

TOPOLOGICAL CORRELATIONS IN A LAYER ADSORBED ON A CRYSTAL SURFACE*

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ABSTRACT. The incoherent scattering of electrons by a layer adsorbed at a single crystal surface is determined by the topological correlations of elements forming the adsorbed layer. The model for the description of atoms or molecules adsorbed on the surface is formulated in terms of occupation operators which are expressed in terms of pseudospin operators with a given spin value. The correlations can be determined by the fluctuation dissipation theorem in connection with the susceptibility or given directly by means of the Green functions properly chosen. An example of the topological or chemical disorder of two components is considered in detail. The calculations of the topological correlations allow us to find the incoherent scattering amplitude as a function of the surface coverage which can be experimentally detected.

1. INTRODUCTION

A knowledge of the surface electronic and ionic topography is one of the most important inputs to the understanding of a surface properties. The main technique used to investigate the geometrical structure of a surface is the low energy electron diffraction (LEED). This technique has established as one of the foremost surface structural techniques for ordered surface [1-4]. In the absence of a long range order at the surface the electrons are scattered out of the discrete beams which characterize the diffraction from an ordered surface, a situation which cannot be described in the framework of the LEED theory. At the same time experimental diffuse LEED intensities contain the structural informations. In a recent paper Pendry and al [5] have shown a non conventional use of LEED technique for the investigations of geometrical arrangement of chemisorbed atoms. Neglecting multiple scattering inside the overlayer, these authors show

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that the spatial distribution of the electrons elastically scattered outside the diffraction channels depends on the statistical arrangement of the adatoms and on the geometry of chemisorption sites. A disordered adsorbate on near perfect substrate was examined by K. Heinz et al. [6]; each electron contributing to the diffuse intensities has scattered at least once from an adsorbate atom and therefore these intensities have concentrated information within them about local environment of the adsorbate. It has been noticed that an accurate measurement of critical exponents by LEED peak intensity analysis requires a detailed knowledge of the multiple scattering processes occurring when a partial order in overlayers exists. Le Bosse et al. [7] introduced a theory of the elastic backscattering of electrons at a disordered surface including multiple scattering processes. This theory is based upon the introduction of field-like operators which define the occupancy of any chemisorption site of the substrate. The wave scattered at a disordered surface is decomposed into the average of the wave performed over a statistical ensemble of overlayer configurations (the coherent wave) and a term corresponding to the deviation from this average (the incoherent wave). It means the backscattered intensities are the sum of a coherent intensity (LEED intensity) and an incoherent intensity (diffuse LEED intensity). It is assumed that the incoherent part of the wave scattered at the adsorbate plus substrate complex depends linearly on the incoherent part of the wave scattered at the disordered overlayer. Furthermore, the coherent part of the wave scattered at the adsorbate plus substrate complex is evaluated by using a mean field like approximation which amounts to do the average transition matrix approximation currently used in energy band alloy theory. So it is possible to preserve the usual theoretical framework of LEED theory and to avoid a time consuming cluster-like treatment of the problem. The expression of the coherent part of the backscattered intensities depends on the occupation number of a site and the incoherent part of the backscattered intensities depends on the pair correlation functions.

In respect of the information about the local environment of the adsorbate, there is an analogy with SEXAFS experiments [5,8–11]. For this technique X-rays are used to ionize an adatom by exciting one of its core level. The wave function of the electron emitted after the ionization process can be roughly considered as the superposition of a primary spherical wave centered at the ionized adatom and waves scattered at its neighbours. Interferences between these waves give rise to oscillations in the transition probability amplitude from the core state to the final state. In SEXAFS, these oscillations which are observed through the adsorption rate of X-rays, are a feature of the local surrounding of the ionized adatoms. A SEXAFS experiment has at the most three datasets corresponding to the polarizations of the X-ray beam. In fact the diffuse LEED has some advantages over SEXAFS because by varying the incident angle of the detections many independent datasets can be gathered and hence a richer mass of structural data is available for analysis.

The aim of this paper is to determine the correlation functions expected for the calculations of the incoherent intensity. For this purpose we should calculate all correlation functions between the sites j and j' (independently of site j) for the occupation operators defined respectively in the states p and p' .

2. STATISTICAL DESCRIPTION OF THE DISORDERED ADLAYER

The chemisorption sites of atoms or molecules are assumed to be located at a two dimensional lattice whose translational symmetry is the same as the surface substrate one. A site occupancy operator is associated with any chemisorption site of the surface. The hamiltonian of the overlayer is expressed in terms of these site occupancy operators and all statistical averages are performed by using the grand canonical ensemble.

2.1. Model of the adsorbate layer

In general case, the model describing properties of an adsorbate layer is definite for the occupation operators $\sigma_j(p)$ which characterize state p of a site occupancy j of the surface lattice. In our case, one site can be occupied at most by one atom or one molecule. Thus the surface coverage, i.e. the ration of atoms or molecules number to chemisorption site number N is necessarily less or equal one. The hamiltonian \mathcal{H} contains a quadratic term describing an interaction between site j in state p and site j' in state p' with energy $U_{j,j'}(p, p')$ and a linear term describing adsorbate substrate coupling with the adsorption energy $E_j^{ads}(p)$. The form of the hamiltonian is [7]:

$$\mathcal{H} = - \sum_{p=1}^{p_{\max}} \sum_{j=1}^N E_j^{ads}(p) \sigma_j(p) + \frac{1}{2} \sum_{p, p'=1}^{p_{\max}} \sum_{j, j'=1}^N U_{j, j'}(p, p') \sigma_j(p) \sigma_{j'}(p') \quad (1)$$

where N is a number of all elements of the adsorbate layer, however $p_{\max} + 1$ is a number of all occupied states of elements.

2.2 Correlation function of an adsorbate layer

The correlation functions are defined as:

$$\gamma_{j, j'}(p, p') = \langle \sigma_j(p) \sigma_{j'}(p') \rangle - \langle \sigma_j(p) \rangle \langle \sigma_{j'}(p') \rangle \quad (2)$$

where the brackets $\langle \dots \rangle$ denote the statistical average in the usual sense i.e. $\langle A \rangle = \text{Tr}(\rho A)$ for the statistical operator of the grand canonical ensemble ρ :

$$\rho = \frac{\exp \left\{ -\beta \left[\mathcal{H} - \sum_p \mu(p) N(p) \right] \right\}}{\text{Tr} \exp \left\{ -\beta \left[\mathcal{H} - \sum_p \mu(p) N(p) \right] \right\}} \quad (3)$$

where $\beta = 1/k_B T$. Moreover $N(p) = \sum_{j=1}^N \sigma_j(p)$ and $\mu(p)$ denotes the chemical potential for the state p . The trace Tr is carried out over the set of configuration states defined further. The correlation function (2) allows us to determine incoherent intensity, which is of the form [7]:

$$I_{\text{incoh}}(k_{\vec{f}} \leftarrow k_{\vec{i}}^+) = \frac{4\pi^4 k}{Ak_{\perp}} \sum_{p=1}^{p_{\text{max}}} \sum_{p'=1}^{p_{\text{max}}} \Gamma(p, p', k_{\vec{f}} \leftarrow k_{\vec{i}}^+) K_1^{(0)}(p, k_{\vec{f}} \leftarrow k_{\vec{i}}^+) * K_1^{(0)}(p', k_{\vec{f}} \leftarrow k_{\vec{i}}^+) \quad (4)$$

where $k_{\vec{f}}$ is the above vector in the detector direction, $k_{\vec{i}}^+$ is an initial wave vector in the electron gun direction. $K_1^{(0)}(p)$ describes the effective transition matrix of the p adsorbate located at the reference site $j=0$ in the presence of the other adsorbates and of the substrate surface, and function $\Gamma(p, p', k_{\vec{f}} \leftarrow k_{\vec{i}}^+)$ is the Fourier transform of the correlation function $\gamma_{j,j}(p, p')$, i.e.:

$$\Gamma(p, p', k_{\vec{f}} \leftarrow k_{\vec{i}}^+) = \sum_{j=1}^N [\gamma_{j,j}(p, p') \exp[-i(k_{\vec{f}} - k_{\vec{i}}^+)(T_j - T_0)] \quad (5)$$

The relation (4) has been established by assuming that all sites j are statistically equivalent.

2.3. Configurations of an adsorbate layer

2.3.1. Topological order

In this case overlayer contains one kind of adsorbate. So, any site can be occupied or unoccupied. Let us define a configuration state $|p_1, \dots, p_N\rangle$ in which site i is in the occupation state p_1 and site N is in the occupation state p_N . For any site j , p_j can take the value 0 for a vacancy or 1 when an adsorbate is present. The operator $\sigma_j(p)$ acts on the configuration state $|p_1 \dots p_j \dots p_N\rangle$ in the following way:

$$\sigma_j(p) |p_1 \dots p_j \dots p_N\rangle = \delta_{p,p} |p_1 \dots p_j \dots p_N\rangle \quad (6)$$

We can notice that $\sigma_j(1) = 1 - \sigma_j(0)$ because occupation and vacancy at site j represent all possibilities. This particular chemisorption problem can be formally written as a problem of magnetism for the spin $S = \frac{1}{2}$. For this purpose let us define the pseudospin operator:

$$S_j^z = \sigma_j(1) - \frac{1}{2} = \frac{1}{2} - \sigma_j(0) \quad (7)$$

Instead of describing the configuration state by $|p_1 \dots p_N\rangle$ we use the notation $|S_1 \dots S_N\rangle$ in which $S_j = (2p_j - 1)/2$. Now (6) is replaced with:

$$S_j^z |S_1 \dots S_j \dots S_N\rangle = S_j |S_1 \dots S_j \dots S_N\rangle \quad (8)$$

In the quantum theory of angular momentum we usually introduce the operator:

$$S_j^\pm = S_j^x \pm iS_j^y \quad (9)$$

and we have:

$$S_j^\pm |S_1 \dots S_j \dots S_N\rangle = \sqrt{S(S+1) - S_j(S_j \pm 1)} |S_1 \dots S_j \pm 1 \dots S_N\rangle \quad (10)$$

Operators S_j^x and S_j^y which have a clear meaning in angular momentum theory cannot be easily interpreted in chemisorption theory. On the other hand, S_j^\pm has a clear meaning in both theories. Let us assume that the different spin states of site j are represented by the steps of a ladder. So, (10) indicates that the action of S_j^+ amounts to climb up the ladder and at the upper step the action of S_j^+ yields zero. Similarly, the action of S_j^- amounts to climb down the ladder and the action on the lower step is zero. In our case, the two ladder steps are associated with the unoccupied and occupied states of chemisorption site j . As a matter of fact, all commutation relations and algebra related to S_j^z , S_j^+ and S_j^- which are established in angular momentum theory can be fully applied to our chemisorption problem. Moreover, they can be extended to the cases where $p_{\max} + 1 = 2S$ is equal to 3, 4 etc.

2.3.2. Stoichiometrical order

The adsorbate layer contains two kinds of atoms and the degree of surface coverage by adatoms is equal 1, $\theta = 1$. So, we have the relation:

$$\sigma_j(1) + \sigma_j(2) = 1 \quad (11)$$

in which 1 denotes the presence of atom A at site j and 2 denotes the presence of atom B . Relation (6) is still valid except that now we consider configuration states $|p_1 \dots p_N\rangle$ in which all p_j are different from zero. We put

$$S_j^z = \sigma_j(1) - \frac{1}{2} = \frac{1}{2} - \sigma_j(2) \quad (12)$$

and change $|p_1 \dots p_N\rangle$ with $|S_1 \dots S_N\rangle$ in which $S_j = (2p_j - 3)/2$ ($p_j = 1$ for atom A corresponds to spin $-\frac{1}{2}$ and $p_j = 2$ for atom B corresponds to spin $\frac{1}{2}$). Let us notice that the simple cases of topological order (2.3.1) and stoichiometrical order (2.3.2) can be described in the same magnetism case $S = \frac{1}{2}$.

2.3.3. Mixed order

The adsorbate contains two kinds of atoms, however, the surface coverage by adatoms $\theta < 1$. It means that one site can be occupied by atom A (with the surface coverage θ_A) or atom B (with the surface coverage θ_B) or it can stay unoccupied (with the surface coverage θ_V), so that $\theta_A + \theta_B + \theta_V = 1$; (for $\theta_A + \theta_B = \theta$ we have $\theta_V = 1 - \theta$). If $\theta_A = \theta'$, then we can put $\theta_B = \theta - \theta'$. In the particular case $\theta_A = \theta_B$, we have $\theta' = \theta/2$.

Operators	vacancy	States	
		atom A	atom B
$\sigma_j(p=0)$	1	0	0
$\sigma_j(p=1)$	0	1	0
$\sigma_j(p=2)$	0	0	1
S_j^z	0	1	-1

Relation (6) is still valid except that p_j can take the value 0, 1 and 2 instead of 1 and 2 as in the previous case. Now, S_j^z has three possible eigenvalues which are $-1, 0, 1$ as shown in the table (left). Now $|p \dots p_N\rangle$ is replaced with $|S_1 \dots S_N\rangle$ in which $S_j = (p_j(5 - 3p_j))/2$. The above

properties can be described by using the operators S_j^z in the following way:

$$\begin{aligned} \sigma_j(p=0) &= 1 - (S_j^z)^2 \\ \sigma_j(p=1) &= S_j^z(S_j^z + 1)/2 \quad \text{for } S_j^z = \pm 1, 0 \\ \sigma_j(p=2) &= S_j^z(S_j^z - 1)/2 \end{aligned} \quad (13)$$

for the pseudospin $S = 1$.

2.3.4. Mixed order with interstitial positions

We assume that each lattice site of the substrate can be occupied by an atom A or B in two positions α or β , and it can be also unoccupied (it means the vacancy of both positions). The position α is a usual position in lattice site of adlayer, while the position β means that an atom A or B is located in the interstitial position i.e. the lattice site of adlayer is shifted with respect to the corresponding lattice site of the substrate. In Fig. 1 we show the positions α and β for the b.c.c. lattice

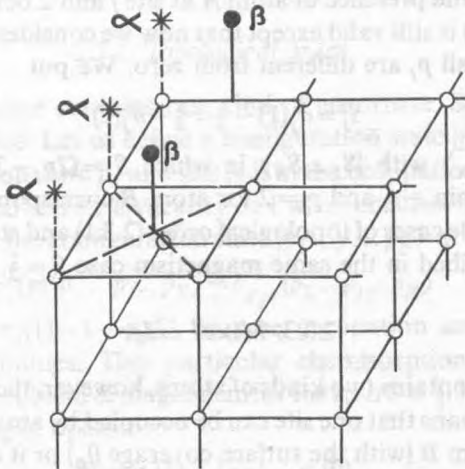


Fig. 1. Positions of adatoms for the b.c.c. lattice; position α is a usual position in this lattice; position β is the interstitial position.

For the description of the situation presented above we introduce the following occupation operators: $\sigma_j(p=0)$ (vacancy operator), $\sigma_j(p=1)$ (occupation operator for an atom A in the position α), $\sigma_j(p=2)$ (occupation operator for an atom B in the position α), $\sigma_j(p=3)$ (occupation operator for an atom A in the position β) and $\sigma_j(p=4)$ (occupation operator for an atom B in the position β).

Operators	States				
	vacancy	atom $A-\alpha$	atom $B-\alpha$	atom $A-\beta$	atom $B-\beta$
$\sigma_j(p=0)$	1	0	0	0	0
$\sigma_j(p=1)$	0	1	0	0	0
$\sigma_j(p=2)$	0	0	1	0	0
$\sigma_j(p=3)$	0	0	0	1	0
$\sigma_j(p=4)$	0	0	0	0	1
S_j^z	0	1	-1	2	-2

The table contains the values of states of the occupation operators, in which, at the same time the values of z -component of pseudospin operator $S=2$ are given. The following representation of the operators $\sigma_j(p)$

$$\begin{aligned}
 \sigma_j(p=0) &= 1 - \frac{5}{4}(S_j^z)^2 + \frac{1}{4}(S_j^z)^4 \\
 \sigma_j(p=1) &= \frac{2}{3}S_j^z(S_j^z+1)\left[1 - \frac{1}{4}(S_j^z)^2\right] \\
 \sigma_j(p=2) &= \frac{2}{3}S_j^z(S_j^z-1)\left[1 - \frac{1}{4}(S_j^z)^2\right] \quad \text{for } S_j^z=0, \pm 1, \pm 2 \\
 \sigma_j(p=3) &= \frac{1}{24}S_j^z(S_j^z+2)\left[(S_j^z)^2-1\right] \\
 \sigma_j(p=4) &= \frac{1}{24}S_j^z(S_j^z-2)\left[(S_j^z)^2-1\right]
 \end{aligned} \tag{14}$$

by the operators S_j^z assure the properties required for the eigenvalues of the operators $\sigma_j(p)$ in the case of the pseudospin $S=2$.

The examples mentioned above point out, that the real situations concerning the order in adsorbate layer can be described in the modelling way as a different configurations expressed with the help of the occupation operators $\sigma_j(p)$ for properly chosen numbers of states p . Simultaneously, these examples show that there is a possibility to represent the operators $\sigma_j(p)$ by the pseudospin operators S_j^z with the adequate values S . We can notice that: $S = \frac{1}{2}$ corresponds to the system of two states ($p_{\max}=2$); $S=2$ to the system of five states ($p_{\max}=4$) in the general case we can find that the pseudospin $S = p_{\max}/2$ corresponds to the system of $(p_{\max}+1)$ states.

2.4. Relation between the occupation operators and pseudospin operators

In Section 2.3 relation between occupation operators and pseudospin operators has been examined for the same particular cases. In this Section we provide a general treatment of this problem.

The relation between the operators $\sigma_j(p)$ and the z -components S_j^z of pseudospin S can be found using the following procedure.

Let us first remark that the set of configuration states $\{|p_1 \dots p_N\rangle\}$ is a complete orthonormal basis set, i.e.:

$$\prod_{i=1}^N \sum_{p_i=0}^{p_{\max}} |p_1 \dots p_N\rangle \langle p_1 \dots p_N| = 1 \quad (15)$$

Using relation (6) it can be straightforwardly shown that:

$$\prod_{\substack{i=1 \\ i \neq j}}^N \sum_{p_j=0}^{p_{\max}} |p_1 \dots p_j \dots p_N\rangle \langle p_1 \dots p_j \dots p_N| = \sigma_j(p_j) \quad (16)$$

On the other hand, for any operator A acting on vectors of the configuration vectorial space, we have the trivial relation:

$$A = \prod_{i=1}^N \sum_{p_i=0}^{p_{\max}} |p_1 \dots p_N\rangle \langle p_1 \dots p_N| A \quad (17)$$

In the particular case where A has a diagonal matrix representation, (17) can be rewritten as:

$$\begin{aligned} A &= \sum_{p_j=0}^{p_{\max}} \prod_{i \neq j} \sum_{p_i=0}^{p_{\max}} |p_1 \dots p_N\rangle \langle p_1 \dots p_N| A |p_1 \dots p_j \dots p_N\rangle \\ &= \sum_{p_j=0}^{p_{\max}} \sigma_j(p_j) A |p_1 \dots p_j \dots p_N\rangle \langle p_1 \dots p_j \dots p_N| \end{aligned} \quad (18)$$

Let us now consider the cases where $A=1$, $A=S_j^z$, ..., $A=(S_j^z)^{2S}$. We obtain a set of $(2S+1)$ linear equations which will have to be solved in order to get the expression of $\sigma_j(p)$ in terms of S_j^z . As an example of this method, let us come back to the case of mixed order with interstitial positions.

In that case $p_{\max}=4$ and thus $S=2$. Five equations can be written:

$$(S_j^z)^n = \sum_{p_j=0}^{p_{\max}} \sigma_j(p_j) [S_j^z(p_j)]^n \quad (19)$$

for $n=0, 1, \dots, 4$. The values of $S_j^z(p_j)$ results from an arbitrary choice of p_j . For example:

$$\begin{aligned} p_j=0 & - S_j^z(0)=0 \\ p_j=1 & - S_j^z(1)=1 \\ p_j=2 & - S_j^z(2)=-1 \\ p_j=3 & - S_j^z(3)=2 \\ p_j=4 & - S_j^z(4)=-2 \end{aligned} \quad (20)$$

We can easily verify that the solutions of the five linear equations (19) obtained for these values are given in (14). The equations (12) and (13) are particular solutions of the system (19) for $S = 1/2$ and $S = 1$, respectively.

3. ENERGY OF CONFIGURATION INTERACTION

The possibility of expression of the occupation operators $\sigma_j(p)$ by the operators $(S_j^z)^n$ allows us to use the well known technique applied to the calculations in Ising model in order to determine the correlation functions. For these purposes we should express the correlation functions, as well as the hamiltonian (1) by the operators $(S_j^z)^n$. At the same time it is a basis for determining the statistical operator occurring in the definition of the correlation functions. Substituting the relation:

$$\sigma_j(p) = \sum_n^{2S} a_n^p (S_j^z)^n \quad (21)$$

to the hamiltonian (1) and the expression (2), the hamiltonian (1) takes the form:

$$\begin{aligned} \mathcal{H} = & - \sum_{j=1}^N \sum_{n=0}^{2S} h_j^{(n)} (S_j^z)^n \\ & + \frac{1}{2} \sum_{j,j'=1}^N \sum_{n=0}^{2S} \sum_{n'=0}^{2S} U_{j,j'}^{n,n'} (S_j^z)^n (S_{j'}^z)^{n'} \end{aligned} \quad (22)$$

where

$$h_j^{(n)} = \sum_{p=0}^{p_{\max}} U_j^{ads}(p) a_n^p$$

and

$$U_{j,j'}^{n,n'} = \sum_{p=0}^{p_{\max}} \sum_{p'=0}^{p_{\max}} U_{j,j'}(p, p') a_n^p a_{n'}^{p'}$$

play the role of external fields of the power (n) and effective interactions of the power ($n + n'$) with respect to the operator S_j^z , respectively. The coefficients a_n^p are determined by the system of equations (19); in the particular cases they are given by the formulas (12), (13) and (14). We would like to remark that these cases represent the most interesting physical configurations.

4. PROPERTIES OF CORRELATION FUNCTIONS

Taking into account the above consideration, we can write the correlations (2) in the following form:

$$\gamma_{j,j'}(p, p') = \sum_{n,n'} a_n^p a_{n'}^{p'} [\langle (S_j^z)^n (S_{j'}^z)^{n'} \rangle - \langle (S_j^z)^n \rangle \langle (S_{j'}^z)^{n'} \rangle] \quad (23)$$

where the average values are calculated with respect to the hamiltonian (22). We can see, that in order to calculate the correlation function $\gamma_{j,j'}(p, p')$ we should know the correlation functions of higher orders, precisely of all the orders $n, n' \in (0, 2S)$ for the pseudospin operators. It is convenient to introduce the functions:

$$\gamma_{j,j'}^{n,n'} = \langle (S_j^z)^n (S_{j'}^z)^{n'} \rangle - \langle (S_j^z)^n \rangle \langle (S_{j'}^z)^{n'} \rangle \quad (24)$$

then

$$\gamma_{j,j'}(p, p') = \sum_{n,n'} a_n^p a_{n'}^{p'} \gamma_{j,j'}^{n,n'} \quad (25)$$

The operator of grand canonical ensemble introduced in form (3) contains now the term:

$$\sum_j \sum_p \mu(p) \sigma_j(p) = \sum_j \sum_n \left[\sum_p \mu(p) a_n^p \right] (S_j^z)^n = \sum_j \mu^{(n)} (S_j^z)^n \quad (26)$$

4.1. Fluctuation dissipation theorem

Let us now consider a small external field h_j and calculate the change in some physical quantities such as $\langle S_j^z \rangle$ resulting from the infinitesimal change of h_j . We assume that the adsorbate - field coupling hamiltonian has the form $-\sum_j h_j S_j^z$ and we now consider

$$\mathcal{H}' = \mathcal{H} - \sum_j h_j S_j^z \quad (27)$$

instead of (22). Taking into account the definition of the statistical average:

$$\langle S_j^z \rangle = \frac{\text{Tr} [S_j^z \exp \beta (-\mathcal{H}' + \sum_j h_j S_j^z)]}{\text{Tr} [\exp \beta (-\mathcal{H}' + \sum_j h_j S_j^z)]} \quad (28)$$

where $\mathcal{H}' = \mathcal{H} - \sum_j \mu^{(n)} (S_j^z)^n$, we have

$$\frac{\partial \langle S_j^z \rangle}{\partial h_j} = \beta \gamma_{jj}^{n=1, n'=1} \quad (29)$$

and by the definition of the susceptibility

$$\chi_{jj'} = \frac{\partial \langle S_j^z \rangle}{\partial h_{j'}} \quad (30)$$

we get

$$1/\beta \chi_{jj'} = \gamma_{jj'}^{11} \quad (31)$$

As h_j is an infinitesimal, the formula (30) is actually fulfilled for the system described by the hamiltonian \mathcal{H} in the case of the grand canonical ensemble, we can see, on the basis of the formula (28), that a derivative with respect to h_j is entirely equivalent to a derivative with respect to the chemical potential $\mu_j^{(1)}$ of site j . Therefore we can write down:

$$\frac{\partial \langle S_j^z \rangle}{\partial \mu_j^{(1)}} = \beta \gamma_{jj}^{1,1} = \chi_{jj} \quad (32)$$

treating $\chi_{j,j}$ as the susceptibility at the point $h_j=0$. As a matter of fact, as it appears in (32) the distribution of chemical potentials is homogeneous and we will have to put $\mu_j^{(1)} = \mu^{(1)}$ at the end of calculations.

4.2 Susceptibility of higher order

The structure of the formula (29) shows that we can arbitrary choose powers of the z-component of the pseudospin operator.

All the correlation functions appearing in the formula (24) can be calculated on the basis of the susceptibility $\chi_{j,j}^{n,n'}$, which can be found from the equations obtained by the differentiation of suitable statistical averages $\langle (S_j^z)^n \rangle$ with respect to $\mu_j^{(n)}$ and considered at the point j ($\mu_x^{(n)} = \mu^{(n)}$). The statistical averages satisfy the conditions imposed for the occupation operators according the assumed degrees of the surface coverage. The formula (32) allows us to determine the correlation functions with a different level of the accuracy which is dependent on the methods used for the calculation of $\langle (S_j^z)^n \rangle$.

4.3. Green function technique

The application of Green function technique is another way to calculate the correlation functions. This technique is well known and wide applied in the statistical physics, but its particular application in order to calculate the correlation function of pseudospins described by the Ising model, requires still certain commentaries. In order to be able to present these commentaries we remind shortly the fundamental properties of Green functions.

The Green function for two operators determined in the Heisenberg representation is defined as:

$$G_{AB}^r(t-t') = \langle \langle A(t) | B(t') \rangle \rangle = -i\theta(t-t') \langle [A(t), B(t')] \rangle \quad (34)$$

or

$$G_{AB}^a(t-t') = \langle \langle B(t) | A(t') \rangle \rangle = i\theta(t-t') \langle [B(t), A(t')] \rangle \quad (35)$$

where the function $\theta(\tau)$ denote heavieside function, and the average value of the commutator is defined for the statistical operator of equilibrium. The Green function $\langle \langle A(t) | B(t') \rangle \rangle$ satisfies the equation:

$$\frac{\partial \langle \langle A(t) | B(t') \rangle \rangle}{\partial t} = -i\delta(t-t') \langle [A, B] \rangle + i \langle \langle [A(t), \mathcal{H}] | B(t') \rangle \rangle \quad (36)$$

where the hamiltonian \mathcal{H} of the system is determined by the operators A and B . The correlation function of the operators A and B is then expressed by the formula:

$$\langle B(t) A(t') \rangle = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\text{Im} \langle \langle A | B \rangle \rangle_{\omega} \exp[i\omega(t'-t)]}{\exp(\omega\beta)} d\omega \quad (37)$$

where $\langle \langle A | B \rangle \rangle_{\omega}$ is the Fourier transform of the function $G'_{AB}(t-t')$, i.e.

$$\langle \langle A | B \rangle \rangle_{\omega} = \int_{-\infty}^{\infty} G'_{AB}(\tau) \exp(i\omega\tau) d\tau \quad (38)$$

and

$$G'_{AB}(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \langle A | B \rangle \rangle_{\omega} \exp(-i\omega\tau) d\omega \quad (39)$$

The operators A and B should fulfil the relations of the commutation or anticommutation rules, which are equivalent to the corresponding relations for the field operators $\Psi(r, t)$, $\Psi^*(r, t)$, namely

$$[\Psi(r, t), \Psi(r', t)] = 0$$

$$[\Psi^*(r, t), \Psi^*(r', t)] = 0 \quad (40)$$

$$[\Psi(r, t), \Psi^*(r', t)] = \delta(r-r')$$

when the Green function is specified for the ensemble of these operators in the well known way:

$$G_n(1, 2, \dots, n; 1', 2', \dots, n') = i^{-(n+n')} \langle \Psi_0 | T[\Psi(1) \dots \Psi(n) \Psi^*(1') \dots \Psi^*(n')] | \Psi_0 \rangle \quad (41)$$

and hence, for instance,

$$G'_1(1, 1') = -i\theta(t-t') \langle [\Psi(1), \Psi^*(1')] \rangle$$

or

$$G'_1(jt, j't') = -i\theta(t-t') \langle [\Psi_j(t), \Psi_j^*(t')] \rangle \quad (42)$$

so the Green function (34) is equivalent to the Green function (42) for certain operators $A_j(t)$ and $B_j(t')$, which fulfil the relations:

$$[A_j, A_{j'}] = 0$$

$$[B_j, B_{j'}] = 0 \quad (43)$$

$$[A_j, B_{j'}] = \delta_{jj'}$$

In particular, this can be easily satisfied in the case when $B_{j'} = (A_j)^*$.

For the correlation functions $\gamma_{j,j'}^{n,n'}$, interesting for the purpose of this paper, the system is described by the hamiltonian (22), which can be treated as a function of the operators S_j^z . The correlations refer to the same moment of time i.e. $t' = t$ or $\tau = 0$ and they are determined for the operators $(S_j^z)^n$. Regarding to the structure of the Green functions in connection with the properties of the commutation rules for the operators forming the Green function in question we cannot construct

directly the Green function $\langle\langle(S_j^z)^n(t)|(S_j^z)^n(t')\rangle\rangle$ which corresponds to the correlations $\langle(S_j^z)^n, (S_j^z)^n\rangle$. It is sufficient to remark that $[S_j^z, S_j^z]=0$, what means that the third condition (43) is not satisfied for $A_j=(S_j^z)^n$ and $B_j=(S_j^z)^n$.

In order to overcome this difficulty we can take advantage of the relation between the components of the pseudospin, namely:

$$S_j^z S_j^z + \frac{1}{2}(S_j^+ S_j^- + S_j^- S_j^+) = S(S+1) \tag{44}$$

where

$$S_j^\pm = S_j^x \pm iS_j^y \tag{45}$$

and the components S_j^\pm, S_j^z fulfil the relations

$$\begin{aligned} [S_j^\pm, S_j^\pm] &= 0 \\ [S_j^+, S_j^-] &= 2S_j^z \delta_{jj'} \end{aligned} \tag{46}$$

We can see that the operators S_j^+, S_j^- correspond to the field operators due to the relations (46), and now $S_j^-(S_j^+)^*$. Thus the Green functions can be expressed by the operators $A=S_j^+$ and $B_j=S_j^-$, or by the operators:

$$A_{jj'}^n = S_j^-(S_j^z)^n \quad \text{and} \quad B_j^n = (S_j^z)^n S_j^+ \tag{47}$$

Next, in a more general case, we should find yet another relations between the correlation functions $\gamma_{j,j'}^{n,n}$, and the correlations (37) at $t=t'$ for the operators (47). As an auxiliary formula we can use here the relation between S_j^z and S_j^\pm resulting from the formula (44). We can notice also that this formula gives the possibility for determination of averages $\langle(S_j^z)^n\rangle$ appearing in $\gamma_{j,j'}^{n,n}$ by the averages of operators S_j^\pm . The formula (44) with help of the commutational relations (46) can be rewritten as

$$S_j^z S_j^z + S_j^z + S_j^- S_j^+ = S(S+1) \tag{48}$$

Multiplying the relation (48) by $(S_j^z)^{n-1}$ and averaging with respect to the statistical operator we get:

$$\langle(S_j^z)^{n+1}\rangle + \langle(S_j^z)^n\rangle = S(S+1)\langle(S_j^z)^{n-1}\rangle - \langle(S_j^z)^{n-1}S_j^-S_j^+\rangle \tag{49}$$

This formula represents a system of $2S$ equations for the average values of successive powers of the pseudospin z -component, i.e. variables $\langle(S_j^z)^n\rangle$ for $n \in (1, 2S+1)$. The missing $2S+1$ equation we obtain by averaging the following relation [13]:

$$\left\langle \prod_{r=-s}^s (S_j^z - r) \right\rangle = 0 \tag{50}$$

The system of equations (49) and (50) allows us to calculate $\langle(S_j^z)^n\rangle$ on the assumption that we know the functions $\langle(S_j^z)^{n-1}S_j^-S_j^+\rangle$. These functions can be found as a solution of the system of equations adequately chosen and arising from the general equation for the Green function, namely on the basis of (36) and (38) we have:

$$\omega \langle \langle S_j^+ | B \rangle \rangle_\omega = \langle [S_j^+, B] \rangle_\omega + \langle \langle [S_j^+, \mathcal{H} | B] \rangle \rangle_\omega \quad (51)$$

where $B = (S_j^z)^{n-1} S_j^-$, and \mathcal{H} is given by the formula (22). Then the functions $\langle \langle (S_j^z)^n S_j^- S_j^+ \rangle \rangle$ fulfil the equation (37). The character of equation (51) is determined by the commutator $[S_j^+, \mathcal{H}]$ independently of the values of operator B . Accuracy of a solution of the problem depends only, but substantially, on the possibility of expression of the Green function $\langle \langle [S_j^+, \mathcal{H} | B] \rangle \rangle$ by the Green function $\langle \langle S_j^+ | B \rangle \rangle$. This possibility is, of course, dependent on the hamiltonian \mathcal{H} . For example, if the hamiltonian $\mathcal{H} = -\sum_r \tilde{h}_r S_j^z$ then $[S_j^+, \mathcal{H}] = \tilde{h}_j S_j^+$, or $\langle \langle [S_j^+, \mathcal{H} | B] \rangle \rangle = h_j \langle \langle S_j^+ | B \rangle \rangle$ and the exact solution of the problem has a form

$$\langle \langle (S_j^z)^{n-1} S_j^- S_j^+ \rangle \rangle = \frac{\langle [S_j^+, (S_j^z)^{n-1} S_j^-] \rangle}{\exp(\tilde{h}_j \beta)} \quad (52)$$

Unfortunately, the form of the hamiltonian (22) is more complicated, and contains the products $S_j^z S_j^z$, and their higher powers. The values of these powers depend on the value of spin (for example $S = \frac{1}{2} \rightarrow n = 1$; $S = 1 \rightarrow n = 2$; $S = \frac{3}{2} \rightarrow n = 3$; $S = 2 \rightarrow n = 4 \dots n_{\max} = 2S$).

5. CORRELATION FUNCTION AND ITS FOURIER TRANSFORM FOR $S = \frac{1}{2}$

It seems to be more convenient to present the computational methods of solving the system of equations (49) and (50) for the individual values of spin, which correspond to the concrete physical situations described in Chapter 2. Moreover, we have to remember that the correlations $\gamma_{jj'}^{n,n'}$ should be expressed by the correlations (37) and it requires the consideration of particular cases with given values of spin.

5.1. Molecular field approximation

According to the formula (28) the average value $\langle S_j^z \rangle$ takes the form

$$\langle S_j^z \rangle = \frac{1}{2} \operatorname{th} \frac{h_j + \sum_{j'} U_{jj'} \langle S_{j'}^z \rangle}{2/\beta} \quad (53)$$

in the molecular field approximation. Next, the formula (31) on the basis of the relation (29) can be rewritten as:

$$\gamma_{jj'} = \theta(1-\theta) [\delta_{jj'} + \sum_r \beta U_{jr} \gamma_{rj'}] \quad (54)$$

where the mean value of $\langle S_j^z \rangle$ is expressed in terms of the degree of the surface coverage θ , namely

$$\langle S_j^z \rangle = \theta - \frac{1}{2} \quad (55)$$

because of $\langle \sigma_j(\frac{1}{2}) \rangle = \theta$

The solution of the equation (54) can be obtained by substituting

$$\gamma_{jj'} = \sum_q T_{qj} \gamma_q T_{qj'} \quad (56)$$

where the coefficients T_{aj} satisfy the relation

$$\sum_r U_{jr} T_{aj} = U_q T_{aj} \quad (57)$$

with the orthogonality condition

$$\sum_q T_{qj} T_{qj'} = \delta_{jj'} \quad (58)$$

Then the Fourier transform becomes

$$\gamma_q = \frac{\theta(1-\theta)}{1-\theta(1-\theta)\beta U_q} \quad (59)$$

and its correlation function is given by

$$\gamma_{jj'} = \theta(1-\theta) \sum_q \frac{T_{qj} T_{qj'}}{1-\theta(1-\theta)\beta U_q} \quad (60)$$

In the particular case, when we take into account only the nearest neighbours interactions and we assume that they are isotropic, we can put

$$T_{aj} = \frac{1}{N} \exp(-iqj) \quad (61)$$

where N denotes the number of elements in the layer. The equation (57) leads to

$$U_q = \sum_{j \in j} U \exp(-iq(j'-j)) = 2U [\cos q_x a + \cos q_y a] \quad (62)$$

for $U_{jj'} = U$ if $j' = j + a$. In the approximation usually applied to the critical scattering process description, i.e. the incoherent diffusion, we can confine our calculations to the formula

$$U_q = 4U - Ua^2q^2 \quad (63)$$

which is sufficient for small values of the scattering vector.

Substituting (59) for U_q given by (62) into the formula (4) for the incoherent intensity, we obtain

$$I_{incoh}(k_f^-) = \frac{4\pi^4 k}{AK_{\perp}} \sum_{p=1}^{p_{\max}} \sum_{p'=1}^{p_{\max}} K_1^{(0)}(p, k_f^- \leftarrow k_i^+) * K_1^{(0)}(p', k_f^- \leftarrow k_i^+) \sum_j \gamma_{1j} \exp[-i(k_f^- - k_i^+)(T_1 - T_j)] \quad (64)$$

where

$$\gamma_{ij} = \theta(1-\theta) \frac{1}{N} \sum_q \frac{\exp(-iqr)}{1-\theta(1-\theta)4U + \theta(1-\theta)Ua^2q^2} \quad (65)$$

We can see from (65) that the maximum of the incoherent intensity is for $kT_c = 4U\theta(1-\theta)$, i.e. it depends on the interaction U as well as the degree of surface coverage θ . It is worth noting that the quantity U refers to the interaction between nearest neighbours, so when there is no nearest neighbours interactions, the intensity (4) reduces to $\theta(1-\theta)\delta_{jj'}$, which corresponds to the case considered in [7] for the same physical conditions.

5.2. Green function method on the Tiablikov decoupling level

For $S = \frac{1}{2}$ we have the Green function:

$$\begin{aligned} \langle\langle [S_j^+ \mathcal{H}] | B \rangle\rangle &= h_j \langle\langle S_j^+ | B \rangle\rangle \\ &+ \frac{1}{2} \sum_r U_{jr}^{11} \{ \langle\langle S_r^z S_j^+ | B \rangle\rangle + \langle\langle S_j^+ S_r^z | B \rangle\rangle \} \end{aligned} \quad (66a)$$

In order to solve the problem we must find the equations for Green function $\langle\langle S_r^z S_j^+ | B \rangle\rangle$, which usually are an infinite chain of equations for function $\langle\langle (S_r^z)^m S_j^+ | B \rangle\rangle$. The solutions with a given accuracy we obtain by cutting this chain for a certain value of m . We can also get the solutions of type (52) by the linearization of hamiltonian or by the fission of Green function $\langle\langle S_r^z S_j^+ | B \rangle\rangle$, which is equivalent to the mean field approximation (molecular field approximation, Hartree-Fock field approximation, Tiablikov decoupling). Taking into account the appearing correlations, on the basis of the de Dominicis theorem, we have:

$$\begin{aligned} \langle\langle S_r^z S_j^+ | B \rangle\rangle &= \langle S_r^z \rangle \langle\langle S_j^+ | B \rangle\rangle - \langle S_r^- S_j^+ \rangle \langle\langle S_r^+ | B \rangle\rangle \\ \langle\langle S_j^+ S_r^z | B \rangle\rangle &= \langle S_r^z \rangle \langle\langle S_j^+ | B \rangle\rangle - \langle S_j^+ S_r^- \rangle \langle\langle S_r^+ | B \rangle\rangle \end{aligned} \quad (66b)$$

It allows us to calculate the correlation in the form:

$$\langle S_j^- S_j^+ \rangle = \sum_q \frac{T_{qj} Q_q T_q}{\exp(\omega_q \beta) - 1} \quad (67)$$

where ω_q and T_{qj} fulfil the equation:

$$\omega_q T_{qj} = (h_j - \sum_r U_{jr}^{11} \langle S_r^z \rangle) T_{qj} - \sum_r U_{jr}^{11} \langle S_r^- S_j^+ \rangle T_{qr} \quad (68)$$

however

$$\begin{aligned} Q_q &= \sum_{jj'} T_{qj} \langle [S_j^+ S_{j'}^-] \rangle T_{qj'} \\ Q_q &= 2 \sum_j |T_{qj}|^2 \langle S_j^z \rangle \end{aligned} \quad (69)$$

If we neglect the correlations $\langle S_r^- S_j^+ \rangle$ appearing in equations (66), we obtain from formula (67)

$$\langle S_j^- S_j^+ \rangle = \frac{2 \langle S_j^z \rangle \delta_{jj'}}{\exp((h_j + \sum_r U_{jr}^{11} \langle S_j^z \rangle) \beta) - 1} \quad (70)$$

It means that we have only the autocorrelations which is in accordance with the assumption made above. Putting the autocorrelation (70) in equation (49), we can find that:

$$S_j^z = \frac{1}{2} - S_j^- S_j^+ \quad (71)$$

and

$$\langle S_j^z \rangle = \frac{\frac{1}{2}}{1 + 2P_j^{(z)}} \quad (72)$$

where

$$P_j^{(z)} = \frac{1}{\exp(\tilde{h}_j \beta) - 1} \quad \text{for} \quad \tilde{h}_j = h_j + \sum_r U_{jr}^{11} \langle S_r^z \rangle$$

and $\langle (S_j^z)^2 \rangle = \frac{1}{4}$ on the basis of equation (50).

The formula (71) is found exactly but the formula (72) determines $\langle S_j^z \rangle$ in a Green function decoupling approximation on the molecular field level, and is well known in that approximation.

The consideration of correlations in the decoupling (68) allows us to find the magnetization $\langle S_j^z \rangle$ in the following form:

$$\langle S_j^z \rangle = \frac{1}{2} - 2 \sum_q |T_{qj}|^2 \frac{\sum_r |T_{qr}|^2 \langle S_r^z \rangle}{\exp(\omega_q \beta) - 1} \quad (73)$$

and so for $1/N \sum_r \langle S_r^z \rangle = \langle S^z \rangle$, we obtain:

$$\langle S^z \rangle = \frac{\frac{1}{2}}{1 + 2\tilde{P}^{(z)}} \quad (74)$$

where

$$\tilde{P}^{(z)} = \sum_q \frac{1}{\exp(\omega_q \beta) - 1} \quad (75)$$

for $|T_{qr}|^2$ independent of j ; this is so, for example, for the coefficients

$$T_{aj} = A \exp(-iqj) \quad (76)$$

which are the solutions of equation (68) for the homogeneous correlations $\langle S_r^- S_j^+ \rangle$, i.e. for the correlations of near neighbours.

The formula (67) allows us, at the same time, to find the correlations which are our objects of interest in this paper, namely $\gamma_{j,j}^{11}$, for $S = \frac{1}{2}$.

6. CONCLUSIONS

The presented description of the topological or stoichiometrical disorder in a layer adsorbed on the crystalline surface opens a large research area for the considerations of two-dimensional systems which can be verified in experiments.

This feature of a natural disorder brings a new example of the system scattering in an incoherent way. For this reason the model of a two-dimensional disordered layer is of a great importance for this new branch of investigations giving contribution to the critical phenomena considered in the surface physics. The low energy electron diffraction finds its natural application in the study of this effect as the method of the incoherent back-scattering by the disordered medium where the incoherent amplitude of the scattered beam is related to the disorder reflected by the correlations between the elements forming an adsorbed layer.

From the point of view of the critical behaviour investigated in the system, the LEED intensities give some information concerning the shape of the correlation functions with respect to their symmetry and the temperature dependence. From the point of interest of the surface physics, the obtained information allows us to describe the properties of the adsorption, its energy, distribution and formation of the surface coverage.

The presented model is general in character. It describes various configurations of the adsorbed atoms, ions or molecules. For a given degree of coverage the spatial distributions and the transitions between different phases of the disordered states can be discussed. The main characteristics are determined by the topological correlations which play the role of an effective potential responsible for the incoherent back scattering as well as the local charge density at the surface. At the same time the influence of adatoms on the boundary conditions can be evaluated by the correlations and their dynamic behaviour. Then the transport properties, first of all the diffusion through the surface barrier may be analysed.

The correlation functions can be calculated by means of different methods at different levels of accuracy. We can divide these methods into four groups, according to the methodological approaches based on (1) the fluctuation dissipation theorem, (2) the Green function technique, (3) the variational principle, and (4) the relations in the form for numerical calculations. In this paper we discuss the first two methods and exemplify them for the case of $S = \frac{1}{2}$ at the level of the molecular field approximation, which is equivalent to the Tiablikov decoupling. Of course, in a more general case all these methods can be applied to various approximations for the statistical averages (e.g. the constant coupling or reaction field approximation), or the methodological approach can be combined with a different kind of approximation, e.g. we can use the fluctuation dissipation theorem for the average values calculated by the Green function technique. It is worth noting that the results in these two approaches are the same in the case of the statistical average of $\langle S_i^z \rangle$. It means that the Tiablikov decoupling is equivalent to the mean field approximation. The decoupling which does not include the nearest neighbour correlations leads directly to the autocorrelations only, while the fluctuation theorem gives the spatial distribution of correlation.

The presented model is equivalent to the generalized Ising model from the formal point of view. Thus, the solutions can be found by means of simple

mathematical analogies. However, the system is now described by the great canonical ensemble. This fact allows us to determine the chemical potential in order to assure the average value of $\langle S_j^z \rangle$ which is related to the coverage degree. This relation leads to the correlations dependent on the coverage and temperature.

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introduction of the propagation constants k_x and k_y of the incident wave has been treated for a long time (see e.g. [1]). The present problem essentially concerns very simplified model systems, being analysed by an approximation technique. Their validity ranges are generally limited by the generally made assumption of both mechanical and electrical isotropy of the substrate. In this paper we use a method based on the Green function technique combined with a well known approach [7] which enables us to define a rough surface by an ideal one with a randomly distributed green function. This enables us to find consistent closed form expressions for both the scattered field and the reflected power spectrum.

Essentially the method can be regarded as a quite general one. For brevity, however, we restrict our considerations to the case of substrate exhibiting isotropy of its mechanical properties along the surface plane. This is exemplified by hexagonal symmetry crystals with (001) surfaces [8], which are common to the typical anisotropic materials.