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**ON COVERAGE DEPENDENCE  
OF CHEMISORPTION CHARACTERISTICS  
ON METALS**

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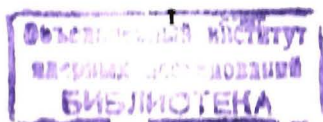
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## INTRODUCTION

In the present paper we investigate the coverage dependence of the basic chemisorption characteristics like the magnetic moment and the electric charge localized on an adatom, the chemisorption energy and the electron density of states induced by the impurities.

The physical effects arising in chemisorption systems are of great practical interest as they are closely connected with our understanding of the physical processes on metal surfaces in heterogeneous catalysis [1], hydrolysis and corrosion. They are widely used in various technologies, for instance, in the cathode technology [2] and others. However, these processes are also interesting from the point of view of fundamental researches. Thus, the discovery of a great number of phase transitions of the order-disorder type [5-6], which arise in the adsorbate components and belong to different classes of universality in their critical behaviour depending on different symmetries of the crystal substrates, allows us to verify and refine the basic assumptions of the theory of second order phase transition for two-dimensional systems [6].

At present the microscopic theory of these systems is developed in two directions. Apparently, the description of the coverage dependence of the properties of chemisorbed overlayers was for the first time realized within the local density functional method (LDF). In the framework of this scheme the adsorbate overlayer is described in the jellium-slab approximation with a positive background proportional to the adsorbate coverage  $\theta$  [7].



The LDF method and its advantages [8] allow us to carry out high precision calculations of the space distribution of the electric charge in the adsorbate-adsorbent systems; nevertheless, some problems of the chemisorption theory have not been solved yet within this approach [9]. Moreover, the LDF-description, as a rule, involves a large amount of computer calculations. Another method of investigating the properties of monolayer coverages is the coherent potential approximation method (CPA) generalized to these systems. In this approach we may start either from the Hamiltonian description [10-12], the Dyson equation for the adsorbate Green-function [13] or the Lipmann-Schwinger equation [14]. However, there are great difficulties within the CPA method in taking into account the many-body effects due to the correlations in both the electronic and the ionic components of the adsorbate. Therefore, the CPA-approach is not yet valid near the critical points [15-16] and for the description of correlation properties in the system.

In the present paper we consistently develop the method of composite Hamiltonians suggested in ref. [17] by one of us. We consider the simplest composite model within the self-consistent Hartree-Fock (H-F) approximation, but we may easily include also correlation effects in both the electronic and the ionic components and additional interactions in the adsorbed system [17].

The paper is organized as follows. In the section 1, we discuss the general assumptions of the formalism of composite Hamiltonians and derive the basic equations. In the section 2, we obtain expressions for the basic chemisorption characteristics and discuss the self-consistency of our approximations. In the section 3, we discuss the numerical results. The section 4 is devoted to the magnetic phase transition and the crossover in the critical behaviour of our model in the phase space of the Hamiltonian parameters. In the conclusion, we give a short summary of the obtained results and a general discussion.

## 1 BASIC EQUATIONS

Let us consider a system of  $N_A$  adsorbed hydrogen-like atoms (adatoms) distributed over  $N$  active centres on the crystal metal surface (substrate) which are called adsorption centres,  $N_A \leq N$ .

Each adatom has a rigid bond with the substrate. The configuration of the adatom arrangement over adsorption centres is not fixed. In the simplest case, the Hamiltonian of this system can be written in the following form [17]:

$$H = \sum_{k,\sigma} \epsilon_k^\sigma n_{k\sigma}^\dagger n_{k\sigma} + \sum_{\alpha} N_{\alpha} \left[ \sum_{\sigma} E_{\alpha\sigma} n_{\alpha\sigma} + U n_{\alpha\uparrow} n_{\alpha\downarrow} + \sum_{k,\sigma} (V_{\alpha k} b_{\alpha\sigma}^\dagger a_{k\sigma}^\dagger + \text{H.c.}) \right]. \quad (1)$$

The model (1) is the generalization of the well-known in the chemisorption theory the Anderson-Newns Hamiltonian [18] to the case of stochastic arrangement of the adatom configuration on the metal surface. The summation over  $\alpha$  in (1) is carried out over all adsorption centres; the operator  $N_{\alpha} = c_{\alpha}^{\dagger} c_{\alpha}$  has eigenvalues equal to 0 or 1, and the operators  $c_{\alpha}^{\dagger}$  and  $c_{\alpha}$  are the Fermi-amplitudes of the creation and annihilation of an adsorbed ion (adion) at the adsorption center  $\alpha$ . It is the proton for the hydrogen chemisorption case. The remaining parameters are the usual parameters of the Anderson model.

All the electronic properties of the system (1) are described by correlators of the type

$$\langle n_{k\sigma}^\dagger \rangle, \langle N_{\alpha} n_{\alpha\sigma} \rangle, \langle N_{\alpha} b_{\alpha\sigma}^\dagger a_{k\sigma}^\dagger \rangle, \dots, \quad (2)$$

whereas the ionic properties are involved in correlators of the Ising type

$$\langle N_{\alpha} \rangle, \langle N_{\alpha} N_{\beta} \rangle, \dots, \langle N_{\alpha} N_{\beta} \dots N_{\delta} \rangle, \dots. \quad (3)$$

The angle brackets in the expressions (2) and (3) mean the statistical averaging with the Hamiltonian (1) [17].

Though the model (1) is linear with respect to the operators  $N_{\alpha}$  it is not equivalent to the ideal lattice gas model. The hopping interaction proportional to  $V_{\alpha k} b_{\alpha\sigma}^\dagger (V_{k\alpha}^\dagger)$ , which describes the adsorbate-adsorbent electron transfer, induces the so-called indirect interaction between impurities when the adatoms exchange electrons through the substrate [19].

The model (1) can not be solved exactly till now, even when there is only one impurity:  $N_{\alpha} = 1$  if  $\alpha = A$  and  $N_{\alpha} = 0$  if  $\alpha \neq A$  because the presence of the Coulomb interaction  $U$  between electrons with opposite spin on an adatom. Therefore, as a first step,

We consider this model within the unrestricted H-F approximation [18]. In the current literature were made many attempts to take into account the Coulomb correlations in the Anderson model [21-22]. Within our model they may be considered in a similar way.

Now we introduce the H-F approximation of the Hamiltonian (1) in the form

$$H = \sum_{k,\sigma} \varepsilon_k^{\sigma} n_{k\sigma}^{\uparrow} + \sum_{\alpha} N_{\alpha} \left[ \sum_{\sigma} E_{\sigma} n_{\alpha\sigma} + \sum_{k,\sigma} (V_{\alpha k} b_{\alpha\sigma}^{\dagger} a_{k\sigma}^{\dagger} + \text{H.c.}) - \gamma \right], \quad (4)$$

where

$$E_{\sigma} = E + e^{-1} U \langle N_{\alpha} n_{\alpha-\sigma} \rangle, \\ \gamma = e^{-2} U \langle N_{\alpha} n_{\alpha\uparrow} \rangle \langle N_{\alpha} n_{\alpha\downarrow} \rangle, \quad \theta = \langle N_{\alpha} \rangle.$$

We have written the factor  $e^{-1}$  in front of the correlator  $\langle N_{\alpha} n_{\alpha\sigma} \rangle$ , to interpret the magnitude  $e^{-1} \langle N_{\alpha} n_{\alpha\sigma} \rangle$  as the conditional probability of finding an electron with spin  $\sigma$  at the adsorption center  $\alpha$ , when this center is already occupied by the adion [17]. The last term is usually added in the H-F scheme and renormalizes the chemical potential of the ionic adsorbate component [23].

For the description of the properties of the system (4) we will use the two-times Green-function formalism [24]. We should like to note that this machinery has some peculiarities for composite models [17]. However, they do not appear here and will not be discussed.

All the electronic properties of the system (4) can be calculated from the following system of Green-function equations

$$\begin{aligned} (\omega - E_{\sigma} + \varepsilon_F) \langle N_{\alpha} b_{\alpha\sigma}; b_{\alpha\sigma}^{\dagger} \rangle &= \frac{i}{2\pi} \theta + \sum_k V_{\alpha k} \langle N_{\alpha} a_{k\sigma}; b_{\alpha\sigma}^{\dagger} \rangle, \\ (\omega - \varepsilon_k + \varepsilon_F) \langle N_{\alpha} a_{k\sigma}; b_{\alpha\sigma}^{\dagger} \rangle &= \sum_k V_{k\alpha} \langle N_{\alpha} b_{\alpha\sigma}; b_{\alpha\sigma}^{\dagger} \rangle, \\ (\omega - \varepsilon_k + \varepsilon_F) \langle a_{k\sigma}; a_{k\sigma}^{\dagger} \rangle &= \frac{i}{2\pi} + \sum_{\alpha} V_{k\alpha} \langle N_{\alpha} b_{\alpha\sigma}; a_{k\sigma}^{\dagger} \rangle, \\ (\omega - \varepsilon_k + \varepsilon_F) \langle N_{\alpha} b_{\alpha\sigma}; a_{k\sigma}^{\dagger} \rangle &= \sum_{\beta} V_{\beta k} \langle N_{\alpha} b_{\alpha\sigma}; b_{\beta\sigma}^{\dagger} N_{\beta} \rangle, \end{aligned} \quad (5)$$

which close in a single Green-function of the form  $\langle N_{\alpha} b_{\alpha\sigma}; N_{\beta} b_{\beta\sigma}^{\dagger} \rangle$ . Here, we have used the Grand statistical ensemble and  $\varepsilon_F$  is the Fermi level of the electron band of the adsorbate-adsorbent system. The last equation of (5) was obtained after the differentia-

tion with respect to the second time. We used also the equality  $\langle N_{\alpha} b_{\alpha\sigma}; N_{\beta} b_{\beta\sigma}^{\dagger} \rangle = \langle N_{\beta} N_{\alpha} b_{\alpha\sigma}; b_{\beta\sigma}^{\dagger} \rangle$ . The first two equations of the system (5) describe the single-electron properties of the chemisorbed overlayer, the remaining equations describe the response of the substrate single-electron ones. Further, we investigate the ground state of the system (4) at zero temperature  $T=0$ .

To close the description we consider the Green-function  $\langle N_{\alpha} b_{\alpha\sigma}; N_{\beta} b_{\beta\sigma}^{\dagger} \rangle$ . There is a chain of recurrent relations for the model (4) which can easily be proved

$$\begin{aligned} (\omega - E_{\sigma} + \varepsilon_F) \langle \prod_{j=1}^m N_{\alpha_j} N_{\alpha} b_{\alpha\sigma}; b_{\beta\sigma}^{\dagger} N_{\beta} \rangle &= \frac{i}{2\pi} \langle \prod_{j=1}^m N_{\alpha_j} N_{\alpha} N_{\beta} \rangle \Delta_{\alpha\beta} + \\ + \sum_{\gamma} P_{\alpha-\gamma}(\omega) \langle \prod_{j=1}^m N_{\alpha_j} N_{\alpha} N_{\gamma} b_{\gamma\sigma}; b_{\beta\sigma}^{\dagger} N_{\beta} \rangle, \end{aligned} \quad (6)$$

where

$$P_{\alpha-\gamma}(\omega) = \sum_k \frac{V_{\alpha k} V_{k\gamma}}{\omega - \varepsilon_k + \varepsilon_F}$$

is the Grimley function introduced in [19] for the description of the indirect interaction between two adatoms,  $\Delta_{\alpha\beta}$  is the Kronecker symbol:  $\Delta_{\alpha\beta}=1$  if  $\alpha=\beta$  and  $\Delta_{\alpha\beta}=0$  in the opposite case. The relations (6) connect the  $(m+1)$ -point Green-function with the  $(m+2)$ -point function,  $m = 0, 1, 2, 3, \dots$

Using the relations (6) one can obtain the following exact representation for  $\langle N_{\alpha} b_{\alpha\sigma}; N_{\beta} b_{\beta\sigma}^{\dagger} \rangle$

$$\begin{aligned} \langle N_{\alpha} b_{\alpha\sigma}; b_{\beta\sigma}^{\dagger} N_{\beta} \rangle &= \frac{i}{2\pi} \frac{1}{(\omega - E_{\sigma} + \varepsilon_F)} \left\{ \Delta_{\alpha\beta} \langle N_{\alpha} N_{\beta} \rangle + \sum_{n=1}^{\infty} \sum_{\gamma_1, \dots, \gamma_n} \langle N_{\alpha} N_{\gamma_1} \dots N_{\gamma_n} N_{\beta} \rangle \right. \\ P_{\alpha-\gamma_1}(\omega) P_{\gamma_1-\gamma_2}(\omega) \dots P_{\gamma_{n-1}-\gamma_n}(\omega) &\left. \frac{1}{(\omega - E_{\sigma} + \varepsilon_F)^n} \Delta_{\gamma_n \beta} \right\}. \end{aligned} \quad (7)$$

The expansion (7) can be summed up if the high Ising type correlators are approximated in the spirit of the cyclic Kirkwood superposite formula

$$\langle N_{\alpha} N_{\gamma_1} \dots N_{\gamma_n} N_{\beta} \rangle \approx e^{-1/n} \langle N_{\alpha} N_{\gamma_1} \rangle \langle N_{\gamma_1} N_{\gamma_2} \rangle \dots \langle N_{\gamma_n} N_{\beta} \rangle \langle N_{\beta} N_{\alpha} \rangle. \quad (8)$$

The approximation (8) keeps the invariance with respect to a cyclic group of index permutations  $(\alpha, \gamma_1, \dots, \gamma_n, \beta)$ . Approximations of the type (8) were first used by Bethe [25] and Peleris

[26] in the theory of lattice systems. In the chemisorption theory they are used in the classical works of Fowler and Guggenheim [27]. It is known that in some cases they are the exact representations of the high correlators [28]. An additional cyclic invariance condition is a quite logical requirement of conservation of as much as possible symmetries of the original expressions when their approximations are constructed. Further, this invariance will provide the conservation of the well known Friedel rule for impurities in metals [29], which shows the self-consistency of the approximation (8).

Let us consider the following function

$$Q_{\vec{q}}^+(\omega) = \sum_{\alpha-\beta} \exp [ i\vec{q}(\vec{\alpha}-\vec{\beta}) ] P_{\alpha-\beta}(\omega) e^{-i\langle N_{\alpha}N_{\beta} \rangle} \quad (9)$$

where the vector  $\vec{q}$  lies within the first Brillouin zone [29] of the reciprocal adsorption lattice formed by the adsorption centers. If the adsorption centers form a square lattice on the metal surface, then  $\vec{q} = \{ q_x, q_y \}$ ,  $-\frac{\pi}{a} \leq q_i \leq \frac{\pi}{a}$  where  $i=x, y$  and  $a$  is the adsorption lattice constant. Here, we choose the axis  $z$  of the coordinate system perpendicular to the metal surface. For the adsorption on a one-dimensional chain  $q$  is a scalar varying within the range  $-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}$ . Further, the dimension of the vector  $\vec{q}$  will be called the dimension  $d$  of the coverage. The summation in the formula (9) is carried out over all vectors  $\vec{\alpha}-\vec{\beta} = \vec{R}_{\alpha} - \vec{R}_{\beta}$  on the surface where  $\vec{R}_{\alpha}$  is the position of the adsorption  $\alpha$ -center.

The inverse transformation from  $Q_{\vec{q}}^+(\omega)$  to  $P_{\alpha-\beta}(\omega)$  is made using

$$\sum_{\alpha-\beta} \exp [ i\vec{q}(\vec{\alpha}-\vec{\beta}) ] = \left( \frac{a}{2\pi} \right)^d \sum_n \delta(\vec{q} - \vec{G}_n) \quad (10)$$

where  $\vec{G}_n$  is a vector of the reciprocal lattice of the adsorption system and the summation in the eq. (10) is carried out over all  $\vec{G}_n$ , finally  $\delta(\vec{q})$  is Dirac's delta function.

Using eqs. (7) - (10) one can obtain the expression for the Green-function  $\langle N_{\alpha} b_{\alpha\sigma}; b_{\beta\sigma}^{\dagger} N_{\beta} \rangle$  in the form

$$\langle N_{\alpha} b_{\alpha\sigma}; b_{\beta\sigma}^{\dagger} N_{\beta} \rangle = \frac{1}{2\pi} \left( \frac{a}{2\pi} \right)^d \int d\vec{q} \frac{\langle N_{\alpha} N_{\beta} \rangle \exp [ i\vec{q}(\vec{\alpha}-\vec{\beta}) ]}{\omega - E_{\sigma} + \epsilon_F - Q_{\vec{q}}^+(\omega)} \quad (11)$$

It follows from the eq. (11) that the expression  $(\omega - E_{\sigma} + \epsilon_F - Q_{\vec{q}}^+(\omega))^{-1}$  may be interpreted as the electron propagator in the adsorption overlayer and the vector  $\vec{q}$  is the electron quasi-momentum in the impurity band. The formula (11) involves the unknown correlator  $\langle N_{\alpha} N_{\beta} \rangle$ . To close the description of the electron properties of the system (4) we use the Bragg-Williams approximation for this correlator [30]

$$\langle N_{\alpha} N_{\beta} \rangle \approx \Delta_{\alpha\beta} \langle N_{\alpha} \rangle + (1 - \Delta_{\alpha\beta}) \langle N_{\alpha} \rangle \langle N_{\beta} \rangle = \Delta_{\alpha\beta} \theta(1-\theta) + \theta^2, \quad (12)$$

where the equality  $N_{\alpha}^2 = N_{\alpha}$  is used.

In the Bragg-Williams approximation the function  $Q_{\vec{q}}^+(\omega)$  has the form

$$Q_{\vec{q}}^+(\omega) \stackrel{BW}{=} (1-\theta)L(\omega) + \theta P_{\vec{q}}^+(\omega) \quad (13)$$

where  $L(\omega) = \sum_k |V_{k\alpha}|^2 \frac{1}{\omega - \epsilon_k + \epsilon_F}$  is the Newns function [20] and  $P_{\vec{q}}^+(\omega)$  is the  $q$ -representation of Grimley's function.

For the single-site Green-function ( $\alpha = \beta$ ) describing the charge distribution on the impurity level we obtain the expression

$$G_{\alpha, \alpha}(\omega) = \frac{1}{2\pi} \left( \frac{a}{2\pi} \right)^d \int d\vec{q} \frac{1}{\omega - E_{\sigma} + \epsilon_F - (1-\theta)L(\omega) - P_{\vec{q}}^+(\omega)} \quad (14)$$

where we have used the approximation (12) and changed the normalization of the Green-function (11) to unity. As  $\theta \rightarrow 0$ , the formula (14) tends to the well-known limit in the Newns theory [20] and as  $\theta \rightarrow 1$  gives another exactly solvable limit of the model (4) when all the adsorption centers are occupied. Note that the model described by the Hamiltonian (4) is exactly solvable at all intermediate values of  $\theta$  in the case of a strictly periodic impurity arrangement.

In the conclusion of this section, we emphasize that the ionic correlator in the formula (11) can be not approximated but calculated within the same composite model scheme [17], and therefore, one can describe self-consistently both the electronic and the thermodynamic properties of the adsorbed overlayers.

## 2. BASIC CHEMISORPTION CHARACTERISTICS

In this section we obtain the expressions for the basic chemisorption characteristics like the impurity induced density of electron states (DOS)  $D(\omega)$ , the electric charge  $q$  and the magnetic moment  $m$  both localized at a single adatom and the binding energy  $\Delta E$  (chemisorption energy) of a single adatom with the substrate.

Using the eq. (14) we can obtain  $D(\omega)$  in the form

$$D(\omega) = \sum_{\sigma} D_{\sigma}(\omega), \quad D_{\sigma}(\omega) = \frac{1}{\Theta} \text{Im} \langle\langle N_{\alpha} b_{\alpha\sigma}; b_{\alpha\sigma}^{\dagger} \rangle\rangle |_{\omega-i0} = \frac{1}{\pi} \left(\frac{a}{2\pi}\right)^d \text{Im} \int d\vec{q} \frac{1}{\omega - E_{\sigma} + \epsilon_F - (1-\Theta) L(\omega) - P_{\vec{q}}(\omega)} \Big|_{\omega-i0} \quad (15)$$

The magnetic moment  $m$  in terms of the Bohr magneton units and the electric charge  $q$  measured in units of the electron charge are

$$m = \langle n_{\alpha\uparrow} \rangle - \langle n_{\alpha\downarrow} \rangle, \quad q = 1 - \langle n_{\alpha\uparrow} \rangle - \langle n_{\alpha\downarrow} \rangle \quad (16)$$

and

$$n_{\sigma} = \int_{-\infty}^{\epsilon_F} d\omega D_{\sigma}(\omega - \epsilon_F).$$

By definition, the chemisorption energy  $\Delta E$  reads as

$$\Delta E = \frac{1}{N_A} \left[ \langle H \rangle - \sum_{k,\sigma}^{\text{occ.}} \epsilon_k \right] - E, \quad (17)$$

where  $H$  is the Hamiltonian (4), and the summation over  $k$  is to be carried out over all occupied states of the unperturbed substrate. It is convenient to introduce the Green-function  $\langle\langle H \rangle\rangle$  as a linear combination of the above introduced ones

$$\langle\langle H \rangle\rangle = \sum_{k,\sigma} \epsilon_k \langle\langle a_{k\sigma}^{\dagger}; a_{k\sigma}^{\dagger} \rangle\rangle + \sum_{\alpha,\sigma} E_{\sigma} \langle\langle N_{\alpha} b_{\alpha\sigma}; b_{\alpha\sigma}^{\dagger} \rangle\rangle + 2 \sum_{k,\alpha,\sigma} V_{\alpha k} \langle\langle N_{\alpha} a_{k\sigma}; b_{\alpha\sigma}^{\dagger} \rangle\rangle. \quad (18)$$

After some rather lengthy algebraic manipulations and using the definitions (17) and (18), the spectral representations of the Green-functions and the equality  $\sum_k V_{\alpha k} \langle\langle N_{\alpha} a_{k\sigma}^{\dagger}; b_{\alpha\sigma}^{\dagger} \rangle\rangle = \sum_k V_{k\alpha} \langle\langle N_{\alpha} b_{\alpha\sigma}; a_{k\sigma}^{\dagger} \rangle\rangle$

we obtain for  $\Delta E$

$$\Delta E = \frac{1}{N_A} \int_{-\infty}^{\epsilon_F} d\omega \omega \rho_0(\omega) + \frac{1}{\pi} \left(\frac{a}{2\pi}\right)^d \text{Im} \sum_{\sigma} \int d\vec{q} \int_{-\infty}^{\epsilon_F} d\omega \omega \frac{d}{d\omega} \times \ln [ \omega - E_{\sigma} - (1-\Theta) \bar{L}(\omega) - \bar{P}_{\vec{q}}(\omega) ] |_{\omega-i0} - E - \gamma. \quad (19)$$

Here,  $\epsilon_F^0$  is the Fermi energy of the unperturbed electron substrate band,  $\rho_0(\omega) = \sum_{k\sigma} \delta(\omega - \epsilon_k) = 2V\bar{\rho}(\omega)$  is the unperturbed substrate density of states normalized to the crystal volume  $V$ ,  $\bar{\rho}(\omega)$  is the same magnitude normalized to unity,  $\bar{L}(\omega) = L(\omega - \epsilon_F)$  and  $\bar{P}_{\vec{q}}(\omega) = P_{\vec{q}}(\omega - \epsilon_F)$ . If the dimension of the adsorbate system is lower than that of the substrate one then  $\epsilon_F$  infinitesimally differs from  $\epsilon_F^0$ ,  $\epsilon_F = \epsilon_F^0 + \frac{S}{V} \xi$ , where  $\frac{S}{V} \rightarrow 0$  as  $S \rightarrow \infty$  and  $V \rightarrow \infty$ . (For  $d=2$   $S$  is the area of the adsorbed crystal surface). However, this change of  $\epsilon_F$  gives a noticeable contribution to the chemisorption energy  $\Delta E$  [19]. Indeed, it follows from the first term in (19)

$$\frac{1}{N_A} \int_{-\infty}^{\epsilon_F} d\omega \omega \rho_0(\omega) = \frac{V}{N_A} \int_{-\infty}^{\epsilon_F^0 + \frac{S}{V} \xi} d\omega \omega \bar{\rho}(\omega) \approx \frac{S}{N_A} \epsilon_F^0 \bar{\rho}(\epsilon_F^0) \xi \approx 1. \quad (20)$$

The condition of conservation of the electron number in our system defines the new position of  $\epsilon_F$

$$\sum_{k,\sigma} \langle n_{k\sigma} \rangle + \sum_{\alpha,\sigma} \langle N_{\alpha} n_{\alpha\sigma} \rangle = N_M + N_A. \quad (21)$$

Here,  $N_M$  is the number of substrate electrons, and  $N_A$  is the number of adsorbate electrons (we consider here one valence electron per adatom). After some algebraic transformations we can rewrite the condition (21) in the form

$$\int_{-\infty}^{\epsilon_F} d\omega \rho_0(\omega) + \frac{\Theta N}{\pi} \left(\frac{a}{2\pi}\right)^d \text{Im} \sum_{\sigma} \int d\vec{q} \int_{-\infty}^{\epsilon_F} d\omega \frac{d}{d\omega} \quad (22)$$

$$\cdot \ln [ \omega - E_{\sigma} - (1-\Theta) \bar{L}(\omega) - \bar{P}_{\vec{q}}(\omega) ] |_{\omega-i0} - \Theta N = 0.$$

It is convenient to reformulate the expression for  $\Delta E$  in a form in which the first term in (19) vanishes when  $\epsilon_F = \epsilon_F^0$ . For

this purpose, we multiply the equality (22) by the factor  $\varepsilon_F/\theta N$  and subtract the resulting expression from the right-hand side of the formula (19). The final result is

$$\Delta E = \frac{1}{N_A} \int_{\varepsilon_F}^{\varepsilon_F} d\omega (\omega - \varepsilon_F) \rho_0(\omega) + \frac{1}{\pi} \left( \frac{a}{2\pi} \right)^d \text{Im} \sum_{\sigma} \int d\vec{q} \int_{-\infty}^{\varepsilon_F} d\omega (\omega - \varepsilon_F) \frac{d}{d\omega} \times \quad (23)$$

$$\times \ln [ \omega - E_{\sigma} - (1-\theta) \bar{L}(\omega) - \bar{P}_{\vec{q}}^+(\omega) ] \Big|_{\omega-i0} - (E - \varepsilon_F) - \gamma.$$

In eq. (22) which defines the Fermi energy of the whole system we may carry out the integration over the energy in the second term and obtain the final equation for  $\varepsilon_F$

$$\frac{1}{N} \int_{\varepsilon_F}^{\varepsilon_F} d\omega \rho_0(\omega) = \frac{\theta}{\pi} \left( \frac{a}{2\pi} \right)^d \sum_{\sigma} \int d\vec{q} \text{arctg} \frac{\text{Im} F(\varepsilon_F - i0)}{\text{Re} F(\varepsilon_F - i0)} + \theta, \quad (24)$$

where  $F_{\sigma}(\omega, \vec{q}) = \omega - E_{\sigma} - (1-\theta)\bar{L}(\omega) - \theta\bar{P}_{\vec{q}}^+(\omega)$  ( $-\pi \leq \text{arctg} \leq 0$ ).

In the conclusion of this section, we note that the equality (22) is the analog of the Friedel sum rule [29] which connects the impurity induced change of the DOS in metals with the phase of the electron scattering  $\eta(\omega)$ . It is the basic relation for the so-called phase-shift approach in the chemisorption theory [31]

$$\eta(\omega) = \frac{\theta}{\pi} \left( \frac{a}{2\pi} \right)^d \text{Im} \sum_{\sigma} \int d\vec{q} \ln [ \omega - E_{\sigma} - (1-\theta) \bar{L}(\omega) - \bar{P}_{\vec{q}}^+(\omega) ] \Big|_{\omega-i0} \quad (25)$$

### 3. NUMERICAL RESULTS

This section contains the numerical results for the coverage dependence of the basic chemisorption characteristics.

As the substrate we take a one-dimensional chain of periodically arranged atoms with lattice constant  $a=1$  interacting only with their nearest neighbours and assume periodic boundary conditions. In this case the energy spectrum of the electron substrate band is  $\varepsilon_k = \Gamma \cos ka$  with respect to the center of the band [32]. The effects of the electron band degeneracy are introduced by the corresponding renormalization of the substrate electron density of states  $\bar{\rho}(\omega) \rightarrow Z\bar{\rho}(\omega)$ . In the calculations we used  $Z=5$ . To some extent, this substrate model is very simple; however, there is an

opinion that integral chemisorption characteristics like  $q$ ,  $m$  and  $\Delta E$  slightly depend on the details of the substrate electron density of states. Therefore, it is widely accepted and used for fitting the experimental data [33]. As we only try to give a correct qualitative description of the chemisorption process, this simple model of the substrate can be used. Further, we assume one adsorption center per site of the substrate surface lattice; so, the adsorbate lattice formed by the chemisorption centers has the same value of the lattice constant  $a=1$ . The type of chemisorption bond [9] is inessential for us here.

For this case the formulae (15) and (19) can be rewritten as

$$D_{\sigma}(\omega) = \frac{\pi}{n} \left( \frac{a}{2\pi} \right)^d \int d\vec{q} (1-\theta) \Delta(\omega) \times \quad (26)$$

$$\times \frac{1}{[\omega - E_{\sigma} + \varepsilon_F - (1-\theta)\gamma(\omega) - \frac{\theta\beta^2}{\omega - \varepsilon_q} + \varepsilon_F]^2 + (1-\theta)^2 \Delta(\omega)^2}$$

and

$$\Delta E = \frac{1}{N_A} \int_{\varepsilon_F}^{\varepsilon_F} d\omega (\omega - \varepsilon_F) \rho_0(\omega) + \frac{1}{\pi} \left( \frac{a}{2\pi} \right)^d \sum_{\sigma} \int d\vec{q} \int_{-\infty}^{\varepsilon_F} d\omega \times \quad (27)$$

$$\times \text{arctg} \left[ \frac{(1-\theta)\bar{\Delta}(\omega)}{\omega - E_{\sigma} - (1-\theta)\bar{\gamma}(\omega) - \frac{\theta\beta^2}{\omega - \varepsilon_q}} \right],$$

where  $\gamma(\omega) + i\Delta(\omega) = L(\omega - i0)$  and  $\bar{\Delta}(\omega) = \Delta(\omega - \varepsilon_F)$ ,  $\bar{\gamma}(\omega) = \gamma(\omega - \varepsilon_F)$ . It leads us to the expressions  $\Delta(\omega) = n \sum_k |V_{k\alpha}|^2 \delta(\omega - \varepsilon_k + \varepsilon_F) = n\beta^2 \bar{\rho}(\omega + \varepsilon_F)$ ,  $\gamma(\omega) = \frac{1}{\pi} \int dy \frac{\Delta(y)}{\omega - y}$  is the Hilbert transformation of the function  $\Delta(\omega)$  and  $-\pi \leq \text{arctg} \leq 0$ .

The corresponding equation for  $\varepsilon_F$  is

$$\frac{1}{N} \int_{\varepsilon_F}^{\varepsilon_F} d\omega \rho_0(\omega) = \frac{\theta}{\pi} \left( \frac{a}{2\pi} \right)^d \sum_{\sigma} \int d\vec{q} \text{arctg} \frac{(1-\theta)\bar{\Delta}(\varepsilon_F)}{\varepsilon_F - E_{\sigma} - (1-\theta)\bar{\gamma}(\omega) - \frac{\theta\beta^2}{\varepsilon_F - \varepsilon_q}} + \theta. \quad (28)$$

Now, it is necessary to specify the basic chemisorption parameters of the theory within the Anderson model. These are the ionization level  $E$ , the electron affinity level  $E+U$ , the Fermi

level  $\epsilon_F^0$  and the width  $2\Gamma = \epsilon_1 - \epsilon_0$  of the unperturbed substrate electron band, where  $\epsilon_1$  and  $\epsilon_0$  are the top and the bottom of the last respectively and, finally, the hybridization parameter  $\beta$ .

There are three situations corresponding to different positions of the ionization and the affinity levels with respect to the Fermi level, which are parametrized by  $\eta = E - \epsilon_F + \frac{U}{2}$ . The case  $\eta=0$  corresponds to the symmetric Anderson model, and  $\eta \neq 0$  corresponds to the asymmetric one. This parametrization is convenient and generally accepted in the Anderson model [34]. We have carried out the investigation of the coverage dependence of the chemisorption characteristics for all these cases. All energies are relative to the substrate band center and measured in half-width band units  $\Gamma$ , and we choose  $\epsilon_F^0 = 0$ .

In the figures 1-11 the results of the numerical calculations for different values of the parameters of the Anderson model are given. The figures 1-3 correspond to the symmetric Anderson model ( $\eta=0$ ). The values of  $\Delta E$  (curve —),  $m$  (-----),  $q$  (-·-·-·) and  $\epsilon_F$  (·····) are plotted vs. the coverage  $\theta$ . If the ratio  $U/\beta$  is large, figure 1, we have the magnetic case with a large value of the magnetic moment  $m$ . This agrees with Anderson's arguments for

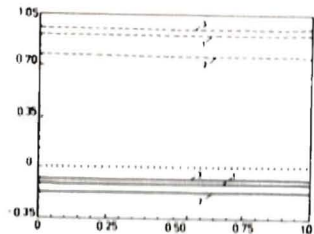


Fig. 1. The values of  $\Delta E$ ,  $m$ ,  $q$  and  $\epsilon_F$  are plotted vs. the coverage  $\theta = \langle N_\alpha \rangle$ .

The Hamiltonian parameters are:  
 1)  $E = -0.95$ ,  $U = 1.9$ ,  $\beta = 0.4$ ;  
 2)  $E = -0.5$ ,  $U = 1.0$ ,  $\beta = 0.4$ ;  
 3)  $E = -1.5$ ,  $U = 3.0$ ,  $\beta = 0.4$ .

For these parameter values:  
 $q(\omega) \approx \epsilon_F(\omega) \approx 0$  ( $\eta = 0$ ).

the impurity magnetism [35]. Figure 2 corresponds to small values

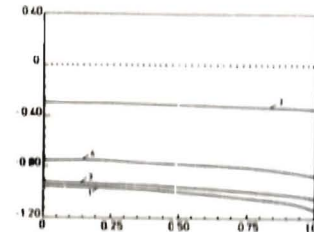


Fig. 2. The values of  $\Delta E$ ,  $m$ ,  $q$  and  $\epsilon_F$  are plotted vs. the coverage  $\theta = \langle N_\alpha \rangle$ .

The Hamiltonian parameters are:  
 1)  $E = -1.5$ ,  $U = 3.0$ ,  $\beta = 1.2$ ;  
 2)  $E = -0.15$ ,  $U = 0.3$ ,  $\beta = 0.4$ ;  
 3)  $E = -0.15$ ,  $U = 0.3$ ,  $\beta = 0.8$ ;  
 4)  $E = -0.5$ ,  $U = 1.0$ ,  $\beta = 0.8$ .

For these parameter values:  
 $q(\theta) \approx \epsilon_F(\theta) \approx m(\theta) \approx 0$  ( $\eta = 0$ ).

of the ratio  $U/\beta$  and the figure 3 shows the intermediate case when  $U/\beta \approx 1.5 - 2$ . The charge transfer between the adsorbate and the

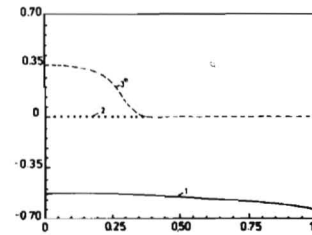


Fig. 3. The values of  $\Delta E$ ,  $m$ ,  $q$  and  $\epsilon_F$  are plotted vs. the coverage  $\theta = \langle N_\alpha \rangle$ . The Hamiltonian parameters are:  
 $E = -0.95$ ,  $U = 1.9$ ,  $\beta = 0.8$ .  
 For these parameter values:  
 $q(\theta) \approx \epsilon_F(\theta) \approx 0$  ( $\eta = 0$ ).

adsorbent is absent in all considered cases of the symmetric Anderson model and all the values of the impurity concentration  $\theta$ . At large values of the impurity magnetic moment, the chemisorption energy slightly depends on  $\theta$ . In nonmagnetic cases it depends on  $\theta$  and  $|\Delta E|$  increases with  $\theta$ . The rate of the chemisorption energy increases with the hybridization parameter  $\beta$ . The region of changing of the chemisorption energy with  $\theta$  is approximately one order smaller than its value. This agrees with current notions about the indirect interaction between adatoms [36]. At intermediate values

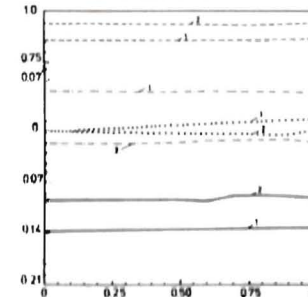


Fig. 4. The values of  $\Delta E$ ,  $m$ ,  $q$  and  $\epsilon_F$  are plotted vs. the coverage  $\theta = \langle N_\alpha \rangle$ .

The Hamiltonian parameters are:  
 1)  $E = -0.5$ ,  $U = 1.5$ ,  $\beta = 0.4$   
 ( $\eta > 0$ );  
 2)  $E = -1.5$ ,  $U = 2.5$ ,  $\beta = 0.4$   
 ( $\eta < 0$ ).

of the ratio  $U/\beta$ , figure 3, we have observed the suppression of the impurity magnetism with the variation of  $\theta$ . In this case  $|\Delta E|$  is approximately constant if  $m \neq 0$  and increases in the region  $m=0$ .

In figures 4-9 we present the numerical results for the asymmetric Anderson model. We interpret the similar behaviour of the chemisorption characteristics at  $\eta > 0$  and  $\eta < 0$  as the appearance of the well-known electron-hole symmetry in the Anderson model [34]. The figure 4 corresponds to large values of the ratio  $U/\beta$ . Here, we have a slight coverage dependence of the chemisorption



characteristics and large values for  $m$ . In the figure 5, we show

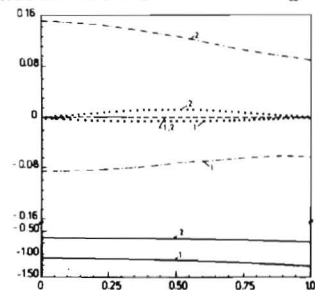


Fig.5. The values of  $\Delta E$ ,  $m$ ,  $q$  and  $\epsilon_F$  are plotted vs. the coverage  $\Theta = \langle N_\alpha \rangle$ .

The Hamiltonian parameters are:

- 1)  $E = -1.5$ ,  $U = 2.5$ ,  $\beta = 1.2$   
 $(\eta < 0)$  ;  
 2)  $E = -0.5$ ,  $U = 1.5$ ,  $\beta = 0.8$   
 $(\eta < 0)$  .

the results for small values of the ratio  $U/\beta \leq 1$ . They indicate

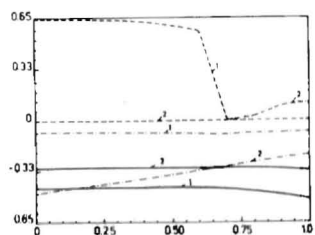


Fig.6. The values of  $\Delta E$ ,  $m$ , and  $q$  are plotted vs. the coverage  $\Theta = \langle N_\alpha \rangle$ .

The Hamiltonian parameters are:

- 1)  $E = -1.5$ ,  $U = 2.5$ ,  $\beta = 0.8$   
 $(\eta < 0)$  ;  
 2)  $E = -0.5$ ,  $U = 0.5$ ,  $\beta = 0.4$   
 $(\eta < 0)$  .

the absence of the magnetic momentum  $m$ , the increase in the chemi-

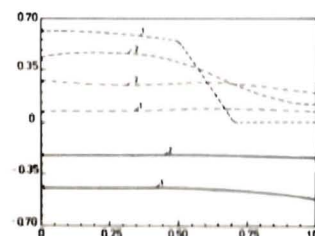


Fig.7. The values of  $\Delta E$ ,  $m$ , and  $q$  are plotted vs. the coverage  $\Theta = \langle N_\alpha \rangle$ .

The Hamiltonian parameters are:

- 1)  $E = -0.95$ ,  $U = 2.4$ ,  $\beta = 0.8$   
 $(\eta > 0)$  ;  
 2)  $E = -0.15$ ,  $U = 0.8$ ,  $\beta = 0.4$   
 $(\eta > 0)$  .

sorption bond  $|\Delta E|$  with  $\Theta$  and the dependence of the sign of the impurity charge on the sign of the parameter  $\eta$ ; if  $\eta > 0$  then  $q > 0$  and  $\eta < 0$  leads to  $q < 0$ . The results for intermediate values of the ratio  $U/\beta$  will be discussed in more detail. In the figure 6, we present the results for  $\eta < 0$  and  $E < \epsilon_F^*$ ,  $E + U > \epsilon_F^*$ . Here, we have both the stimulation (1) and the suppression (2) of the impurity magnetism with increasing  $\Theta$ . We do not present the coverage dependence of  $\epsilon_F^*$  in the figures 6,7,9 but it conforms

with the charge coverage dependence. In the figure 7 the results

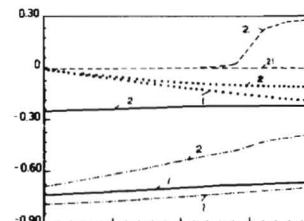


Fig.8. The values of  $\Delta E$ ,  $m$ ,  $q$  and  $\epsilon_F$  are plotted vs. the coverage  $\Theta = \langle N_\alpha \rangle$ .

The Hamiltonian parameters are:

- 1)  $E = -1.5$ ,  $U = 1.0$ ,  $\beta = 0.5$   
 $(\eta < 0)$  ;  
 2)  $E = -0.5$ ,  $U = 0.4$ ,  $\beta = 0.3$   
 $(\eta < 0)$  .

for  $\eta > 0$  and the same configuration of the levels  $E$ ,  $E+U$  and  $\epsilon_F^*$ .

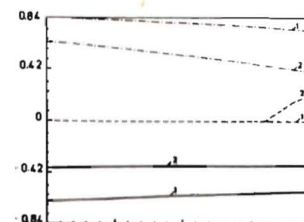


Fig.9. The values of  $\Delta E$ ,  $m$ , and  $q$  are plotted vs. the coverage  $\Theta = \langle N_\alpha \rangle$ .

The Hamiltonian parameters are:

- 1)  $E = 0.5$ ,  $U = 0.5$ ,  $\beta = 0.4$   
 $(\eta > 0)$  ;  
 2)  $E = 0.15$ ,  $U = 0.5$ ,  $\beta = 0.4$   
 $(\eta > 0)$  .

are given. In addition to the impurity magnetism suppression we see here a transition between two different states of adatoms with magnetic momenta  $m \approx 0.6$  and  $m \approx 0.15$ , respectively. In figures 8 and 9 the high asymmetric events when both the ionization and the electron affinity levels lie above or below the substrate band Fermi level  $\epsilon_F^*$  are given. Here, as could be expected, there is a strong charge transfer between the adsorbate and the adsorbent, which is damped with increasing  $\Theta$ . However, the chemisorption bond between an adatom and the metal substrate decreases with increasing  $\Theta$ . The sets of parameters 1) correspond to the nonmagnetic behaviour. We have observed here also the stimulation of the impurity magnetism with increasing  $\Theta$ , parameter sets 2). Note that the charge transfer damping is observed in all considered cases independently of the parameter values. It agrees with the calculations of other authors [8,2].

The appearance and disappearance of the impurity magnetism with increasing  $\Theta$  in the system (4) is interpreted by us as a se-

cond order phase transition. This question will be discussed more attentively in the next section.

In the remaining figures we present the coverage dependence of the electron density of states on adatoms. We should like to

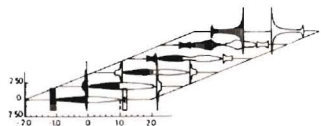


Fig.10. The electron density of states on adatoms are plotted vs. the coverage  $\theta = \langle N_{\alpha} \rangle$ . The Hamiltonian parameters are:  $E = -0.15$ ,  $U = 0.3$ ,  $\beta = 0.8$ . The curve  $D(\omega) > 0$  are the states with spin up and  $D(\omega) < 0$  are spin down ( $\eta < 0$ ). It is a nonmagnetic case.

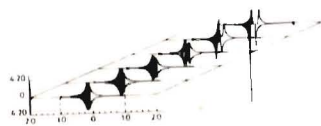


Fig.11. The electron density of states on adatoms are plotted vs. the coverage  $\theta = \langle N_{\alpha} \rangle$ . The Hamiltonian parameters are:  $E = -0.5$ ,  $U = 0.5$ ,  $\beta = 0.4$ . The curve  $D(\omega) > 0$  are the states with spin up and  $D(\omega) < 0$  are spin down ( $\eta < 0$ ). It is a coverage stimulated magnetic case.

note that it is the most model dependent information therefore, we give only a brief discussion. The dashed regions correspond to occupied states lying below  $\epsilon_F$ . The localized delta-like states in the DOS at  $\theta = 0$  [20] are showed as columns of area equal to its occupation number and their positions are marked by the arrows. In all considered cases we have the splitting of the DOS in two parts (bonding and antibonding states) when the coverage  $\theta$  tends to 1. The impurity magnetism is due to the asymmetrization between the densities of the electron states with spin up and down

#### 4 MAGNETIC PHASE TRANSITION

In this section, we discuss in more detail the phase transition when the appearance or disappearance of the magnetism in the adsorbed layer is observed in the model (4) at certain values of  $\theta$  and the model parameters:  $E$ ,  $U$ ,  $\beta$ ,  $\Gamma$  and  $\epsilon_F$ . These cases are presented in figures 3, 6 - 9 and 11. The sign of  $m$  is inessential

because the symmetry of equations (16) with respect to the substitution  $n_{\downarrow} \rightarrow n_{\uparrow}$  and  $n_{\uparrow} \rightarrow n_{\downarrow}$ . Therefore, there are always both solutions of (16) with  $m_1 > 0$ ,  $m_2 < 0$  and  $|m_1| = |m_2|$  if the magnetic case is realized.

In all the considered cases of appearance and disappearance of magnetism we did not observe the broken of the smooth behaviour of the other chemisorption characteristics near the critical points  $\theta_c$ . Thus, we interpret this as a second order phase transition.

Using the representations (16) and (26) we can obtain the following equations for the magnetic moment and the impurity charge

$$m = -\frac{m}{\pi} \left( \frac{a}{2\pi} \right) \int_{-\frac{a}{2}}^{\frac{a}{2}} \int_{-\infty}^{\epsilon_F} dq \int d\omega \frac{2U I(\omega, \theta) G_q(\omega, \theta)}{[G_q^2(\omega, \theta) + I^2(\omega, \theta) + (\frac{Um}{2})^2]^2 - [UmG_q(\omega, \theta)]^2} \quad (29)$$

$$1 - q = \frac{1}{\pi} \left( \frac{a}{2\pi} \right) \int_{-\frac{a}{2}}^{\frac{a}{2}} \int_{-\infty}^{\epsilon_F} dq \int d\omega \frac{2I(\omega, \theta) [G_q^2(\omega, \theta) + I^2(\omega, \theta) + (\frac{Um}{2})^2]}{[G_q^2(\omega, \theta) + I^2(\omega, \theta) + (\frac{Um}{2})^2]^2 - [UmG_q(\omega, \theta)]^2}$$

where

$$G_q(\omega, \theta) = \omega - \frac{(1-q)U}{2} - (1-\theta)\bar{\gamma}(\omega) - \frac{\theta\beta^2}{\omega - \epsilon_F}$$

$$I(\omega, \theta) = (1-\theta)\bar{\Delta}(\omega)$$

From the equations (29) we see that there is always a nonmagnetic solution with  $m = 0$ . Then, the system (29) transforms into a single equation for  $q$

$$1 - q = \frac{1}{\pi} \left( \frac{a}{2\pi} \right) \int_{-\frac{a}{2}}^{\frac{a}{2}} \int_{-\infty}^{\epsilon_F} dq \int d\omega \frac{2I(\omega, \theta)}{G_q^2(\omega, \theta) + I^2(\omega, \theta)} \quad (30)$$

At the same time there is a certain region of the model parameters where magnetic solutions may be realized too. If we fix a certain magnetic solution of eq. (29),  $m=m^*$  and  $q=q^*$  at some value of  $\theta$  and change the model parameters  $E$ ,  $U$ ,  $\beta$ ,  $\Gamma$  and  $\epsilon_F$  with satisfaction of the condition  $m=m^*$  and  $q=q^*$ , then the equations (29) will define a hypersurface in the phase space of the model parameters. This hypersurface may be topologically very complex. If we choose  $m^{**} \rightarrow 0$  and  $q \rightarrow q^{**}$  at some  $\theta = \theta_0$  where  $\theta_0$  is the

point where the magnetic solutions disappear, we obtain the critical hypersurface which divides the phase space on magnetic and nonmagnetic regions. The corresponding equations are

$$-1 = \frac{1}{\pi} \left( \frac{a}{2\pi} \right) \int_{-\frac{a}{2}}^{\frac{a}{2}} \int_{-\infty}^{\epsilon_F} d\omega \frac{2UJ(\omega, \theta) G_q(\omega, \theta)}{[G_q^2(\omega, \theta) + I^2(\omega, \theta)]^2}, \quad (31)$$

$$1 - q^{**} = \frac{1}{\pi} \left( \frac{a}{2\pi} \right) \int_{-\frac{a}{2}}^{\frac{a}{2}} \int_{-\infty}^{\epsilon_F} d\omega \frac{2I(\omega, \theta)}{G_q^2(\omega, \theta) + I^2(\omega, \theta)} \Big|_{q=q^{**}}.$$

It is convenient to rewrite the conditions (31) in terms of  $n = n_{\uparrow} = n_{\downarrow}$ . Then, the second equation of (31) is written as

$$n_{\uparrow} = \int_{-\infty}^{\epsilon_F} d\omega D_{\uparrow}(\omega - \epsilon_F) \Big|_{n_{\downarrow} = n_{\uparrow}} \quad (32)$$

and for the first one we have:

$$-1 = \frac{d}{dn_{\downarrow}} \int_{-\infty}^{\epsilon_F} d\omega D_{\uparrow}(\omega - \epsilon_F) = \frac{d}{dn_{\downarrow}} n_{\uparrow} \Big|_{n_{\uparrow} = n_{\downarrow} = n} \quad (33)$$

The last means that the critical hypersurface involves those points of the model parameter phase space which realize the non-magnetic solutions of the equations (29) and, at the same time, satisfy the well-known Anderson criterion for the existence of the impurity magnetism [35].

Let us calculate the critical exponent  $\nu$  which defines the behaviour of the magnetic moment  $m$  near the critical point  $\theta_c$  at a fixed value of the impurity electric charge,  $q = \text{const}$ ,

$$m \frac{1}{m} = Z \left[ \frac{\theta - \theta_c}{\theta_c} \right]. \quad (34)$$

For this purpose we consider another hypersurface near the critical one which is defined by the equations (29) when  $\theta = \theta_c + \delta\theta$  and  $|m| \ll 1$  at the same value  $q$ . Let us define the variations of the functions  $G_q(\theta, \omega)$  and  $I(\theta, \omega)$  when the transition from this hypersurface to the critical one takes place

$$G_q(\omega, \theta) = G_q(\omega, \theta_c) + \delta\theta \left[ \bar{\gamma}(\omega) - \frac{f\beta^2}{\omega - \epsilon_q} \right] = G_q(\omega, \theta_c) + \delta\theta \varphi_q(\omega),$$

$$I(\omega, \theta) = I(\omega, \theta_c) - \delta\theta \bar{\Delta}(\omega), \quad \delta\theta = \theta - \theta_c. \quad (35)$$

Then, we substitute the formulae (36) into the equality (29-I), expand the obtained expression over small values of  $\delta\theta$  and  $m$  and limit ourselves only to the lowest contributions over  $\delta\theta$  and  $m$  in it. The result is

$$m^2 \left[ \int_{-\infty}^{\epsilon_F} d\omega 4 \left( \frac{U}{2} \right)^2 [2G_q(\omega, \theta) - C_q(\omega)] \frac{UG_q(\omega, \theta_c) I(\omega, \theta_c)}{C_q^4(\omega)} = \right.$$

$$\left. = \delta\theta \left[ \int_{-\infty}^{\epsilon_F} d\omega \left[ \frac{\varphi_q(\omega) - \Delta(\omega)}{C_q^2(\omega)} - \frac{4UG_q(\omega, \theta_c) I(\omega, \theta_c) A_q(\omega)}{C_q^3(\omega)} \right] \right] \quad (36)$$

where

$$C_q(\omega) = G_q^2(\omega, \theta_c) + I^2(\omega, \theta_c),$$

$$A_q(\omega) = 2 [\varphi_q(\omega) G_q(\omega, \theta_c) - \bar{\Delta}(\omega) I(\omega, \theta_c)].$$

Here, we have taken into consideration the conditions (31). Comparing the expressions (34) and (36) one with the other we get the value  $\nu = 1/2$ . However, at some values of the model parameters one (or both) of the coefficients in (36) may be equal to zero. Then, we need to continue the expansion over  $m$  and  $\delta\theta$  and, as a result, we may obtain another functional dependence between  $m$  and  $\delta\theta$ . This means the change of the critical behaviour of our model or crossover [36]. The sign of the coefficients in front of  $m^2$  and  $\delta\theta$  defines the direction of the phase transition: the appearance or disappearance of magnetism with increasing  $\theta$ . We can see both the cases in our model that indicates the existence of crossover in the phase space of the model parameters.

In the conclusion of this section we note that the particular formula (27) ( $d=1$ ) is used here only to make the expressions for coefficients more evident. We are hopeful of the universality of the results obtained in this section.

## CONCLUSION

In this paper we used the composite Hamiltonian method to investigate the coverage dependence of the basic chemisorption characteristics, both analytically and numerically for the case of hydrogen-like chemisorption on metals. Our choice of the model (1) is governed only by reasons of simplicity. At the same time, it is to be emphasized that this model is quite profound if its parameters are fitted to the experimental data [9].

Now, we summarize the main results obtained here.

It was shown that at strong impurity magnetism in the adsorbate the basic chemisorption characteristics slightly depend on the adatom coverage  $\theta$ . In the nonmagnetic cases, when the ionization and electron affinity levels lie on different sides of the Fermi level  $\epsilon_F^0$ , the chemical bond between the adatom and the metal substrate increases with  $\theta$ . This conforms with the results obtained within other approaches [8,38]. In the case of strong asymmetry, when both the ionization and the electron affinity levels lie on the same side of the Fermi level, the chemisorption bond  $|\Delta E|$  decreases with  $\theta$ . At intermediate values of the ratio  $U/\beta$  we observed a magnetic phase transition in both directions: appearance or disappearance of the impurity magnetism with increasing  $\theta$ . It was shown that the Anderson criterion for the impurity magnetism in metals [35] holds for this phase transition, which is interpreted as a second order phase transition with the critical exponent  $s = 1/2$ . Further, we discussed the existence of crossover in our model. In all the considered cases we observed the damping of the charge transfer between the adsorbate and adsorbent with increasing  $\theta$ . It conforms with the experimental data and the results obtained within other methods [2,8]. At last, we demonstrated the splitting of the DOS on adatoms when  $\theta$  tends to 1.

The above developed scheme may be easily generalized to the case when other interactions [17] and correlations effects in the electronic and the ionic components of the adsorbate are taken into consideration. In the present paper we did not aim at getting a quantitative agreement of our model with experimental data. We

were hopeful of revealing here the qualitative behaviour of the coverage dependence of the basic chemisorption characteristics for the chemisorption of hydrogen-like adatoms on metals in a wide region of the Hamiltonian parameters. However, some of the considered cases can be associated with particular situations. At last, we should like to emphasize the possibility of calculate the ionic correlators within the same composite Hamiltonian model in order to obtain a self-consistent description of both the electronic and the thermodynamic properties of the adsorbed overlayers within a unified parametrization for different thermodynamical conditions of adsorption.

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Гавриленко Г.М., Карденас Р., Федянин В.К. E17-88-664  
О влиянии степени покрытия на характеристики хемосорбции

В рамках формализма составных гамильтонианов изучается зависимость от степени покрытия подложки адсорбатом плотности электронных состояний на адатомах, энергии хемосорбции, электрического заряда и локализованного на них магнитного момента. Расчеты выполнены в самосогласованной хартри-фоковской схеме в рамках приближения Брэгга-Вильямса для ионной компоненты адсорбата. Наблюдены происходящие здесь магнитные фазовые переходы по концентрации адатомов, которые интерпретируются как фазовые переходы второго рода. Рассчитан критический индекс и обсуждена проблема кроссовера в пространстве параметров модели.

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Gavrilenko G.M., Cardenas R., Fedyanin V.K. E17-88-664  
On Coverage Dependence of Chemisorption Characteristics on Metals

Within the composite Hamiltonian method the coverage dependence of the chemisorption characteristics like the chemisorption energy, the electric charge and magnetic moment localized at impurities (adsorbed atoms) and at last the impurity electron density of states are investigated. Calculations are carried out within the self-consistent unrestricted Hartree-Fock scheme for an electron component and the Bragg-Williams approximation for an ionic adsorbate component. The magnetic phase transition in coverage dependence is obtained. It is interpreted as a second order phase transition with the critical exponent  $s = 1/2$ . The crossover problem in the phase of the model parameters is also discussed.

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

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