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1995 J. Phys.: Condens. Matter 7 2687

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The influence of hydrogen at pressures up to 2000 Pa on the work function of Cu(111)

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Received 9 November 1994, in final form 26 January 1995

Abstract. (111) surfaces of copper, grown epitaxially on a clean (001) face of a ruthenium crystal, were exposed to hydrogen or deuterium at pressures p up to 2000 Pa, at temperatures from 290 to 440 K. The concomitant changes of the work function ϕ were recorded photoelectrically. While coadsorbed impurities influenced the absolute value of ϕ , the slope $d\phi/dp$ was found to be roughly constant and independent of the temperature in the pressure range $400 \leq p \leq 2000$ Pa. The slope of the coverage $d\theta/dp$, calculated from low-temperature adsorption data in the literature, is also constant in the above temperature and pressure range. Thus the variation of ϕ follows the chemisorption of hydrogen atoms due to the tail of the Boltzmann distribution. The effects of impurity adsorption and desorption are discussed.

1. Introduction

The adsorption of gases on *well-defined metal crystal surfaces* is usually studied under UHV conditions. In these experiments surfaces are exposed to small doses of gases, introduced to the system at low pressures ($p \leq 10^{-4}$ Pa). Under these conditions most of the tools of surface science can be applied and the impurity level of the gases introduced into the system will have a negligible effect on the measured quantities. On the other hand, at high pressures impurities with high sticking coefficients, even at very low concentration, will have a major effect on the adsorption properties. Even though it is difficult to isolate the various parameters at high pressures, investigation of this regime is of great practical importance, e.g., for heterogeneous catalysis, adsorption-induced embrittlement, and hydrogen absorption in hydride-forming metals and alloys. Moreover, adsorption at high pressure is intriguing from a theoretical point of view as well: under these conditions reversible adsorption may play an important role. In cases with activation barriers for adsorption, the tail of the Boltzmann distribution function may supply enough molecules to overcome the activation barrier.

This work was intended to bridge partially the pressure gap mentioned. We looked for a clear ‘fingerprint’ of the adsorption in a given gas/metal system at high pressures. It was planned to refer to the high-pressure adsorption results in the literature on the same system, obtained by ‘state of the art’ surface science techniques, under fully controlled conditions, at low pressures.

Adsorption of hydrogen on copper was chosen as a model case. This system is usually considered to be a relatively simple one, both since hydrogen is the simplest atom and since copper has a closed d shell. An activation barrier of ~ 0.7 eV [1] (for hydrogen molecules in their ground state, see below) is involved in the process. Accordingly the sticking coefficient for H_2 is very low [2] at room temperature ($S_0 \sim 10^{-5}$). The studies

closely related to this work, reported in the literature, can be divided into two categories, according to the manner of overcoming the activation barrier.

(i) *Molecular beam studies.* In these experiments the surface is exposed to a supersonic molecular beam of hydrogen and the sticking coefficient is measured as a function of energy of the hydrogen molecules. The first experiments yielded an activation barrier $E_{\text{act}} = 0.2\text{--}0.3$ eV. These included the pioneering study by Balooch *et al* [3], the determination of the angular dependence of the sticking coefficient by Anger *et al* [2], and the investigation of the sticking of a seeded beam by Berger *et al* [4]. The latter authors observed that the vibrational energy of the hydrogen molecule contributes 20% to the sticking coefficient. In a very recent (1992) set of experiments Rettner *et al* [5] varied the vibrational temperature up to 2100 K. From analyzing the data they deduced that the height of the activation barrier for a hydrogen molecule in the ground vibrational and rotational state is $E_{\text{act}} = 0.67$ eV. They attributed the lower values obtained in the past to contribution of excited molecules.

(ii) *Permeation experiments.* The back side of a copper crystal, heated to ~ 1000 K, is exposed to a high pressure of hydrogen (10^{-5} Pa). Hydrogen atoms diffuse through the copper bulk and desorb to the vacuum on the front side of the crystal. In 1982 Comsa and David [6] performed time of flight measurements on the desorbed hydrogen and found that the hydrogen molecules carry a very narrow distribution of kinetic energies centred around kT_s , where T_s is the surface temperature. In later experiments Kubiak *et al* [7] and Michelsen *et al* [1] also studied the internal energies of the outcoming hydrogen molecules, using multiphoton ionization. They found that these molecules are highly excited.

We measured changes in ϕ of a (111) face of copper with hydrogen present at pressures up to 2000 Pa at room temperature and above. For this system and under these conditions the relaxation time for equilibrium between adsorption and desorption is very low (much less than 1 s). We found that in the pressure range 400–2000 Pa the effect of impurities on the slopes $d\phi/dp$ is negligible: in this range the work function change is due to reversible chemisorption of hydrogen atoms on clean copper. This conclusion is strongly supported by an analysis of the data, involving both low-temperature, low-pressure adsorption [2–5] and desorption [1, 6, 7] results by other authors. The room-temperature results are also in accord with work function measurements on copper, deposited on glass, in the presence of hydrogen.

The method chosen for the determination of the work function changes was based on the photoelectric threshold, since, at the pressures employed, methods involving a reference electrode (such as the Kelvin probe method) could have given results distorted by adsorption at the reference electrode.

2. Experimental details

The experimental system comprises two UHV chambers: one chamber for the characterization of the samples and another one where the sample can be exposed to high ambient gas pressures. This second chamber is built on top of the first one, and separated from it by a gate valve. The sample can be transferred from one chamber to the other by means of an extension of a commercial manipulator using a telescopic system, described elsewhere [9]. This enabled the transfer of the sample from cell to cell within minutes.

In the lower UHV chamber, serving for the characterization of the sample, a Ru single-crystal platelet with a (0001) main face, covered by Cu, was studied. It is well known [10–12] that Cu grows epitaxially, with the (111) face, on such a Ru surface. Prior to

depositing Cu, the Ru crystal underwent a series of cleaning and annealing treatments [10–13]. This involved several repeats of the following sequence: (i) Ar sputtering at room temperature and at 1100 K; (ii) baking in the presence of O₂ at 1100 K; (iii) desorbing oxygen and annealing at 1570 K. After each sequence the sample was cooled down to room temperature, and the Auger and LEED spectra were checked. Subsequently a controlled amount of O₂ (20 L) was let in and the sample was checked by TDS for desorption of CO. The sequence was repeated until all these tests gave satisfactory results. Cu was always deposited only on clean Ru surfaces; before each set of H₂ adsorption experiments the old Cu layers were flashed away and a fresh Cu deposit was prepared. The evaporation was preceded by outgassing of the W basket and the ultraclean (99.999%) Cu at about 850 K for an hour or more, until the background pressure (2×10^{-7} Pa) was not affected by the outgassing from the W basket. The thickness of the Cu layers was established by calibrating the evaporation time by TDS of Cu, and establishing the Cu coverage from the ratio of two TDS peaks, using literature data [10, 14–18]. Good crystallinity of the Cu layer was checked by means of LEED patterns and by the ratio between the intensities of the Cu 920 eV line to the Ru 273 eV line, confirming that the Cu growth was, indeed, epitaxial. The work function of the Cu samples was determined by means of the photoelectric threshold, using the Fowler theory for photoemission from a metal into a dilute medium the square root of the photocurrent is a linear function of the photon energy, with the exception of the immediate vicinity of the threshold [19, 20]. From such Fowler plots (figure 1) we found the value of the work function of clear Cu(111) surfaces to be 4.91 ± 0.03 eV, in good accord with literature data [21]. The Cu surfaces referred to below belonged to deposits at least 10 monolayers thick, with work functions in the above range.

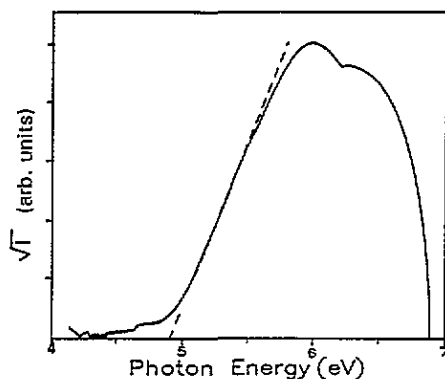


Figure 1. The square root of the normalized photoresponse of a Cu(111) surface at room temperature, as a function of photon energy. The small currents below the threshold are mainly due to photoemission from other metal surfaces.

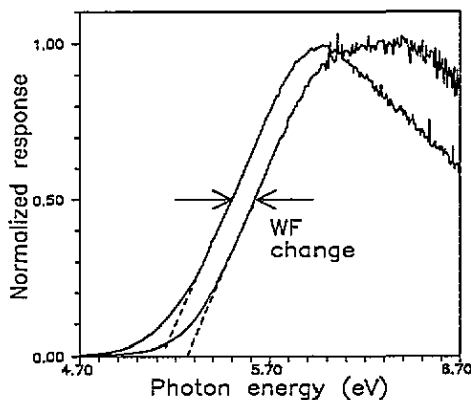


Figure 2. The normalized photoresponse as a function of photon energy: left-hand curve, clean Cu(111); right-hand curve, the Cu(111) surface with 920 Pa H₂ present. Room temperature in both cases.

The upper chamber could be evacuated independently of the lower one. H₂ of research grade purity was let into the chamber through a long tube, cooled to liquid N₂ temperature to freeze out H₂O and other impurities. The chamber is equipped with a sapphire window, allowing illumination of the sample for photoelectric work function measurements. A high-pressure Xe arc lamp, monochromated by a low-resolution monochromator, served as light source. The wavelengths of the illumination were set by the positions of a stepping motor.

For the determination of the changes in the work function, the sample was held at a potential of -100 V and a collecting electrode (made of fine Ni mesh) at $+9$ V, to suppress photoemission from the latter. The sample-collector distance was 0.5 cm. The currents measured were of the order of 10^{-12} – 10^{-11} A. The raw photocurrents were deconvoluted in order to eliminate the effect of the slit widths (2 mm) and corrected for the spectral distribution of the Xe arc. To avoid divergence of the correcting procedure at short wavelengths, where the light intensity drops to zero, a very small constant (equal to 0.02 times the light intensity measured at 5 eV) was added to the actual intensities. In most cases only the change $\Delta\phi$ of the work function was of interest, not its absolute value. To determine $\Delta\phi$, we normalized the corrected photocurrents to the same maximum height. The ascending parts of the resulting current against photon energy plots had extensive linear parts (determined consistently by least-squares fitting between the 30% and 60% points), very nearly parallel to each other. $\Delta\phi$ was determined from the horizontal shift of these parts (figure 2). The similar photon energy dependence of the current in the threshold region vindicates the validity of the photoelectric method as applied in this work.

3. Results

After preparing and characterizing the sample in the bottom chamber, it was lifted into the top chamber and the valve between the two chambers was closed. Closing the valve caused a transient increase of pressure (up to 10^{-3} Pa in the worst cases) and triggered an increase of the work function ϕ by up to several tenths of an electronvolt (figure 3). Moreover, letting in a small controlled amount (of the order of several pascals) of H_2 or D_2 caused further increases of the work function. The initial rises (due to closing the gate valve and letting in H_2 at low pressure) varied from experiment to experiment and thus must be attributed to impurities stuck on the surface. However, further increase of the H_2 pressure always caused a decrease of the work function, starting with a steep drop that turns gradually to a moderate descent with a constant slope of $\sim -2 \times 10^{-5}$ eV Pa $^{-1}$ (figure 3, table 1); the slope was similar in all experiments. The vertical shifts (e.g. between the H_2 and D_2 curves at 290 K) are fortuitous, depending on the initial coverage by impurities. It will be shown in section 4 that the decreasing part of each curve is predominantly governed by the hydrogen itself and, in particular, the part with constant moderate slope is due to chemisorption of pure hydrogen on clean areas of the Cu(111) surface. Figure 4 is relevant to this claim. It shows $\Delta\phi$ against p both during the increase in the ambient pressure and during pumpout. It is clear that the two curves are almost identical, apart from a small vertical shift (see above) that could be due to a slight accidental contamination before starting the pumpout. The main difference is at the lowest pressures: pumping out did not restore the work function to its value corresponding to a clean Cu(111) surface, but left the sharp rise. This confirms our suspicion that the initial rise is due to impurities, adsorbed non-reversibly, while the part with a negative slope should be attributed to reversible adsorption of hydrogen. The non-reversible adsorption of impurities was confirmed repeatedly upon complete pumpout following the experiments depicted in figure 3: the work function was always considerably higher after pumpout than before closing the gate valve. In this context we also mention the result of an experiment (not shown) on a 'used' Cu(111) surface, i.e., a surface that had been exposed to H_2 up to 2000 Pa and from which the gas was subsequently pumped away. When this surface was exposed again to H_2 the $\Delta\phi$ against p curve was very similar to that of a virgin surface shown, e.g., in figure 3. For the quantitative interpretation of the results that will be presented in section 4 it is also important to emphasize that no

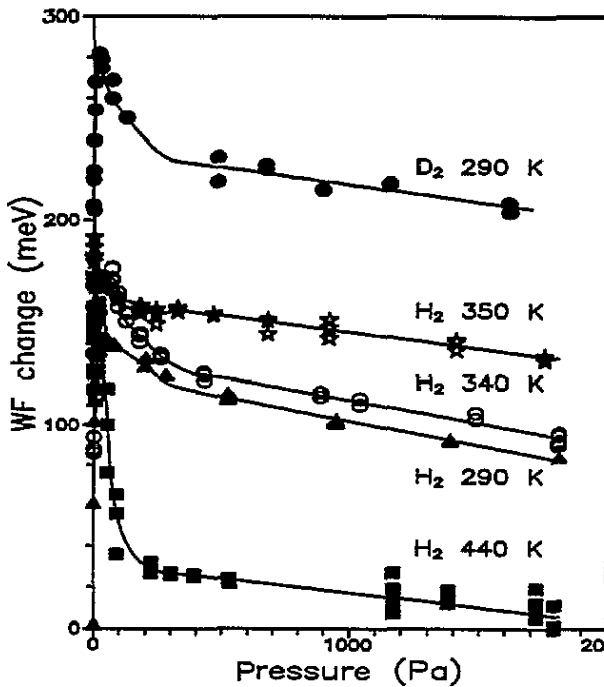


Figure 3. The work function change of Cu(111) against the pressure of ambient H₂, or D₂, during pressure increase, at various temperatures. The graphs are not staggered vertically.

Table I. The slope of the $\phi(p)$ curves ($d\phi/dp$) and calculated $d\theta/dp$ values (1) for pressures above 400 Pa.

	$-d\phi/dp$ (10^{-5} eV Pa $^{-1}$)	$d\theta/dp$ (10^{-5} Pa $^{-1}$)
D ₂ 290 K	1.7	3.7
H ₂ 350 K	1.6	4.0
H ₂ 340 K	2.1	4.0
H ₂ 290 K	2.4	3.7
H ₂ 440 K	1.5	3.5

systematic temperature dependence of the constant slopes (between 400 and 2000 K) could be discerned.

Three questions about the eventual role of gaseous impurities arose naturally.

(i) What are the impurities that stick irreversibly to the surface during the initial sharp rise of $\Delta\phi$? The impurities introduced into the system while closing the gate valve and along with the H₂ were identified (by means of a mass spectrometer) as O₂, N₂, CO, CO₂, CH₄ and H₂O. Among these only O₂ is irreversibly bound to Cu in the temperature range of our measurements, therefore it is the chief suspect. Oxygen was, indeed, detected on the Cu surface by Auger electron spectroscopy (AES) after lowering the sample into the bottom chamber upon completion of a series of $\Delta\phi$ against p measurements. Oxygen adsorption increase the work function of a pure Cu surface [22, 23]; we confirmed this fact in our system as well. In some cases sulphur (originating from the Viton gasket of the gate valve) was also detected by AES. Sulphur also binds irreversibly to Cu at room temperature and it is known to increase its work function [24], thus it also might play a role.

(ii) During the moderate decrease of $\Delta\phi$, between 400 and 2000 Pa, does any impurity contribute to the value of $d\phi/dp$? This is very unlikely, since oxygen and sulphur adsorb

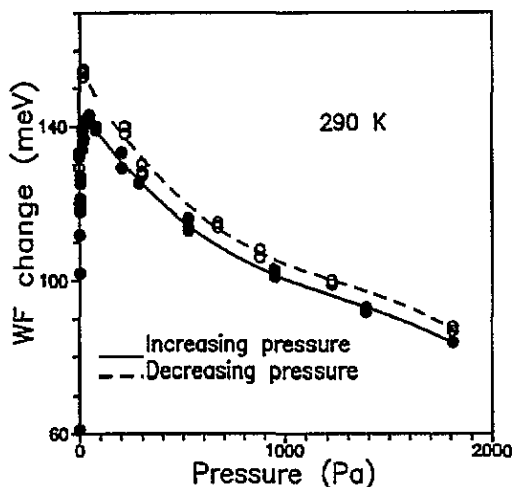


Figure 4. The work function change of Cu(111) against the pressure of ambient H_2 , during both pressure increase and decrease.

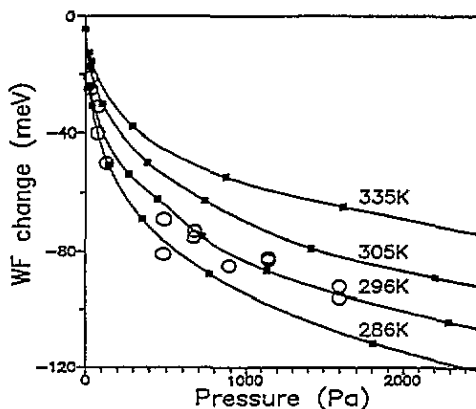


Figure 5. A comparison between photoelectric work function measurements at 290 K (open circles) of $H_2/Cu(111)$ (figure 2, referred to the initial rise of the work function), and Kelvin probe results on H_2/Cu on glass (full squares, [8]).

irreversibly, while in the experiments $\phi(p)$ was found to be reversible. On the other hand, the rest of the observed impurities (in the gas) have appreciably lower binding energies on Cu(111) than hydrogen [25–27], their concentration is also much lower, and thus their effect on ϕ must be negligible.

(iii) Are there appreciable changes in the coverage by impurities during the steep decrease of $\Delta\phi$ with p just after the initial rise? This important question will be answered in section 4, after presenting a model on the adsorption and concomitant work function changes.

4. Discussion

4.1. The 400–2000 Pa range

We claimed above that in this pressure range the changes of the work function are due to adsorption of hydrogen on clean parts of the Cu(111) surface. This claim was supported by qualitative arguments, based on our experiments alone. The claim will now be further justified by comparison with results in the literature.

Alexander and Pritchard [8] measured the surface potential of Cu in the presence of H_2 by means of a Kelvin probe. Five different Cu films were evaporated on glass: each film was deposited and sintered at different temperatures. Because of the simplicity of the set-up used (a glass vessel) [8] they were able to work under very clean conditions. Furthermore, the H_2 introduced into the vessel was filtered through a Pd filter, ensuring an extremely high purity. They worked at pressures of up to 13 000 Pa, and temperatures starting from 242 K up to 337 K. In figure 5 the close resemblance of our $\phi(p)$ curve to that of [8], at room temperature, to one of the five films is shown. Even so it should be pointed out that the other films prepared by these authors had different structures and/or textures, since there were appreciable differences between the sets of isotherms of the films. Moreover,

the agreement with our results below 400 Pa may be fortuitous as will transpire from our discussion of this range.

It will now be shown that calculating Langmuir adsorption isotherms [28], based on low-temperature, low-pressure data on *pure* hydrogen adsorbed on *clean* Cu(111) leads to agreement with our results.

The assumptions involved are as follows.

(i) In the range discussed the dipole moment induced by each hydrogen atom is dependent neither on the coverage nor on the surface temperature.

(ii) In the range discussed the number of sites of the surface not blocked by adsorbed impurities varies neither with the hydrogen coverage nor with the temperature. This can happen if the number of blocked sites is small compared with their total number. Such a situation may prevail due to 'cleaning' the surface by hydrogen due to chemical reaction followed by desorption; see below. An alternative assumption might be that the number of blocked sites is constant, but this seems rather unlikely.

(iii) The dependence of the adsorption energy E_{ad} on the hydrogen coverage θ can be calculated from desorption E_{des} energies, obtained by Anger *et al* [2], utilizing thermal desorption of hydrogen from Cu(111). The hydrogen had been deposited by means of a molecular beam [2] at low temperatures.

The details of this procedure are as follows. Anger and his coworkers analysed the TDS spectra on the basis of the Polanyi–Wigner equation [29], using two mathematical approaches: the 'complete method' of King [29] and the threshold method TTPD [30]. The TTPD analysis determined the desorption energy to be $E_{des} \cong 0.8 - 0.3\theta$ eV, where $\theta = n/n_0$, i.e. θ is the relative coverage. The King method gave a zero-coverage value of ~ 0.89 eV and approximately the same dependence on θ . Now $E_{ad} = E_{des} - E_{act}$, where E_{act} is the activation barrier for hydrogen adsorption. As stated in section 1, the value of E_{act} is 0.67 eV for a hydrogen molecule in the ground vibrational and rotational state [1, 5]. However, for a highly excited hydrogen molecule steric effects reduce the value of E_{act} to ≈ 0.25 eV [2–4]. It is this latter value one has to take into account when estimating E_{ad} , since in the process of thermal desorption the hydrogen atoms combine to form hydrogen molecules through saddle points in the surface potential of the copper surface. By doing so the molecule is stretched and the outcoming hydrogen molecules are highly excited. It follows that $E_{ad} = E_0 - 0.3\theta$, with $E_0 = 0.60 \pm 0.08$ eV. Here we have assumed that the lateral interaction term 0.3θ is the same for adsorption and desorption. On this basis we tried to reproduce the experimental results by using the Langmuir isotherms to calculate the dependence of the coverage θ on the pressure p .

The Langmuir equation for second-order adsorption is given by

$$n(p) = n_0 / \left\{ 1 + \sqrt{[(kT)^{5/2} (M/2\pi\hbar^2)^{3/2} / p] e^{-E_{ad}/kT}} \right\}. \quad (1)$$

Here n is the number density of adsorbed hydrogen atoms, n_0 is the number density of adsorption sites, M is the mass of the hydrogen molecule, T is the surface temperature, E_{ad} is the adsorption energy, and p is the pressure of the ambient hydrogen molecules. For a clean surface n_0 is equal to one half of the density [2] of the copper atoms on a (111) face. We calculated $\theta = n(p)/n_0$ from the above equation. It turned out that $\theta(p)$ is very sensitive to the value of E_0 . We looked for a value of E_0 that gives an approximately constant slope $d\theta/dp$ for $400 \leq p \leq 2000$ Pa and for $290 \leq T \leq 440$ K. This could be achieved with $E_0 = 0.58$ eV, well within the predicted range (0.60 ± 0.08 eV, see above) of E_0 . The Langmuir isotherms calculated in this way are shown in figure 6. It follows

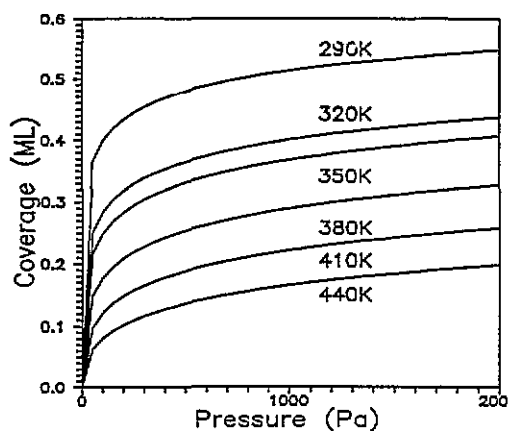


Figure 6. Langmuir isotherms for hydrogen adsorption on Cu(111). The adsorption energy as a function of coverage is calculated as described in the text.

that this choice of E_0 , along with assumption (i) leads to agreement with the experimental result of the slope $d\Delta\phi/dp$ being independent of the pressure and the temperature in this range.

In order to calculate μ we use the Helmholtz relation $\Delta\phi = -4\pi n\mu$. From table 1 one may see that in the pressure range discussed the change in ϕ for one monolayer ($(d\phi/dp)/(dn/dp)$) is approximately 0.5 eV. If none of the hydrogen adsorption sites on the Cu(111) surface is blocked by impurities then $n = 8.9 \times 10^{14} \text{ cm}^{-2}$ [2]. With this assumption one obtains $\mu = (0.032 \pm 0.006)e \text{ \AA}$, where e is the electronic charge. We emphasize again that this is a lower bound for μ , assuming that the number of adsorption sites is equal to that of clean Cu(111). The variations of $d\phi/dp$ in table 1 may be attributed to variations in the number of adsorption sites actually blocked by impurities.

4.2. The 10–400 Pa range

If the analysis presented above were correct for $p < 400 \text{ Pa}$ as well, then figures 3 and 6 ought to be identical except for a negative proportionality factor. In order to make the actual comparison, we present in figure 7 the experimental and calculated (see previous section) values of $\Delta\phi$ as a function of p . The calculated curves are vertically shifted so as to have the best fit in the 400–200 Pa pressure range. It is seen that below this range the correspondence is only qualitative; the discrepancy varies from curve to curve. This means that in the range 10–400 Pa the above Langmuir isotherm analysis is *not* adequate. Since the initial rise in figure 3 is due to impurities, it is natural to assume that in the 10–400 Pa range the number of non-blocked adsorption sites varies considerably: the hydrogen reacts with the non-reversibly adsorbed impurity (oxygen and in some cases sulphur as well) and the reaction products (probably H_2O and H_2S) desorb. In other words, the hydrogen cleans away some of the impurities that had been previously adsorbed. One cannot make any statement about the variation of $\Delta\phi$ itself in this range, since the work function is influenced simultaneously by several factors: the impurities, the hydrogen, and the reaction product or products. It should be noted that this qualitative model supports assumption (ii) in the previous section, namely that in the 400–2000 Pa range the number of blocked adsorption sites is small.

In summary, the analysis of the results on the basis of independent experimental data, using the Langmuir isotherms, strongly supports the claim that in the 400–2000 Pa range $\Delta\phi$ is due reversible chemisorption on clean parts of the Cu(111) surface, while in the range

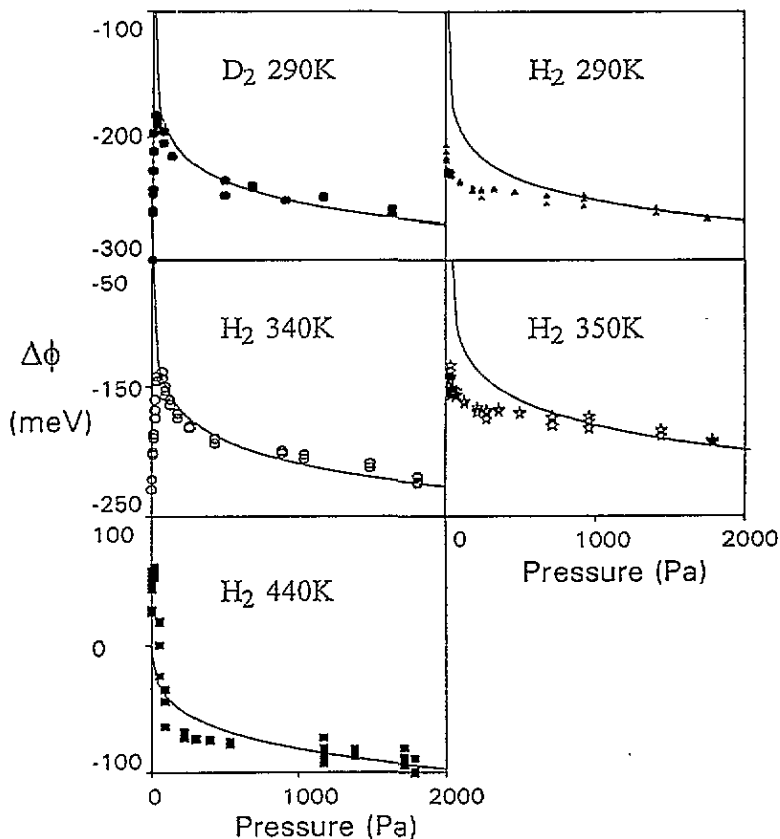


Figure 7. The data of figure 3 compared with calculations based on Langmuir isotherms (see the text). The calculated curves are shifted vertically so as to obtain a good fit to experiment between 400 and 2000 Pa.

10–400 Pa this process takes place in parallel with cleaning of the surface from irreversibly adsorbed impurities, by surface reactions with hydrogen.

5. Conclusions

It has been demonstrated that hydrogen at room temperature and above (290–440 K), at pressures up to 2000 Pa, adsorbs reversibly on Cu(111) surfaces. The concomitant work function changes were consistently interpreted by means of a simple model based on low-temperature adsorption parameters [2], and assuming a constant dipole moment associated with each adsorbed hydrogen atom. It follows that measuring the photoelectric work function of the surfaces led to information on hydrogen adsorption of the surface at relatively high ambient hydrogen pressures even with impurities present. In view of the results the applicability of the photoelectric method for the study of other gas/surface systems under non-conventional conditions should be examined.

Acknowledgments

The authors wish to thank M Asscher (Jerusalem), K Wandelt (Bonn), and R Dus (Warsaw) for most helpful discussions and the Deutsche Forschungsgemeinschaft (DFG) for a grant financing the project.

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