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R.Cardenas, G.M.Gavrilenko, V.K.Fedyanin

**CHEMISORPTION ON METALS
AT FINITE SUBMONOLAYER COVERAGES^o**

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In the present work we study the influence of the coverage θ on some chemisorption characteristics as the one-impurity binding energy ΔE , the charge transfer between the adsorbate and the substrate Δq and the magnetic momentum in the impurity layer Δm . We use the formalism of composite Hamiltonians [1] as it gives the possibility of treating both the electronic and the thermodynamic characteristics of chemisorption in a self consistent way, allowing for a relatively clear microscopic description of this problem. A detailed discussion of this method is given in paper [1], here we only show its application to a simple model oriented to the description of hydrogen chemisorption on metals.

We assume that adsorption sites form a regular lattice over the surface with a unit distance between nodes. The arrangement of adatom ions within this lattice is not fixed, but we consider only the case when there is no more than one adatom ion in each adsorption site. Further, adatoms are considered to be in their ground states and effects related to its migration and other degrees of freedom are neglected. The Hamiltonian of this system may be written as

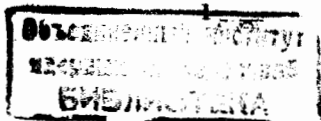
$$H = \sum_{k\sigma} \xi_k n_{k\sigma} + \sum_{\alpha\sigma} N_{\alpha} \left\{ \xi_{\alpha\sigma} n_{\alpha\sigma} + \frac{U}{2} n_{\alpha\sigma} n_{\alpha-\sigma} + \sum_k V_{\alpha k} \left(\delta_{\alpha\sigma}^{\dagger} a_{k\sigma} + \text{H.c.} \right) \right\}, \quad (1)$$

where $N_{\alpha}=0,1$ is the occupation number of the adsorption site α and the summation is carried out over all adsorption sites on the surface. The other parameters are the usual parameters of the Anderson model [2]. In the unrestricted Hartree-Fock approximation it becomes

$$H = \sum_{k\sigma} \xi_k n_{k\sigma} + \sum_{\alpha\sigma} \xi_{\alpha\sigma} N_{\alpha} n_{\alpha\sigma} + \sum_{\alpha k\sigma} V_{\alpha k} \left(N_{\alpha} \delta_{\alpha\sigma}^{\dagger} a_{k\sigma} + \text{H.c.} \right) - N_{\alpha} U n_{\alpha\sigma} n_{\alpha-\sigma} \quad (2)$$

$$\xi_{\alpha\sigma} = \xi + U n_{\alpha-\sigma}; \quad n_{\alpha\sigma} = \langle N_{\alpha} n_{\alpha\sigma} \rangle / \langle N_{\alpha} \rangle; \quad \langle N_{\alpha} \rangle = \theta;$$

here N_{α} is the total number of adsorbed atoms and the average is made using (1). The renormalization of n_{σ} is needed to interpret



this quantity as the probability of finding an electron at an adsorption site when the latter is already occupied by an adatom ion, this arises directly from the fact that the configuration of adatoms is not fixed. The last term in (2) renormalizes the chemical potential of the ion subsystem and is usual within the Hartree-Fock scheme.

Using the two-time Green function machinery [3], it may be shown that all the electronic characteristics of the system may be calculated from the following system of Green's function equations

$$\begin{aligned}
 (\omega - \varepsilon_\sigma) \langle \langle N_\alpha b_{\alpha\sigma} : b_{\alpha\sigma}^+ \rangle \rangle &= \frac{1}{2\pi} \theta + \sum_k V_{\alpha k} \langle \langle N_\alpha a_{k\sigma}^+ : b_{\alpha\sigma}^+ \rangle \rangle \\
 (\omega - \varepsilon_k) \langle \langle N_\alpha a_{k\sigma}^+ : b_{\alpha\sigma}^+ \rangle \rangle &= \sum_\beta V_{k\beta} \langle \langle N_\beta b_{\beta\sigma} : N_\alpha b_{\alpha\sigma}^+ \rangle \rangle \\
 (\omega - \varepsilon_k) \langle \langle N_\alpha a_{k\sigma}^+ : a_{k\sigma}^+ \rangle \rangle &= \frac{1}{2\pi} + \sum_\alpha V_{\alpha k} \langle \langle N_\alpha b_{\alpha\sigma} : a_{k\sigma}^+ \rangle \rangle \\
 (\omega - \varepsilon_k) \langle \langle N_\alpha b_{\alpha\sigma} : a_{k\sigma}^+ \rangle \rangle &= \sum_\beta V_{\beta k} \langle \langle N_\alpha b_{\alpha\sigma} : N_\beta b_{\beta\sigma}^+ \rangle \rangle.
 \end{aligned} \tag{3}$$

The first two equations describe the single-electron properties of the adsorbate and the remaining ones describe the response of the single electron properties of the substrate. It may be seen that the system is solved if one can compute the single Green function of the form $\langle \langle N_\alpha b_{\alpha\sigma} : N_\beta b_{\beta\sigma}^+ \rangle \rangle$.

When the coverage is fixed by external parameters and adatoms are randomly distributed it may be shown that the Bragg-Williams approximation [4] gives

$$\langle \langle N_\alpha b_{\alpha\sigma} : N_\beta b_{\beta\sigma}^+ \rangle \rangle = \left[\frac{1}{2\pi} \right]^d \int d\vec{q} e^{i\vec{q}(\vec{\alpha}-\vec{\beta})} G_\beta(\omega, \vec{q}) \left[\Delta_{\alpha\beta} \theta(1-\theta) + \theta^2 \right], \tag{4}$$

with

$$G_\beta(\omega, \vec{q}) = \frac{1}{2\pi} \frac{1}{\omega - \varepsilon_\sigma - (1-\theta)L(\omega) - \theta P(\omega, \vec{q})}, \tag{5}$$

here \vec{q} is a vector of the reciprocal lattice of the adsorption sites and may be interpreted as a quasi-momentum of the electron in the adsorbed layer, d is the coverage dimension, $P(\omega, \vec{q})$ is the Fourier transform of Grimley's chemisorption function $P_{\alpha\beta}(\omega) = \sum_k \frac{V_{\alpha k} V_{k\beta}}{\omega - \varepsilon_k}$ [5] and $L(\omega) = P_{\alpha\alpha}(\omega)$ is the Newns chemisorption function [2]. We note that the system (3) allows an exact solution in all cases where a strictly ordered arrangement of adatoms occurs and only the explicit form of $G(\omega, \vec{q})$ will change. For the more general case when θ is not

fixed the system must be complemented with the corresponding equations for the ionic component of the adsorbate.

At zero temperature the electron occupation number in the adsorbed layer is obtained as usual

$$n_\sigma = \left[\frac{1}{2\pi} \right]^d \int d\vec{q} \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \operatorname{Im} G_\sigma(\omega, \vec{q}) \Big|_{\omega-i\varepsilon}, \tag{6}$$

where E_F is the Fermi level of the system after chemisorption. In the zero coverage limit (6) becomes the well-known expression of the Newns theory [2]. The charge transfer in the electron units and the magnetic momentum in terms of the Bohr magnetons are given by

$$\Delta q = 1 - \langle \bar{n}_\uparrow \rangle - \langle \bar{n}_\downarrow \rangle, \quad \Delta m = | \langle \bar{n}_\uparrow \rangle - \langle \bar{n}_\downarrow \rangle |, \tag{7}$$

where the modulus is taken as we do not distinguish between the two possible orientations of the spin. Finally, the one-impurity binding energy is defined as

$$\Delta E = \frac{1}{N_A} \left\{ \langle H \rangle - \sum_{k\sigma}^{\text{occ}} \varepsilon_k \right\} - \varepsilon; \tag{8}$$

where the summation is over all the occupied states in the unperturbed substrate. After some manipulations one finds

$$\begin{aligned}
 \Delta E = 2Z \frac{M}{N_A} \int_{E_F}^{E_F} \rho(\omega) d\omega + \sum_\sigma \left[\frac{1}{2\pi} \right]^d \int d\vec{q} \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \omega \frac{\partial}{\partial \omega} \operatorname{Im} \ln \left[G_\sigma(\omega, \vec{q})^{-1} \right] \Big|_{\omega-i\varepsilon} \\
 - \varepsilon - U n_\sigma n_{-\sigma},
 \end{aligned} \tag{9}$$

where $2Z$ stands for spin and orbital momentum degeneracy of the substrate band, $\rho(\omega)$ is the local density of electronic states in the unperturbed substrate normalized to unity, E_F^0 is the unperturbed substrate Fermi level and M is the number of cells in the substrate. It is of interest to note that even infinitesimal changes in the Fermi energy may lead to finite contributions to the chemisorption characteristics and must be properly taken into account to avoid violation of charge conservation laws. The position of the Fermi level after chemisorption is found by solving the equation

$$\frac{1}{N_A} \int_{E_F}^{E_F} \rho(\omega) d\omega = \theta \left[1 + \sum_\sigma \left[\frac{1}{2\pi} \right]^d \int d\vec{q} \frac{1}{\pi} \operatorname{Im} \ln \left[G_\sigma(E_F, \vec{q})^{-1} \right] \Big|_{E_F-i\varepsilon} \right], \tag{10}$$

which simply expresses the conservation of the total number of electrons in the system.

Now it is necessary to choose the form of $L(\omega)$ and $P(\omega, \vec{q})$. $L(\omega)$ may be expressed through a unique function of the energy

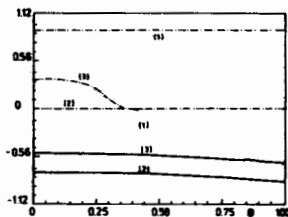


Fig.1 Results for $\eta=0$. The parameter values are $\xi=-0.95$, $U=1.9, \beta=0.4$ (1); $\xi=-0.5, U=1.0, \beta=0.8$ (2); $\xi=-0.95, U=1.9, \beta=0.8$ (3). Δq and E_F are zero in this case.

$$\Delta(\omega) = \begin{cases} \beta^2 (1-\omega^2)^{-1/2} & |\omega| \leq 1 \\ 0 & |\omega| > 1 \end{cases}, \quad P(\omega, q) = \frac{\beta^2}{\omega + \cos q}, \quad (11)$$

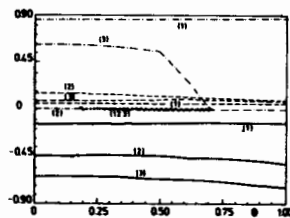


Fig.2 Results for $\eta>0$. The parameters values are $\xi=-0.5$, $U=1.5, \beta=0.4$ (1); $\xi=-0.5, U=1.5, \beta=0.8$ (2) and $\xi=-0.95, U=2.4, \beta=0.8$ (3).

In the Anderson model the parameter ξ is identified with the ionization level and $\xi+U$ is the electron affinity level A . It is convenient to introduce a new parameter $\eta=\xi-E_F^0+U/2$, when $\eta=0$ we have the symmetrical Anderson model with ξ and A lying at equal distances from the Fermi level and if $\eta<0$ we have the asymmetrical case. The

$L(\omega)=A(\omega)-i\Delta(\omega)$ [5] with $\Delta(\omega)=\pi \sum_k |V_{\alpha k}|^2 \delta(\omega-\xi_k) \cong \pi \beta^2 \rho(\omega)$ and $A(\omega)$ its Hilbert transformation. The case of $P(\omega, q)$ is more complicated, the simplest model that gives an analytical expression for it is a linear chain with one adsorption site per elementary cell of the substrate and the interaction only between nearest neighbours. In the tight binding approximation we have

where energies are relative to band center and are measured in units of its halfwidth. This is a very crude approximation but it is known that integral chemisorption characteristics are not so sensitive to the detailed structure of the band [6] and one could expect that at least the qualitative behaviour may be correctly described even in this simple model.

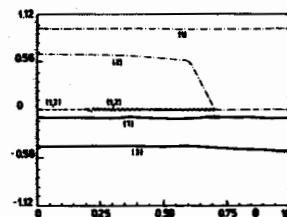


Fig.3 Results for $\eta<0$. The parameter values are $\xi=-1.5$, $U=2.5, \beta=0.4$ (1) and $\xi=-1.5, U=2.5, \beta=0.8$ (2).

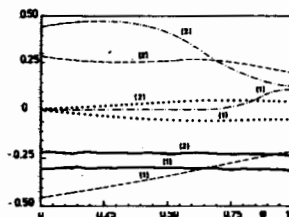


Fig.4 Results for the parameter values $\xi=-0.5, U=0.5, \beta=0.4$ $\eta<0$ (1) and $\xi=-0.15, U=0.8, \beta=0.4$ $\eta>0$ (2).

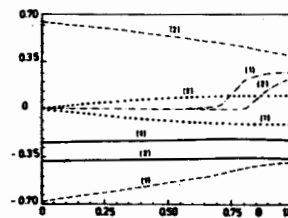


Fig.5 Results for the parameter values $\xi=-0.5, U=0.4, \beta=0.3$ $\eta<0$ (1) and $\xi=0.15, U=0.5, \beta=0.4$ $\eta>0$ (2).

numerical calculations were made for these three topologically different situations, $E_F^0=0$, $Z=5$ and different values of the hybridization parameter β . In all figures the curves (—) correspond to ΔE , curves (---) to Δq , curves (---) to Δm and the curves (.....) to the position of E_F .

In Fig.1 the results for the symmetrical case are shown. We observe no charge transfer and no displacement of the Fermi level in the full range of θ . When the ratio U/β is great, there is a strong magnetism, and when $U/\beta \leq 1$, only nonmagnetic solutions appear in concordance with the Anderson criterion [7]. However, at intermediate values, when $U/\beta \cong 2$, it was found that the coverage may eliminate the surface magnetism.

The binding energy is not sensitive to the coverage in the magnetic region and decreases more rapidly in the nonmagnetic region.

The results for the asymmetrical Anderson model given in Figs.(2-5) show a similar dependence of magnetic solutions of the ratio U/β , the only difference is that the surface magnetism is not only damped but also induced by the coverage at intermediate values of U/β . The chemisorption parameters are not sensitive to θ in the

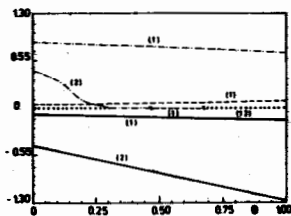


Fig.6 Results for the Newns substrate and the parameter values $\xi = -0.5, U = 1.5, \beta = 0.4$ (1) and $\xi = -1.5, U = 3.0, \beta = 1.2$ (2).

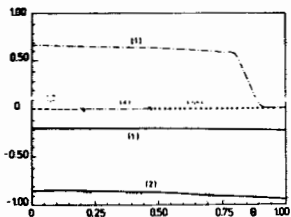


Fig.7 Results for a constant density of electronic states in the substrate and the parameter values $\xi = -0.5, U = 1.0, \beta = 0.4$ (1) and $\xi = -0.5, U = 1.0, \beta = 0.8$ (2).

magnetic region, Δq is damped and $|\Delta E|$ increases with θ when magnetic solutions do not occur. We can also see that the sign of Δq is in concordance with the sign of η and the changes in E_F . In Fig.4 the case is shown when Δm is damped from $\Delta m \approx 0.6$ at $\theta = 0$ to $\Delta m \approx 0.15$ at $\theta = 1$.

Fig.5 shows the case when both ξ and A lie on one side of the Fermi level. As could be expected a strong charge transfer is found in this case. Δq is damped by the coverage and appearance of magnetism with increasing θ is found, too. In this case $|\Delta E|$ decreases with the coverage. The similar behavior of the parameters in both the asymmetrical cases ($\eta > 0$ and $\eta < 0$) is an evidence of the presence of electron-hole symmetry in our model. The appearance and disappearance of magnetism after some value of the coverage θ_c is interpreted by us as a phase transition of second order due to the observed smooth behaviour of the resting characteristics. The critical exponent ν given by $\mu \propto |1 - \theta/\theta_c|^\nu$

is estimated as $\nu = 1/2$. We consider that these two cases in the coverage dependence of the surface magnetic momentum are an evidence of a possible crossover in the critical exponent behaviour.

In fig.6 we show some results for a substrate of the Newns type $\Delta(\omega) = 2\beta^2(1-\omega^2)^{1/2}$, $|\omega| \leq 1$ [2]; and in fig.7, the results for a constant density of k states in the substrate $\Delta(\omega) = \beta^2/2$, $|\omega| \leq 1$. These types of the substrate are widely used for fitting of experimental data.

The results will not be discussed in detail, we only note that a similar qualitative behaviour obtained is in concordance with the assumption that our simple linear model can give a reasonable qualitative description of the main features of the coverage dependence of the chemisorption characteristics.

Considerable divergence is found for this simple model. It is of great interest to study open systems where the coverage is not fixed and the effects are due to ordering in the adsorbed layer. These investigations are now in progress.

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Карденас Р., Гавриленко Г.М., Федянин В.К. E17-88-631
Хемосорбция на металлах при конечных
субмонослойных покрытиях

В рамках метода составных гамильтонианов изучены зависимости некоторых характеристик хемосорбции от концентрации покрытия для различных моделей подложки. Расчеты выполнены в самосогласованной хартри-фоковской схеме для электронной компоненты и в рамках приближения Брэгга-Вильямса для ионной компоненты.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1988

Cardenas R., Gavrilenko G.M., Fedyanin V.K. E17-88-631
Chemisorption on Metals at Finite
Submonolayer Coverages

In the framework of the composite Hamiltonian method the coverage dependence of some chemisorption characteristics is investigated for different substrate models. All calculations are carried out within the self-consistent Hartree-Fock approximation for the electron component and the Bragg-Williams approximation for the ion one.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna 1988