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Magnetic behavior of Fe atoms on the surface of palladium

Gerd Bergmann
Institut für Festkörperforschung der KFA Jülich, Postfach 1913, D-5170 Jülich, Germany
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The magnetic properties of thin Pd films with Fe surface impurities are investigated by means of the anomalous Hall effect (AHE). The AHE measures the z component (perpendicular to the surface) of the magnetization and is sufficiently sensitive to investigate Fe coverages down to 0.01 atomic layers (atola). The magnetization varies strongly nonlinearly with magnetic field. For small Fe coverages, in the range from 0.01 to 0.1 atola the susceptibility is temperature independent. The author concludes that the Fe has lost its moment and represents a local spin-fluctuating system. For Fe coverages above 0.5 atola the magnetization shows a hysteresis which disappears with increasing temperature. In this range of coverage the Fe atoms possess a magnetic moment. The moments prefer the orientation perpendicular to the film and form an Ising ferromagnet. In the intermediate range around 0.3-atola Fe the susceptibility follows a Curie law. The large value of the susceptibility either requires the existence of super large moments of about $100\mu_B$ or is due to an indirect exchange enhancement of the magnetic field. Covering the dilute Fe-surface atoms with a few layers of Pd changes the magnetic behavior of the Fe completely. The magnetization follows a Brillouin function with $S = 8$ and $g = 2$ and describes the magnetization of free giant moments.

I. INTRODUCTION

Pd, as a nearly ferromagnetic metal, has rather interesting magnetic properties. Its Stoner enhancement factor is about 10 and describes the easy polarizability of the Pd matrix. Magnetic ions such as Mn, Fe, and Co when they are dissolved in Pd possess giant moments with a magnetic moment up to $15\mu_B$.[1-7] The magnetic ions polarize the Pd matrix so that about 200 Pd atoms contribute to the magnetic moment of the magnetic center. Among the magnetic ions Ni plays an exceptional role because it requires a threshold concentration to form magnetic moments.[8,9]

In this paper we investigate the magnetic properties of Fe atoms at the surface of Pd. The magnetic properties of metallic surfaces are rather interesting from a theoretical point of view as well as from an experimental and technical one. Unfortunately, there is little reliable information concerning the magnetic properties of surfaces. There are, for example, two controversial computer calculations for the change of the magnetic moment of Ni at the surface.[10,11] Of large technical interest is the question of whether the magnetic surface properties influence catalytic properties.

A surface atom is subject to several different influences. First, its electronic wave functions have only an overlap with a reduced number of nearest neighbors and decay exponentially into the vacuum at the surface. This influences the bandwidth and the electronic density of states at the Fermi surface.[11-13] Second, the surface atom experiences a strong noncubic "surface" field which removes the degeneracy of the d states and which yields a considerable shift of the local energy levels. This applies particularly to surface impurities such as Fe on a Pd surface, which we shall investigate.

Recent experiments by the author[14] showed an interesting behavior of the resistance of Pd. The resistance of quench-condensed Pd films increases at low temperature when a magnetic field is applied. The superposition of Fe (or Ni) atoms causes a similar increase in the resistance, whereas Cu atoms have no influence. This raised the question of whether the magnetoresistance has a magnetic origin and what the magnetic properties of the Pd film and the Fe atoms are.

Since the interaction between different Fe atoms at the Pd surface should be as small as possible, the measurements are extended to Fe coverages of less than $\frac{1}{100}$ atomic layers (atola).[15] This small concentration of Fe atoms can hardly be investigated by classical magnetization measurements. Other (bulk) magnetic impurities which are always present spoil the measurement even for thin foils. The use of thin Pd films does not help in this case since the thin film must be condensed onto a substrate which itself contains magnetic impurities. In addition, very high sensitivity is required. We use, therefore, the new and extremely sensitive method of the anomalous Hall effect (AHE).[16] The AHE is based on the fact that magnetic atoms in the interior and on the surface of a metal scatter the conduction electron asymetrically and produce an electric field (the AH field) perpendicular to the current and the magnetic moment. The AH resistance is essentially proportional to the z component of the magnetization. (The z direction is defined

perpendicular to the surface.) Besides the fact that this measuring method is extremely sensitive, it has the advantage that only the magnetic moment in or on top of the metallic film contributes, whereas magnetic impurities in the nonmetallic substrate do not effect the measurement because they are not felt by the current. Therefore the thin film with its favorable ratio of surface to bulk can be utilized. This method has already been applied to investigate the magnetic properties of thin Ni films on a nonmagnetic metal.[17]

II. EXPERIMENTAL PROCEDURE AND RESULTS

The apparatus in which the experiment is performed has been described in Refs. 17 and 18. In an ultrahigh vacuum of at least 10^{-11} Torr a Pd film is condensed onto a crystalline quartz plate at temperatures in the range between 5 and 40 K. The thickness of the Pd films lies between 50 and 70 Å. The Pd film is polycrystalline and has an electronic mean free path of 40 Å.[19] The Pd is evaporated by direct heating of a Pd wire with an impurity concentration of less than 10 ppm. The concentration of magnetic impurities is below 1 ppm.[14] The thickness of the film is measured by a quartz balance, which runs at helium temperature, with an accuracy of $\frac{1}{30}$ atola.[17] The Fe is evaporated with a condensation rate of about 0.1 atola per min after careful preheating of the Fe wire. The evaporation rate is calibrated before each evaporation step with an accuracy of 10%. The evaporation of the Fe is performed in steps of 5–10 sec at low Fe coverages. This yields an additional absolute error in the thickness of about 0.002 atola per evaporation step.

After each condensation the Hall resistance has been measured between -7 and $+7$ T with an accuracy of about 2×10^{-4}.[20] It is measured by means of two opposite electrodes. Since such a measurement always contains an Ohmic part, the Ohmic resistance R_{xx} is also determined for each field. Both values are fed into an on-line calculator and the Ohmic part is subtracted. The Hall resistance varies essentially linearly with the applied field

$$R_{xy}\sim -1100\times10^{-5}B\ (\Omega/\mathrm{T}).$$

The small deviation from linearity (less than 10^{-3}) is shown in Fig. 2 as crosses and is considerably less than the effect of $\frac{1}{100}$-atola Fe. The HE of the Pd is temperature independent in the temperature range between 6 and 25 K. In Fig. 1 the slope of the H curves of pure Pd is plotted as a function of the temperature. The total variation of the HE in this temperature range is less than 5×10^{-4}.

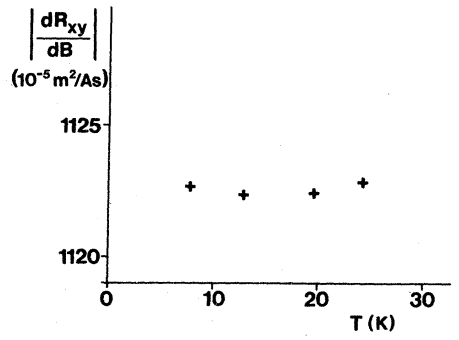

FIG. 1. Temperature dependence of the slope of the (linear) Hall curves of pure Pd films (thickness 60 Å).

The condensation of Fe yields an additional AH resistance. (The separation of normal and anormal Hall resistance is discussed in Appendix A.) Figure 2 shows the additional AH resistance of the Pd film superimposed with 0.004 ±0.001-atola and 0.01 ±0.002-atola Fe. The measurement was performed at 6.5 K.

The temperature is measured with a calibrated AuFe-chromel thermocouple which is glued with epoxy onto the bottom of the quartz plate. It has an accuracy of 2% or better in the experimental range. The thermocouple is in thermal equilibrium with the Pd film due to the high thermal conductivity of the crystalline quartz. The quartz plate can be heated by a resistor which is also glued with epoxy onto the bottom of the quartz plate.

The shape of the AH curves is almost independent of the Fe coverage up to about 0.2 atola as we shall see below (Fig. 5). This, however, changes drastically when the Fe coverage exceeds 0.5 atola. Figure 3 shows the AH curves for Fe coverages of 0.74 atola. At the lowest

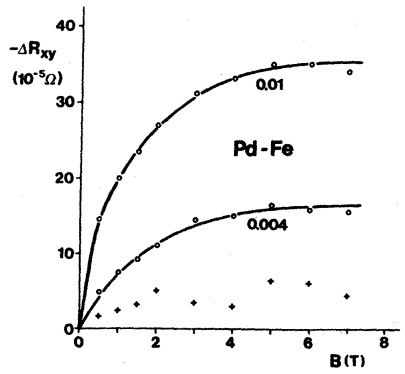

FIG. 2. Magnetization curves (measured by means of the anomalous Hall effect) of a Pd surface covered with a small fraction of an atomic layer (atola) of Fe. The numbers at the curves give the coverage in units of atola.

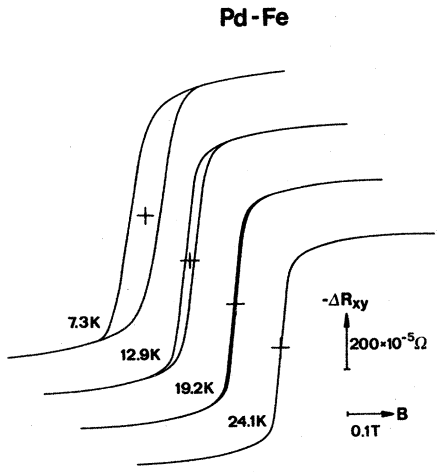

FIG. 3. Magnetization curves of Pd with 0.74-atola Fe at different temperatures.

temperature of about 7 K the AH curves show a hysteresis which disappears at higher temperatures. The hysteresis is due to a remanent magnetization in zero-field perpendicular to the surface. In addition the magnetization saturates at much lower fields.

The temperature dependence of the AHE of dilute Fe coverages is also rather interesting. In Fig. 4 the AH curves of a Pd film with a coverage of 0.034-atola Fe are plotted. The low-field values—within the accuracy of the measurement—are almost independent of the temperature.

In Fig. 5 the AH curves of three different Fe coverages (0.046-, 0.1- and 0.2-atola Fe) are plotted at two different temperatures. Since we

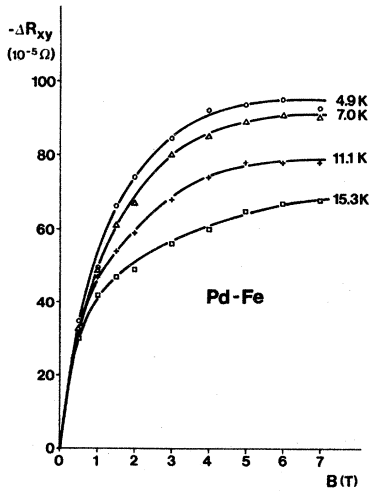

FIG. 4. Magnetization curves of Pd with 0.034-atola Fe at different temperatures.

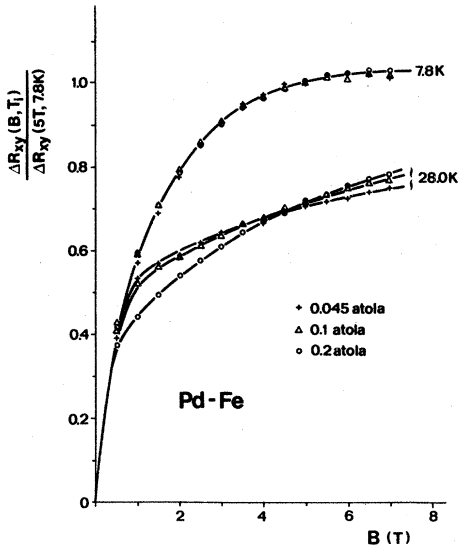

FIG. 5. Magnetization curves of Pd with three different coverages of Fe at two temperatures (7.8 K and 27.0 K). The three sets of curves are divided by their low-temperature value at 5 T.

wish to compare the field and temperature dependence for the different thicknesses, the set of curves for each thickness is divided by the value at 5 T of the low-temperature curve. Indeed the three low-temperature curves are almost superposed in this plot, indicating that they have the same shape. In addition, the high-temperature curves show almost the same fraction of ΔR_{xy} from the low-temperature curves and also behave rather similarly. In particular they have—independent of the coverage—a slope which hardly depends on the temperature. This behavior of the susceptibility is rather surprising because it rules out the possibility that the Fe possesses free magnetic moments. One knows, however, that Fe impurities in bulk Pd form free giant moments. Therefore an additional superposition of Pd on top of the Fe should change the temperature-dependent behavior of the magnetization of the Fe. For a check of this expectation the Pd film with an Fe coverage of 0.034 atola—plotted in Fig. 4—is superimposed by a second Pd film with a coverage of 4.6 atola. Figure 6 shows the AH curves of the inner- or bulk-impurity Fe. The magnetization is now indeed temperature dependent and represents, as we will discuss later, free magnetic moments. The magnitude of the AHE is considerably larger when the Fe atoms are bulk impurities than when they are surface impurities. The reason for this behavior is discussed in Appendices A and B.

Films with an Fe coverage larger than the critical value of about 0.5 atola show hysteresis

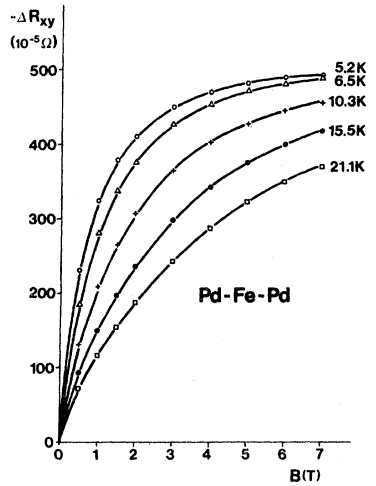

FIG. 6. Magnetization curves of the same system as in Fig. 4 after an additional coverage with 4.6-atola Pd. Now the Fe represents a bulk impurity.

at low temperature. In the intermediate range one finds an interesting temperature dependence of the intitial slope of the AH curves. In Fig. 7(a) the low-field part of the AH curves is plotted for a Pd film with 0.32-atola Fe at different temperatures. The initial slope is proportional to the reciprocal temperature as Fig. 7(b) demonstrates. We shall discuss below that the magnitude of the initial slope corresponds to magnetic moments of more than $100\mu_B$—or a strong exchange enhancement of the magnetic field.

III. DISCUSSION

A. The anomalous Hall effect

Phenomenologically the AHE is proportional to the z component of the magnetization. The use of the method for determining the magnetic behavior of a sample is discussed in detail in Appendix A.

B. Fe coverages above the critical value

Pd films with an Fe coverage above the critical value of about 0.5-atola Fe show a hysteresis. For these large coverages the Fe atoms at the surface possess a magnetic moment. The moments prefer the orientation perpendicular to the surface and are ferromagnetically ordered. This corresponds to a two-dimensional Ising model.

With increasing temperature the hysteresis decreases and finally vanishes. One may suggest that this happens at the Curie temperature. However, a temperature dependence of the anisotropy can not be excluded. The Curie temperature is at least equal to or larger than the temperature

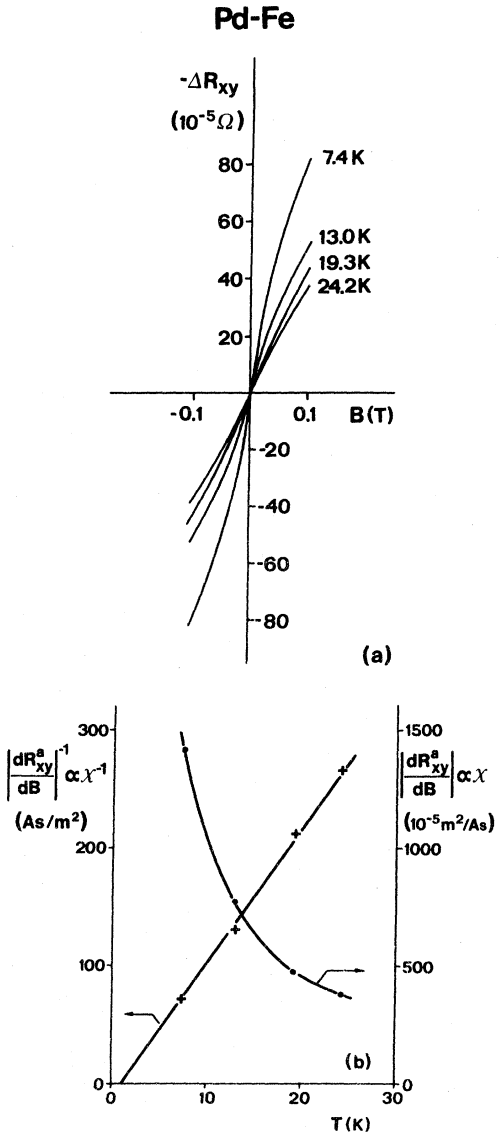

FIG. 7. (a) The low-field part of the magnetization curve of Pd with 0.32-atola Fe for different temperatures. (b) The reciprocal initial slope of these curves as a function of the temperature.

where the hysteresis disappears, which is about 20 K for the coverage of 0.74-atola Fe.

C. Small Fe coverages

For small Fe coverages much below 0.5 atola the interpretation of the measurements requires a detailed discussion. If the magnetic state is not known *a priori*, magnetization measurements do not generally permit an identification of the magnetic state. This limitation also applies, of course, to the measurements of the AHE. One realizes immediately that the Fe atoms do not possess free magnetic moments because the

initial slope of the AH curves, i.e., the susceptibility, is not inversely proportional to the temperature T but is temperature independent. Such a temperature independent susceptibility permits several different explanations and we shall discuss three possible models.

(a) The Fe atom does not possess a magnetic moment in the sense of the Anderson model,[21] which means in a mean-field approximation that $N_d(U+4J)<1$, where U and J are the Coulomb and exchange integrals between two electrons localized at the d impurity (see, for example, Ref. 22). Then the Fe plus its Pd environment represents a local spin-fluctuating system. Doniach[23] pointed out (for Ni impurities in bulk Pd) that for such a system the magnetization curve is nonlinear because the Stoner enhancement factor depends on the magnetization.

(b) The Fe atom forms a magnetic moment in the sense of the Anderson model. Owing to an antiferromagnetic interaction with the conduction electrons of the Pd (not the d electrons which show a ferromagnetic interaction) its magnetic moment is compensated at low temperature (Kondo effect). The magnetization curve of a Kondo system is nonlinear and shows the temperature-independent susceptibility[24] at low temperatures.

(c) The Fe atoms possess a magnetic moment and are ferromagnetically ordered within the x-y plane due to anisotropy. Although the magnetic structure of such a system in the x-y plane is very complicated (and known as the X-Y model), its magnetization J_z in a field perpendicular to the plane should be described qualitatively correctly by a mean-field theory. Such a calculation shows that the z component of the susceptibility is temperature independent between zero and the Curie temperature. In addition the curve of magnetization as a function of the field is, of course, rounded.

1. Model (c): Magnetic moments and two-dimensional order

Several arguments oppose model (c). First, the AH curves show the same shape down to thicknesses of 0.004-atola Fe. It seems questionable that the interaction is strong enough to form a ferromagnetic state in such a dilute system. Second, the AH curves show almost the same temperature dependence up to an Fe coverage of 0.2 atola. Model (c) suggests, however, an increasing transition temperature with increasing Fe concentration as for Fe impurities in bulk Pd.[4] Therefore the more concentrated films with their larger transition temperature should show a reduced temperature dependence in contrast to Fig. 5. In addition this model requires an explanation for the change of the smoothest direction from parallel to the film for small Fe coverages to perpendicular to the film for Fe coverages above 0.5 atola.

2. Model (b): Magnetic moment and Kondo effect

At first sight the Kondo effect appears to be an attractive explanation for the measurements, because the superposition of the Pd with Fe atoms causes a resistance minimum as a function of temperature as the author recently showed.[14] However, this argument weakens if one takes into account that (i) a magnetic field has the same effect as the Fe atoms and (ii) the resistance minimum does not change when the Fe coverage is increased and the Fe becomes ferromagnetic.

Nevertheless, a Kondo system at low temperatures has a constant, i.e., temperature-independent susceptibility and the magnetization saturates at large fields. However, the parameters do not fit with the Pd-Fe system under consideration. For the Kondo system the susceptibility is constant only at very low temperatures.[21] At finite temperature it follows approximately the law $\chi(T) \propto 1/(kT+2kT_K)$.[25] Since the measurements do not show a temperature dependence up to 20–30 K the Pd-Fe system should have a rather large Kondo temperature T_K above 100 K. On the other hand, the low-temperature magnetization curve of a spin-$\frac{1}{2}$ system follows the law[26]

$$\frac{M}{M_0} = \frac{\frac{1}{2}\mu_B g B}{[k_B^2 T_k^2 + (\frac{1}{2}\mu_B g B)^2]^{1/2}}.$$

Therefore the magnetization reaches $1/\sqrt{2}$ of the saturation value when the magnetic energy $\frac{1}{2}\mu_B g B$ is equal to the energy $k_B T_K$. In the Pd-Fe system this value is, however, already reached at fields between 1 and 2 T, which correspond in the spin-$\frac{1}{2}$ system to a Kondo temperature of 1–2 K. Although these relations will be changed in a magnetic system with large magnetic moments it is hard to believe that this discrepancy can be removed. Therefore the Kondo effect is a rather improbable explanation of the experimental results.

3. Model (a): Suppressed magnetic moment and local spin fluctuations

Although Fe impurities in bulk Pd possess a giant moment it is quite possible that their moment is suppressed at the surface. We shall discuss a simple model of a d-metal impurity at the surface which shows that the density of d states of an impurity atom may be quite different from

that in the bulk. The details are treated in Appendix B.

We consider first the d states of the atom in the crystal field of the surface. The potential splits the states with different $|m|$. Higher terms in the potential remove the degeneracy for $m = +2$ and -2 so that one obtains the energy levels drawn in Fig. 8. Only the states with $m = +1$ and -1 are degenerated. Of course, the Pd electrons hybridize with the local d states of the Fe impurity. The strong surface field causes a marked change of the resonance states of the Fe atom compared with an Fe atom dissolved in bulk Pd, which results in the splitting of the d states and a change in the widths of the resonance curves because the overlap is reduced. The first effect generally reduces the density of states at the Fermi energy whereas the second one may have the opposite effect. The total change can only be obtained by a (difficult) quantitative calculation. It appears, however, that clear differences in comparison with the bulk impurity occur and may change the magnetic moment. The latter may even be suppressed. If, however, the impurity forms a magnetic moment it is shown in Appendix B that under simplified conditions the magnetic moment possesses a lower energy in the orientation perpendicular to the surface, due to spin-orbit coupling. This is the experimentally observed anisotropy in the range of coverage where the Fe possesses uniquely a magnetic moment, i.e., for $c \geq 0.5$.

Anderson solved the problem of the magnetic impurities first in the resonance picture of Friedel,[27] which does not use a fixed set of eigenfunctions. Since the set of eigenfunctions changes with the moment of the impurity, it will also be altered by the application of a magnetic field. In the picture of the density of states the additional d density which forms a resonance curve may move up and down on the density of states of the host, minimizing the energy. For Pd as a host this picture is no longer correct since the Pd neighbors are polarized and therefore their local density of states also moves up or down in a magnetic field. This has been neglected in the calculation of the magnetization of Ni impurities in Pd (Ref. 23), which only considered the shift of the local density of the impurity atom.

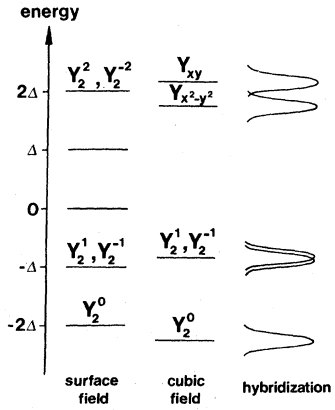

FIG. 8. Energy spectrum of a d atom at a surface of a metal.

The susceptibility of a homogeneous spin-fluctuating system has been calculated by Misawa[28] and Barnea,[29] who obtained

$$\chi(T) = \chi(0) - bT^2 \ln(T/T_2) + cT^3 \ln(T/T_3),$$

where b, c, T_2, and T_3 are adjustable parameters. (For pure Pd the formula gives only a small temperature dependence below 25 K.) The logarithmic term $T^2 \ln T$ goes beyond the results of former calculations[30,31] which had difficulties reproducing the maximum in the susceptibility. Similar corrections must be considered for local spin-fluctuating systems which are defined by the Wolff model[32] (see, for example, Refs. 33 and 34).

On the other hand, the application of the Landau theory provides us with a phenomenological description of the Pd system (for small magnetization). Here the free energy is written in powers of the magnetization[35]

$$F = \int d^3r \left[\tfrac{1}{2}\alpha(r) M^2(r) + \tfrac{1}{4}\beta M^4(r) - B M(r) + \tfrac{1}{2}\gamma |\nabla M(r)|^2\right],$$

where $\sqrt{\gamma/\alpha} = \mathcal{K}^{-1}$ is the correlation length in Pd. Minimization of F yields the expression for the space-dependent magnetization

$$B = \alpha M(r) + \beta M(r)^3 - \gamma \nabla^2 M(r). \qquad (1)$$

At the impurity the coefficients change so strongly that the power expansion is not sufficient and therefore one solves the equation only outside the impurity with boundary conditions (which are not known and fitted to the experimental results).

Although the cubic term of Eq. (1) yields a deviation from linearity for the magnetization in large fields, the expansion is not sufficient for the experimental range.

An appropriate calculation of the magnetization at finite temperature in high fields does not exist for a local spin-fluctuating system, at least to the knowledge of the author.

D. The intermediate range

Model (a) gives an explanation for the temperature dependent slope in the intermediate range

of Fe coverage. If the Fe atoms reach a critical concentration at the Pd surface they form a magnetic moment. This can be due either to the direct exchange interaction between the d orbitals of the Fe atoms or due to a critical indirect polarization of the Pd matrix.

One expects that the critical concentration of Fe atoms is already reached locally when the average concentration is still below the critical value. This phenomenon, which is well known for bulk systems such as CuNi, is due to statistical fluctuations in the concentration. The value of the moments formed is generally quite large. If one divides the saturated AH resistance by the initial slope $\Delta R_{xy}/(d\Delta R_{xy}/dB)$, one obtains a value with the units of a magnetic field. For Pd with 0.32-atola Fe this field has the value $B_0 = 0.2$ T at 7.4 K. For free magnetic moments one obtains from B_0 the effective number of μ_B according to

$$Sg = 4.46 \frac{T(K)}{B_0(T)} - g .$$

This yields an effective moment of about $150\mu_B$. If one assumes a strong Ising anisotropy, then one obtains a magnetic moment of about $50\mu_B$ from B_0 (setting $S' = \frac{1}{2}$ and $\mu = g'S'\mu_B$ and using the above relation). An alternative explanation for the large susceptibility may be an enhancement of the external field by the polarization of the Pd.

The magnetic behavior in the intermediate range of Fe coverage links the nonmagnetic range with the Ising ferromagnetic range because it shows the gradual formation of magnetic moments.

E. The magnetoresistance measurements

The lack of an Fe moment for dilute Fe coverages caused the author some difficulty in connection with the magnetoresistance measurements which were discussed in the Introduction. For the interpretation of these experiments the model of a magnetic sheet below the Pd surface has been discussed.[36-39] The present experiments do not support the existence of a magnetic sheet in the Pd film. In particular, the old question is raised in a new light: Why do nonmagnetic (fluctuating) Fe atoms cause the same resistance anomaly at low temperature as do both ferromagnetic Fe atoms and a magnetic field? The present experiment lets the magnetoresistance measurements appear in a new light, but further measurements will be necessary to solve the problem.

F. Fe impurities in the bulk of Pd

A superposition of the Fe atoms at the Pd surface by a few atomic layers of Pd changes the magnetic properties of the Fe centers dramatically (see Fig. 6). The AH curves show a temperature-dependent initial slope proportional to $1/T$. This corresponds to the magnetic behavior of free magnetic moments. The latter possess a universal behavior since their magnetization depends only on B/T. Therefore the AH curves are plotted in Fig. 9 for different temperatures as a function of B/T. The experimental points fall on one curve. The full curve is a Brillouin function for $S = 8$ and $g = 2$. This agrees quite nicely with giant moments which are known for bulk Fe impurities. McDougald and Manuel[40] could fit their magnetization measurements of bulk Fe impurities with an even larger S value of $S = 10$ and $g = 2$. The present measurement by the AHE demonstrates quite clearly that the bulk impurities behave very differently from the surface impurities and—for those who have reservations about this method—that the AHE is a successful method to measure magnetic properties.

IV. CONCLUSION

The method of the anomalous Hall effect is used to measure the magnetization of Fe impurities on the surface of Pd in the coverage range between 0.01- and 1-atola Fe. The experimental results are interpreted in a model which is quite analogous to the magnetic behavior of Ni in Ni_xCu_{1-x}, where the Ni is nonmagnetic at small concentrations and ferromagnetic at concentrations above

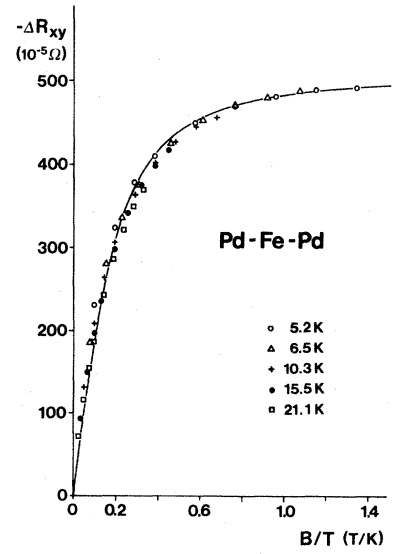

FIG. 9. The same magnetization curves as in Fig. 6, now plotted as a function of B/T.

40%. In the intermediate range the Ni may form a moment if the number of nearest Ni neighbors exceeds a critical value.

For a small coverage of the Pd surface by Fe atoms the Fe looses its magnetic moment. For large concentration with Fe coverages above 0.5 atola the Fe atoms possess a magnetic moment with an anisotropy favoring the orientation perpendicular to the surface and behave as an Ising ferromagnet. In an intermediate range of Fe coverage the Fe concentration locally reaches the critical concentration in statistical clusters and forms large moments which show superparamagnetism.

According to the author's interpretation, the single Fe atom on top of the Pd surface represents a local spin-fluctuating system. It is suggested that its behavior, which is quite different from an Fe impurity in bulk Pd, is due to the strong gradient of the electric field at the surface, which splits the energy of the *d* states of the Fe. If the Fe atoms are covered with as little as two layers of Pd they already approach the magnetic behavior of bulk Fe impurities.

APPENDIX A: THE ANOMALOUS HALL EFFECT AS A MEASURING METHOD FOR THE MAGNETIZATION

The author hopes that the present experiment shows that the AHE is a useful method to learn about the magnetic properties of metals. Therefore it is necessary to discuss the properties of the AHE critically and in some detail in light of our present knowledge.

1. Angular momentum

The AHE is due to the asymmetric scattering of the conduction electrons by the magnetic impurities. This requires, however, that the magnetic system possess a nonvanishing angular momentum.[41] Only then can the spin-orbit coupling which is responsible for the AHE cause an asymmetry in the scattering. For the AHE of single magnetic atoms in a matrix, Fert and Jaoul[42] showed within the Friedel-Anderson model that the position of the Fermi level with respect to resonance energy determines the magnitude (and sign) of the AHE. Therefore one may expect that the sensitivity of the AHE for a magnetic moment in the bulk and at the surface is different. We show in Appendix B that the position of the resonance energies and the Fermi energy may be quite different in the two positions.

2. Space-dependent sensitivity

Since the angular momentum of magnetic atoms at the surface is generally different from the bulk value, the sensitivity of the AHE will also be different. In addition, the AHE is proportional to the drift velocity of the conduction electrons. At the surface half of the conduction electrons have a reduced drift velocity because they are diffusely scattered at the surface. In addition, the asymmetrically scattered wave can only propagate into a half sphere which reduces the magnitude of the AHE at the surface. The increase of the sensitivity as a function of the distance from the surface is quite dramatic and plotted in Fig. 10. It will be examined in more detail in the future.

This different sensitivity of the AHE at the surface and in the bulk makes a quantitative comparison between the magnetic moment at the surface and in the bulk difficult. However, it also has advantages because it allows the measurement of the magnetization of bulk impurities in the presence of different concentrations of surface impurities whose magnetization is almost suppressed in the measurement.

3. Field-dependent scattering

One may speculate that the magnetic field can change the local distribution of the current. If, for example, the ratio of specular to diffuse reflection at the surface increases with the magnetic field, then the current density at the surface increases and it decreases in the bulk (if the total current is kept constant). A similar effect occurs for magnetic Fe atoms which are sandwiched between layers of Pd. If their moments are oriented perpendicular to the surface they may scatter the conduction electron differently from when it is disoriented. Again this changes the relative distribution of the current density. As a consequence the longitudinal and transverse (Hall) conductance of the film are changed. How-

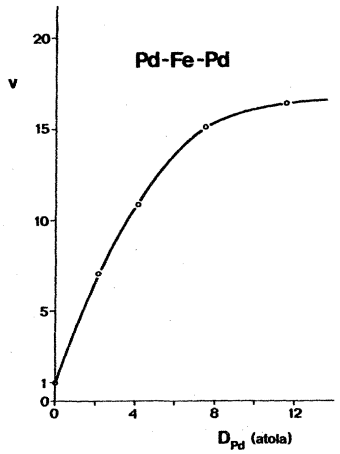

FIG. 10. Sensitivity ratio of the AHE of an Fe layer (0.10-atola) as a function of the distance from the surface. The surface sensitivity is set equal to 1.

ever, the Hall *resistance* is not altered to a first approximation. This shall be demonstrated in the case where the mean free path of the conduction electrons l_0 is much less than the thickness D and the fraction of conduction electrons which are specular reflected at the surface is p. The longitudinal and transverse conductance L_{xx} and L_{xy} may be derived by following Chambers[43]:

$$L_{xx} = Al_0 D\left(1 - \frac{3}{8}\frac{l_0}{D}(1-p)\right),$$

$$L_{xy} = Al_0 D\omega\tau\left(1 - 2\frac{3}{8}\frac{l_0}{D}(1-p)\right),$$

where ω is the cyclotron frequency and τ is the collision time of the conduction electrons. $A = S_F(e^2/12\pi^3\hbar)$ is proportional to the area of the Fermi surface. The Hall resistance is

$$R_{xy} = \frac{L_{xy}}{L_{xx}^2} = \frac{\omega\tau}{Al_0}\frac{1}{D}\left[1 + O\left(\left(\frac{l_0}{D}\right)^2\right)\right].$$

Obviously the Hall resistance does not involve the scattering mechanism at the surface because of the rearrangement of the current. This means that the Hall resistance is not influenced by (small) changes in the scattering mechanism. The same applies if the mean free path of the conduction electrons changes in one part of the film. This independence of R_{xy} of the scattering mechanism is of particular importance in the Pd system since Pd shows a magnetoresistance both without Fe and with small coverages of Fe. This means that the scattering mechanism of the conduction electrons changes with the magnetic field. According to the last argument, however, this should not alter the linear field dependence of the Hall resistance. The (almost) linear dependence of the Hall resistance of pure Pd and its temperature independence confirms the conclusion. The only effect of the magnetoresistance is that it reduces the accuracy of the measurement at low temperatures for small fields and small Fe coverage.

4. Separation of normal and anomalous Hall effect

It is at least desirable that the normal Hall effect is a linear function of the magnetic field. This is particularly important when the contribution of the AHE is only a small fraction of the total Hall effect. In the case of Pd covered with Fe atoms, the linear term of the normal Hall effect was separated by assuming that the AHE saturates at low temperature in the highest field. In practice it turned out that this normal Hall effect was—for small Fe coverages—identical with the normal HE of the pure Pd. Still, one cannot exclude the possibility that the correct AHE differs by a small linear correction from the AHE so determined. This separation—performed at low temperature—could then be used for all temperatures up to 25 K because the normal Hall effect of pure Pd was temperature independent in this range. The possible small uncertainty of the linear term hardly effects the results and the conclusions.

5. Temperature-dependent sensitivity

The AH constant R_s depends on the resistivity and is proportional to ρ^v, where v is between 1 and 2 depending on the model of the AHE. Since the resistivity changes by only 0.3% between 5 and 25 K this does not influence the experimental results.

6. Spin-flip processes

The normal, i.e., nonspin-flip scattering processes of the conduction electrons by the magnetic impurities show an asymmetry which is proportional to the z component of the moment. The contribution of spin-flip processes is not known in the resonance picture. (Hartree-Fock approximation and rotational symmetry are not mutually consistent.) For magnetic moments in Pd this problem is not so serious because the large polarization cloud of the Pd reduces the importance of spin-flip processes.

7. Dependence of the AHE on the magnetic moment

If the Coulomb energy U in the Anderson model is increased continously there is a critical value of U at which the impurity atom develops, a magnetic moment which further increases with increasing U. For small moments the contribution to the AHE increases linearly with magnetic moment. When spin-up and -down densities of states at the Fermi energy begin to differ considerably, then the AHE is no longer proportional to the moment and must be calculated as a function of the moment. (This is not always a disadvantage because it allows the position of the Fermi level to be localized with respect to the spin-up and -down density of states.) However, this causes no serious problems for magnetic moments in Pd because here the large number of polarized Pd atoms contributes much more strongly to the AHE than the central impurity atom. The Pd atoms are, however, only slightly polarized and their AHE is proportional to the magnetic moment. [In the present case the Fe atoms should show a positive AHE (Refs. 42 and 44), whereas the Pd should show a negative one which is obviously much larger.]

APPENDIX B: ENERGY STATES OF d IMPURITIES AT THE SURFACE

We consider the d states of a transition-metal atom at the surface of a metal. The surface is treated as a plane. The leading term in the potential is (see, for example, Ref. 45)

$$v(x,y,z)=A(x^2+y^2-2z^2).$$

An additional term proportional to $r^2=x^2+y^2+z^2$ shifts the energy of all d states but does not split them. One obtains the split energy levels as they are drawn in Fig. 8. The level separation Δ follows from the radial matrix element

$$\Delta=\tfrac{2}{7}A\int dr\, r^2R^2(r).$$

The sign of Δ depends on the sign of A. The degeneracy of the states Y_2^{-2} and Y_2^{+2} is removed by higher terms in the potential. Since the d states overlap, the wave function of the substrate one obtains a hybridization and the d levels are smeared to resonance curves.

It is obvious that the splitting of the d states generally changes the density of states at the Fermi energy and influences the formation of magnetic moments since the product $N_d(U+4J)$ is altered in comparison with the case where the d atom is a bulk impurity. Therefore it is not surprising that the magnetic moment of the impurity is different at the surface from its value in the bulk and it may even vanish at the surface.

Let us now consider the case of a surface impurity forming a magnetic moment. For the sake of simplicity we assume the distribution of resonance states as indicated in Fig. 8. The resonance curves shall be well separated (with the exception of the $m=+1$ and -1 state), i.e., so that the individual linewidth is smaller than the level separation Δ. (Otherwise the hybridization mixes the d states a second time and the problem becomes rather complicated.) The (strong) exchange interaction shifts the spin-down states below the spin-up states and the Fermi level crosses the $m=\pm1$ state of spin up. We want to consider the anisotropy of the spin and discuss first the case when the magnetic moment points into the z direction. The anisotropy of the orientation of the magnetic moment is due to the spin-orbit coupling

$$v_{so}=\lambda\vec{s}\cdot\vec{l}.$$

In the present orientation the spin-orbit coupling yields only two diagonal matrix elements which do not vanish:

$$\langle Y_2^1|v_{so}|Y_2^1\rangle=-\langle Y_2^{-1}|v_{so}|Y_2^{-1}\rangle=\lambda\langle S_z\rangle.$$

This causes a splitting of the two degenerated states as drawn in Fig. 8 and lowers the energy by $\frac{1}{2}N_{\pm1}(\lambda)^2$. ($N_{\pm1}$ is the density of states of the $m=\pm1$ resonance curve at the Fermi energy. The decrease of energy is quite analogous to Pauli paramagnetism where the field shifts the two density-of-states curves relative to each other by $2\mu_B B$.) In second-order perturbation theory the off-diagonal matrix elements also yield contributions proportional to λ^2 which are, however, much smaller in the present model because they contain an energy denominator.

When the magnetic moment is oriented within the plane then all diagonal matrix elements of the spin-orbit coupling vanish. Now one has only contributions in second-order perturbation theory. Again their terms are smaller [$1/\Delta$ is smaller than $N_{\pm1}$ (non-spin-flip matrix elements) and the inverse of the separation of spin-up and spin-down states is smaller than $N_{\pm1}$ (spin-flip matrix elements)]. Within the simplified model the spin-orbit interaction favors the orientation of the magnetic moment perpendicular to the surface.

Since the AHE, i.e., the asymmetric scattering of the conduction electrons, is due to the spin-orbit coupling and since the latter is particularly effective when the Fermi energy cuts the resonance curves with opposite m (Fert-Jaoul model[42]) and depends strongly on δ_m^2 one realizes easily that the sensitivity of the AHE at the surface may be different from the bulk.

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