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

**A MODEL FOR CHEMISORPTION  
AT FINITE SUBMONOLAYER COVERAGES**

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The variety of physical processes connected with the heterogeneous catalysis [1], cathod technology [2] and phase transitions in the adsorbate component [3] stimulate the growing interest in the chemisorption problem both theoretically and experimentally. Here we describe the coverage dependence of some chemisorption values within the composite Hamiltonian method [4].

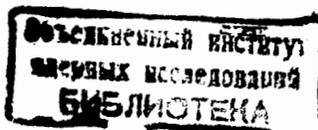
Suppose we have a system of  $N_A$  atoms, e.g. hydrogen-like, interacting with a clean crystal metal surface with lattice constant  $a=1$ . We assume that adsorption sites form a regular lattice with nodes at points with radius vector  $\vec{\alpha}$ . The distribution of adatoms within this lattice is not fixed. Migration of adatoms and further degrees of freedom are neglected. Such a system is described by the Hamiltonian

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

here  $N_{\alpha}=0,1$  is the occupation number of the adsorption site  $\alpha$  and the summation is carried out over all adsorption sites on the surface. The other parameters are usual parameters of the Anderson model of single atom chemisorption [5]. The Hamiltonian (1) may be deduced from first principles in the framework of an Anderson-Ising composite model [4]. Within unrestricted Hartree-Fock approximation it becomes

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

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



The unusual form of  $\langle \bar{n}_{\alpha\sigma} \rangle$  arises from the fact that the configuration of adatoms is not fixed and the electronic correlation function  $\langle \bar{n}_{\alpha\sigma} \rangle$  should be interpreted as the probability of finding an electron at the adsorption center  $\alpha$  when the latter is already occupied, so if we are interested in the electron occupation number for the adsorbed layer, the electronic correlation function must be renormalized. This fact is discussed in detail in ref. [4].

At fixed coverages it may be shown that the system is fully described by a unique single-electron propagator with the Fourier transform given by

$$G(\omega, \vec{q}) = \frac{i}{2\pi} \frac{1}{\omega - \xi_{\sigma} - (1-\theta)L(\omega) - \theta P(\omega, \vec{q})} \quad (3)$$

here  $\vec{q}$  is a reciprocal vector of the lattice of the adsorption sites and may be interpreted as the quasi-momentum of the electron in the adsorbed layer.  $P(\omega, \vec{q})$  is the Fourier transform of Grimley's chemisorption function  $P_{\alpha\beta}(\omega) = \sum_{\vec{k}} \frac{V_{\alpha\vec{k}} V_{\vec{k}\beta}}{\omega - \xi_{\vec{k}}}$  [6] and  $L(\omega) = P_{\alpha\alpha}(\omega)$  is the Newns chemisorption function [5]. Here we used the Bragg-Williams approximation [7] for ion-ion correlation functions. The electron occupation number in the adsorbed layer is obtained as usual

$$\langle \bar{n}_{\alpha\sigma} \rangle = \frac{1}{\Omega} \int d\vec{q} \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \operatorname{Im} G(\omega, \vec{q}) \Big|_{\omega-i\epsilon} \quad (4)$$

where integration over  $\vec{q}$  includes all vectors lying in the first Brillouin zone of the lattice of the adsorption sites,  $\Omega$  is the area of the metal surface.

The one-impurity binding energy is given by

$$\Delta E = -\frac{2Z}{e} \int_{E_F}^{E_F} \rho(\omega) d\omega + \frac{1}{\Omega} \int d\vec{q} \frac{1}{\pi} \int_{-\infty}^{E_F} d\omega \omega \frac{\partial}{\partial \omega} \operatorname{Im} \ln \left[ G(\omega, \vec{q})^{-1} \right] \Big|_{\omega-i\epsilon} \quad (5)$$

$$- \xi - U \langle \bar{n}_{\alpha\sigma} \rangle \langle \bar{n}_{\alpha\sigma} \rangle$$

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. 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 conservation laws. This nontrivial fact as far as we know was for the first time pointed out by Grimley [6]. The position of the Fermi level after chemisorption is found by solving the equation

$$2Z \int_{E_F^0}^{E_F} \rho(\omega) d\omega = e \left[ 1 - \frac{1}{\Omega} \int d\vec{q} \frac{1}{\pi} \operatorname{Im} \ln \left[ G(E_F, \vec{q})^{-1} \right] \Big|_{E_F-i\epsilon} \right] \quad (6)$$

The equations (4-6) must be solved self-consistently. At this stage one must choose the appropriate form of  $L(\omega)$  and  $P(\omega, \vec{q})$ . It is well known that  $L(\omega)$  may be expressed through a unique function of the energy  $L(\omega) = \Lambda(\omega) - i\Delta(\omega)$  [8], with  $\Delta(\omega) = \pi \sum_{\vec{k}} |V_{\alpha\vec{k}}|^2 \delta(\omega - \xi_{\vec{k}}) \cong \pi \beta^2 \rho(\omega)$  and  $\Lambda(\omega)$  its Hilbert transformation. The case of  $P(\omega, \vec{q})$  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 interaction only between nearest neighbours, in the tight binding approximation we have:

$$\Delta(\omega) = \begin{cases} \beta^2 (1-\omega^2)^{-1/2} & |\omega| \leq 1 \\ 0 & |\omega| > 1 \end{cases}, \quad P(\omega, q) = \frac{\beta^2}{\omega + \cos q} \quad (7)$$

here energies are relative to band center and 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 [8] and one could expect that at least the qualitative behaviour may be correctly described even in this simple model. Therefore one-dimensional models are often used in interpreting experimental data and they are realized in quasi-one dimensional compounds as polymers.

The electric charge  $q$  and the magnetic momentum  $\mu$  of the adsorbed layer are easily obtained by evaluation of the expressions  $q = 1 - \langle n_{\alpha\uparrow} \rangle - \langle n_{\alpha\downarrow} \rangle$ ,  $\mu = \langle n_{\alpha\uparrow} \rangle - \langle n_{\alpha\downarrow} \rangle$ . These quantities complete the set of chemisorption characteristics investigated in the present work.

The calculations have been made for the case when the substrate band is half filled. The model parameters were taken in the range  $U < 4$ ,  $|\xi| < 2$ ,  $\beta \leq 1.2$ ,  $Z = 5$ . Typical results are shown in Figs. (1-4). The energies are normalized to the halfwidth of the band, the electric charge is expressed in terms of electron charges; and the magnetic momentum, in terms of Bohr magnetons.

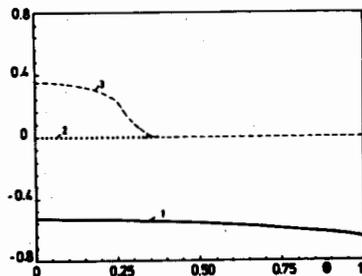


Fig. 1. Coverage dependence of  $\Delta E$  (1),  $E_F$  (2) and  $\mu$  (3) for  $\xi = -0.95$ ,  $U = 1.9$ ,  $\beta = 0.8$ .

It has been found that the surface magnetism may be eliminated (Figs. 1-2) or induced (Figs. 3-4) after some critical value of coverage  $\theta_c$ . We interpret this behaviour as a second order magnetic phase transition and estimate the critical exponent  $\nu$  given by  $\mu \propto |1 - \theta/\theta_c|^\nu$  as  $\nu = 1/2$ . We consider that these two cases in the coverage dependence of the surface magnetic momentum are an evidence of crossover in the critical exponent behaviour.

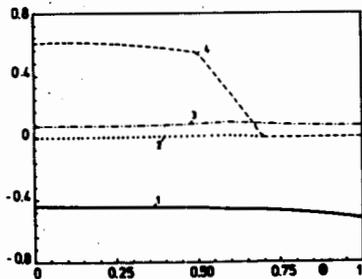


Fig. 2. Coverage dependence of  $\Delta E$  (1),  $E_F$  (2),  $q$  (3) and  $\mu$  (4) for  $\xi = -0.95$ ,  $U = 2.4$ ,  $\beta = 0.8$ .

In all the considered cases the charge transfer between the substrate and the impurity layer is damped. The binding energy was found to decrease with the coverage when both the ionization potential  $\xi$  and the electron affinity level  $A = \xi + U$

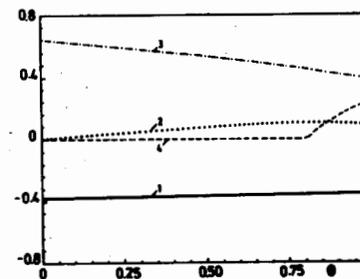


Fig. 3. Coverage dependence of  $\Delta E$  (1),  $E_F$  (2),  $q$  (3) and  $\mu$  (4) for  $\xi = +0.15$ ,  $U = 0.5$ ,  $\beta = 0.4$ .

lie at one side of the Fermi level (Figs. 3-4), but when only  $\xi$  lies below  $E_F$ , one can see from Figs. 1-2 that  $\Delta E$  is not so sensitive to the coverage in the magnetic region up to  $\theta_c$  and increases more rapidly beyond the critical point. A similar charge transfer and increasing of the binding energy with the coverage in the nonmagnetic region have been found in other works within the coherent potential approximation [9] and the local density functional method [2].

Considerable divergence is found for this simple model. It is of great interest to study the influence of different substrates and the effects due to ordering in the adsorbed layer. Such investigations are now in progress.

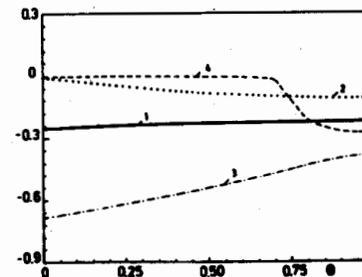


Fig. 4. Coverage dependence of  $\Delta E$  (1),  $E_F$  (2),  $q$  (3) and  $\mu$  (4) for  $\xi = -0.5$ ,  $U = 0.4$ ,  $\beta = 0.3$ .

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Карденас Р., Гавриленко Г.М., Федянин В.К. E17-88-316  
Модель хемосорбции при конечных субмонослойных  
покрытиях

Дается выражение для энергии хемосорбции в зависимости от покрытия  $\theta$ . Обсуждается поведение электрического заряда и магнитного момента, локализованных на примесном слое. Для некоторых наборов параметров модели найдены магнитный, фазовый переход второго рода и признаки кроссовера в критическом поведении.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Gardenas R., Gavrilenko G.M., Fedyanin V.K. E17-88-316  
A Model for Chemisorption at Finite  
Submonolayer Coverages

The binding energy is given as a function of the coverage  $\theta$ . Behaviour of the surface electric charge and magnetism is discussed. For some sets of the model parameters the magnetic phase transition and evidence of crossover of the critical behaviour are found.

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

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