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First observation of a fully magnetic $4d$ impurity on the surface of Au

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Abstract. – We observe for the first time a fully magnetic $4d$ surface impurity on the surface of a noble metal. Au films are covered with 1/100 of a monolayer of Mo. The Mo atoms cause a dephasing of the conduction electron coherence which is of the same order of magnitude as the dephasing by magnetic Fe atoms. The dephasing is measured by weak localization and proves the strong magnetic character of the Mo atoms. The magnetic character of Mo is investigated up to a coverage of one monolayer. The dephasing per Mo atom strongly diminishes with increasing Mo coverage.

The study of magnetic single transition metal atoms on the surface of a noble metal dates back more than 10 years [1]-[3]. 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 only a fraction of an atom's moment is parallel to the magnetic field at finite temperature. In many cases, the moment is much further reduced (sometimes by a factor of 100) due to Kondo screening or other effects at the borderline of magnetism. The first successful method was the anomalous Hall effect (AHE) which is sensitive enough to study a coverage of a few percent of a monolayer of magnetic impurities. A similarly successful method was tunneling with polarized electrons, see, for example, the review article [4]. The most successful method is weak localization, which is so sensitive that it can easily detect a coverage of 10^{-4} of a monolayer of magnetic atoms. We used this method to investigate the properties of magnetic $3d$ surface impurities [5].

The field of magnetic surface impurities recently received a great boost from new theoretical predictions by the Dederichs group in Jülich [6]. They investigated the magnetic properties of single transition metal impurities on the surface of Ag and Cu. They concluded that on the (100) surface of Ag the $4d$ atoms Nb, Mo, Tc and Ru should possess a magnetic moment in the adatom position as well as in the in-surface position. All the moments are 1 μ_B or larger.

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The moment for a Mo surface impurity, for example, is predicted to lie between 3 and 4 μ_B in the adatom position. We recently investigated the properties of Nb atoms on the surface of Ag and Au [7].

In this paper we investigate the magnetic properties of Mo atoms on the surface of Au. We show that Mo atoms on the surface of Au represent the first system for which a fully magnetic $4d$ surface impurity is experimentally identified. Our experimental method is weak localization, which is a powerful tool to study characteristic scattering times in thin disordered metal films [8]. Magnetoresistance measurements correspond to time-of-flight experiments which yield the inelastic, spin-orbit, and magnetic scattering times. The fact that the coherence of the conduction electrons is destroyed by magnetic scattering roughly after the magnetic-scattering time results in an increase of the width of the magnetoresistance curves, which can be well evaluated with the theory by Hikami *et al.* [9]. This method does not depend on the formation of a ferromagnetic state, it is very sensitive to the existence of magnetic moments.

The experimental details of the preparation of the films, rate calibration and the experimental technique have been published in earlier work [10]. Therefore, we give here only a brief summary. Our film samples are prepared by *in situ* condensation onto a quartz substrate at helium temperature. This reduces the diffusion of the Mo into the Au substrate to an absolute minimum. We prepare our Au/Mo samples in the following manner. First we evaporate 25 to 30 monolayers of the substrate film Au. In a typical experiment the Au film is condensed with a resistance per square of about $100\,\Omega$. The vacuum is better than 10^{-11} Torr. The quench condensed Au film is homogeneous and polycrystalline. After the evaporation the film is annealed to 40 K. The magnetoresistance of the Au film is then measured in the temperature range between 4.5 and 20 K.

In the next evaporation step 0.01 of a monolayer of Mo is condensed on top of the Au film. The Mo is evaporated from a thin wire with a radius of 0.25 mm and its evaporation rate is carefully calibrated. After the Mo evaporation the film is annealed to 35 K and the measurements are repeated.

In the third evaporation step the Au/Mo film is covered with five additional layers of Au and again the measurements of the magnetoresistance curves are repeated. The experimental results are generally reproducible within 10%. However, the calibration of the Mo evaporation is quite delicate at these small rates of 0.1 to 0.2 atomic layers per minute. Therefore, we prefer to use a very conservative estimate of the accuracy of the Mo coverage of about 20–25%.

Figure 1 shows three magnetoresistance curves measured at 4.5 K. The top one is for pure Au, the second one is for the Au film covered with 1/100 of a monolayer of Mo and for the third one the Au/Mo is again covered with 5 atomic layers of Au. Note that for the second curve the ordinate is stretched because the magnetoresistance curve is much wider. 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 dephasing by inelastic- and magnetic-scattering processes. This allows us to extract the strength of magnetic dephasing with high accuracy.

The width of the magnetoresistance curve is described by the dephasing field H_i^*. This field is proportional to $1/\tau_i + 2/\tau_s$, where τ_i is the inelastic and τ_s the magnetic dephasing time of the conduction electrons. The latter is due to magnetic scattering by the Mo atoms. (The proportionality constant is about 0.3 psT for this film). We evaluated the magnetoresistance curves with the theory of weak localization by Hikami *et al.* [9]. By fitting this theory to the experimental curves, one obtains the dephasing field H_i^* of the conduction electrons. From the broadening of the magnetoresistance curves, *i.e.* from the increase of the dephasing field H_i^*, one obtains the magnetic-scattering cross-section σ_s of Mo. It is convenient to measure the cross-section in units of $4\pi/k_F^2$, which yields a dimensionless number. For 1/100 coverage with

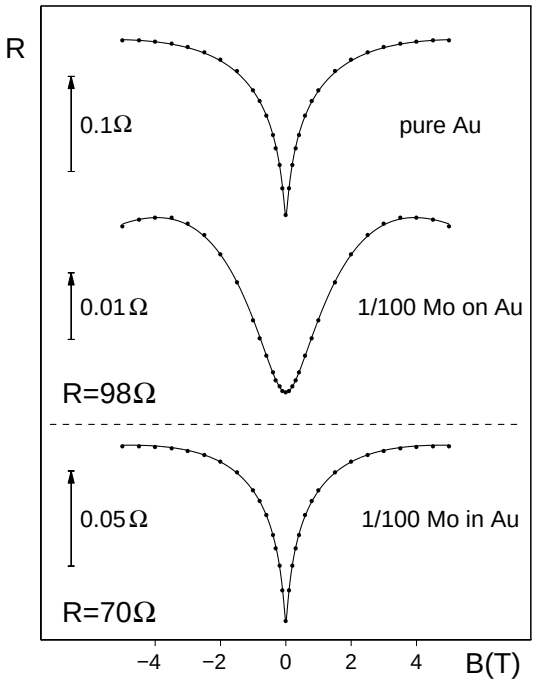

Fig. 1.

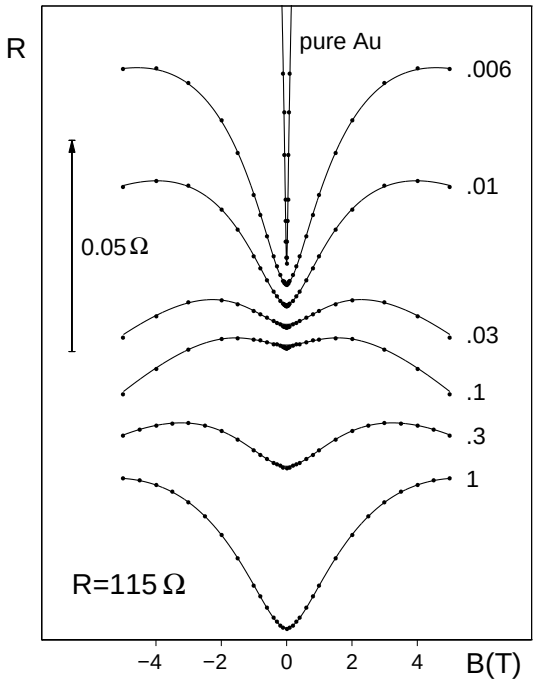

Fig. 2.

Fig. 1. – Three magnetoresistance curves for the system of Au/Mo/Au measured at 4.5 K. The top curve is for pure Au. For the second curve the Au is covered with 1/100 atomic layers of Mo. In the third curve the Au/Mo is covered with 5 atomic layers of Au. The points are the experimental values. The curves are fitted with the theory of weak localization.

Fig. 2. – Several magnetoresistance curves for increasing coverage with Mo. The coverages are given by the number beside the curves. Again the points are the experimental values while the curves are fitted with the theory of weak localization.

Mo we find the magnetic cross-section per Mo atom $\sigma_s k_F^2/4\pi = 180 \cdot 10^{-3}$. For a comparison with a typical magnetic atom the corresponding values for Fe and Mn on the surface of Au are $270 \cdot 10^{-3}$ and $55 \cdot 10^{-3}$, respectively, while Nb on Au has essentially the value 0 and Nb on Ag yields at 4.5 K the value of $18 \cdot 10^{-3}$. Obviously, Mo is much closer to the fully magnetic surface atoms Fe and Mn than to Nb. Although our experiment does not directly measure the magnetic moment, we consider the result as a confirmation of the theoretical prediction by Lang *et al.* that Mo has a large magnetic moment on the surface of a noble metal.

It should be mentioned that we did not include in the theoretical evaluation of the magnetoresistance curves the classical spin-scattering contribution of the Mo atoms [11]-[13]. Here as in earlier investigations we tried to include the theoretical contribution of spin scattering as given by Beal-Monod and applied by [14]. The resulting theoretical curves disagreed completely with the experimental curves. At best we could include 10% of the theoretical spin-scattering contribution without losing a reasonable agreement with the experiment.

The third curve in fig. 1 corresponds to bulk Mo impurities in Au because the Mo atoms are embedded in Au. The width of the magnetoresistance curve is so narrow that within

the experimental accuracy there is no magnetic broadening. (A possible broadening due to magnetic impurities is a factor of $2 \cdot 10^{-3}$ smaller than for the same Mo atoms on the surface of the Au.) From this result we conclude i) that bulk Mo impurities in Au are non-magnetic and ii) that the concentration of magnetic $3d$ impurities in our Mo is smaller than $2 \cdot 10^{-3}$. This agrees with the specifications of Johnson and Matthews that the Fe concentration in the Mo wire is less than 200 ppm and all the other magnetic $3d$ impurities are an order of magnitude smaller. As a matter of fact, the destructive effect of magnetic transition metal atoms on weak localization is so strong that the method can be used to determine the concentration of magnetic $3d$ atoms with high sensitivity.

In our next experimental series we investigate the magnetic dephasing as a function of the Mo coverage on top of an Au film. We cover an Au film successively with 0.006, 0.01, 0.03, 0.1, 0.3 and 1 atomic layers of Mo. Figure 2 shows several magnetoresistance curves measured at 4.5 K. The top one is for pure Au. (Since the same resistance scale is used for all magnetoresistance curves, the one for pure Au would extend over several pages). The numbers beside the curves give the Mo coverage in units of monolayers of Mo. The points are the experimental results while the full curves are theoretical curves where the magnetic-scattering strength has been optimally adjusted. The magnetic dephasing rate is given by $2/\tau_{\mathrm{s}}$. This rate is given in fig. 3 by the field H_{s}, which is directly obtained from the fit between experiment and theory and which is proportional to $2/\tau_{\mathrm{s}}$, since $H_{\mathrm{s}} = \hbar e \rho N / 4\tau_{\mathrm{s}}$. We observe the maximum dephasing for a coverage of the order of 0.1 atomic layers of Mo.

Wildberger *et al.* [15] recently calculated the magnetic properties of small clusters of $4d$ atoms on the surface of Ag. They considered mainly a possible ferromagnetic alignment of neighboring Mo atoms. Their numerical calculation predicted that besides single surface impurities, pairs and linear chains of four Mo atoms should possess a magnetic moment, while triples and square-shaped clusters of four were non-magnetic. It appears that compact clusters tend to be non-magnetic. One may wonder what the magnetic properties of linear chains of an even number of Mo atoms or even zig-zag chains might be. However, they mention that anti-ferromagnetic clusters of Mo have larger moments and are more stable. Despite these uncertainties, we wish to make a first comparison between our experimental dephasing results and the theoretical cluster prediction. The first apparent difficulty for such a comparison is that we do not have a theoretical model to calculate the dephasing of magnetic atoms in a cluster when the moment in the cluster varies from atom to atom and is not identical with the moment of a single Mo atom. In the absence of such a theory and only for a first estimate we treat all magnetic atoms as equal. In fig. 3 we consider two simplified models. *a*) Only Mo singles are magnetic. Their number is given by $c(1-c)^6$, where c is the coverage in units of atomic layers. The dashed curve gives the number of single Mo atoms as a function of the Mo coverage. Here the dephasing effect is proportional to the number of singles. We adjusted the height of the maximum so that it agrees with our experimental curve. The curve shows a maximum dephasing at a coverage of about 0.14. *b*) Only singles and pairs are magnetic and yield the same dephasing per atom. The dephasing is given by the dash-dotted curve (again the height of the maximum is adjusted). The maximum is at a coverage of 0.17.

There are two important deviations between the experimental and both theoretical curves. i) For coverages above 0.3 to 0.4 the experimental dephasing is much larger than the theoretical one. ii) At small coverages of the order of 0.01 the experimental initial slope is a factor of four-to-six larger than for the two theoretical curves.

The first fact means that experimentally the magnetic Mo moments persist to much higher concentrations than the simple models predict. Of course, magnetic linear chains would extend the dephasing range to higher coverage. However, even for a monolayer of Mo we find a finite dephasing although the dephasing per Mo atom is a factor of almost 100 smaller than for the

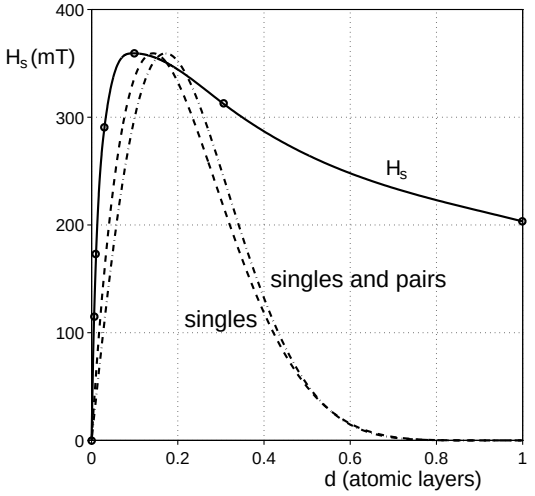

Fig. 3.

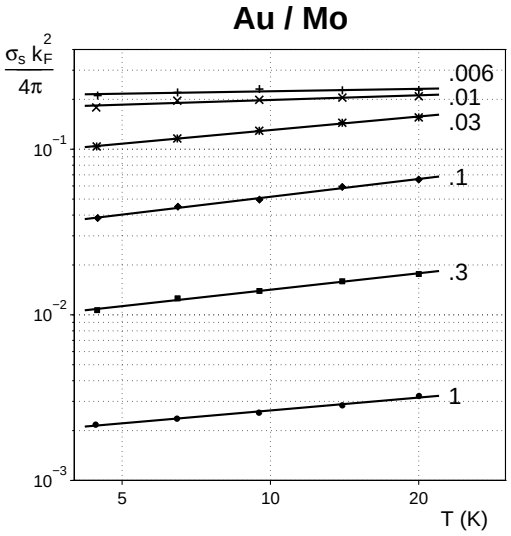

Fig. 4.

Fig. 3. – The strength of the dephasing by magnetic Mo surface atoms as a function of the Mo coverage. The strength is given in terms of the magnetic dephasing field H_s which is directly proportional to $1/\tau_s$. The dashed and dash-dotted curves are discussed in the text.

Fig. 4. – The temperature dependence of the magnetic-scattering cross-section of Mo on the surface of Au (in units of $4\pi/k_F^2$) for different Mo coverages. The numbers besides the curves give the Mo thickness in units of monolayers.

coverage of 0.01. This experimental finding shows a qualitative similarity to our results for V on the surface of Au [5]. On the other hand, the theoretical predictions for a monolayer of Mo on Ag and a monolayer of V on Ag are very different [16], [17]. While the first is predicted to be non-magnetic, the latter should be anti-ferromagnetic. Of course, one has to keep in mind that the theoretical model assumes that the substrate surface is a perfect (100)-plane, while experimentally we have a smooth but disordered surface. This experimental situation cannot yet be modeled by the theory.

The large initial slope of our experimental dephasing curve is rather unusual. It means that even for a coverage of 0.01 of a monolayer the neighboring Mo moments not only feel each other but their interaction is so strong that it changes the dephasing rate per atom. At the present time we cannot give an explanation for this behavior.

The magnetic dephasing cross-section of the Mo shows a small temperature dependence which is plotted in fig. 4 in a log-log plot for the different coverages of Mo on Au. The exponents are 0.05 for the smallest coverage, 0.26 for the monolayer and have the largest value of 0.36 for a coverage of 0.1 of a monolayer.

In summary we find that single Mo atoms on the surface of Au are magnetic and from the strength of the dephasing of weak localization we conclude that they have a large moment. The magnetic character of the Mo surface atoms decreases when the coverage is increased. Our measurements indicate that there is a strong interaction between the magnetic Mo atoms, even at a concentration of 1/100. Our measurements identify for the first time a fully magnetic 4*d* atom on the surface of a noble metal.

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