

Success and failure of the Friedel-Anderson resonance model for magnetic impurities: $3d$ impurities on the surface of Au

H. Beckmann and G. Bergmann

Department of Physics, University of Southern California, Los Angeles, California 90089-0484

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The magnetic character of $3d$ atoms on the surface of Au is investigated using the method of quantum interference (weak localization). We find that single atoms of V, Cr, Mn, Fe, and Co are magnetic on the surface of Au while single atoms of Sc and Ni are nonmagnetic. Single atoms of Ti are locally spin fluctuating. The magnetic dephasing due to the $3d$ impurities has two maxima, one for iron and a smaller one for chromium impurities and a minimum for manganese. This behavior can be qualitatively described within the Friedel-Anderson model although the experimental values are smaller by roughly a factor of 5 than our theoretical estimates within this model. [S0163-1829(96)01825-5]

I. INTRODUCTION

The magnetism of the $3d$ impurities Mn, Fe, Co, and Ni in different metallic hosts has been studied for several decades. In this paper we go a step further and ask ourselves: What is the magnetic character of single $3d$ atoms on the surface of a host metal? For this purpose we study the magnetic scattering of single $3d$ impurities on the surface of Au. Parallel to our investigation Lang *et al.*¹ used the spin-density functional theory to calculate the magnetic moments of $3d$ atoms on the surface of Cu. They considered the $3d$ atoms at two different positions, on top of a Cu(100) surface (adatom position) and in the surface layer (in-surface position). They found that V, Cr, Mn, Fe, and Co should have a magnetic moment in both locations. Generally they found a larger moment for the adatom position. The size of this moment has its maximum for Cr and Mn with about $4\mu_B$. The magnetic moment for Ni should vanish at the surface of Cu. Of particular interest is Ti on Cu. According to their calculation it should be nonmagnetic in the in-surface position and have a magnetic moment of $1.5\mu_B$ in the adatom position.

Experimentally the anomalous Hall effect (AHE),^{2,3} tunneling with polarized electrons⁴ and weak localization^{5,6} (WL) have been used to study the properties of magnetic impurities on metal surfaces. The method of WL is particularly suited for this kind of investigation because it is extremely sensitive to magnetic impurities. We find that one can easily detect a coverage of 10^{-4} monolayer of a magnetic $3d$ surface impurity. Recently we have used WL to study the properties of mono- and multilayers of V at the surface of Au.⁶

In this paper we investigate the magnetic character of single $3d$ atoms on the surface of Au films. The smallest coverage of the $3d$ atoms is of the order of 1/100 of a monolayer. The underlying Au film has an area of $2 \times 5 \text{ mm}^2$. A coverage of 1/100 corresponds to about 10^{12} $3d$ atoms. The magnetic moments of these surface atoms experience a strong anisotropy perpendicular to the surface. In addition, there is experimental evidence that the interaction of moments at the surface is much larger than in the bulk. Therefore the field and temperature dependence of the magnetiza-

tion does not follow a Brillouin function, and its analysis is difficult. As a consequence, the investigation of dilute magnetic moments at the surface requires special care. In our experiments we use the dephasing effect of magnetic moments on the quantum interference of the conduction electrons (generally called weak localization). This method is extremely sensitive to the scattering by magnetic moments and yields the magnetic interaction between the conduction electrons and the magnetic moment (see, for example, the review articles^{7,8}). Even a hundredth of a monolayer of magnetic $3d$ atoms yields a large dephasing.

II. EXPERIMENT

Our film samples are prepared by *in situ* condensation onto a quartz substrate at liquid-helium temperature. In a typical experiment a Au film with a thickness of about 25 atomic layers and a resistance per square of about 110Ω is condensed onto a quartz substrate. The Au is evaporated from a tungsten boat by direct electrical heating. The vacuum is better than 10^{-11} torr. After the condensation the Au film is annealed to about 40 K. The magnetoresistance of the Au film is then investigated in the temperature range between 4.5 and 20 K. In the following evaporation steps the $3d$ impurity is condensed on top of the Au film. The $3d$ metals Ti, V, Fe, Co, and Ni are available in the form of thin wires. Scandium is available in the form of a thin narrow foil with a thickness of about $50 \mu\text{m}$ and a width of 3 mm. The purity of the $3d$ materials is generally 99.99%. Only Cr with 99.9% and V with 99.95% have a lower purity. For the evaporation the wires or the foil are directly heated with an electric current and the evaporation rates are carefully calibrated. The $3d$ metals Cr and Mn are not available in the form of thin wires and are too brittle for the preparation of a thin foil. They can be evaporated by indirect heating in a tungsten boat. However, because of the indirect heating, the power input is so high that it makes a reliable calibration of the evaporation rate impossible. In addition, due to the high temperature of the tungsten boat the chances are that rest gases are set free from the walls. Since we need only a very small evaporation rate of the $3d$ metal the rest gases could severely dirty the $3d$ atoms. Instead, we prepare the

Mn evaporation source in the high vacuum of a pumpstand. We heat a small piece of Mn in a tungsten boat to such a high temperature that the Mn melts and coats the tungsten boat. This requires some care because the Mn sublimates long before it melts. Therefore precautions are taken so that other parts of the evaporation source are not polluted. Chromium, with a much higher melting temperature than Mn, could not be prepared in this manner. Here we evaporate a piece of Cr from one tungsten boat onto a second tungsten boat which is only a few millimeters away. (Of course, both tungsten boats are cleaned beforehand by annealing to a very high temperature.) This yields a sufficiently thick layer of Cr on the second tungsten boat. The latter can then be used in the actual evaporation of Cr in the cryostat because now the Cr assumes the same temperature as the tungsten boat and a more modest heating of the tungsten boat yields a sufficient evaporation rate due to sublimation. This enables us to accurately calibrate the evaporation rate. This "distillation" of the Cr is in one experiment performed in a pumpstand and the evaporation source then transferred into the evaporation cryostat. In another experiment the distillation is performed in the evaporation cryostat itself so that the Cr is not exposed to atmospheric air before the actual evaporation. The experimental results agree for both procedures to within 10%.

Each $3d$ surface impurity is investigated in at least two or three different experiments. The agreement between different experiments is generally better than 10%. However, we prefer a more conservative estimate of 20% in the uncertainty of the $3d$ impurity coverage. For reliable results it is absolutely important that the impurity coverages are perfectly clean. This is achieved by the ultrahigh vacuum during the evaporation and the fact that most of our evaporation sources are thin wires, which have been carefully preannealed and are directly heated during the evaporation. This keeps the thermal radiation to a minimum. Since the condensation of the Cr requires such a complex distillation process we expect that the quality of the Cr coverage is somewhat poorer than for the other $3d$ metals.

After completing the investigation of the Au film, the evaporation rate of the $3d$ metal is calibrated and a rate of the order of $1/5$ atomic layer per minute is chosen. Then $1/100$ of a monolayer of the $3d$ impurity is condensed on top of the Au film. The total film is annealed up to 35 K and the magnetoresistance measurement is repeated at different temperatures. Generally the coverage of the $3d$ metal is increased by a factor of 2 in several evaporation steps as long as the magnetoresistance curves can be evaluated.

Figure 1 shows several magnetoresistance curves. The top one is for a pure Au film. The bottom curve shows the corresponding magnetoresistance curve after a coverage with 0.011 of a monolayer of Mn. (Notice that the field and resistance scales are different for this curve.) The two other curves are discussed below. The broadening of the magnetoresistance curves is proportional to the magnetic scattering. We evaluate the magnetoresistance curves with the theory of weak localization by Hikami *et al.*⁹ The full curves give the best theoretical fit and yield the dephasing field H_i^* , which is proportional to $(1/\tau_i + 2/\tau_s)$, where τ_i is the inelastic lifetime of the conduction electrons and τ_s the magnetic scattering time due to the $3d$ atoms. Since for the pure Au film $1/\tau_s$ is zero we can first determine $1/\tau_i$ and then evaluate the

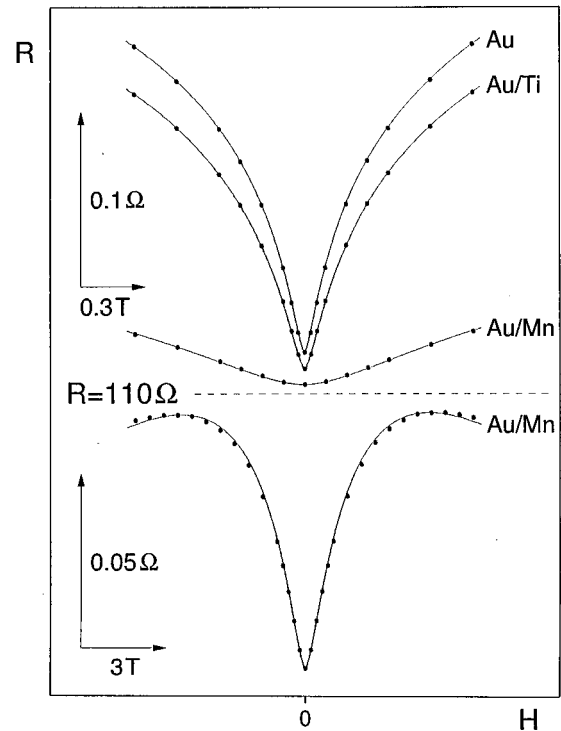


FIG. 1. Several magnetoresistance curves for a Au film with $3d$ surface impurities. The top curve is for pure Au, the second curve is for Au with a coverage of 0.045 atomic layer of Ti, the third curve for a coverage of Au with 0.011 atomic layer of Mn (the same field scale is used as for the first two curves). The bottom curve is the same magnetoresistance curve as number three but plotted with a compressed field scale. The points are the experimental values measured at 4.5 K. The curves are fitted with the theory of weak localization.

magnetic scattering rates for the different coverages. For a quantitative evaluation it is important that one works in the spin-orbit scattering dominated case. Then one has a positive magnetoresistance for small fields and, generally, a maximum at large fields. With increasing coverage of magnetic atoms the minimum at zero field disappears, and then the evaluation of the magnetoresistance curve becomes less accurate.

The broadening of the magnetoresistance curves by Ti is smaller by a factor of 100–500 than for V, Cr, Mn, Fe, and Co. To demonstrate the dephasing due to the Ti the second magnetoresistance curve in Fig. 1 is plotted for a Ti coverage of 0.045 atomic layers. One clearly recognizes the broadening of the magnetoresistance. However, if we plot the magnetoresistance of the Au with about $1/100$ of a monolayer of Mn (i.e., the bottom curve in Fig. 1. The $3d$ impurities Cr, Mn, Fe, and Co cause so much dephasing that in some cases a coverage of less than $5/100$ of an atomic layer removes the minimum at low fields and prevents a quantitative analysis for larger concentrations. Only for V does the dephasing cross section per V atom decrease dramatically with increasing coverage so that its dephasing can be studied up to many vanadium monolayers.⁶ The requirement of being in the dominant spin-orbit scattering regime is also the reason why we prefer to have Au as a substrate because Au films have a large spin-orbit scattering. If one wishes to use a Cu sub-

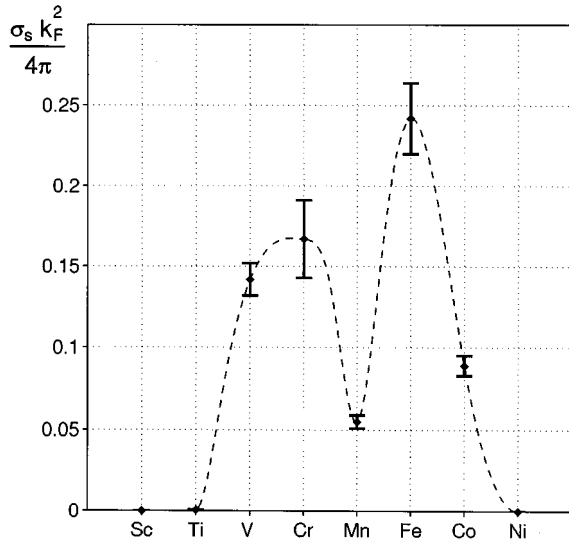


FIG. 2. The magnetic scattering cross section σ_s in units of $4\pi/k_F^2$ for the different 3d atoms on the surface of Au.

strate then additional experimental steps are required to be in the dominant spin-orbit scattering regime.

From the magnetic scattering rate $1/\tau_s$ one obtains the magnetic free path $l_s = v_F \tau_s$. We determine the magnetic scattering cross section σ_s with the relation $\sigma_s l_s n_{3d} = 1$ where n_{3d} is the concentration of the 3d atoms (given by the coverage).

In Fig. 2 the magnetic scattering cross section is plotted for the different 3d surface impurities on Au. The diamonds give the average experimental results and the bars the estimated experimental errors. The ordinate gives the magnetic scattering cross section in units of $4\pi/k_F^2 \approx 8.7 \times 10^{-20} \text{ m}^2$. The magnetic scattering cross section has two maxima, one for Fe and another one for Cr, and it has a minimum for Mn. It vanishes for Ni and Sc. For Ti $\sigma_s k_F^2 / 4\pi$ is only 0.5×10^{-3} , almost too small to be distinguished from zero in Fig. 2.

Furthermore we observe, that for Fe, Co, and Ni, neighboring 3d atoms support each other in the formation of magnetic moments and couple ferromagnetically. This is particularly obvious for Ni atoms. Here we observe that the magnetic scattering increases roughly with the square of the Ni coverage. This suggests that pairs of Ni atoms already possess a magnetic moment while single Ni atoms are non-magnetic. For coverages above half a monolayer a measurement of the anomalous Hall effect confirms our earlier result that the Ni becomes ferromagnetic.¹⁰

On the other hand, for the 3d atoms V, Cr, and Mn the anomalous Hall effect does not show ferromagnetic order. Furthermore, we observe that for Cr and V, neighboring atoms hinder each other in the formation of a magnetic moment. This we conclude from the dependence of the magnetic scattering rate on the concentration of the 3d atoms. For example, a coverage of 0.02 atomic layer of Cr results in a strong reduction of the magnetic scattering per atom. The same behavior we observed for V.⁶

In Fig. 3 we plot the temperature dependence of the magnetic scattering. It shows $\sigma_s k_F^2 / 4\pi$ for 1/100 of a monolayer of the different 3d impurities as a function of the tempera-

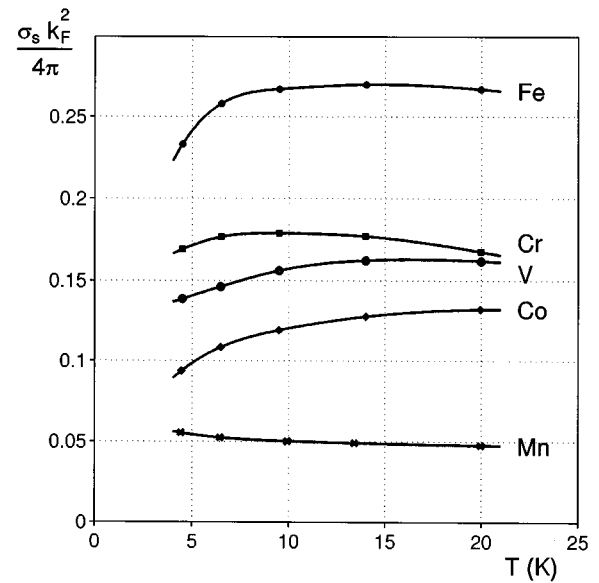


FIG. 3. The temperature dependence of the magnetic scattering cross sections of the different magnetic 3d atoms on the surface of Au (in units of $4\pi/k_F^2$) for a coverage of 1/100 of an atomic layer.

ture. There is, with exception of Mn, a clear decrease of σ_s at helium temperature. However, the main result of this plot is that the magnetic scattering is essentially temperature independent.

III. DISCUSSION

Lang *et al.*¹ calculated the magnetic moment of 3d impurities on a Cu(100) surface for two different positions, the adatom and the in-surface position. For both positions they found a clear maximum of the magnetic moment in the middle of the 3d row for Mn and Cr with about $4\mu_B$. On the other hand, our experimental magnetic scattering cross section for the 3d surface impurities on Au shows two maxima as a function of the 3d impurities and a minimum for Mn. We ask ourselves whether we can explain the experimental behavior of σ_s with the theoretical magnetic moments.

In the theory of weak localization by Hikami *et al.*⁹ the magnetic impurities are described by an exchange Hamiltonian $H_{\text{ex}} = J\mathbf{sS}$. However, the value of the exchange interaction J is, despite intensive research over many decades, still an adjustable experimental parameter. Therefore we can consider our magnetic dephasing cross sections as an experimental determination of the exchange interaction J , but this in itself does not improve our physical understanding.

There is, however, an alternative model of a magnetic impurity, the Friedel-Anderson (FA) resonance model. Within this model the magnetic impurity is described by two d resonances, one for spin-up and the other one for spin-down electrons. The scattering of the conduction electrons by 3d impurities is dominated by d scattering and can be described in terms of the Friedel phase shifts δ_2 for d scattering. The value of δ_2 is essentially given by the occupation of the d states. For a magnetic impurity one has two different d phase shifts for spin-up and spin-down electrons δ_{2+} and δ_{2-} . The scattering amplitude of a spin-up or spin-down conduction electron is do-

minated by the d scattering amplitude $f_{2\pm}(\Omega) = (5/k_F) \exp[i\delta_{2\pm}] \sin(\delta_{2\pm}) P_2(\cos\Theta)$. [$P_2(u)$ is the Legendre polynomial for $l=2$. The factor 5 comes from the $(2l+1)$ degeneracy.] As a consequence a conduction electron with spin up experiences a different scattering than a spin-down conduction electron. This description of a d impurity has several shortcomings: (a) the magnetic impurity points with its magnetization either up or down, i.e., $S_z = \pm S$ and intermediate magnetic quantum numbers are not permitted (we take the preferred direction parallel to the z axes), (b) as a consequence spin-flip processes with $\Delta S_z = \pm 1$ are absent and the spin dynamics is strongly reduced. Nevertheless, this model is quite successful in describing the (residual) scattering of the conduction electrons by $3d$ impurities. Podloucky *et al.*¹¹ calculated the phase shifts for $3d$ impurities in Cu and Ag in the local spin-density approximation of the density-functional theory. With these phase shifts they calculated the contribution of the magnetic $3d$ impurities to the residual resistivity and they compared their numerical results with the experimental data. They found a rather satisfactory agreement between their numerical results and the experimental data.

Furthermore, the FA model is generally used to conclude from the residual resistivity of a host with $3d$ impurities whether the $3d$ impurities are magnetic (see the review article, Ref. 12). For example, the contribution of the $3d$ impurities to the resistivity of Cu and Au at room temperature shows a double-peak structure, while the same impurities in Al possess a single maximum in the middle of the $3d$ series. The generally accepted conclusion is that the $3d$ impurities possess a moment in Cu at room temperature while they are nonmagnetic in Al.

It would be desirable to understand why this model is so successful in describing the residual resistivity despite its shortcomings. However, here we will take a more pragmatic point of view. We will try to check how well the same model works for the dephasing contribution of the $3d$ impurities on weak localization. We recently studied the dephasing effect of local spin-density fluctuations on weak localization within the Friedel-Anderson model.¹³ This calculation is quite general and can be directly applied to our present question. Therefore, we give a very brief sketch of the derivation.

In the following we consider only the $l=2$ or d contribution of the scattering amplitude. Then the $3d$ impurity contributes to the decay rate $1/\tau$ of the electron propagator (i.e., the Green's function) $(5/2)n_{3d}v_F(4\pi/k_F^2)[\sin^2\delta_{2+} + \sin^2\delta_{2-}]$. We then calculate the contribution to the particle-particle propagator in weak localization and obtain that each magnetic impurity contributes to the dephasing of the singlet channel (which is the important one for dominant spin-orbit scattering) with a cross section of

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

Here μ is the magnetic moment of the $3d$ impurity in units of μ_B . This result is surprisingly simple. The dephasing depends only on the value of the magnetic moment and has its maximum for $\mu = 2.5(\mu_B)$.

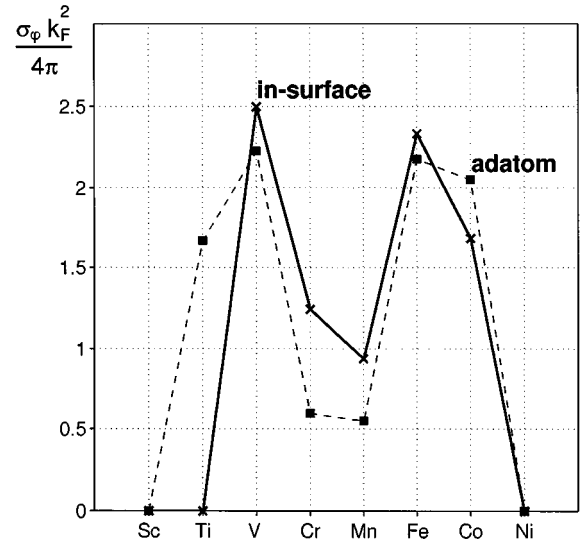


FIG. 4. The theoretical dephasing cross section for the $3d$ surface impurities with the Friedel-Anderson resonance model, using the magnetic moments of Lang *et al.* Details are given in the text.

The above calculation explains qualitatively the two maxima and the minimum of the magnetic scattering cross section. We take the magnetic moments from Ref. 1 for $3d$ atoms on a Cu(100) surface and use Eq. (1) to calculate the theoretical dephasing cross section. In Fig. 4 we plot these theoretical cross sections for the different $3d$ surface impurities in the adatom position (dashed line) and in the in-surface position (full line). We expect that the magnetic moments are somewhat larger on a Au substrate than on a Cu substrate, because the electron density in Au is smaller than in Cu. However, the difference in the substrate should have no dramatic effect. For a quantitative comparison between the dephasing cross section σ_φ in the FA model and the evaluated experimental σ_s in the exchange model we note that $\sigma_\varphi = 2\sigma_s$ because the dephasing rate in the exchange model is $1/\tau_\varphi = 2/\tau_s$ (see above and Ref. 9). We find that the experimental dephasing cross section is roughly by a factor 0.2 smaller than the averaged theoretical ones calculated within the FA model (V, 0.12; Cr, 0.3; Mn, 0.16; Fe, 0.2; Co, 0.1).

This calculation uses the Friedel-Anderson model which has been successful in the calculation of the residual scattering. Therefore it is very desirable to understand why this model works so well in calculating the total scattering rate $1/\tau_0$ and fails in the calculation of the dephasing rate $1/\tau_\varphi$. One might speculate that the surface position of our $3d$ impurities with its nonspherical potential might be of importance. That may be so. It would also be desirable to measure the dephasing cross sections for bulk $3d$ impurity where the phase shifts for the $T2g$ and Eg states are almost the same.¹¹ The original goal of this investigation was the investigation of surface impurities, and the derivation of the dephasing cross section was only inspired by the experimental data. However, during the meantime we have obtained some (incomplete) experimental results for bulk $3d$ impurities. We find that, with exception of Mn, their dephasing cross sections are either close to or smaller than the surface values.

Therefore the discrepancy between our experimental results and the FA model for the dephasing of weak localization is a fact.

IV. CONCLUSIONS

We have measured the magnetic behavior of $3d$ surface impurities on Au. We find the formation of magnetic moments for V, Cr, Mn, Fe, and Co. Titanium shows a magnetic scattering which is strongly temperature dependent and by 2 orders of magnitude smaller than the other magnetic surface impurities. Single Sc and Ni atoms are nonmagnetic. We have derived a theoretical result for the dephasing effect of $3d$ impurities within the Friedel-Anderson model.

Our experimental results are in qualitative agreement with our theoretical calculation using the predicted magnetic mo-

ments for $3d$ atoms on a Cu surface by Lang *et al.* However, the absolute value of the theoretical dephasing cross section within this model is roughly a factor 5 larger than our experimental results. On the other hand the same model yields rather good values for the residual resistance of $3d$ impurities in Au and Cu. It would mean a rather important step in the understanding of magnetic moments in metals if the success on one hand and the failure on the other hand of the Friedel-Anderson model could be explained.

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