Magnetism of Rh and Ru atoms, clusters, and monolayers on Au and Ag surfaces

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The magnetic character of Rh and Ru on the surface of Au and Ag is investigated by means of weak localization (WL) and the anomalous Hall effect (AHE). Dephasing of the conduction electrons in WL is the most sensitive method to detect magnetic surface impurities. The Au/Rh and Au/Ru systems are investigated in the range between 1/100 of a monolayer of Rh (Ru) and several monolayers of Rh (Ru). We observe a small dephasing by Rh clusters and no dephasing by single Rh surface impurities, while single Ru surface impurities cause already a finite but small dephasing. We suggest that the dephasing is caused by small fluctuating magnetic moments of the order of 0.1 $(0.4)\mu_B$. For a coverage of one monolayer of Rh we observe a maximum in the dephasing. However, we do not observe a ferromagnetic Rh monolayer as predicted in a number of theoretical papers. Similarly, a Ru monolayer on the surface of Au or Ag does not show ferromagnetism. The absence of an AHE in the Rh and Ru monolayers excludes ferromagnetism as well. For Rh the dephasing increases again when the Rh coverage exceeds two monolayers, suggesting that pure bulk Rh shows spin fluctuations. [S0163-1829(97)02622-2]

I. INTRODUCTION

Materials at the borderline of magnetism belong to the most interesting electronic systems in solid-state physics. Examples are the heavy fermions and high-T_c superconductors. Both materials are magnetic either at higher temperatures or at different electron concentrations. This proximity to a magnetic state creates physics which is very challenging.

In recent years theory and experiment have opened the door to a whole class of new systems with unexpected magnetic properties: (i) monolayers of transition metals on the surface of noble metals and (ii) single transition-metal atoms on the same substrate. The first topic started with the prediction by the Freeman group[1] that monolayers of V on the surface of Ag and Au should be ferromagnetic. This prediction was then later modified by Blügel *et al.*,[2] who predicted that monolayers of the $3d$ elements V, Cr, and Mn on the surface of Ag should be antiferromagnetic (see also the review article[3]). These theoretical papers used the local spin-density-functional theory. Later a number of papers[4–6] predicted that monolayers of the $4d$ metals Tc, Ru, and Rh on the surface of Ag or Au are ferromagnetic.

Experimentally, the existence of a ferromagnetic monolayer is particularly interesting. Already in the late 1970's, it was shown that monolayers of Fe, Co, and Ni are ferromagnetic on the surface of the noble metals,[7,8] while Ni monolayers loose their moment on the surface of polyvalent metals.[9] The recent predictions of ferromagnetism in adlayers of the conventionally nonmagnetic transition metals started an intensive search. A number of different experimental methods have been used to observe such a ferromagnetic layer, such as spin-polarized secondary electrons, the surface magneto-optic Kerr effect, photoemission effect, the anomalous Hall effect, and weak localization. For a monolayer of V on the surface of Ag the observation of ferromagnetism[10] could not be confirmed by later experiments.[11–14]

Two particularly interesting systems are monolayers of Rh and Ru on the surface of Ag and Au. In a number of theoretical papers Rh and Ru monolayers on both of these substrates were predicted to be ferromagnetic with a moment per atom varying between $0.6\mu_B$ and $1\mu_B$ for Rh and $1.7\mu_B$ for Ru.[4–6,15]. While experimental studies by means of the surface magneto-optic Kerr effect[16,17] do not show any ferromagnetism for a Rh monolayer, Li *et al.*[18] found a splitting of the $4s$ level in their photoemission experiment. Although this splitting can have nonmagnetic origins, they favored the explanation that the Rh atoms possess a magnetic moment. Diffusion presents a serious problem in these investigations and is intensively discussed in several of these papers. Pfandzelter, Steierl, and Rau,[19] recently reported that they observed a ferromagnetic monolayer of Ru on the surface of carbon.

The magnetic properties of single transition-metal impurities on the surface of Ag and Cu were investigated by Lang *et al.* in Jülich.[20] They concluded that the $4d$ atoms Nb, Mo, Tc, and Ru on the surface of Ag possess a magnetic moment. (Zr atoms should only have a moment in the adatom position). All the moments are $1\mu_B$ or larger. Single Rh atoms on the surface of Ag (and Au) present an interesting case as well. In the first calculation by Lang *et al.*[20] they obtained a magnetic moment for Rh which was smaller than their error margins, and as a consequence they published the value zero for the magnetic moment. In a more recent paper[21] they found a small but finite moment of $0.3\mu_B$ at the single Rh impurity on the surface of Ag.

The experimental study of single magnetic transition-metal atoms on the surface of a noble metal dates back more than 10 years.[22–24] One needs an extremely sensitive detection method because the concentration of the ''surface impurities'' should be very small (of the order of 1/100 of a monolayer), and at finite temperature the atoms align only a fraction of their moment parallel to the magnetic field. In many cases the moment is much further reduced (sometimes by a factor of 100) due to Kondo screening or other effects.

One successful method is the anomalous Hall effect, which is sensitive enough to study a coverage of a few percent of a monolayer of magnetic impurities. However, the most sensitive method is weak localization, which can easily detect a coverage of 10^{-4} of a monolayer of magnetic atoms.

Obviously the transition metals Rh and Ru on the surface of the noble metals Au and Ag represent very interesting magnetic systems. In this paper we investigate the magnetic properties of Rh and Ru on the surface of Au (and Ag) as isolated surface impurities, as clusters, and as monolayers. As our experimental tools we use weak localization (WL) and the anomalous Hall effect (AHE). The AHE measures the magnetization of the sample,[35] while in WL one studies the interference of the conduction electrons. Magnetoresistance measurements correspond to time-of-flight experiments, which yield (among other information) the dephasing time of the conduction electrons (see, for example, Ref. 25). We first study the pure Au (Ag) film and determine the (small) dephasing rate of the conduction electrons. It is essentially caused by inelastic electron-phonon processes. In the next step the Au (Ag) film is covered with a fraction of a monolayer of Rh or Ru. The Rh (Ru) introduces an additional dephasing of the conduction electrons. This results in an increase of the width of the magnetoresistance curves. The experimental magnetoresistance curves evaluated with the theory by Hikami, Larkin, and Nagaoka[26] yield the dephasing time of the conduction electrons, from which we obtain the dephasing cross section σ_φ.

II. EXPERIMENT

A. Film preparation

Our film samples are prepared by *in situ* condensation onto a quartz substrate at helium temperature. This reduces diffusion of the $4d$ metal into the Au (Ag) substrate to an absolute minimum. We prepare our Au/$4d$ metal sample in the following manner. We evaporate about 25 to 30 atomic layers of Au with a resistance per square of about 120 Ω. The vacuum is better than 10^{-11} Torr. After the evaporation the film is annealed to 40 K, because quench-condensed films have many lattice defects, with atoms being in local energy minima. Since some of the measurements are performed at 20 to 25 K these defects would anneal and the film change its local structure irreversibly. This is undesirable and can be avoided by the annealing to 40 K, so that the structure does not change during the experiment. The magnetoresistance of the Au film is then measured in the temperature range between 4.5 and 20 K.

In the next evaporation step about 1/100 of a monolayer of the $4d$ metal is condensed on top of the Au (Ag) film. After the $4d$ metal evaporation the film is annealed to 35 K, and the measurements are repeated. Up to 11 different thicknesses between 0.002 and 5 atomic layers of the $4d$ metals were investigated during a single experiment.

It is quite obvious that an extremely clean evaporation source is required to prepare single $4d$ impurities or $4d$ monolayers on the host metal. Any pollution by other elements or rest gases would be rather disastrous. The cleanest and most desirable evaporation source of the impurity is a thin, high purity wire of the transition metal. For the $3d$ metals we generally use a wire with a diameter of 1 mm. Since the $4d$ metals have a considerably higher evaporation temperature we use for the Rh evaporation a thin Rh wire with a diameter of 0.25 mm, i.e., its cross section is by more than an order of magnitude reduced. This makes the calibration of the evaporation rate and the evaporation of thicker films much harder than for the $3d$ elements.

One great difficulty in the investigation of Ru atoms on the surface of Au and Ag lies in the evaporation of Ru. Unfortunately the $4d$ metal Ru is not available as a thin wire but only as a sponge or powder. We used Ru sponge with a grain size between 10 and 100 μm and a purity of 99.95%. Another difficulty is that Ru easily alloys with the typical boat materials like W, Ta, or Mo. Already in the $3d$ series we encountered two materials, Cr and Mn, which were not available in the form of wires. Here we applied special procedures, such as distillation from one evaporation source with indirect heating to one with direct heating.[27] However, these procedures cannot be applied in the case of Ru. As a $4d$ metal its evaporation temperature is by several hundred degrees higher than those of Mn and Cr. We developed a small electron gun specifically for the $4d$ and $5d$ metals, which fitted into the limited space of our cryostat. However, despite carefully cooling with liquid N_2 the electron gun was not clean enough to produce the high purity films which are required in our experiments. Most likely the collisions between accelerated ions and the walls cause a pollution of the films which is intolerable.

Finally we resorted to the following method. We prepared a carefully cleaned W boat made from a 40 μm thick W foil, 2 mm wide. The boat was carefully sprinkled with a thin layer of the Ru sponge. Then the boat with the Ru powder was directly heated in UHV to a sufficient high temperature so that the Ru grains sintered and became attached to the W. This process was performed three times so that a reasonable number of Ru grains were attached to the W boat. More than three sintering processes resulted in a destruction of the W boat due to alloying between the W and the Ru. The preparation of the evaporation source (and the performance of the experiment) represents a walk on a narrow ridge.

An evaporation source prepared in this way, contains relatively little of the material to be evaporated, i.e., Ru. Therefore it was not possible to measure the evaporation rate of the Ru before each Ru evaporation. Therefore we have to trust that the rate does not change between two evaporations. When the evaporated Ru coverage is larger than 0.1 atomic layer, the Ru thickness can be directly determined from the change in frequency of the oscillator. For smaller thicknesses we have another control: We observed experimentally that the evaporation of a transition metal onto a noble metal increases the resistance of the film and, for small thicknesses, this increase is proportional to the coverage. Therefore we can detect any anomaly in the evaporation rate.

With this procedure we prepared a series of Ru coverages ranging from 2/1000 of a monolayer to about one monolayer. We performed three series of experiments with a Au substrate and one series with a Ag host. We estimate the upper limit of the error in the Ru thickness to be about 30% although the relative accuracy might be considerably better.

B. The Rh system

Figure 1 shows several magnetoresistance curves measured at 4.5 K. The top one is for pure Au. The following

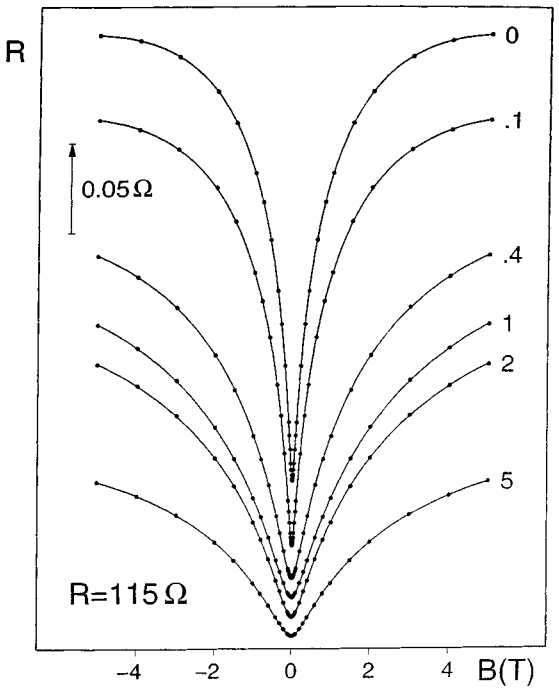

FIG. 1. The magnetoresistance curves of several Au/Rh films measured at 4.5 K. The top one is for pure Au. The following curves are a selection of magnetoresistance curves with increasing Rh coverage. The numbers on the curves give the Rh coverage in units of monolayers. The points are the experimental values. The curves are fitted with the theory of weak localization.

curves are a selection of magnetoresistance curves with increasing Rh coverage. The numbers on the curves give the Rh coverage in units of monolayers. The accuracy of the coverage lies between 15 and 20 %. The experimental curves show a positive magnetoresistance. This demonstrates that our samples are in the ''strong spin-orbit scattering limit.'' In this limit the broadening of the magnetoresistance curve is only due to the dephasing by inelastic and magnetic scattering processes. This allows us to extract the strength of the magnetic dephasing with high accuracy.

The width of the magnetoresistance curve is described by the dephasing field H_i^*. This field is proportional to the total dephasing rate $1/\tau_i + 1/\tau_\varphi$ of the conduction electrons. Here $1/\tau_i$ is inelastic rate in the pure Au film and $1/\tau_\varphi$ is the dephasing rate due to the Rh atoms. (The proportionality constant is $\hbar e \rho N_0/4 = 0.33$ ps T for this film, ρ = resistivity of the film, N_0 = density of states). We evaluate the magnetoresistance curves with the theory of weak localization by Hikami, Larkin, and Nagaoka.[26] This theory yields the dephasing field H_i^* of the conduction electrons. From the broadening of the magnetoresistance curves, i.e., from the increase ΔH_i of the dephasing field one obtains the dephasing time τ_φ caused by the Rh atoms. The dephasing cross section σ_φ of the Rh is obtained with the relation $n_d l_\varphi \sigma_\varphi = 1$ where n_d is the concentration of the Rh atoms, $l_\varphi = v_F \tau_\varphi$, v_F = *Fermi* velocity. It is convenient to measure the cross section in units of $4\pi/k_F^2$, which yields a dimensionless number. Whenever we give values for the cross section they are in units of $4\pi/k_F^2$ and therefore dimensionless.

In Fig. 2 we have plotted the additional dephasing rate

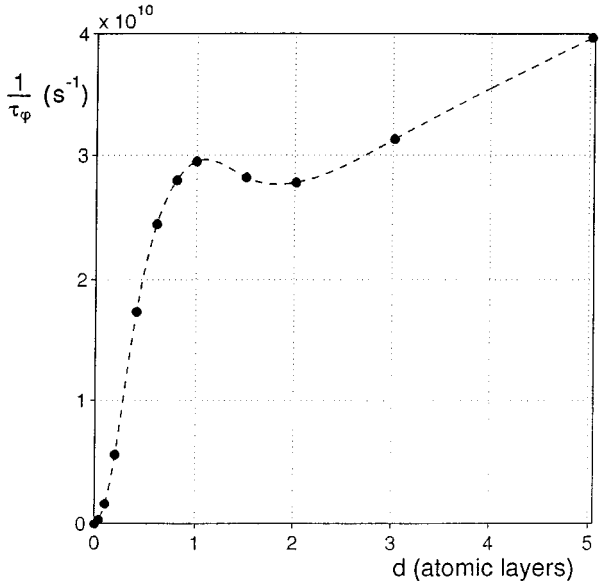

FIG. 2. The additional dephasing rate $1/\tau_\varphi$ due to the Rh coverage as a function of the Rh coverage. The data are taken at 4.5 K.

$1/\tau_\varphi$ of the conduction electrons due to the Rh atoms on top of the Au film. The error bars are about 1/10 of the diameter of the full circles. The curve has a number of interesting features: (a) it is quadratic at low concentrations, (b) it has a maximum at one atomic layer of Rh, and (c) after a short decline it rises almost linearly for more than two monolayers of Rh. Below we will discuss these features in detail.

In Fig. 3 we have plotted the resulting dephasing cross section σ_φ in units of $4\pi/k_F^2$. One recognizes that σ_φ increases linearly at low Rh coverage. This means that single Rh atoms do not contribute to the dephasing (since σ_φ is the dephasing contribution per Rh atom). The dephasing cross section at the maximum is 1.4×10^{-3}. This value is smaller by more than a factor of 100 than the value we found for

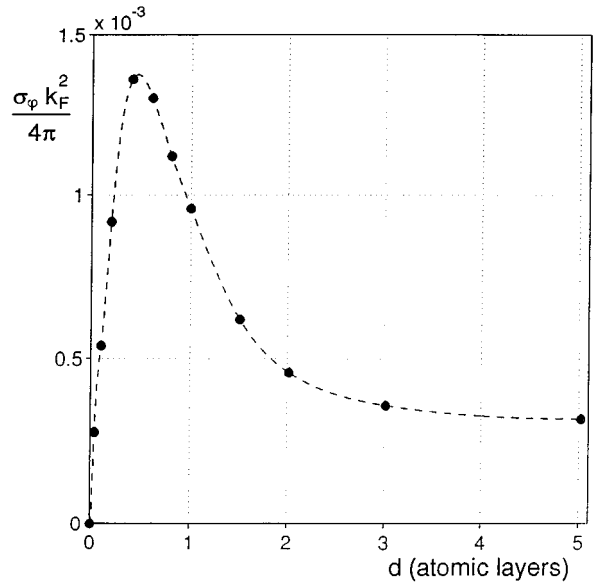

FIG. 3. The dephasing cross section per Rh atom on top of the Au film as a function of the Rh coverage. The data are taken at 4.5 K.

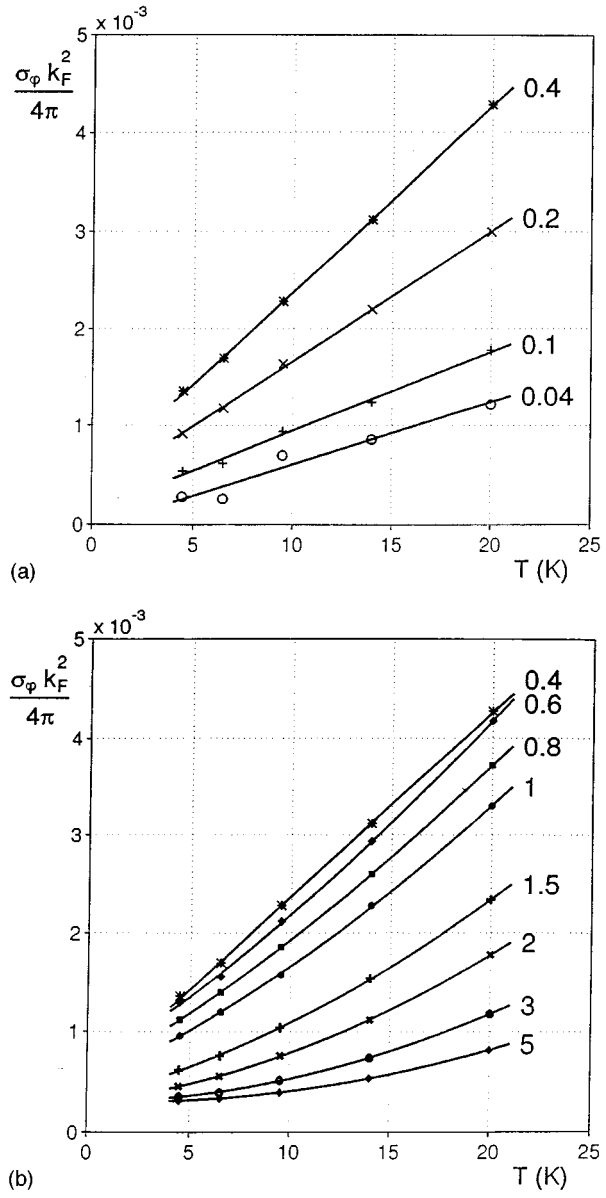

FIG. 4. The temperature dependence of the Rh dephasing cross section σ_φ (in units of $4\pi/k_F^2$): (a) for Rh coverages between 0.04 and 0.4 monolayers of Rh; (b) for Rh coverages between 0.4 and 5 monolayers of Rh.

single fully magnetic Mo atoms on Au (which is 360 $\times 10^{-3}$). Therefore we have to check very carefully whether the origin of the dephasing is magnetic.

The evaluation of our magnetoresistance curves yields the dephasing rate and therefore the dephasing cross section as a function of the temperature. This temperature dependence is plotted in Figs. 4(a) and 4(b) for the different Rh coverages. The numbers on the right side of the curves give the Rh coverage in units of monolayers. The coverage with the largest dephasing is on the top in both figures. The dephasing cross section increases strongly with temperature. In addition to the linear plot in Fig. 4 we also made a log-log plot. With the exception of the Rh coverages below 0.4 monolayers, we do not find a simple power law $\sigma_\varphi \alpha T^p$.

In addition to the magnetoresistance we have also measured the Hall effect to check whether it contains a noticeable magnetic contribution, i.e., an anomalous Hall effect. We find that the Hall curves are linear within the accuracy of the measurement (which is about 2×10^{-4}). This excludes the presence of a ferromagnetic Rh layer as predicted by many theoretical papers. Furthermore the Hall resistance shows only a minor temperature dependence, which can be explained by the Coulomb anomaly.[28] In Fig. 5 we plot the Hall conductance L_{xy} at a field of 7 T as a function of the Rh thickness. For Rh thicknesses d_{Rh} above 2 monolayers L_{xy} increases essentially linearly with the Rh thickness. The slope approaches the value of $-1.1\times10^{-7}\ \Omega^{-1}$. Within the free-electron model this corresponds to 1 conduction electron per Rh atom. The decrease of $|L_{xy}|$ for $d_{\mathrm{Rh}}<0.5$ monolayers is caused by a similar decrease of the longitudinal conductance L_{xx} as shown in Fig. 6. This is a behavior which so far

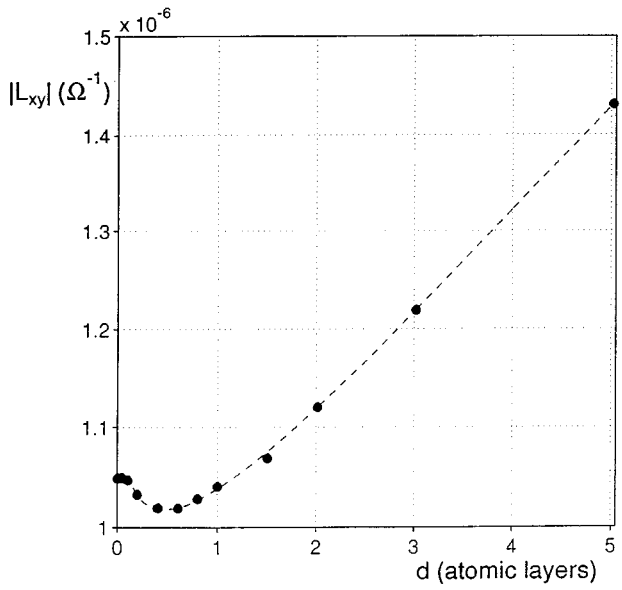

FIG. 5. The Hall conductance $|L_{xy}|$ at a field of 7 T as a function of the Rh thickness.

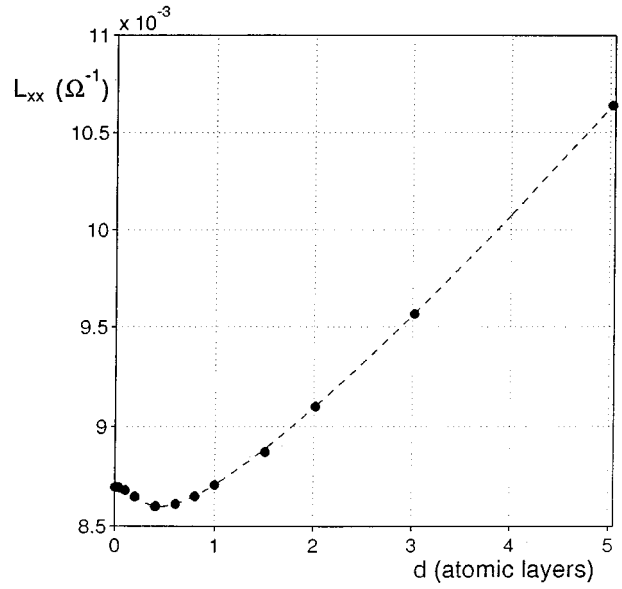

FIG. 6. The (longitudinal) conductance L_{xx} as a function of the Rh thickness.

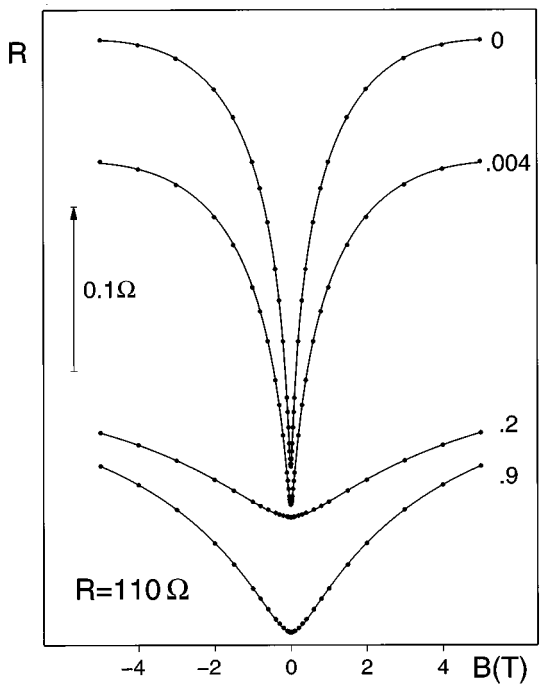

FIG. 7. The magnetoresistance curves of several Au/Ru films measured at 4.5 K. The top one is for pure Au. The following curves are a selection of magnetoresistance curves with increasing Ru coverage. The numbers at the curves give the Ru coverage in units of monolayers. The points are the experimental values. The curves are fitted with the theory of weak localization.

we have observed for all transition-metal coverages. We always find an increase of the resistance with the first coverage by a $3d$ or $4d$ metal. We interpret this increase of the resistance as follows. Although our films are quench condensed, their surfaces still reflect a finite fraction of the conduction electrons specularly. Covering a surface with transition-metal atoms increases the diffuse scattering at that surface and therefore the resistance.

C. The Ru system

Figure 7 shows several magnetoresistance curves of the Au/Ru system, measured at 4.5 K. The top curve is for pure Au. The curves below are a selection of magnetoresistance curves with increasing Ru coverage. The numbers on the curves give the Ru coverage in units of monolayers. The experimental curves show a positive magnetoresistance.

In Fig. 8 we have plotted the additional dephasing rate $1/\tau_\varphi$ of the conduction electrons due to the Ru atoms on top of the Au film. The curve has a number of interesting features: (a) it increases (almost) linearly at low coverages, (b) it has a maximum at about 0.2 atomic layers of Ru and decreases for larger Ru coverages. This means, of course, that the dephasing efficiency per Ru atom decreases much stronger. This efficiency is measured by the dephasing cross section of a Ru atom.

In Fig. 9 we have plotted the resulting dephasing cross section σ_φ in units of $4\pi/k_F^2$ at 4.5 K. The circles are for the system Au/Ru and the crosses for Ag/Ru. One recognizes that σ_φ is finite at (very) small Ru coverages, increases slightly, and has a maximum at about 0.05 atomic layers.

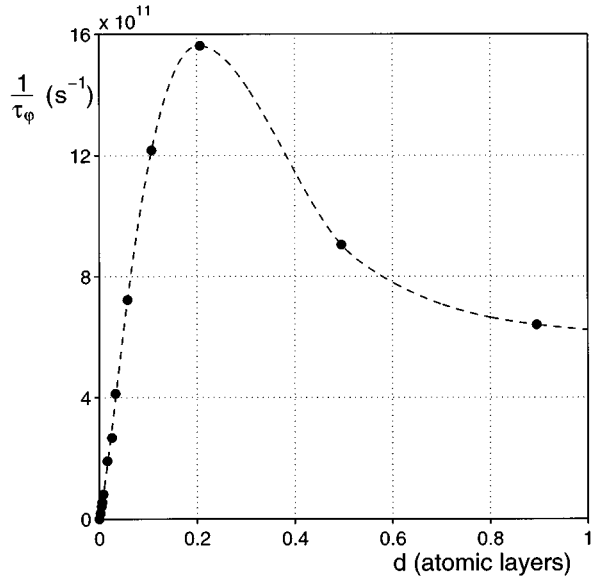

FIG. 8. The additional dephasing rate $1/\tau_\varphi$ due to the Ru coverage as a function of the Ru coverage. The data are taken at 4.5 K.

The maximum dephasing cross section is 38×10^{-3}. For a monolayer of Ru on Au the dephasing cross section is strongly reduced to about 2×10^{-3}.

The evaluation of our magnetoresistance curves yields the dephasing rate and therefore the dephasing cross section as a function of the temperature. This temperature dependence is plotted in Fig. 10 for the different Ru coverages. The numbers on the right side of the curves give the Ru coverage in units of monolayers. We find a strong temperature dependence of the dephasing cross section.

As for the Au/Rh system we have also measured the Hall effect. Again we find that the Hall curves are linear within the accuracy of the measurement which excludes the presence of a ferromagnetic Ru layer.

The experimental results for Ru on a substrate of Ag are quite similar to those of Au/Ru. The dephasing cross section

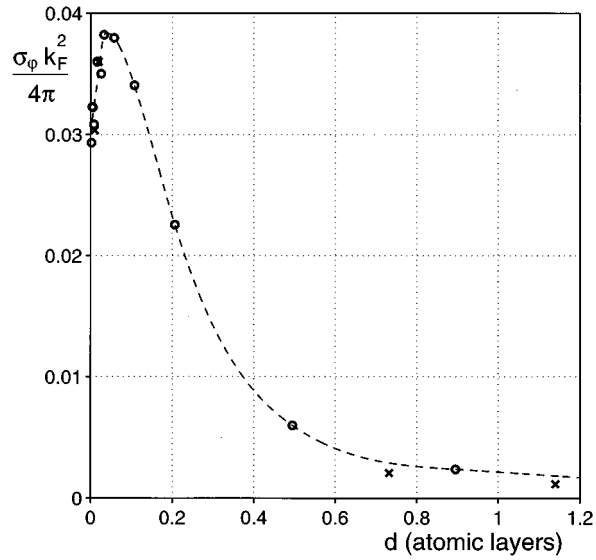

FIG. 9. The dephasing cross section per Ru atom on top of a Au surface (open circles) and a Ag surface (crosses) as a function of the Ru coverage. The data are taken at 4.5 K.

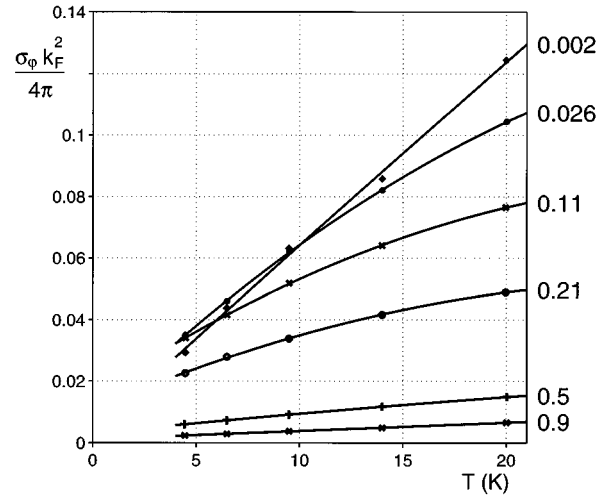

FIG. 10. The temperature dependence of the Ru dephasing cross section σ_φ (in units of $4\pi/k_F^2$) for Ru coverages between 0.002 and 0.9 monolayers of Ru.

for 1/100 of a monolayer of Ru on Ag is 30×10^{-3} which is almost the same as the value on Au (see Fig. 9). For the dephasing cross section of a monolayer of Ru on Ag we find the value 1.4×10^{-3} which is somewhat smaller than for a Au substrate. The temperature dependence is also similar to the Au/Ru system.

III. DISCUSSION

A. The dephasing mechanism

The method of weak localization measures essentially the (additional) dephasing due to the $4d$ atoms on the Au surface. This additional dephasing is not due to weak localization but is a property of the $4d$ atom on the surface of Au. The first and most important question is: what is the origin of this dephasing, is it of magnetic character? We discuss this question by using the experimental results for the Au/Rh system. The conclusions apply also to the Au/Ru and Ag/Ru systems.

Since the dephasing cross section of Rh on Au increases linearly with coverage at small Rh coverages, it follows that single Rh atoms essentially do not contribute to the dephasing. We compare the dephasing cross section of Rh with the corresponding values of the $4d$ metal Mo and the $3d$ metal Co, one being in the same row and the other in the same column as Rh. We have investigated both as surface impurities on a Au substrate and consider that both of them are magnetic.[27,29]

The interaction between conduction electrons and magnetic impurities with a full moment is generally described by the exchange Hamiltonian $H_{\rm ex}=J\mathbf{sS}$ where $\mathbf{s}$ is the spin of the conduction electron and $\mathbf{S}$ is the spin of the impurity. With this Hamiltonian one obtains a magnetic scattering cross section σ_s. Such a magnetic impurity has a strong dephasing effect on weak localization and its dephasing cross section σ_φ is equal to $2\sigma_s$. In this paper we prefer to describe the $4d$ impurities by their dephasing cross section σ_φ. Therefore we have to multiply the former σ_s values by a factor of 2 if we want to compare them with the experimental σ_φ of this paper. The reason for using σ_φ here is, as we will see below, that the moment of the Rh (Ru) impurities is of the order of 0.1 $(0.4)\mu_B$ and therefore much too small to be described by a spin quantum number S. We rather describe it by a small polarization of the d resonance. We recently derived the dephasing of weak localization within this Friedel-Anderson resonance model.[27] For Mo we found a dephasing cross section of $\sigma_\varphi=2\sigma_s=360\times10^{-3}$, while Co on Au yielded the value of 175×10^{-3} for σ_φ. We recognize that the dephasing caused by Rh atoms is smaller than for typical magnetic impurities by more than two orders of magnitude. We have no doubt, that the Rh atoms on the surface of Au are not fully magnetic. The dephasing is just much too small.

The normal contributions to the dephasing of the conduction electrons are thermal atomic vibrations (the electron-phonon interaction) and the electron-electron interaction. We ask ourselves how the Rh surface atoms could contribute to either of them. Furthermore, we have to account for the fact that single Rh atoms do not noticeably contribute to the dephasing, only pairs and larger clusters do.

For a comparison we calculate the dephasing by the individual Au atoms in the Au film (mainly due to the thermal vibration of atoms). At 4.5 K the inelastic field is $H_i=13$ mT, which yields a dephasing time of $\tau_i=25$ ps. Using the atomic volume of Au, $\Omega=17\times10^{-30}$ m^3, we find $\sigma_\varphi^{\rm Au}\approx5.6\times10^{-6}$ (in units of $4\pi/k_F^2$). Therefore we see that the dephasing per Rh atom is still stronger than that of a Au atom by a factor of 250.

Thermal Vibrations: It is difficult to see that the thermal oscillation of the Rh should cause 250 times the dephasing of a Au atom. In addition it is difficult to understand that the vibrational dephasing does not occur for single Rh atoms on the Au surface but only for pairs and larger clusters. One would rather expect that the vibrations of single Rh atoms are less restricted, and therefore larger in amplitude and stronger in their dephasing.

Conduction electron-electron interaction: The electron-electron interaction between the conduction electrons contributes to the dephasing of weak localization.[30,31] Since the Rh atoms are transition-metal atoms with a high (resonance) density of states one might speculate that the condensation of the Rh atoms increases the electron-electron interaction in the Au film. However, the electron-electron interaction (between the conduction electrons) in a metal is screened. As a consequence its effective strength is inversely proportional to the density of states. This means that the electron-electron interaction is reduced by the Rh atoms. (The final contribution to the inelastic rate should be essentially unchanged because the integration over all states cancels the density of states). Furthermore it is again hard to see that this mechanism should only contribute for pairs and larger clusters.

We believe that the main mechanism that could cause the dephasing is the Coulomb interaction within the Rh atoms. Here we have to distinguish two different processes. In the first process we consider two conduction electrons which are d scattered by one Rh atom. In the intermediate state the two electrons occupy two d states within the Rh atom with different l_z. If we ignore the dynamics of the Coulomb interaction within the Rh atom then the two electrons scatter back into the conduction band and the whole process can be described by Friedel resonance scattering for each electron,

since each electron independently obeys energy conservation. However, within the Rh atom there is a finite probability that the Coulomb interaction causes the two electrons in their d states to perform a transition into a new set of d states, $|m_1 m_2\rangle$ to $|m_1' m_2'\rangle$, and then to leave the atom. Now we suppose each of the two electrons can change its energy; only the total energy of both electrons has to be conserved. We expect that this process yields a dephasing rate for the conduction electrons which is proportional to T^2, although we have not performed a calculation. However, we doubt that this process causes the additional dephasing by the Rh atoms. The strongest argument against this process is the fact that single Rh atoms do not contribute to the dephasing.

Then we are left with the other consequence of the Coulomb interaction in a d atom: The fact that the exchange interaction repels spin-up and spin-down d electrons. This is, however, just the mechanism which creates a magnetic moment in a transition-metal atom provided the interaction is strong enough.

We will assume for the following that the dephasing is caused by a polarization of the d resonance resulting in a magnetic moment μ. From the dephasing cross section we cannot directly determine the size of this moment. However, recently with the Friedel-Anderson resonance model of a magnetic impurity we derived the size of the dephasing cross section. We obtained

$$\frac{\sigma_\varphi k_F^2}{4\pi} = \frac{5}{2}\sin^2\left(\frac{\pi\mu}{5}\right). \tag{1}$$

This formula reproduces qualitatively the dephasing cross section of $3d$ impurities on the surface of Au. However, it overestimates its value by a factor of the order of five. We will use this formula to estimate the size of the magnetic moment of the $4d$ atoms by comparing it with the dephasing cross section of the corresponding $3d$ atom on the surface of Au. Our estimates yield for Rh atoms about $\mu^2 = (0.12\mu_B)^2$ and for Ru atoms $\mu^2 = (0.4\mu_B)^2$.

These moments are considerably smaller than the moments predicted by Wildberger *et al.*[21] for small Rh clusters on Ag (which is of the order of 0.6 to $1\mu_B$) and Ru singles on Ag (about $2\mu_B$). It should be emphasized that our theoretical formula yields only the (averaged) square of the magnetic moment. It is quite likely, that the moment fluctuates in time and, in an average, vanishes.

We have essentially the following reasons for this suggestion:

(i) With exception of Mo we find for all investigated $4d$ surface impurities, Nb, Rh, and Ru a dephasing cross section which corresponds to very small moments. Within the mean-field approximation of the Anderson model[32] one obtains a moment at the impurity when the product of the exchange interaction U and the resonance density g_2 is larger than one. The larger the product, the larger the moment. A small moment requires a product of Ug_2 very close to one. It is very unlikely that this condition is equally fulfilled for the different $4d$ impurities since the resonance density at the Fermi energy depends strongly on the number of d electrons. In addition, the numerical calculation by Dederichs' group also excludes this possibility. It appears more likely that the $4d$ impurity forms a moment which is then screened or hidden by other effects, such as the Kondo effect or local spin fluctuations.

(ii) The strong temperature dependence of the dephasing cross section indicates that the $4d$ atoms develop a magnetic moment at high temperature which is suppressed at low temperatures. (For small coverages it extrapolates roughly to zero dephasing.) This is a behavior which is well known for Kondo impurities and local spin fluctuations which are nonmagnetic at $T=0$ and fully magnetic at a temperature sufficiently above the corresponding critical temperature. The dephasing rate of magnetic impurities is particularly well suited to detect the disappearance of the magnetic moment by a strong temperature dependence of the dephasing in contrast to magnetic measurements such as the susceptibility which shows only a saturation at low temperatures.

B. No ferromagnetic monolayers

We find neither for a monolayer of Rh on Au nor for Ru on Au or Ag any trace of ferromagnetism. In the contrary we can definitely exclude ferromagnetism and even the formation of a moment. In particular for Ru we find that larger (two-dimensional) clusters reduce dramatically the tendency towards magnetic moments.

The absence of a ferromagnetic Rh (Ru) monolayer presents a theoretical challenge. From the theoretical side as well as from experimentalists who work with epitaxial surfaces, we often hear the argument that the disordered surface of the Au substrate is the reason that we do not observe ferromagnetic or antiferromagnetic order. Although we cannot completely rule out such a possibility, we consider it as rather unlikely. First, we have observed ferromagnetic monolayers for Fe and Co on disordered noble metals.[22,33] Secondly, we believe that the main effect of a perfect crystal surface [as a Ag (001) plane] is that it imposes its lattice parameter on the monolayer of the $4d$ metal. If the lattice parameters do not fit, the monolayer will be compressed or dilated. Then, of course, it is not surprising if the magnetic properties of the cover layer are dramatically altered. Fe, for example, can be forced into a fcc structure. In a disordered substrate, as our Au film, one has only short-range order. The influence of the substrate on the $4d$ structure is incoherent over larger distances. We expect that this reduces the overall effect of the substrate on the (average) lattice parameter of the $4d$ monolayer. Of course, the structure within the $4d$ monolayer is far from perfect. But as we mentioned above the ferromagnetism of Fe or Co layers proves that this deviation from a perfect structure is not essential for the formation of a magnetic monolayer.

This absence of a ferromagnetic monolayer increases the puzzle about magnetic monolayers. During the last decade there have been numerous predictions of ferromagnetic or antiferromagnetic monolayers[2–6,15] of (normally) nonmagnetic metals such as V, Ru, and Rh on the surface of Ag or Au. During the meantime we have studied a number of transition-metal monolayers on Au. This includes vanadium, whose magnetic structure was predicted to be antiferromagnetic, molybdenum (predicted to be nonmagnetic) and now rhodium and ruthenium (both predicted to be ferromagnetic). In all cases we neither observed strong dephasing for the

monolayer, nor the absence of dephasing. Rather, all monolayers behaved similarly with a dephasing cross section between 1×10^{-3} and 6.5×10^{-3} and have therefore strongly reduced moments. On the other hand, the properties of these transition metals differ strongly when we evaporate them in small concentrations (1/100 of a monolayer) on the substrate. So far, there has been only a single unconfirmed experiment which claims the observation of a magnetic V monolayer.[10] No ferromagnetic monolayer could be detected otherwise. Since WL is much more sensitive than other experimental methods, we could prove the absence of magnetic monolayers for these predicted systems. And this applies for ferromagnetic as well as for antiferromagnetic layers. It should be emphasized that we easily observe magnetic monolayers of the $3d$ metals, Cr, Mn, Fe, Co, and Ni on top of the noble metals (see, for example, Ref. 22).

Why does the theory obtain large magnetic moments in these monolayers, of the order of $1\mu_B$ or larger, while they are not observed experimentally? Let us assume for a moment that the theory, which is a mean-field theory, is correct. Could there be fluctuation effects, which reduce the moments in the monolayer? Although, as a two-dimensional system, the monolayer should be subject to large fluctuations, these fluctuations should be much smaller than in a zero-dimensional single impurity. Since we observe a much larger dephasing cross section for single surface impurities than for the corresponding monolayers this cannot be the explanation for the strong suppression of a moment. Therefore this discrepancy between theory and experiment represents a large gap in our understanding of moment formation and creates a great theoretical challenge. We now discuss the Au/Rh and the Au/Ru, Ag/Ru systems in some detail.

C. The Au/Rh system

Our experiments yield a number of remarkable results: (a) Single Rh atoms on the surface of Au do not contribute a detectable dephasing, since ΔH_i increases quadratically with the coverage and σ_φ extrapolates linearly towards zero. (b) The dephasing has a maximum at one atomic layer of Rh. (c) The maximum dephasing cross section of Rh (for a coverage of about 0.45 monolayers of Rh) has the value of $\sigma_\varphi=1.4\times10^{-3}$. This value is two orders of magnitude smaller than for a typical magnetic atom. (d) For Rh coverages above one monolayer the dephasing rate first decreases, but beyond two monolayers it increases almost linearly. This suggests that even bulk Rh causes an additional dephasing. (e) The dephasing cross section is strongly temperature dependent for all coverages. Between 20 and 4.5 K it reduces roughly by a factor of 4, but it does not extrapolate to zero dephasing at zero temperature except for the smallest coverages.

With the help of Eq. (1) we estimate the size of the magnetic moment of the Rh by comparing it with the dephasing cross section of Co on the surface of Au. The ratio of the cross sections is proportional to the ratio of $\sin^2(\pi\mu/5)$. The maximum dephasing cross section of Rh at a coverage of 0.45 atomic layers is 1.4×10^{-3}, while the corresponding value for Co is 175×10^{-3}. The ratio of the cross sections is 1/125. Taking the magnetic moment of Co on Cu as $1.7\mu_B$ from the paper of Lang *et al.*[20] we estimate the moment of Rh on Au to be $0.12\mu_B$.

It is remarkable that the total dephasing by the Rh has a maximum for one monolayer of Rh. As we discuss above there have been several predictions that a monolayer of Rh should be magnetic with a moment of the order of $1\mu_B$.[6] Recently Turek *et al.*[34] considered a monolayer of Rh on Ag (001) which was covered with an additional submonolayer of Rh. According to their numerical calculation the Rh atoms lose their moments in both layers, the original monolayer, and the additional submonolayer. Our observed maximum of the total dephasing appears to point out that the monolayer is an optimal structure for magnetism. However, the magnetic moment is again very small. There is absolutely no ferromagnetic monolayer with a moment of the order of $1\mu_B$. This is confirmed by our Hall-effect measurement. We do not find any indication of an anomalous Hall effect. The Hall resistance as a function of the magnetic field is, within the accuracy of the measurement, perfectly linear. The Hall resistance of the substrate Au film is about 0.1 Ω at the maximum field of 7 T. Since we cannot detect an AHE resistance its value must be smaller than 2×10^{-5} Ω. For a comparison we refer to the earlier measurement of 0.8 and 1.6 atomic layers of Co on the surface of Ag of similar thickness.[22] In that measurement we observed an AHE resistance of the order 1×10^{-2} Ω. This is larger by a factor 500 than the upper experimental limit for the Rh monolayer.

We were rather surprised when the (total) dephasing started to increase again for Rh coverages above 2 atomic layers. In this respect the Rh behaves differently from the other nonmagnetic d metals (such as V, Mo, Nb) which we have investigated so far. Our measurements suggest that pure bulk Rh causes an anomalous dephasing which is not caused by phonons but may have some magnetic component. Nonlocal spin fluctuations in the Rh metal are the most likely mechanism responsible for this dephasing. It appears worthwhile to study theoretically the effect of spin fluctuation in Rh and its effect on the dephasing of weak localization. Among the $4d$ metals Pd is generally considered as a material with strong spin fluctuations. We plan to investigate the effect of Pd on the dephasing of a Au substrate. It should give us a comparison with the effect of Rh.

D. The Au/Ru, Ag/Ru system

Our main experimental results for the Au/Ru system are the following: (a) Single Ru atoms on the surface of Au contribute to a dephasing of WL. Their dephasing cross section is $\sigma_\varphi=32\times10^{-3}$. (b) The dephasing cross section has a maximum at 0.05 atomic layer of Ru. (c) The dephasing cross section per Ru atom in a monolayer of Ru on Au, $\sigma_\varphi=2\times10^{-3}$, is much smaller than for a single Ru atom. (d) The dephasing cross section is strongly temperature dependent for all coverages. We discuss these results one by one.

(a) Single Ru atoms on the surface of Au and Ag both have a dephasing cross section of about $\sigma_\varphi=32\times10^{-3}$. This value is more than ten times smaller than for Mo and Fe on Au,[29,27] but also by a factor of 10 larger than for atoms of Rh clusters on the surface of Au. We conclude from this experimental result that single Ru surface impurities show a weak magnetic character. They do not have a moment of the order of $1\mu_B$.

Again we use Eq. (1) to estimate the magnetic moment for Ru on Au or Ag. From the comparison with Fe we obtain

for the Ru moment $\mu_{\mathrm{Ru}}=0.39$, using $\sigma_{\varphi,\mathrm{Fe}}=480\times10^{-3}$ and $\mu_{\mathrm{Fe}}=3.0$. In complete analogy we also obtain from the comparison with Mo in the $4d$ row the moment $\mu_{\mathrm{Ru}}=0.38$, using $\sigma_{\varphi,\mathrm{Mo}}=360\times10^{-3}$ and $\mu_{\mathrm{Mo}}=3.5$. Therefore we estimate the moment of Ru on the surface of Au to be $0.4\mu_B$.

(b) We observed a maximum in the dephasing cross section of Ru at a coverage of about 0.05 atomic layer. For larger Ru coverages σ_φ reduces and for a monolayer of Ru it is more than an order of magnitude smaller. We conclude that two Ru atoms in a pair support each other in forming a magnetic moment. For larger clusters the tendency towards magnetism, in particular towards ferromagnetism is reduced. This makes the formation of a ferromagnetic monolayer very unlikely.

(c) Indeed, we do not observe a ferromagnetic monolayer, but only a very weak dephasing at a coverage of 1 atomic layer of Ru.

(d) The strong temperature dependence of the dephasing cross section (see Fig. 4) supports the interpretation that single Ru atoms possess a hidden magnetic moment because it demonstrates that energies of k_BT, i.e., energies of the order of 1 meV, alter the magnetic properties strongly. This energy scale is not included in the local spin-density-functional theory calculations. It has to be treated separately.

The experimental results for Ag/Ru are qualitatively quite similar to those of Au/Ru. Although we have not studied the properties of most other $3d$ and $4d$ impurities on Ag our experimental results suggest that single Ru atoms on the surface of Ag have a similar moment of about $0.4\mu_B$ which fluctuates in time. Again a monolayer of Ru on Ag is not ferromagnetic.

IV. CONCLUSION

We use the method of weak localization and the anomalous Hall effect to study the magnetic properties of Rh and Ru atoms and monolayers on the surface of Au and Ag. We detect the magnetic moments by their dephasing effect on weak localization. We do not find a fully stable moment for Rh or Ru atoms on the surface of Au or Ag. In particular, single Rh atoms cause no noticeable dephasing at all. We observe, however, an increased dephasing by Rh clusters. We give a rough estimate of the corresponding moments of the Rh atoms and find about $0.1\mu_B$ per Rh atom. The same estimate yields about $0.4\mu_B$ for Ru atoms on Au and Ag. We do not believe that this moment is stable but rather that it is a locally fluctuating moment. This is supported by the strong temperature dependence of the dephasing cross section. The dephasing rate due to the Rh coverage reaches a maximum for a single monolayer of Rh on the surface of Au. This coincides with theoretical predictions that a monolayer of Rh on the surface of Au and Ag is ferromagnetic, while the magnetism decreases for smaller and larger coverages. However, our Rh monolayer is not ferromagnetic. Neither is a monolayer of Ru on Au or Ag ferromagnetic. This is a pattern which we observed in several systems. V is another example. The large magnetic moment for single V atoms on the surface of Au was confirmed by our measurements. However, a monolayer of V also behaved very differently than the theory predicted. We believe that in all cases we see small fluctuating moments in the monolayers. We also believe that the absence of a ferromagnetic monolayer is not caused by our polycrystalline Au (Ag) substrate. Rather the closeness of our systems to the borderline of magnetism yields physics which is not yet included in the local spin-density-functional theory. Finally we observe that for Rh coverages larger than two monolayers the dephasing increases again. This suggests that bulk Rh shows (nonlocal) spin fluctuations of the d electrons similar to those in Pd. We intend to investigate the Au/Pd system in the future for a comparison.

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