

EFFECT OF HYDROGEN AND OXYGEN CHEMISORPTION ON THE HALL VOLTAGE IN THIN LAYERS OF PALLADIUM AND PLATINUM

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Results of measurements of changes of the Hall voltage in thin layers of palladium and platinum are reported during chemisorption of hydrogen, oxygen, and during interaction of preadsorbed oxygen with hydrogen. In all the systems studied the prevailing effect is the decrease of the Hall voltage during chemisorption of the gas. The reasons of this decrease are geometrical (the effective cross section of the metal layer decreases as a result of the formation of a surface compound) and electronic. Hydrogen chemisorption leads to a decrease in the mobility of conduction electrons, as it is shown in the discussion based on the two-band model of metal. The possible influence of virtual levels formed in the chemisorption is discussed. Variation of the Hall voltage during hydrogen chemisorption exhibits an extreme which may be accounted for either by the existence of two forms of the adsorbed particles, or by an indirect interaction among the adsorbed particles.

Gas adsorption over clean surfaces of thin metal layers (thickness 100–1000 Å) prepared by condensing metal vapours on a cooled, dielectric, usually amorphous substrate in ultra-high vacuum leads to changes of values of some physical characteristics of the metal. These changes are a consequence of the formation of a chemical bond between surface metal atoms and molecules of the adsorbate. Therefore, it may be expected that information on the nature of this bond may be obtained by studying these changes. One of the most frequent methods, comparatively easiest to carry out experimentally, is the investigation of variation of the electrical conductivity of thin layers^{1–3} during chemisorption. From these studies conclusions have been made concerning the polarity of the chemisorption bond, the role of various groups of electrons in the formation of this bond, the role of adsorption intermediates in a catalytic reaction *etc.*^{1–6}.

The interpretation of variation of the electrical conductivity has been, however, prevalently speculative. This is because the final expression for the electrical conductivity of a thin metal layer contains a series of parameters and direct experimental data on their changes during chemisorption have not been so far available. Besides it, so far there has not been put forward a general theory of transport phenomena in thin metal layers based on a sufficiently realistic model. It is evident, therefore, that achieving an unambiguous interpretation of the above mentioned data – namely in connection with elucidation of the nature of the chemisorption bond – requires a combination of several experimental methods. Results of measurements of electri-

cal conductivity changes can be conveniently combined with results of measurements of changes of other transport coefficients (galvanomagnetic, thermomagnetic, thermoelectric *etc.*). This communication is a part of a more extensive study⁷ of the galvanomagnetic phenomena in thin metal layers and the influence of chemisorption on these phenomena. Results on the measurements of changes of the Hall voltage of palladium and platinum films during hydrogen and oxygen chemisorption will be reported here.

The isothermal Hall voltage U_H for a sample in the form of a rectangular parallelepiped can be written as

$$U_H = R_H I_s B / d, \quad (1)$$

where R_H is the Hall coefficient, I_s the current passing through the sample in the longitudinal direction, B the induction of the outer magnetic field, and d the sample thickness. The expression for the Hall coefficient can be obtained by solving the Boltzmann transport equation in the effective mass and isotropic relaxation time approximations⁸

$$R_H = (12\pi^3 \hbar / ec) (\tau / \langle m^* \rangle l A), \quad (2)$$

which reduces in the case of free electrons to

$$R_H = \pm (n^* |e| c)^{-1}, \quad (3)$$

τ is the relaxation time, $\langle m^* \rangle$ the average value of the effective mass of current carriers, l their mean free path, A the area of the Fermi surface, n^* the density of current carriers; \hbar , c , e , π are the usual constants. The sign of the coefficient R_H determines the type of the dominant conductivity; ($R_H < 0$: *n*-type conductivity; $R_H > 0$: *p*-type conductivity). For transition metals the two-band model has been often used^{8,9}. Within the framework of this model the Hall coefficient is given (in the approximation of independent bands and free electrons) by

$$R_H = \frac{1}{N|e|c} \frac{n_h \mu_h^2 - n_e \mu_e^2}{(n_h \mu_h + n_e \mu_e)^2}, \quad (4)$$

where n is the number of current carriers per one metal atom, μ their mobility, and N the number of atoms in a volume unit of the metal. The subscripts *e* and *h* refer to electrons and holes, respectively. When passing from a three dimensional bulk sample to a thin layer in which the mean free path is comparable to the layer thickness, the Hall coefficient becomes a function of the layer thickness. According to the Fuchs-Sondheimer theory¹⁰ this dependence is given by

$$R_{Hf} = R_H, \quad d \geq l \quad (5)$$

$$R_{Hf} = R_H \frac{1-p}{1+p} \frac{4}{3} \frac{1}{d[\ln(1/d) + 0.423]^2}, \quad d < l$$

Here, $0 \leq p \leq 1$ means the probability of specular reflection of the current carriers on the film surface, R_{Hf} is the Hall coefficient of the thin layer, and R_H that one of the bulk material (as given by (2) or by (5)).

EXPERIMENTAL

The experimental arrangement and the procedure of data evaluation was described elsewhere^{7,11}. Thin metal layers, *i.e.* films 200–700 Å thick, were prepared by evaporating the metal of spectral purity from a resistively heated filament (diameter 0.3 mm) and by condensing its vapours onto a cooled (~ 200 K) hard-glass substrate. The distance between the filament and the substrate was 10 ± 2 mm; the evaporation rate varied from film to film in the range 5–40 Å/min, and the evaporation was carried out at background gas pressures 10^{-9} – $5 \cdot 10^{-8}$ Torr. The films were annealed at 80–90°C for 30–60 min. During the annealing the value of their electric resistance decreased to 10–40% depending on the evaporation rate and film thickness. Measurements were carried out at 273 K using the direct-current method in magnetic fields up to 4 kG. The magnetoresistance effect was unmeasurably small for all the films. A thermocouple gauge was used to measure the stationary pressures. Electrolytic hydrogen was purified by means of a palladium diffusion unit. Oxygen was prepared by thermal decomposition of potassium permanganate degassed in high vacuum.

RESULTS AND DISCUSSION

The electric resistance of the films was measured during film condensation. Typical results for palladium and platinum are shown in Fig. 1. The dependence can be approximated in bi-logarithmic coordinates by two straight lines which cross each other (with thicker films still another break can be observed sometimes – see Fig. 1). Such a type of dependence of the film electric resistance on the evaporation time is probably typical for the films formed by metal agglomerates whose size is a function of the evaporation rate, temperature and chemical nature of the substrate, pressure and composition of the residual gases. With films of metals characterized by a high

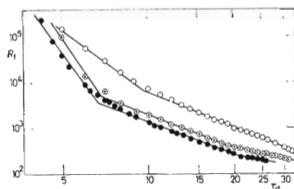


FIG. 1

Typical Dependences of Film Resistance R_f (Ω) on Evaporation Time τ_d (min) at a Constant Evaporation Current

- Pd, evaporation rate $v_d = 10$ Å/min;
- Pd, $v_d = 12$ Å/min; ● Pt, $v_d = 6$ Å/min.

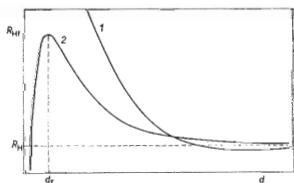


FIG. 2

Schematic Presentation of the Hall Coefficient R_{HF} vs Metal Layer Thickness d Dependence

R_H the Hall coefficient of the bulk sample; 1 theoretical curve¹⁰; 2 experimental dependence, films of copper¹³, gold¹⁵, platinum¹⁴, several other metals¹⁶.

cohesion energy (*e.g.*, tungsten) the film grows practically in monolayers in view of the small mobility of atoms over the substrate surface; the electric resistivity vs evaporation time dependence is then given by a single straight line in the bi-logarithmic coordinates¹².

It is important from the point of view of the measurements discussed here that very thin layers formed by metal agglomerates exhibit an anomalous behaviour. The dependence of the Hall coefficient upon the layer thickness does not obey equation (5), but at a certain critical thickness goes through a maximum (Fig. 2). One of the reasons of the anomalous behaviour of the Hall coefficient in the region of low film thickness is presumably the presence of voids in the metal layer, *i.e.* the presence of regions in which the substrate surface is exposed into the gaseous phase. The real value of the current density is then higher than its value calculated from the mean thickness as determined with the use of the film weight. Besides it, with the change of the film thickness the size of film microcrystals varies and this results in a variation of the magnitude of contributions of the current carriers scattering at grain boundaries to the value of transport coefficients¹⁷. Platinum films, *e.g.*, exhibit lateral grain dimensions¹⁸ about 100 \AA^2 , while reported values¹⁴ of the mean free path of current carriers in the metal are about 500 \AA . This together with some other factors leads to a complicated dependence¹⁹ of the transport coefficient values on the layer thickness, namely for thin films. In the case of the Hall coefficient these factors lead to a substantially different dependence than that one given by equation (5). Let us note here that the results of our measurements⁷ on films of twelve various metals showed that a good agreement of the experimental data with equation (5) was rather an exception than a rule, namely for thinner films.

In all measurements reported in this communication the Hall voltage U_H was a linear function of the external magnetic field induction B (Eq. (1)) and its relative change during chemisorption was independent of the magnitude of this field. Variations of electric conductivity during chemisorption in all systems studied were in agreement with the published results^{4,20-22}; therefore, this fact will not be mentioned explicitly in the following text.

Palladium. The value of U_H during hydrogen chemisorption decreases for films $200-600 \text{ \AA}$ thick. The observed character of changes shows that the dependence of U_H on the amount of adsorbed hydrogen exhibits a minimum which is analogous to the extremes observed in the same system when variations of the electrical conductivity²¹ and the thermoelectric power²³ were measured (Fig. 3). A part of the change at the minimum of U_H is reversible and corresponds to the weakly bound hydrogen.

During the chemisorption of oxygen the value of U_H decreases (Fig. 4); with some thicker films, however, it increases ($d > 600 \text{ \AA}$). The electric resistance of the films increases in both cases. Over some films the interaction of preadsorbed oxygen with hydrogen was studied. The changes of U_H (Fig. 4) show unambiguously that pre-

adsorbed oxygen reacts with hydrogen to form a product, evidently water⁴ which desorbs. The reaction can be repeated on the same surface practically without limitations. It may be concluded from the observed variation (Fig. 4) that after product desorption the excess unreacted hydrogen from the gaseous phase is chemisorbed on the freed adsorption sites. A part of this chemisorbed hydrogen is weakly bound (similarly as in the chemisorption of hydrogen on a clean surface), and desorbs when the gas phase pressure over the adsorbent decreases.

Over some films the temperature dependence of the electric resistance and of the Hall voltage were measured, too. Values of the temperature coefficients of the electric resistance varied in the range $\alpha = 1-2 \cdot 10^{-3} \text{ grad}^{-1}$ (for bulk palladium $\alpha = 3.7 \cdot 10^{-3} \text{ grad}^{-1}$)²⁴ and the value of the ratio $\beta = R_{\text{Hf}}(273 \text{ K})/R_{\text{Hf}}(80 \text{ K}) = 1.12$, i.e. nearly the same as for the bulk metal²⁴. Values of both these coefficients decrease after covering the surface with hydrogen (α by 15%, β by 5.5%).

Platinum. The value of U_{H} decreases during hydrogen chemisorption (Fig. 5), and this change is quite reversible within the experimental error: after pumping off the gaseous phase from the measuring cell the U_{H} value settles at the value of the clean-surface film. Similarly, oxygen chemisorption causes a decrease of U_{H} in films

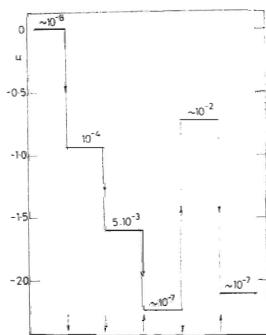


FIG. 3

Hall Voltage Changes $u = \Delta U_{\text{H}}/U_{\text{H}}$ (%) During Hydrogen Chemisorption over a Palladium Film

↓Hydrogen dose; ↑gaseous phase pumped off; values of gaseous phase pressure after reaching the stationary state ($B, I_s = \text{const}$).

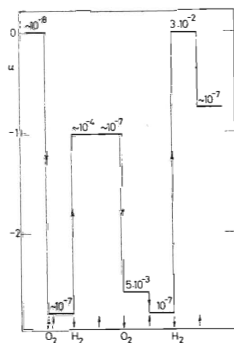


FIG. 4

Hall Voltage Changes u (%) during Oxygen Chemisorption and in Reaction of Pre-adsorbed Oxygen with Hydrogen over the Palladium Film Surface

↓Gas introduced; ↑gaseous phase pumped off; gas species indicated at the particular dose; $B, I_s = \text{const}$.

100–300 Å thick. Neither the magnitude nor the character of these changes depended on whether the chemisorption took place over a clean surface or a surface previously treated with hydrogen (adsorption and desorption). For that reason, data for both hydrogen and oxygen are presented in one figure (Fig. 5). Preadsorbed oxygen reacts with hydrogen to form water over platinum surfaces, too. Unlike with palladium, however, the stationary values of U_H (reached after the reaction took place) are not always the same. The scatter of the U_H values was with some films as large as 6% (*i.e.* more than half of the entire change of U_H caused by oxygen chemisorption over a clean film surface) after multiple repetition of the process. Possible reasons of this phenomenon are: *a*) incomplete desorption of the reaction product or incomplete consumption of all preadsorbed oxygen in the reaction; *b*) recrystallization of the film or of its surface layer due to the evolved reaction heat. As it is known²⁵ that during chemisorption over a platinum surface a migration of metal atoms occurs which results in a reconstruction of the surface layer of the metal, the second reason (*b*) appears to be more plausible.

The results reported here are in agreement with a more general rule^{7,19} stating that the prevailing effect during hydrogen chemisorption is a decrease of the Hall voltage over *n*-type conductors (*e.g.*, Ti, Ni, Pd, Pt), and its increase over *p*-type

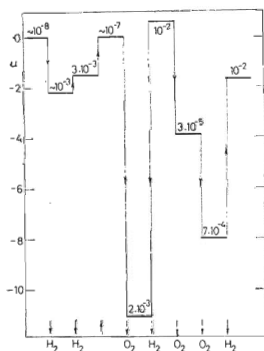


FIG. 5

Typical Hall Voltage Changes (%) during Hydrogen and Oxygen Chemisorption and Their Reaction over the Platinum Film Surface (Thickness 160 Å)

Designation of gas doses and stationary pressure values the same as in Fig. 3 and 4.

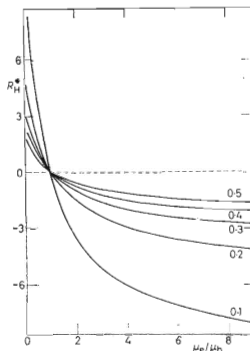


FIG. 6

Dependence of the Hall Coefficient $R_H^* = R_H N |e| c$ for a Compensated Metal ($n_e = n_b = n$) on the Mobility Ratio μ_c/μ_h of Current Carriers, Calculated from Eq.(4)

The number of carriers n per one metal atom is the parameter of the curves.

conductors (Nb, Re, Mo, W, Fe). The effects taking place over thin metal layers may be classified into two categories. To the first category belong those effects which are due to the finite dimensions of the sample: the disturbed translational symmetry at the film surface manifests itself in a limitation of the mean free path of electrons in the metal. The second category form those effects that hang together with a different coordination of the surface atoms of the metal and with a different electron density close to the surface in comparison with the bulk of the metal. Thus, the effects of the first type are rather geometrical, while those of the second type show themselves directly in the differences of the electron structure of thin layers in comparison with the electron structure of the corresponding metal as derived assuming the validity of the Born-von Kármán conditions. Besides it, in reality films are usually polycrystalline and contain many defects which scatter the conduction electrons. Scattering of electrons in real films, namely the scattering at grain boundaries (largely ignored so far) may have significant consequences as far as the interpretation of the variation of transport coefficients due to chemisorption is concerned¹⁹. By the geometrical effects we mean the change in the effective film thickness due to a shift in the position of the potential barrier near the metal surface caused by chemisorption. The simplest model of chemisorption assumes that a compound is formed from the surface atoms of the metal and the adsorbate. As a result, the contribution of the surface atoms to the collective and cooperative properties of the metal is limited or entirely eliminated ("demetalization")²⁶. The concept of demetalization makes it possible to explain changes in values of some transport coefficients of thin layers in those cases where a strong chemisorption bond is formed (*e.g.*, oxygen). However, this concept cannot be applied in a general way — as it was shown earlier^{7,27} — and represents a considerable simplification. The concept of demetalization, together with the Fuchs-Sondheimer relations, was sometimes used^{13,16,28,29} to calculate the absolute value of the film thickness change during chemisorption. Because of the reasons indicated in this communication and because of a considerable arbitrariness in the choice of numerical values of some parameters, the values resulting from such calculations may be regarded at best as rough estimates only. Changes in the effective thickness of the metal layer are probably responsible for a larger part of the change of the Hall voltage as observed in the systems O₂/Pd, Pt. This view is supported by the character of the dependence U_H vs film thickness as observed for O₂/Pd.

Main factors of the electronic nature are: *a*) formation or disappearance of localized surface electronic states; *b*) a shift in the position of the Fermi level or a change of the area and/or of the shape of the Fermi surface; *c*) a change in the magnitude of relative contributions of various mechanisms of the current carriers scattering. In a correct interpretation one has to consider that none of the changes mentioned above occurs independently. Thus, *e.g.*, the existence of localized surface states modifies the surface potential barrier and in this way also the effective layer thickness,

conditions of the surface scattering of current carriers and – consequently – their mobility *etc.* The resulting effect – as determined experimentally – is then a superposition of several contributions differing in magnitude and even in the sign.

The surface localized states which originate (in the case of transition metals) in gaps on the boundary of the Brillouin zone or within the Brillouin zone in gaps formed as a consequence of the *s-d* hybridization³⁰ and spinorbital splitting³¹ can play a role in hydrogen chemisorption, especially if they do not lie too deep below the Fermi level.

With respect to the interpretation of the electric transport properties, those surface states which lie very close to the Fermi surface are important. To determine the precise position of these states the complex band structure of the metal must be known; this is, however, not the case for platinum and palladium. Another serious complication represents the non-ideal structure of the surface of the real metal (reconstruction of the surface layer, defects, impurities *etc.*). For polycrystalline materials the situation is complicated by the lack of information on the abundance of various crystal planes in the surface. The question concerning the role of surface states during chemisorption is thus not clear, namely with regard to the quantitative aspects. However, interesting results can be expected in this field.

The change in the position of the Fermi level during chemisorption does not seem to be probable in the systems H_2/Pd , Pt , as the density of states in the non-fully occupied *d*-band of the metals is high and the number of hydrogen atoms adsorbed is small in comparison with the total number of metal atoms (ratio $\sim 10^{-2}$). The main effect would be rather an indirect one even in this case: a change in the contribution of the *s-d* conduction electrons scattering to the over-all value of the transport coefficient^{7,23}.

Therefore, variation of the mobility of the current carriers can be regarded as the most probable reason of the observed changes of the Hall voltage. Fig. 6 represents the dependence of the Hall coefficient on the mobility ratio μ_c/μ_h calculated from equation (4). It can be seen from this figure that for palladium and platinum ($\mu_c \gg \mu_h$) a decrease in the electron mobility leads to a decrease in the absolute value of the Hall coefficient and, consequently, of the Hall voltage, too. For palladium $n_e = n_h = 0.375$; for platinum³² $n_e = n_h = 0.405$.

The main fraction of the electric current is thus carried in palladium and platinum by the *s*-electrons. If we restrict ourselves to these electrons only, their mobility can be calculated as

$$\mu = (U_H/R_f)(Lc/BI_s w), \quad (6)$$

where R_f is the electric resistance of the metal sample, L and w its length and width, respectively. The mobility of electrons in the metal and its changes during chemisorption can thus be calculated from the measured values of U_H and R_f . The calculated mobility values decrease during hydrogen chemisorption, too. However, no quantita-

tive conclusions can be made from them in view of the simplifying assumptions under which equation (6) was derived.

It was found³³ with the use of the autocorrelation formalism that the value of the Hall coefficient is indirectly proportional to the square of the state density at the Fermi level. The decrease of the absolute value of this coefficient, which evidently causes the observed decrease of U_H during hydrogen chemisorption over palladium and platinum, can be then explained as a result of an increase of state density at the Fermi level. This increase³⁴ may be due to the formation of virtual levels in the vicinity of the Fermi level during the chemisorption.

The dependence of the U_H value on the amount of adsorbed hydrogen (Fig. 3) indicates that presumably two forms of bound hydrogen exist on the palladium surface which differ in their influence on the current carriers mobility. These conclusions support to a certain extent the theoretical calculations of Toya⁶. It follows from his results that during hydrogen chemisorption first of all the free surface valences of the metal are saturated and polarized covalent bonds $\text{Pd}^{\delta+}-\text{H}^{\delta-}$ (*r*-type bond) are formed. Further hydrogen is chemisorbed in the protonized form (*s*-type bonds). Relative abundance of the *r*- and *s*-forms is a function of the surface coverage, the temperature at which the chemisorption occurs, chemical nature of the adsorbent, and structure of its surface.

Let us add here that the extremes on the curves expressing the dependence of the transport coefficient values on the surface coverage may be caused also by indirect interactions between adsorbed particles mediated by a residual oscillating electron density which screens the charge of the adsorbed particle¹⁹.

It is essential to realize that the variation of the values of transport coefficients in thin layers during chemisorption cannot be consistently explained in a general way as a result of the change of one single parameter: *e.g.*, the changes which are essential in interpreting conductivity data may not be always essential in interpreting galvanomagnetic data and *vice versa*. In any case, however, combination of the results of several experimental methods reduces the number of unknown parameters involved in an interpretation.

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