coverage yields a small additional contribution to the Hall conductance (reducing the normal Hall resistance slightly). The dashed curve gives our best fit for the normal Hall slope as a function of the Ru thickness. The difference of the two curves represents the anomalous Hall slope. One recognizes that it increases strongly for small Ru coverages, reaches a maximum at around 0.1 monolayers of Ru and decreases for larger Ru coverages.

For the evaluation of the Hall curves one has to subtract the normal Hall effect. Figure 2 shows the AHR contribution for the Pd covered with 0.075 atomic layers of Ru. It is essentially proportional to the magnetization. One recognizes that the magnetization depends on the magnetic field and on the temperature. This indicates the presence of magnetic moments (in contrast to the Pauli susceptibility). But it is not the magnetization of free magnetic moments. For free magnetic moments the susceptibility (*i.e.*, the initial slope) is inversely proportional to the temperature, $\chi \propto 1/T$. In Figure 3 the initial slope of the anomalous Hall resistance is plotted *versus* $1/T$. One does not find a straight line through the origin but a relatively flat line. This means that the Ru on Pd does not behave as single independent magnetic impurities. The saturation AHR (for sufficient large magnetic field) shows, as a function of the Ru coverage, a very similar behavior as the initial slope. This suggests that the saturation magnetization has a maximum at about 0.1 atomic layers of Ru.

If one tries to fit the field dependence of the AHR with a Brillouin function then one obtains the best fit at $T = 9.5$ K for a magnetic moment of 10 μ_{B}. (Since the initial slope shows only a weak temperature dependence the optimally fitted moment increases with temperature.)

Besides the AHR we also used weak localization to investigate the magnetic properties of Pd/Ru. In weak

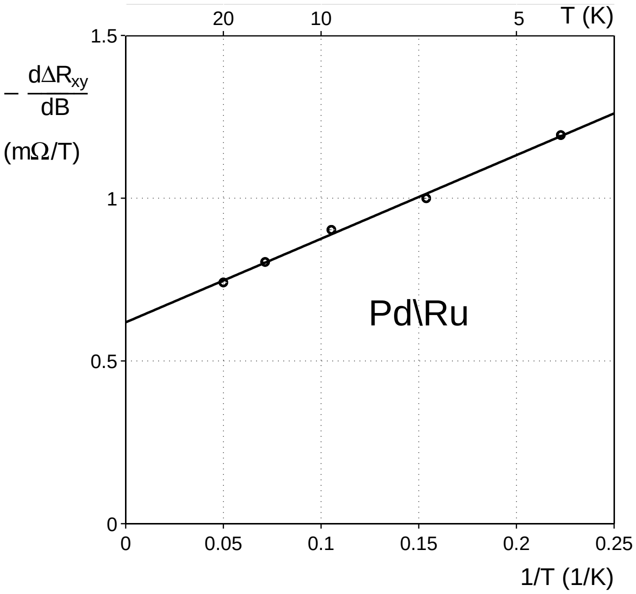

Fig. 3. The initial slope of the anomalous Hall resistance as a function of the inverse temperature $1/T$.

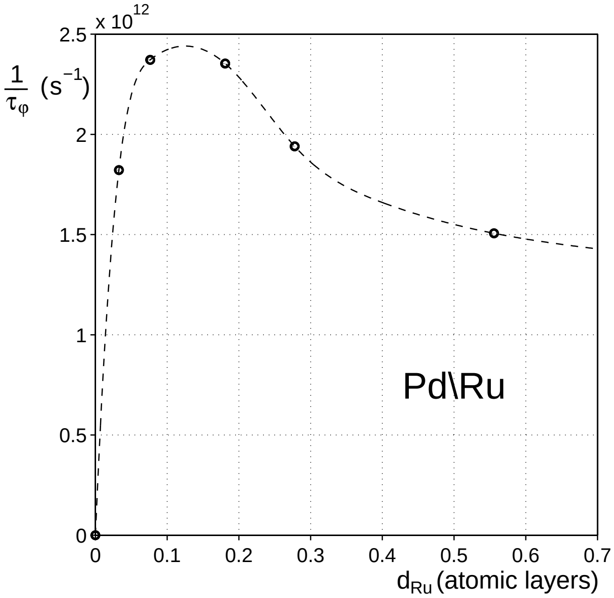

Fig. 4. The magnetic dephasing rate of the conduction electrons as a function of the Ru coverage.

localization one studies the interference of conduction electrons. Magnetoresistance measurements correspond to time-of-flight experiments which yield (among other information) the dephasing rate of the conduction electrons (see for example [16]). If one measures the resistance of a thin disordered film then the coefficient of B^2 is proportional to the square of the dephasing time. Magnetic moments scatter the conduction electrons differently for different electron spin and cause a magnetic dephasing rate of weak localization. The total dephasing rate is $1/\tau_\varphi = 1/\tau_\mathrm{i} + 2/\tau_\mathrm{s}$, where τ_i is the inelastic and τ_s the magnetic scattering time. To obtain the magnetic scattering rate one simply has to determine the quadratic field dependence of the resistance. This additional dephasing rate due to the Ru is evaluated as a function of the Ru thickness and the temperature. A temperature independent dephasing rate satisfies the experimental data. This rate is plotted in Figure 4 as a function of the Ru thickness. It shows the same behavior as the AHR. It has a maximum around 0.1 atomic layers.

Before we discuss the magnetic structure of the sample it should be emphasized that our experiments prove that Ru atoms on the surface of Pd possess a magnetic moment. The magnetic dephasing cross section of 1/100 atomic layers Ru on Pd is $\sigma_\varphi = 0.20$ in units of $4\pi/k_\mathrm{F}^2$. This is quite similar to the value of Fe on Au ($\sigma_\varphi = 0.48$) and much larger than for Ru on Au ($\sigma_\varphi = 0.032$).

For the interpretation of the experimental results we recall our findings:
(a) the initial slope and the saturation of the AHR as a function of the Ru coverage have a maximum at about 0.1 atomic layers;
(b) the initial slope of the anomalous Hall resistance has a temperature independent component;
(c) the magnitude of the AHR is quite similar to that of Fe on the surface of Pd [19];
(d) if one tries to fit the anomalous Hall resistance for a temperature of 9.5 K with a Brillouin function one obtains the best fit for a moment of 10 μ_B;
(e) the magnetic dephasing of weak localization as a function of the Ru coverage shows a maximum at about 0.1 atomic layers.

Now we discuss which model of the magnetic structure is consistent with our experimental findings.

1) Free magnetic moments. This can be excluded because the initial slope of the AHR would be inversely proportional to the temperature.

2) Anti-ferromagnetic order or spin glass. Both structures can not explain the experimental findings. In case that the characteristic temperature is larger then 20 K (the largest experimental temperature) one would expect an almost linear magnetization curve. In the opposite case one expects a small initial slope at low temperature which increases when one approaches the characteristic temperature.

3) This leaves essentially a ferromagnetic order. If we ignore for a moment the spin wave excitations then we expect for a ferromagnetic layer a temperature independent initial slope as long as the temperature is much smaller than the Curie temperature. Furthermore, the similarity between the AHR and the dephasing rate of weak localization as a function of the Ru thickness strongly supports a ferromagnetically ordered structure. In the ferromagnetic structure the effect of all moments add up in the AHR as well as in weak localization. However, in the anti-ferromagnetic state Ru atoms with opposite moment would cancel each others contribution to the AHR while they still add their contribution in weak localization.

Therefore we find a strong indication that the Ru atoms on the surface of Pd possess a ferromagnetic structure. However, we expect that strong thermal effects (due to spin waves) are present which weakens the magnetization already at the experimental temperatures. The saturation magnetization has a maximum at about 0.1 atomic layers, this is far below a monolayer of Ru. This suggests that the Ru moments polarize the Pd and couple ferromagnetically over distances of the order of three atomic layers. This agrees with the well known effect that magnetic atoms dissolved in Pd possess giant moments and that the magnetic coherence length is increased by the Stoner enhancement factor which is of the order of several atomic distances.

However, there is one puzzling fact. The magnetic moment per Ru atom decreases with increasing Ru coverage. For Ru coverages larger than 0.1 atomic layers even the total magnetization decreases. This means that Ru atoms hinder each other in the formation of magnetic moments. This is a behavior which we had previously observed for (fluctuating) Ru moments on the surface of Au [10]. In contrast Pfandzelter *et al.* [20] reported that they had recently observed a ferromagnetic monolayer of Ru on carbon. They did not notice a suppression of the Ru moment by Ru neighbors.

Our former experiments contradicted the theoretical predictions of ferromagnetic monolayers of Ru and Rh on the surface of Au and Ag and an anti-ferromagnetic monolayer of V on Cu substrates [10,21]. Our present results go one step further because they demonstrate in two independent measurements that magnetic Ru atoms on the surface of Pd do not like to have other Ru atoms at a close distance. Obviously the field of surface magnetic moments is still full of open questions and challenges.

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